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(Photochemistry-Carbohydrates, Cellulose)
Project Reports (2)

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THE INSTITUTE OF PAPER CHEMISTRY

QUARTERLY RESEARCH REPORT

Prepared by: R. D. McKelvey, Project Leader

DIVISION: Natural Materials and Systems

DATE: October 22, 1975

✓ PROJECT NO.: 313⁴ - "A Fundamental Study of the Photochemistry of Carbohydrates, Cellulose, and Related Compounds"

Class: I

OBJECTIVE:

1. Investigate the ultraviolet spectra of carbohydrates and related model compounds.
2. Mechanistic and exploratory studies on the photochemistry of carbohydrates and related models.
3. Extension into cellulose systems. Examine uses related to the modification and stabilization of cellulose.

BUDGET:

July 1, 1975 - September 30, 1975	\$5,956.95
Amount spent previously	\$45,006.60

SCHEDULE:

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:

Three project reports were submitted summarizing recent results. A manuscript on the vacuum photosizing work was submitted to the Journal of Colloid and Interface Science and was accepted. The model compound studies with 2-methoxy-4-methyl-tetrahydropyran were brought to a point suitable for publication of a communication to the editor. A manuscript has been written but has not been sent to the journal yet.

Future work will be limited severely due to other time commitments of the project leader.

PROJECT REPORT FORM

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✓ PROJECT NO. 3134
COOPERATOR Institute of Paper Chemistry
REPORT NO. 11
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SIGNED Ronald D. McKelvey
Ronald D. McKelvey

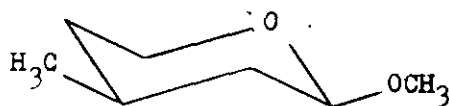
A FUNDAMENTAL STUDY OF THE PHOTOCHEMISTRY OF CARBOHYDRATES, CELLULOSE, AND RELATED COMPOUNDS

SUMMARY

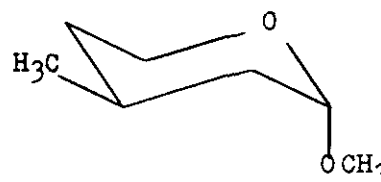
The syntheses of cis- and trans-2-methoxy-4-methyltetrahydropyran and the photoproducts expected from these compounds are presented. These syntheses are based on literature methods. In addition, some preliminary observations on the photochemistry are reported.

INTRODUCTION

Earlier studies (1) on the photochemistry of 2-methoxytetrahydropyran indicated that conformational effects might be important. Therefore, a study of another model system, 2-methoxy-4-methyltetrahydropyran, was undertaken. Since this is a ring system with two substituents, cis and trans isomers exist. The cis isomer exists almost entirely in the conformation with the methoxy group equatorial, since in the alternative conformation a severe 1,3 diaxial interaction is destabilizing. The trans isomer exists almost entirely in



cis



trans

the conformation in which the methyl group is in the more stable equatorial

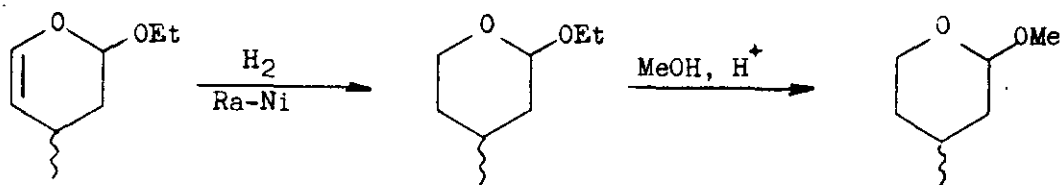
orientation and the methoxy group is axial, which is more favorable due to the anomeric effect. Thus, the two isomers simulate the two boat conformations in the original model system and also provide a model system capable of distinguishing between alpha and beta glycosides.

RESULTS AND DISCUSSION

SYNTHESIS OF MODEL COMPOUNDS AND PHOTOPRODUCTS

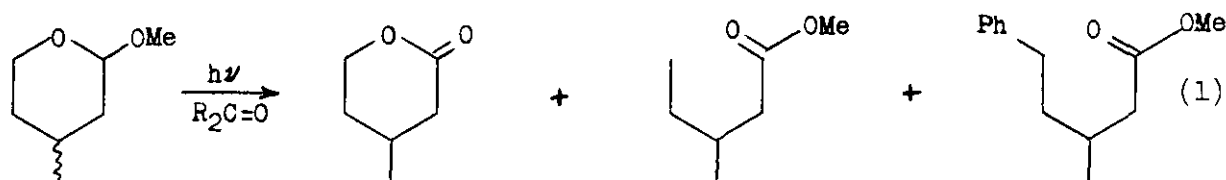
Since the desired compounds were not readily available, it was necessary to synthesize them. All are known compounds so literature methods with minor modifications were followed. Literature references are given in the Experimental Section.

The synthetic route for the isomeric mixture of 2-methoxy-4-methyl-tetrahydropyran is shown in Scheme 1. The starting material was reduced by catalytic hydrogenation and acid catalyzed alkoxy exchange gave an equilibrium mixture of about 60% of the trans isomer and 40% of the cis isomer. The mixture could be used for some purposes. When the individual isomers were needed, small quantities were separated by preparative gas chromatography.

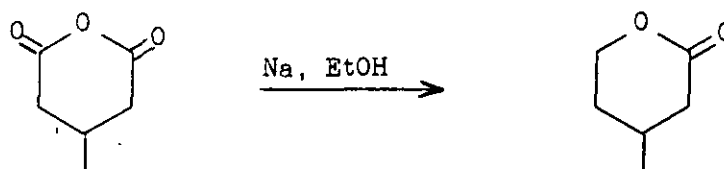


Scheme 1. Synthesis of cis- and trans-2-methoxy-4-Methyltetrahydropyran

The expected photochemistry, based on previous work, is shown in Equation 1. Three major photoproducts were expected. The synthesis of the lactone, the product derived from the reaction analogous to chain cleavage in polysaccharides, is shown in Scheme 2. The one-step synthesis involves reduction of 3-methylglutaric anhydride with sodium in ethanol. Sodium borohydride, which is reported to reduce glutaric anhydride, failed to react in the present system.

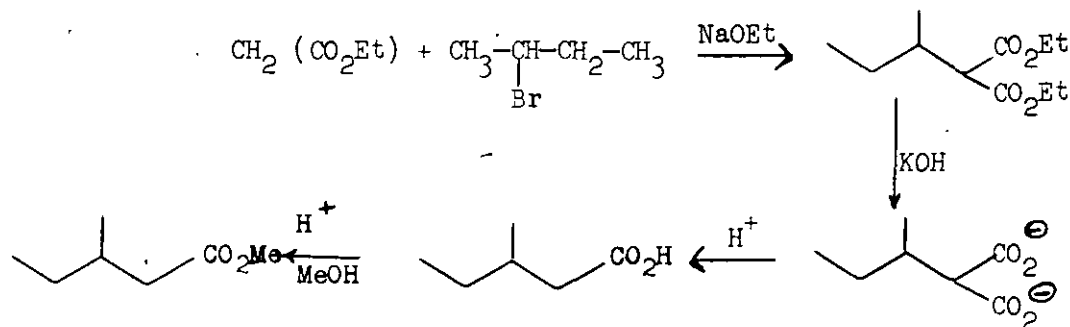


Two products were expected from the ring opening reaction. The first of these, methyl 3-methylpentanoate, results from the open-chain free



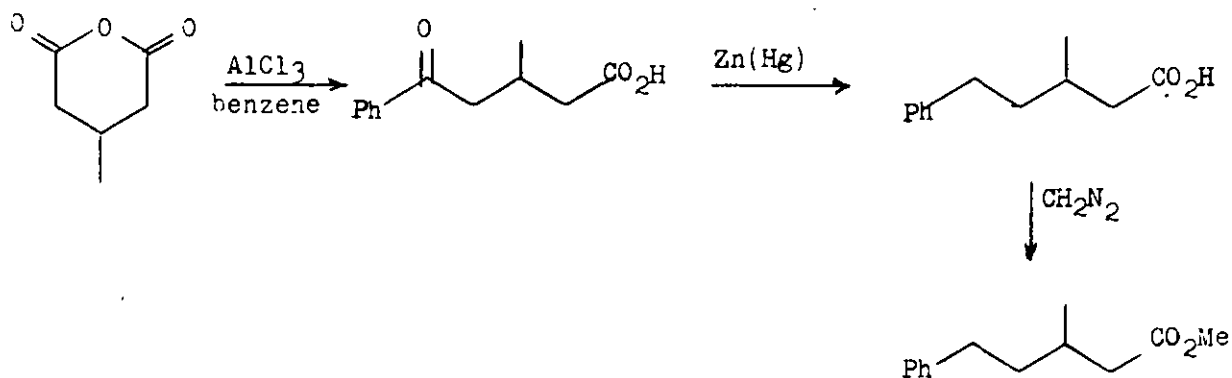
Scheme 2. Synthesis of 4-Methyltetrahydropyran-2-one

radical picking up a hydrogen atom. The synthesis, shown in Scheme 3, involves alkylation of diethylmalonate with 2-bromobutane followed by hydrolysis, decarboxylation, and esterification.



Scheme 3. Synthesis of Methyl 3-Methylpentanoate

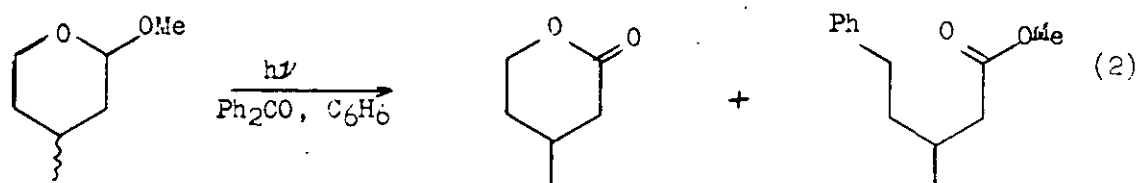
The other product derived from the ring opening reaction is methyl 3-methyl-5-phenylpentanoate. This product is formed when the open-chain free radical reacts with benzene and thus, is only a product when the photochemistry is carried out in benzene. The synthesis is shown in Scheme 4. Friedel-Crafts reaction of 3-methylglutaric anhydride with benzene gave 4-benzoyl-3-methylbutyric acid. Reduction of the ketone with zinc amalgam followed by esterification with diazomethane completed the synthesis.



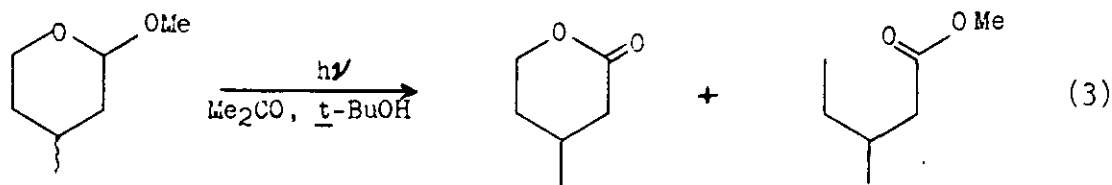
Scheme 4. Synthesis of Methyl 3-Methyl-5-Phenylpentanoate

PHOTOCHEMISTRY OF 2-METHOXY-4-METHYLTETRAHYDROPYRAN

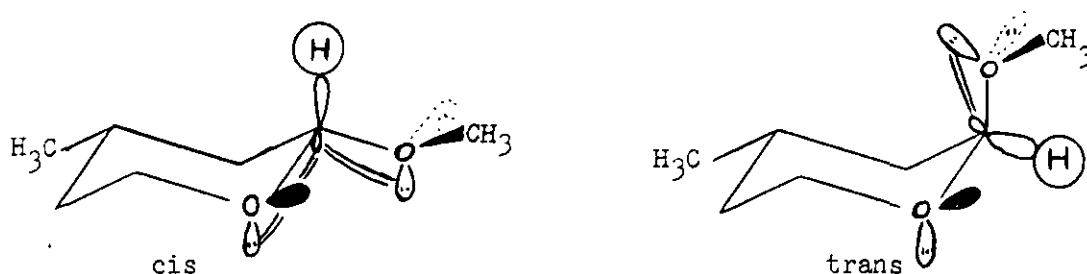
Irradiation of the isomeric mixture of cis- and trans-2-methoxy-4-methyltetrahydropyran and benzophenone in benzene gave 4-methyltetrahydropyran-2-one and methyl 3-methyl-5-phenylpentanoate, as shown in Equation 2. No methyl 3-methylpentanoate was detected, although small amounts would not have been found due to incomplete separation of the ester and the trans starting material on the gas chromatograph. In addition, it was noted that the cis isomer of the starting material was consumed much faster than the trans isomer. Irradiations of the individual isomers under the same conditions gave the same products and confirmed the difference in reactivity. No large difference in the product ratio was found, although analytical difficulties caused problems in obtaining accurate ratios.



Irradiation of the isomeric mixture in acetone and t-butyl alcohol gave the lactone and methyl 3-methylpentanoate as shown in Equation 3. In this case, the open chain radical picked up a hydrogen atom, since there was no benzene with which to react. As in the previous irradiation, the cis isomer was consumed more rapidly than the trans.



The greater reactivity of the cis isomer can be explained by orbital overlap. In the cis isomer, the carbon-hydrogen bond being broken is axial. The orientation of the bond is such that there is a hybrid orbital with nonbonding electrons antiperiplanar to the bond on each of the two oxygens attached to the carbon. This allows overlap to be developed while the bond is being broken and thus stabilizes the transition state leading to the free radical. In the case of the trans isomer, the equatorial C-H bond cannot be antiperiplanar to an orbital on the ring oxygen. Thus, stabilization can be gained from only one oxygen.



Similar reasoning has helped rationalize the selective carbon-oxygen bond cleavage in anionic transesterification (2) and also the difference in reactivity of alpha and beta glycosides to ozone (3). The interaction is somewhat related to the anomeric effect, in that the ring oxygen preferentially stabilizes one anomeric configuration over another.

Work on accurately determining the relative rates of decomposition of the two isomers and the product distribution is incomplete and will be reported at a later date.

EXPERIMENTAL SECTION

2-Ethoxy-4-methyltetrahydropyran. A solution of 15.3 g of 2-ethoxy-4-methyl-3,4-dihydro-2H-pyran (Aldrich) in 35 ml of hexane was hydrogenated in the presence of 1.0 g of W-2 Raney nickel (4) for 1.5 hr at room temperature and 1700 psi of hydrogen. The mixture was filtered through celite, concentrated, and distilled to give 11.6 g (75%) of the title compound. bp 62-65° (20 mm) [Lit. (5) 56-60° (20 mm)].

2-Methoxy-4-methyltetrahydropyran. A solution of 0.215 g of toluene-sulfonic acid, 9.95 g of 2-ethoxy-4-methyltetrahydropyran, 37 ml of methanol, and 37 ml of acetonitrile was allowed to react at room temperature for 44 hr. A solution of sodium methoxide in methanol was added until the mixture was alkaline, at which point the mixture was concentrated, filtered, and distilled to give 3.2 g of cis- and trans-2-methoxy-4-methyltetrahydropyran, bp 60-69° (150 mm) [Lit. (5) 54-55° (28 mm)]. These isomers could be separated by preparative gas chromatography on a 1/4" x 5' column of 5% SE-30 on 60-70 mesh Anakrom ABS. The trans isomer came off first and showed a broad doublet in the nmr at δ 4.58 with a width at half-height of 6 Hz, consistent with the "anomeric proton" being equatorial. The cis isomer gave a signal in the nmr at δ 4.15 which was a doublet of doublets ($J=8.5$ Hz, 2.0 Hz) consistent with the "anomeric proton" being axial.

4-Methyltetrahydropyran-2-one. The method of Sircar (6) was used. Sodium (1.44 g, 0.066 mol) was added in small pieces to a refluxing mixture of 1.99 g (0.015 mol) of 3-methylglutaric anhydride and 7.5 ml of absolute ethanol over a 30-minute period. More ethanol (ca. 3 ml) was added when

the mixture would not reflux. The mixture was cooled, 10 ml of water was added and the ethanol was distilled. The residue was acidified with ca. 6 ml of hydrochloric acid, refluxed for 10 minutes, cooled, and extracted with ether. The ether extracts were concentrated and distilled to give 0.25 g (14%) of the title compound, bp 72° (1 mm) [Lit. (6) 90° (12 mm)].

Diethyl sec-butylmalonate. To a solution of sodium ethoxide in ethanol prepared by adding 4.19 g (0.181 mol) of sodium to 100 ml of dried absolute ethanol, was added 30.1 g (0.188 mol) of diethyl malonate over a 15-minute period. The mixture, which partially solidified, was warmed somewhat until it cleared and then 25.0 g (0.182 mol) of 2-bromobutane was added over a 10-minute period. The mixture, which was protected with a drying tube containing Drierite and Ascarite, was refluxed for 20 hr. during which time the pH dropped to ca. 9. Most of the ethanol was distilled, water (80 ml) was added, and the organic layer was separated and distilled to give 31.5 g (76%) of the title compound, bp $95-103^{\circ}$ (7-8 mm) [Lit. (7) $124-132^{\circ}$ (28 mm)].

3 Methylpentanoic acid. This compound was prepared by the method of Eliet, et al. (7). Diethyl sec-butylmalonate (24.4 g, 0.113 mol) was added to a warm solution of 25.0 g (0.38 mol) of 85% potassium hydroxide in 25 ml of water over a 15-minute period. The solution was refluxed for 1.5 hr., water (25 ml) was added, and the ethanol was removed by distilling 25 ml of solvent. The solution was cooled and then a solution of 40 g (0.41 mol) of sulfuric acid in 55 ml of water was added over a 15-minute period

and the resulting solution was refluxed for 17 hours. The mixture was continuously steam distilled using a water separator (8) for 7 hours at which time the distillate was clear. This crude product was used in the next step.

Methyl 3-methylpentanoate. The crude product from above (14.8 g) which contained ca 1 g of water. was refluxed for 16 hours with 30 ml of methanol, 30 ml of benzene, and 10 mg of toluenesulfonic acid using a Dean-Stark trap. Most of the solvent was distilled, the residue was poured into benzene, washed with sodium bicarbonate solution, dried with sodium sulfate, concentrated, and distilled to give 1.5 g of methyl 3-methylpentanoate. The bicarbonate washings were acidified with 50% sulfuric acid and extracted twice with benzene. The benzene extracts were dried and concentrated to give 8.9 g of recovered 3-methylpentanoic acid. Thus, it appears that the water present in the crude starting material reduced the yield of ester. Drying the starting material and/or diazomethane esterification would probably have given a better yield.

4-Benzoyl-3-methylbutyric acid. The method of Mathur and Saharia (9) was used. Aluminum chloride (6.1 g) was added to ice-cold solution of 3-methylglutaric anhydride (3.2 g, 0.025 mol) in 15 ml of benzene. The mixture was then stirred at room temperature overnight and then for three hours on a steam bath. Cold hydrochloric acid was added to the cooled mixture and after stirring for one hour, two liquid phases separated. The water layer was filtered and extracted with benzene and ether. The organic extracts were combined with the above organic phase and extracted with 10%

sodium carbonate. This aqueous layer was acidified with 50% sulfuric acid and extracted with ether. This ether layer was dried and concentrated to give 4.0 g of product which crystallized on standing. Recrystallization from hexane gave 3.0 g (58%) of the title compound, mp 75-77° [Lit. (10) 78.5-79.5°].

3-Methyl-5-phenylpentanoic acid. Amalgamated zinc was prepared by adding 8 ml. of a solution of 1.0 ml of hydrochloric acid in 35 ml of water to a mixture of 0.43 g (0.0016 mol) of mercuric chloride and 4.26 g (0.065 mol) of granulated zinc which had been activated by heating almost to the melting point and then pouring into water (11). To this was added 3 ml of water, 7 ml of hydrochloric acid, 5 ml of toluene, and 2.00 g of 4-benzoyl-3-methylbutyric acid. The mixture was refluxed for 28 hours. Additional hydrochloric acid (ca. 2 ml) was added during this reflux after 6, 21, and 25 hours. The mixture was allowed to stand overnight at room temperature. The aqueous layer was washed with ether. The washings were combined with the organic layer and washed with water, dried, and concentrated to give 1.73 g of crude acid. A 1.5 g portion of this material was distilled to give 0.7 g of the desired compound, bp 138° (0.5 mm) [Lit. (9) 168° (4 mm)].

Methyl 3-methyl-5-phenylpentanoate. Etherial diazomethane was prepared by adding dropwise a solution of 2.22 g (0.010 mol) of Diazald (Aldrich) in 15 ml of ether to a mixture of 3.5 ml of diethylene glycol monoethyl ether, 1.0 ml of ether, and 1.2 ml of 37% sodium hydroxide solution which was heated to 65°. The distillate was trapped in an ice-cooled flask containing 15 ml of ether. This solution was added in small portions to a solution of 0.550 g of 3-methyl-5-phenylpentanoic acid until the yellow

color persisted for 5 minutes. This solution was concentrated to give 0.620 g (105%) of the methyl ester.

Irradiations. All irradiations were carried out in the Rayonet Photochemical Reactor using RPR 3000 lamps and pyrex glassware to assure that only the ketone was absorbing light. Solutions were degassed by sealing under vacuum after several freeze-pump-thaw cycles. Reactions were monitored and analyzed by gas chromatography on either or both of the following two columns: 10% Carbowax 20M on Chromosorb W, 1/8" x 6'; 3% OV-17 on 100/120 mesh Chromosorb Q, 1/8" x 4'. High column bleed made analysis of the lactone and phenyl ester difficult on the Carbowax column, whereas the unsubstituted ester was not separated from the trans starting material on the OV-17 column. These compounds were not completely separated on the Carbowax column, but no better column was found.

Numerous irradiations were carried out on both the mixture of cis and trans isomers and on the individual isomers. The following example is illustrative. More specific details and product analysis will be given when these results are complete.

A solution of 98.5 mg of 2-methoxy-4-methyltetrahydropyran (60% trans, 40% cis), 139.4 mg of benzophenone, and benzene to give a total of 10 ml was prepared and 1.0 ml aliquots were sealed in pyrex ampoules under vacuum after two freeze-pump-thaw cycles. Samples were irradiated as described above. After 260 minutes, 79.4% of the cis isomer had been consumed, while only 15.5% of the trans isomer was consumed. The products were 4-methyltetrahydropyran-2-one and methyl 3-methyl-5-phenylpentanoate, as shown by

retention time. Using the following equation, the ratio of rate constants was found to be about 9.4.

$$\frac{k_c}{k_t} = \frac{\ln [\text{cis}]/[\text{cis}]_0}{\ln[\text{trans}]/[\text{trans}]_0}$$

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Ronald D. McKelvey

A FUNDAMENTAL STUDY OF THE PHOTOCHEMISTRY OF CARBOHYDRATES, CELLULOSE, AND RELATED COMPOUNDS

SUMMARY REPORT

Results obtained to date and reported previously are discussed briefly. Some implications of this work are discussed. Areas for possible future work in photosizing and model compound studies are suggested.

INTRODUCTION

This project has been involved with three aspects of the photochemistry of carbohydrates. The first is a study of the ultraviolet spectra of carbohydrates, since any photochemical system requires a chromophore. The second is a model compound study of light-initiated free radical reactions of carbohydrate model compounds. The third is a study of the photochemistry of cellulose, with emphasis, so far, on the photochemical sizing of cellulose. This report will briefly summarize work completed to date in these areas and suggest areas where future work, if desired, might be done. For more details on the work completed, the reader is referred to earlier project reports (1) and manuscripts for publication (2).

WORK COMPLETED TO DATE

Ultraviolet Spectra of Carbohydrates

Ultraviolet spectra of carbohydrates often show a weak absorption at about 275 nm. Primary and secondary alcohols do not absorb in this region; neither do ethers. Therefore, the appearance of such a band in saturated

compounds such as carbohydrates, is somewhat controversial. Some people have assigned the band to the "acetal chromophore" (3) while other workers have attributed it to carbonyl groups present either as impurities or as the open chain form of sugars.

In the present work, such a band was found in virtually all commercial samples examined. In all but two cases, this band could be completely eliminated by purification of the compound. The two exceptions were the only ketoses studied. There is some literature evidence that ketoses have measurable amounts of open chain form present in solution (4).

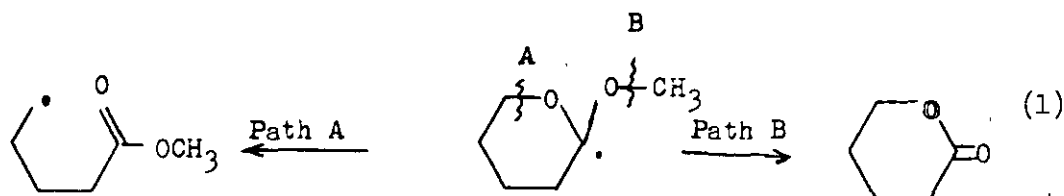
The conclusion drawn from this study was that the absorbance in this region is, with the exception of the ketoses mentioned, due to impurities. Based on the position of the band and the chemistry of carbohydrates, the most reasonable possibility would be carbonyl-containing impurities formed by oxidation. A similar band has been found in the spectrum of cellulose (5). In this case, the "impurities" would be irregularities in the cellulose chain. Such irregularities could not be removed by normal purification techniques, but would require chemical reduction. Such chemical reduction does stabilize cellulose to thermal aging (6).

Model Compound Studies

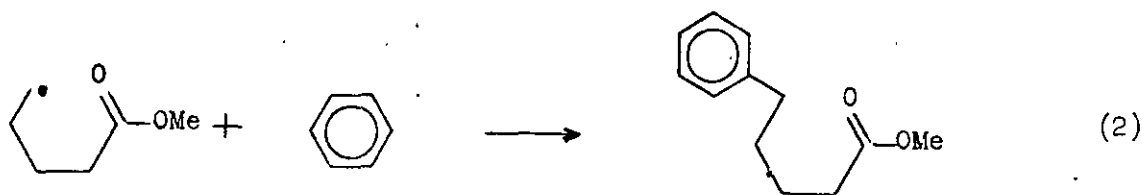
Model compound studies have emphasized free radical reactions initiated by light. The polyfunctionality of sugars result in a large number of degradation products. Therefore, a simpler system was studied which simulated only the acetal group of glycosides. Two methods of initiation were studied: decomposition of N-bromosuccinimide and hydrogen abstraction by ketones. Similar reactions were observed in both systems but

the ketones gave fewer secondary products. A portion of this work was recently published (2a).

Both methods resulted in the formation of a free radical at the "glycosidic" carbon of the model compound, 2-methoxytetrahydropyran. Once formed, the free radical could undergo either of two reactions as shown in Eq. 1. One of these (path A) is a ring opening reaction, while the other

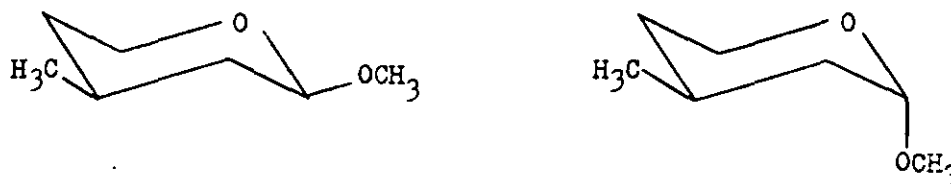


corresponds to a chain cleavage reaction in polysaccharides. Similar processes had been observed previously (7) but the importance of the ring ring opening pathway had been underestimated by the failure to find the major product, methyl 5-phenylvalerate which was formed by reaction with the solvent, as shown in Eq. 2. This reaction is important in later work (vide infra) because it shows that such radicals can react with hydrocarbons



to form covalent bonds. Extrapolation of this to cellulose is somewhat risky, however, since such radicals on cellulose would be in a hydrophilic environment and interaction with a hydrocarbon would be less favorable.

A similar model system with a methyl group at C-4 of the tetrahydropyran ring provided two isomers, one corresponding to β -glycosides and the other corresponding to α -glycosides. The isomer corresponding to



the β -glycosides was approximately ten times as reactive as the isomer corresponding to the α -glycosides. This leads to the prediction that, other things being equal, amylose should be more stable than cellulose to such hydrogen abstraction reactions. This prediction has not been tested.

The two processes observed in the model systems, chain cleavage and ring opening, help explain the photochemical reactions of cellulose. A decrease in molecular weight is observed (8) and an increase in carbonyl and carboxyl content (9). The infrared band at 1740 cm^{-1} observed by Desai (9) is consistent with the formation of an ester similar to that found in the model system. This reinforces the hypothesis that carbonyl groups in cellulose initiate free radical reactions which result in the degradation of cellulose.

Photosizing of Cellulose

A note by Desai and Shields (10) indicated that paper became sized when irradiated with ultraviolet light under vacuum. Initial experiments aimed at reproducing these results indicated that rubber was essential to obtain sizing. It was hypothesized that a volatile material from the rubber, such as an olefin, was responsible for the effect. This led to the development of a sizing system using olefins, ultraviolet light and an inert atmosphere.

It was found that paper could be completely sized by irradiating in the presence of olefins in a nitrogen atmosphere or under vacuum (0.05 mm). Water droplets placed on the sized paper exhibited contact angles of about 125° and did not wet the sheet before evaporating. With linear, terminal olefins of 16 to 20 carbons, vapor transport occurred under vacuum from the olefin source to the paper, resulting in sizing. Under nitrogen, sheets which were dipped in a dilute olefin solution were sized after irradiation. Benzophenone enhanced the effect and extended the active wavelength range.

A chemical bond between cellulose and olefin was suggested by solvent extraction experiments. An upper limit of 0.2% olefin incorporation, based on the weight of the paper, was established, although the actual amount might be considerably less.

AREAS FOR POSSIBLE FUTURE WORK

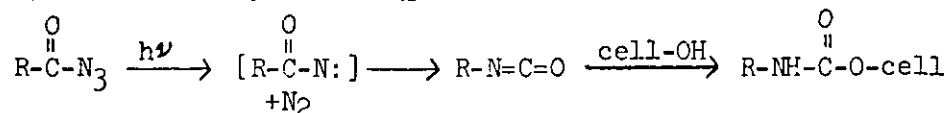
Photochemical Sizing

It is important to determine the actual amount of olefin incorporated into the paper. Indications are that it is a small amount and this system might give information on the effectiveness of partial monolayers for sizing. An approach involving the use of radioactive olefin would give a very sensitive measure of the amount of olefin in the paper. This would also provide the possibility of demonstrating a chemical bond to cellulose directly, since it might be possible to hydrolyze the paper and find radioactive fragments which contain carbohydrate.

Several applications of the photochemical sizing can be envisioned. The olefin system is probably not photochemically efficient enough for routine sizing of paper. However, the imaging capability which photochemistry adds to the sizing process brings up several applications in the graphic arts area. Continuous tone printing might be a possibility with such a system. Offset printing plates might be made by this method. Although the sized surface on filter paper was somewhat fragile and subject to loss of sizing upon surface abrasion, it might be that a more durable sized surface could be obtained on smoother surfaces, such as cast films.

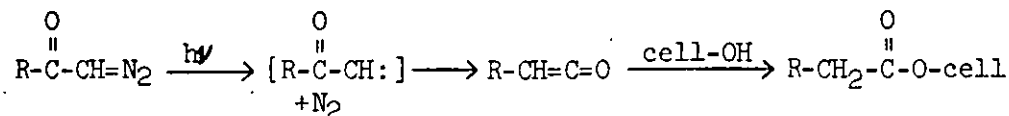
Perhaps a more fruitful research area would be to take a different approach to photochemical sizing. The olefin system probably involves the formation of free radicals on cellulose which then react with olefin to form a bond. The photochemical production of free radicals on cellulose is an inefficient process which occurs only because there is nothing else for cellulose to do. There is no good chromophore in cellulose, so impurities and irregularities tend to dominate the photochemistry. An approach which might stand a good chance of being more efficient would be that of generating the reactivity in the additive which would then react with the cellulose to give sizing. Several systems come to mind, some of which are shown in the following examples. The efficiency is expected to be high due to the energy gained by releasing the stable molecule, nitrogen, and a good chromophore is present to capture most of the light.

1. Isocyanate from acyl azide (photo-Curtius rearrangement)



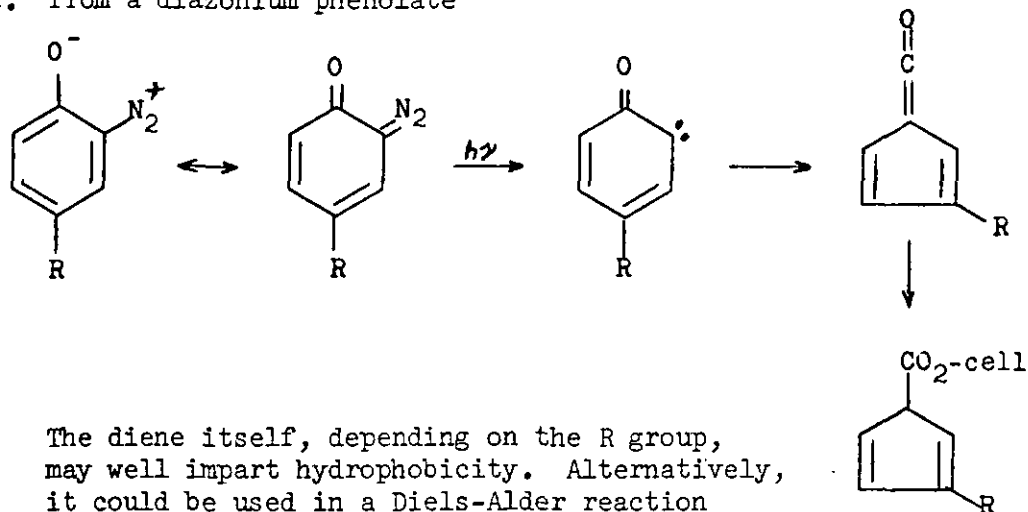
2. Generation of a ketene

a. from a diazoketone



b. from a diazoester (same as above except replace R with RO-)

c. from a diazonium phenolate



The diene itself, depending on the R group, may well impart hydrophobicity. Alternatively, it could be used in a Diels-Alder reaction with an olefin to attach a large aliphatic chain onto the cellulose.

Model Compound Studies

There are a few loose ends in this area that it would be nice to tie up. Analytical problems were encountered in the model system mentioned earlier where cis and trans isomers were possible. This made the getting of an accurate ratio for the relative reactivity of the alpha and beta glycoside models impossible. It also made it difficult to say whether the two isomers were interconverted photochemically. It might be possible to get this information with the new high pressure liquid chromatography equipment or with other gas chromatographic columns. It would also be interesting to note any differences in the product ratios obtained from the two isomers, since this would tell us whether the mechanism is concerted or not.

Some of these areas of research might be pursued in our academic research program. However, some of them might deserve immediate attention and, if so, should be continued through Institute research.

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THE INSTITUTE OF PAPER CHEMISTRY
QUARTERLY RESEARCH REPORT

DIVISION: Natural Materials and Systems

DATE: July 1, 1975

✓ PROJECT NO.: 3134 "A Fundamental Study of the Photochemistry of Carbohydrates, Cellulose, and Related Compounds." (Institute Project)

Project Leader: R. D. McKelvey

OBJECTIVE:

1. Investigate the ultraviolet spectra of carbohydrates and related model compounds.
2. Mechanistic and exploratory studies on the photochemistry of carbohydrates and related models.
3. Extension into cellulose systems. Examine uses related to the modification and stabilization of cellulose.

BUDGET:

\$42,400.00 (2 yrs)

\$45,006.60 spent through May 31, 1975

SCHEDULE: Original schedule--October 20, 1972 to October 24, 1974

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:

Results on this project have reached a plateau. Although certain questions remain unanswered, the work is at a point suitable for publication. The vacuum photosizing of cellulose with olefins appears to be a free radical process with the vacuum functioning to remove oxygen and to facilitate vapor transport.

PROJECT NO.: 3134

DATE: July 1, 1975

Two mechanisms are still possibilities. The first involves light absorption by the olefin to generate hydrocarbon free radicals. The second is hydrogen abstraction on cellulose to form cellulose free radicals. In both cases, subsequent free radical reactions result in a bond between hydrocarbon and cellulose.

An upper limit of 0.2% olefin incorporation, based on the weight of the paper, was established. The actual amount is presumably much less. A chemical bond between cellulose and hydrocarbon is implicated by the fact that the sizing could not be removed by extraction with four different solvents.

A report has just been written summarizing these results and should be available shortly.

The work in the model compound area is incomplete. It would be nice to see this work finished, but it might be best to pursue this in the academic research program. Likewise, questions on photosizing, such as the actual amount of olefin incorporation, could be followed up by students.

PROJECT REPORT FORM

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J. W. Swanson
J. C. Wollwage
G. A. Baum
R. M. Leekley
D. C. Johnson
R. D. McKelvey (2)
Editorial

✓ PROJECT NO. 3134
COOPERATOR Institute of Paper Chemi
REPORT NO. 9
DATE July 1, 1975
NOTEBOOK 1787 PAGE 101-160
2111 143-147
SIGNED Ronald D. McKelvey
Ronald D. McKelvey

A FUNDAMENTAL STUDY OF THE PHOTOCHEMISTRY OF
CARBOHYDRATES, CELLULOSE, AND RELATED COMPOUNDS

EXPERIMENTS ON THE VACUUM PHOTOSIZING OF PAPER WITH OLEFINS

SUMMARY

The effect of various operating parameters on the photosizing of paper was evaluated. Photosizing with olefins could be obtained in an inert nitrogen atmosphere when vapor transport was not required. Under vacuum, photosizing with vapor transport was obtained. Typically, contact angles of ca 125° were measured. Extraction with four different solvents did not remove the sizing agent, providing evidence for a covalent bond. Vycor and pyrex filtered out the active wavelength unless benzophenone sensitizer was added. An upper limit on the amount of olefin utilized in the paper for sizing was established as 0.2% of the weight of the paper. The sized paper lost some of its repellency when overirradiated or subjected to abrasion.

INTRODUCTION

Earlier work (1) had shown that vacuum photosizing of paper, as described in the literature (2), could only be duplicated when the apparatus used contained rubber. It was then found that sizing could be obtained if olefins were present instead of rubber. A reasonable mechanism was proposed (1) and the present work was undertaken to test that mechanism. The main objectives were to identify the photochemically reactive species and to

determine whether a covalent bond was formed between the olefin and paper. Determining the role of the vacuum was also desired.

RESULTS AND DISCUSSION

Irradiation of Whatman No. 1 filter paper with a 450-watt medium pressure mercury lamp through an evacuated quartz tube in the presence of olefins gave sizing of the paper. High contact angles were obtained and the water droplets placed on the paper generally evaporated without wetting the sheet. Early experiments were carried out with straight-chain, terminal olefins of 12, 16, 18, and 20 carbons. Although sizing was obtained with all of these olefins, some variability of results was noted, indicating that the system was sensitive to operating parameters such as temperature, pressure, and olefin volatility. Much more reproducible results were obtained when a mixture of C_{16} , C_{18} , and C_{20} olefins was used. This blend covered a volatility range such that the system was much less sensitive to fluctuations in conditions from run to run.

1076 In a typical experiment, a sample of paper (ca. 100 mg) was dipped into a hexane solution containing 2% (w/v) each of 1-hexadecene, 1-octadecene, and 1-eicocene, and the hexane allowed to evaporate. Olefin uptake was ca. 10 mg. The sample was then placed in the quartz tube along with one or more undipped sheets, the tube was evacuated to 0.05 mm, and the sample was irradiated (typically 25 minutes) as described above. Under these conditions "complete" sizing was observed on the irradiated side of both dipped and undipped samples. Water drops placed on the paper did not wet the surface,

remaining on the surface until evaporation. Contact angles measured for such sheets ranged from 117 to 134°. The unirradiated side of the sheets generally showed slight sizing.

Amount of Olefin Incorporated

At the end of a typical run, most of the olefin had left the paper and condensed on the cooler portions of the quartz tube. This indicated that considerably less than the 10 mg of olefin added were used in sizing the sheets. Attempts to determine the amount of olefin incorporated into the paper by weighing were not successful. Typically, a weight loss of ca. 3% was observed and no detectable difference was noted between treated sheets and controls irradiated without olefin. This put an upper limit for olefin incorporation of about 0.5% of the weight of paper. In a second attempt at putting an upper limit on the amount of olefin incorporation, multiple irradiations were carried out in series in the same tube without cleaning out the residual olefin between samples. In this manner, 5.6 mg of olefin was sufficient to size a total of 2.62 g of paper (on the irradiated side), indicating an upper limit of about 0.2% for olefin incorporation. Even in this system, a significant fraction of the olefin probably went into the vacuum pump. A direct measure of olefin uptake would require a sensitive, specific method, such as scintillation counting of radioactive olefin.

The Role of the Vacuum

Previous workers (2) had claimed that the vacuum was necessary for photosizing of paper and that an inert, nitrogen atmosphere could not

be substituted. The role of the vacuum was not clear but it was suggested that it might remove volatile cellulose decomposition products. In the present work it was found that a nitrogen atmosphere was sufficient to get sizing in sheets which were dipped in the olefin solution. Undipped sheets in the same tube showed varying degrees of incomplete sizing. Under vacuum (0.05 mm or less required), undipped sheets were consistently sized. These results indicate that the lack of oxygen is required and that vacuum serves to assist olefin migration. In the above mentioned work (2) the vacuum was presumably needed because migration of the active material was required from rubber (or some other organic material in the system) to the paper.

Migration of the olefin is probably through vapor transport. Irradiations done with paper held away from the glass gave results equivalent to treatment with the paper touching the glass. Thus, transport on the glass surface is not likely to be important.

Sizing is a Surface Effect

The sizing effect appears to be operative only on the top surface of the paper. The back side (unirradiated) of the paper showed only slight sizing unless longer irradiation times were used. Furthermore, scratching the sized surface with a probe made the scratched area absorbent. Finally, overirradiation of sized sheets destroyed the effect. Since it has been shown that irradiation results in cellulose decomposition predominantly on the surface of the paper (3) and if it is assumed that this releases the hydrophobic groups attached, it can be inferred that the groups are at the surface.

Mechanism for Photosizing

Two possible mechanisms come to mind. Free radicals are known to be produced upon ultraviolet irradiation of cellulose (4). These free radicals would be expected to react with olefins, as shown in Equation 1



to form covalent bonds. The product radicals could then be quenched by the system, forming a monomeric graft, or react with more olefin to give a graft polymer on the cellulose.

The second mechanism involves light absorption by the olefin. Since olefins are known to form free radicals upon photolysis (5), this would be a source of hydrocarbon radicals. These hydrocarbon radicals could then combine with radicals on cellulose, which were formed either by photolysis or chain transfer, to produce a covalent bond.

Two types of experiments were carried out to try to distinguish between these two possibilities. Unfortunately, the results are consistent with either mechanism. In the first set of experiments it was found that pyrex ($\lambda > 290$ nm) and even vycor filters ($\lambda > 225$ nm) removed the active wavelengths from the incident light. Hence, only the very short components were responsible for sizing. Either of these filters would prevent the olefins from absorbing light, whereas cellulose does absorb some of the longer wavelength components (6). One might be tempted to infer from this that the second mechanism is operative. However, Kujirai (7) has

shown that cellulose is more sensitive to the 184.9 nm component of a low pressure mercury lamp than to the 253.7 nm component in spite of the much lower intensity of the former. Although some degradation was observed with 253.7 nm light, the author was measuring reduction in degree of polymerization, not radical formation. Phillips, et al., (4) found maximum radical formation of cellulose when irradiation was at ca. 360 nm. This, however, is probably a reflection of the spectral output of their high pressure mercury lamp and not cellulose sensitivity. A high pressure mercury lamp probably has a smaller percentage of the very short wavelength light than does the medium pressure lamp used in the present work (8), although this will vary with the condition of the lamp.

Since hydrogen abstraction by carbonyl "impurities" in cellulose might be important in the formation of free radicals in cellulose, the effect of the addition of carbonyl groups in the form of benzophenone might be such as to enhance reaction by Mechanism 1. Several irradiations were carried out in which one strip of paper which was dipped in a 1% solution of benzophenone in 95% ethanol, one which was dipped in the olefin solution used previously, and a third, undipped strip were irradiated under vacuum simultaneously. The presence of benzophenone reduced the irradiation time required for sizing in the quartz tube by a factor of about two. Sizing was observed on all three sheets. Furthermore, benzophenone extended the wavelength range so that sizing was observed even with a pyrex filter. This is what would be expected if light absorption by benzophenone were important in this system. Benzophenone has an $n \rightarrow \pi^*$ absorption band extending from 300 nm to 400 nm.

It is interesting to note that benzophenone gave sizing of paper, even in the absence of olefin. Irradiation through quartz gave sizing of both benzophenone dipped and undipped sheets when irradiated together. Through vycor, only the undipped strip was sized. Through pyrex, neither strip was sized unless the irradiation time was doubled, in which case only the undipped strips were sized. It is conceivable that radicals derived from benzophenone might combine with radicals formed on cellulose to make the paper hydrophobic.

The enhanced rate of sizing with olefins in the presence of benzophenone is consistent with either mechanism. Hydrogen abstraction reactions of benzophenone with cellulose or olefin would introduce free radicals into the system. On the other hand, energy transfer from benzophenone to olefin would generate the triplet excited state of the olefin. Direct irradiation of olefins produces the singlet excited state, but intersystem crossing would produce triplets.

If benzophenone had not had an effect, then the singlet excited state of the olefin would have been implicated. However, the fact that benzophenone did have an enhancing effect means that a choice in mechanism cannot be made by these results. Additional experiments to determine the mechanism might be somewhat tedious. One approach would be to look for benzophenone reduction products which would be formed if it were acting as a hydrogen abstractor. A rather sensitive method, such as isotopic dilution, would be required. The amount of reduction product would be meaningful only if one knew how much olefin was grafted onto the cellulose, if it was grafted in the form of polymer or monomer and whether a radical chain mechanism is involved. It is possible that these reduction products

would be formed in a side reaction. Also, the mechanism in the presence of benzophenone might be different from the mechanism without benzophenone

Demonstration of a Chemical Bond

Direct evidence for a chemical bond between cellulose and olefin is difficult to obtain. In cellulose grafting studies it is generally assumed that homopolymer will be soluble in an appropriate solvent while graft copolymer will remain attached to cellulose and thus be insoluble. This assumption was made in the present work. Several samples which had been sized photochemically with olefins were soxhlet extracted with benzene, toluene, acetonitrile, and decalin. None of these solvents removed the sizing agent. Hence, it appears that at least some of the olefin is covalently bonded to the cellulose. A more direct proof of a chemical bond would be difficult to obtain due to the small amount of olefin incorporated.

EXPERIMENTAL SECTION

General

All irradiations were carried out with a Hanovia 450-watt medium pressure mercury arc lamp. The distance from the center of the lamp to the paper was 10 cm. Unless otherwise indicated, all irradiations were done under a vacuum with a pressure of less than 0.05 mm (0.1 mm was inadequate). The vacuum was maintained by continuous pumping. Irradiations were done in quartz or pyrex tubes, as indicated, 3.0 cm O.D. x 42 cm long attached to the vacuum line by a ground glass joint using a minimum amount of vacuum grease.

For vycor-filtered light, a vycor filter was placed around the lamp and the quartz tube was used. Unless otherwise noted, irradiations were for

25 minutes with a new lamp or 60 minutes with an older lamp. Whatman No. 1 filter paper was used throughout.

Contact angles were measured with a rame-hart contact angle goniometer. Sizing was evaluated qualitatively by placing small droplets of water (ca. 2 microliters) on the sheet. Sizing was said to be "complete" if the water did not penetrate the sheet during the 5-10 minute observation period. Sizing was said to be "partial" if penetration occurred in 10 to 60 seconds, and "slight" if it occurred in 3 to 10 seconds. Unless otherwise stated, results given are for the exposed side of the paper.

Solutions for Dipping Paper

An olefin solution was prepared by dissolving 0.8 g each of 1-hexadecene, 1-octadecene, and 1-eicocene in 40 ml of hexane. Dipping strips of paper in this solution and allowing the hexane to evaporate resulted in the uptake of ca. 10% of the weight of the paper. Similarly, a 1% solution of benzophenone in 95% ethanol resulted in an uptake of ca. 5%. Typically, most of the material left the paper during irradiation, since both dipped and undipped strips of paper lost 3% of their weight.

Determination of Upper Limit for Olefin Incorporation

A strip of filter paper was dipped in the olefin solution. The weight before and after indicated an olefin uptake of 5.6 mg. This strip was irradiated with two other, undipped strips under the usual conditions. All three strips were removed and three new, undipped strips were put in the tube. Nine such irradiations were carried out without cleaning the tube between runs. During this time, the olefin gradually migrated to the ends

of the tube where it was cooler. A total of 2.62 g of paper was treated. In the first three irradiations, sizing was complete for all three sheets. In the last six irradiations, complete sizing was observed for the two strips closest to the ends of the tube (where more olefin was present) but only partial for the center strip. At the end of the series a very small amount of olefin could still be seen in the tube.

Irradiations in a Nitrogen Atmosphere

Olefin-dipped and undipped strips of paper were placed together in the quartz tube and oxygen was removed by pumping to 0.05 mm pressure and then filling the tube with nitrogen by means of a three-way stopcock. This was repeated for a total of three times. The final pressure was 630 mm, the partial vacuum being used to hold the joint together. Irradiation was for 25 minutes. This experiment was repeated several times. In all cases the dipped strips showed complete sizing. The undipped strips showed varying degrees of sizing.

Overirradiation and Surface Abrasion of Sized Sheets

An olefin-dipped and undipped strip of filter paper were irradiated together under the usual conditions to give complete sizing on the irradiated side. The quartz tube was then cleaned thoroughly and the samples were irradiated for two hours without olefin. The olefin-dipped sample absorbed water in 5-10 seconds while the undipped strip absorbed water in 1-5 seconds. Overirradiations for shorter times had a greater effect on the undipped strip than on the dipped one. It was also found that scratching the surface of a sized sheet lightly with a pointed metal probe resulted in absorbance if the drop was placed exactly on the scratch.

Solvent Extractions of Sized Paper

Samples of the photochemically sized paper were extracted by placing them in the upper part of a small Soxhlet extractor and extracting with solvent for two hours. This was done with benzene, toluene, decahydro-naphthalene, and acetonitrile (1-hr extraction). The sizing was not lost by the extraction. Control samples of untreated filter paper were extracted with the hydrocarbon solvents and did not show any sizing.

Miscellaneous Control Experiments

Paper irradiated without olefin or benzophenone did not give sizing even after extended irradiation. Olefin-dipped strips did not show sizing before irradiation. Strips dipped in a 2% solution of 1-eicocene in hexane and then warmed to 45° for 30 minutes did show sizing, but this was removed by toluene extraction. Irradiation of olefin-treated sheets in air, or at pressures of greater than 0.05 mm, did not give sizing.

Irradiation Without Contact With the Quartz Tube

Two clips were fashioned out of paper clips to hold the paper strips away from the tube. An olefin-dipped strip was placed in one clip and an undipped strip was placed in the other. Irradiation under vacuum with the usual conditions gave complete sizing of both strips.

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THE INSTITUTE OF PAPER CHEMISTRY

QUARTERLY RESEARCH REPORT

DIVISION: Natural Materials and Systems

DATE: Mar. 31, 1975

✓ PROJECT NO.: 3134 "A Fundamental Study of the Photochemistry of Carbohydrates, Cellulose, and Related Compounds." (Institute Project)

Project Leader: R. D. McKelvey

OBJECTIVE:

1. Investigate the ultraviolet spectra of carbohydrates and related model compounds.
2. Mechanistic and exploratory studies on the photochemistry of carbohydrates and related models
3. Extension into cellulose systems. Examine uses related to the modification and stabilization of cellulose

BUDGET:

\$42,400.00 (2 yrs)

37,676.68 spent through Dec. 31, 1974

3,668.41 spent Jan, Feb, 1975

SCHEDULE:

Original schedule--October 20, 1972 to October 24, 1974

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:

Due to other commitments, activity on this project was decreased this quarter. Additional work on conformational effects in the model compound studies (objective 2) was done by Miss Kim Hayday, who was here during the month of

PROJECT NO.: 3134

DATE: Mar. 31, 1975

January from Gustavus Adolphus College. She looked at the photochemistry in a different solvent system. Quantitative differences could not be proved, due to incomplete separation on the gas chromatograph (perhaps high pressure liquid chromatography will overcome this problem). Spectral data (infrared and mass spectra) were obtained on several of the photoproducts, which will be of use in product identification. The structure of one photoproduct was confirmed by the spectra and synthesis.

Additional work was also done on the use of olefins for photochemical sizing. Hexadecene was found to be better than dodecene. The sizing could not be removed by benzene extraction, implicating a chemical bond. Attempts to preform the free radical (proposed) on cellulose and then add the olefin were unsuccessful at giving sizing.

Immediate plans for future work involve a few experiments to get the photosizing work in a form suitable for publication. Further work, including the use of other sizing agents, and other aspects of vapor sizing in general, will be limited by available time.

PROJECT REPORT FORM

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J. W. Swanson
R. D. McKelvey
R. M. Leekley
Editorial

✓ PROJECT NO. 3134
COOPERATOR IPC
REPORT NO. 8
DATE February 7, 1975
NOTEBOOK 2111 PAGE 132-143

SIGNED R. D. McKelvey
R. D. McKelvey

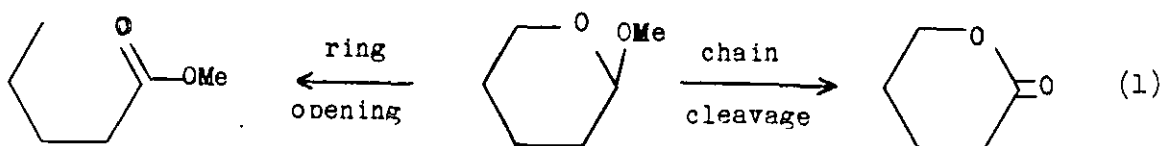
A FUNDAMENTAL STUDY OF THE PHOTOCHEMISTRY OF CELLULOSE, CARBOHYDRATES, AND RELATED SYSTEMS

SUMMARY

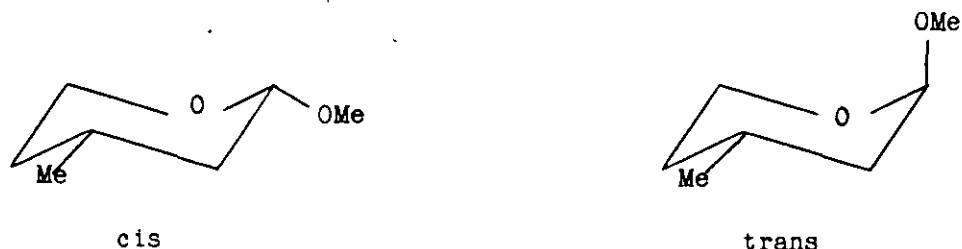
During the month of January 1975, Miss Kim Hayday, a sophomore at Gustavus Adolphus College, worked on this project in order to gain research experience during her one month winter term. She worked on the model compound studies, described herein, while the principle investigator worked on the photosizing of paper. Approximately 30% of the time charged to the project during that month was related to these model compound studies.

INTRODUCTION

Previous model compound studies had shown that two processes are important in the hydrogen abstraction reactions of acetals, a ring opening and a "chain cleavage" reaction (Eq. 1). There was some indication that conformational effects could be important (1) and, therefore, the cis- and trans-



isomers of 2-methoxy-4-methyltetrahydropyran were synthesized (2). The cis-isomer has the methoxy group equatorial (as in β -glycosides) while the trans-

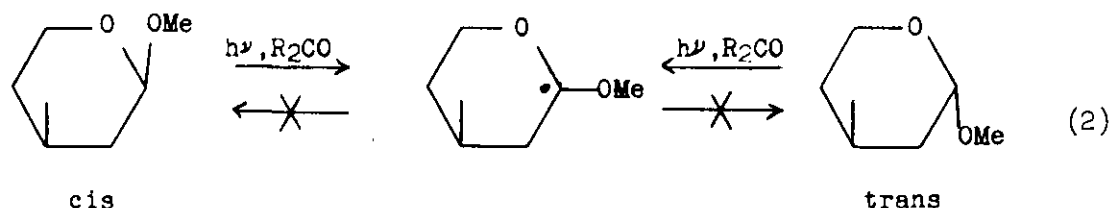


isomer has the methoxy group axial (as in α -glycosides). Previous irradiations in benzene with benzophenone as hydrogen abstractor had indicated that the cis-isomer was much more reactive than the trans-isomer while the product distribution was similar for the two isomers (2). It was of interest to see how the system differed in the more polar system of t-butyl alcohol and acetone. It is on this aspect of the problem that Kim worked.

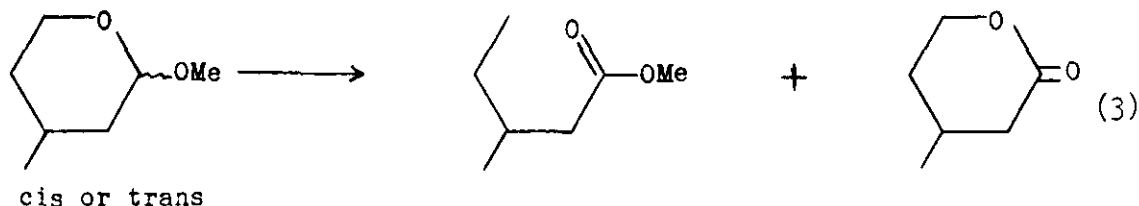
RESULTS AND DISCUSSION

The first task was to separate the previously synthesized mixture of cis- and trans-isomers. This was done by preparative gas chromatography. The trans-isomer had to be chromatographed a second time, after which samples of each compound were available of ca. 98% purity. Several irradiations were run to determine the optimum irradiation times. During these irradiations, it was found that a larger number of products appeared to be formed in this system than in the benzene-benzophenone system. A blank irradiation of the t-butyl alcohol-acetone mixture demonstrated that some of these products did not result from the acetal. These were generally formed in small amounts.

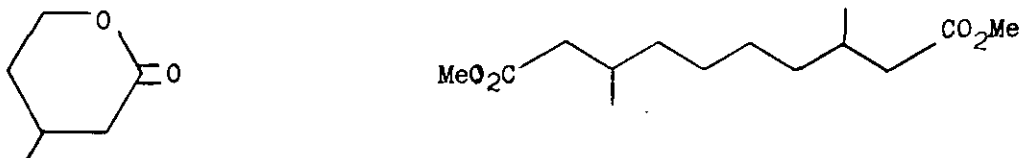
It was found that the cis-compound was ca. 10 times as reactive as the trans-compound in this solvent system as well. The cis- and trans-compounds did not interconvert, indicating that the hydrogen abstraction step is not reversible. The retention times of two of the products were



identical to the retention times of two of the expected photoproducts, the lactone and methyl ester (Eq. 3). Infrared spectra were obtained for three



photoproducts after preparative gas chromatography and mass spectra were obtained for five photoproducts by gc-ms. Two of the mass spectra are consistent with the lactone and open chain dimer, respectively. The others have not yet been interpreted.



Quantitative analysis of the photoproducts was again frustrated by two problems--nonreproducibility of recorder integrals and an overlap of the methyl ester peak with the trans- starting material. No other available gas

chromatographic columns improved the separation of these two compounds. It is hoped that, when high-pressure liquid chromatographic equipment becomes available, the separation can be accomplished.

A more detailed report, including the benzene system, synthetic work, and experimental details, will follow at a later date.

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1. R. D. McKelvey, The Institute of Paper Chemistry, Project 3134, Project Report 5.
2. Details will be reported in another report.

JAN 21 1975

THE INSTITUTE OF PAPER CHEMISTRY

QUARTERLY RESEARCH REPORT

DIVISION: Natural Materials and Systems

DATE: Jan. 20, 1975

✓ PROJECT NO.: 3134 "A Fundamental Study of the Photochemistry of Carbohydrates, Cellulose, and Related Compounds." (Institute Project)

Project Leader: R. D. McKelvey

OBJECTIVE:

1. Investigate the ultraviolet spectra of carbohydrates and related model compounds.
2. Mechanistic and exploratory studies on the photochemistry of carbohydrates and related models.
3. Extension into cellulose systems. Examine uses related to the modification and stabilization of cellulose.

BUDGET:

\$42,400 (2 yrs)

37,676.68 spent through Dec. 31, 1974

SCHEDULE: Original schedule--October 20, 1972 to October 24, 1974.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:

Prior to the previous quarterly review, work had been concentrated on Objectives 1 and 2. Work on ultraviolet spectroscopy (objective 1) was complete while work on model compounds (objective 2) was in progress. No work had been done on cellulose (objective 3).

PROJECT NO.: 3134

DATE: Jan. 20, 1975

During the last quarter, the emphasis has shifted to cellulose, although work is continuing in the model compound studies. Work on cellulose has been concerned with vacuum photosizing. Previously published work and exploratory Institute work (S. C. Nagel, project 1102-32) had shown that paper is sized when irradiated with ultraviolet light under vacuum.

Work done during the last quarter has shown that rubber is necessary for the sizing effect. Apparently volatile material from the rubber is attached to the surface of the paper photochemically. A mechanism was proposed in which an olefin from the rubber reacted with a free radical on the cellulose to form a chemical bond. The olefin made the cellulose hydrophobic.

This proposed mechanism is presently being tested. Olefins have been found to work. Experiments are being carried out to determine whether a free radical on cellulose is involved and whether a chemical bond is formed.

The implications of the above are much broader than that of explaining the results in the literature. The modification of the surface properties of cellulose with minute amounts of chemically bonded material has important applications as well as being of theoretical interest to surface chemistry.

FUTURE WORK

As indicated above, the proposed mechanism for olefin sizing is being tested. This will constitute necessary but insufficient evidence that this is what is happening in the case of rubber. In addition, a rather limited amount of work is planned in the area of generating other reactive intermediates photochemically which can modify the properties of cellulose. The model compound studies are also continuing on a limited scale to pin down a few leads turned up previously.

PROJECT REPORT FORM

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J. W. Swanson
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✓ PROJECT NO 3134
COOPERATOR IPC
REPORT NO. 7
DATE December 26, 1974
NOTEBOOK _____ PAGE _____
SIGNED Ronald D. McKelvey
Ronald D. McKelvey

A FUNDAMENTAL STUDY OF THE PHOTOCHEMISTRY OF CARBOHYDRATES, CELLULOSE, AND RELATED COMPOUNDS

SUMMARY OF THE LITERATURE ON RUBBER DECOMPOSITION

The emphasis in the literature on rubber decomposition is very much in the areas of changes in physical properties and the use of stabilizers. Thus, a considerable amount of work has been published on what materials will stabilize rubber to photolysis and thermolysis while only a few papers have dealt with the volatile decomposition products.

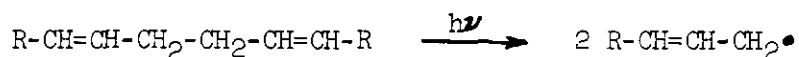
In addition to the relative paucity of papers on decomposition products, the majority used rather extreme conditions--temperatures of ca. 400°C or gamma irradiation with cobalt. These extreme conditions may have been chosen to give isolable amounts of degradation products. A few papers do seem to indicate that olefins are reasonable products to expect from rubber degradation.

Straus and Madorsky (1) found that pyrolysis of crude pale crepe and compounded crepe, before and after vulcanization, at 390° under vacuum gave two volatile fractions. The first fraction, bp -80° to 25°, was claimed to be an isoprene fraction (isoprene bp 34-35°) and constituted 5% of the original rubber weight. The second fraction was claimed to be the isoprene dimer fraction and amounted to 9-18% of the original weight.

Small but significant amounts of isoprene were also found by Batemen (2) when he photolyzed "rubber hydrocarbon", but only when the temperature was above 150°. At lower temperatures the gaseous mixture of products was claimed to be mainly hydrogen.

A more recent study (3) under milder conditions (100-150°) also found olefinic thermal decomposition products. Styrene-butadiene rubber gave styrene, "hydrocarbons", carbon monoxide, and carbon dioxide. Acrylonitrile-butadiene rubber gave acrylonitrile, "hydrocarbons", carbon monoxide, carbon dioxide, and dibutyl phthalate. Natural rubber gave "hydrocarbons", carbon monoxide, carbon dioxide, and dibutyl phthalate.

Carstensen and Ranby (4) used electron spin resonance to detect free radicals formed from various rubbers upon ultraviolet irradiation. With light of wavelength shorter than 300 nm they found evidence for the formation of allylic radicals. These could be readily formed by carbon carbon bond cleavage between the residual double bonds from butadiene



polymerization. Although their technique does not allow detection of stable products, it is reasonable to expect that these radicals would ultimately lead to relatively low molecular weight olefinic products. An unzipping mechanism (5) would give back monomers, while chain transfer (hydrogen abstraction) would give olefins of intermediate molecular weight.

Cummins (6) looked at the infrared spectra of pyrolysates from rubbers which had been heated in vacuo. Plasticizers and processing oils

had been removed by extraction. No numbers were given in the abstract, but it was claimed that peroxide cross-linked rubber gave more olefinic material than sulfur cross-linked rubber.

Rubbers contain many materials in addition to the basic polymer or copolymer. Sulfur is used to cross-link the rubber during vulcanization. Sulfide and disulfide links are generally considered to be formed. A wide variety of accelerators are used although they are generally free radical sources. Metallic oxides are used to activate the accelerator. Zinc oxide is commonly used. A rubber-soluble soap is needed to make the activator available and an antioxidant is usually added for stability. A typical composition is shown in the table. In addition, most rubbers also contain a filler, such as carbon black. Rubber, therefore, is a complex mixture,

Table. Typical composition of pure gum vulcanizate of natural rubber^a.

Material	Parts by Weight
Rubber	100
Sulfur	0.25-1.5
Accelerator	0.25-1.5
Zinc oxide (activator)	1-10
Stearic acid or zinc laurate	1-5
Antioxidant	0-1.5

^aBillmeyer, F. W., Jr., Textbook of Polymer Science, New York, Interscience, 1962, p. 540.

and could be a source of other materials in addition to olefins, such as stearic acid, which could be capable of sizing paper.

The study of the photochemical sizing of paper in the presence of rubber is complex. In addition to the plethora of possible volatile products, there is the problem of selective attachment to paper. Thus, the major volatile component may not be as photochemically reactive as other minor components. Even if one considers only the material on the paper, it is possible that well distributed and/or chemically bonded material, which might be present in small amounts, could contribute more to the sizing effect than adsorbed material.

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PROJECT NO. 3134
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REPORT NO. 6
DATE December 12, 1974
NOTEBOOK 1787 PAGE 94-96

SIGNED Ronald D. McKelvey
Ronald D. McKelvey

A FUNDAMENTAL STUDY OF THE PHOTOCHEMISTRY OF CARBOHYDRATES, CELLULOSE, AND RELATED COMPOUNDS

SUMMARY

A brief examination of the photochemical sizing of paper under vacuum indicated that the effect is likely to be the result of volatile materials from rubber O-rings or rubber stoppers which become attached to the surface, rendering it hydrophobic. Results to date are consistent with a mechanism in which free radicals or other active sites are created on the cellulose. Volatile materials, such as olefins, which might be generated photochemically from rubber stoppers, could then be trapped by these free radicals. The vacuum could serve both to stabilize the free radicals by removing oxygen and to mobilize the volatile materials. Although the evidence to date is not compelling, more definitive experiments might require a lot of time and effort.

INTRODUCTION

The report is 1969 by Desai and Shields (1) that cellulose was sized when irradiated with ultraviolet light, stimulated considerable interest here at the Institute. Potential applications could include sizing without chemicals and, if imaging capabilities could be incorporated into the system, several graphic arts uses. In addition, an understanding of the surface chemistry involved might lead to improved sizing by other means.

A considerable amount of exploratory work was done here (2) with the intent of making the method efficient enough to be practical. Many additives were tested, some of which were fairly effective at reducing the irradiation time. The present report describes some results obtained while doing some orientational work preliminary to an investigation of the surface chemistry.

RESULTS

A series of irradiations were carried out under a variety of conditions. In all cases, a vacuum of 0.03 mm was maintained by continuous pumping. Qualitative observations were made as to the degree of sizing by placing small drops (2-3 microliters) of water on the irradiated surface with a syringe.

In one set of irradiations, strips of filter paper were placed loosely in quartz test tubes and irradiated with a medium-pressure mercury lamp for one hour. In one case, a 25-mm i.d. tube fitted with a rubber stopper was used, with the stopper protected from direct exposure by wrapping from outside the test tube with aluminum foil (considerable reflected light could still hit that portion of the stopper which was inside the test tube). In the other case, a long (42 cm), 22-mm i.d. tube fitted with a ground glass joint was used. In this case, a minimum amount of vacuum grease was used, and only near the top of the joint so that diffusion into the tube would be minimal. In addition, the paper was at least 28 cm from the joint.

In the first case, which utilized the rubber stopper, the paper was completely sized on the exposure side. In the second case, little if any sizing was observed.

In a second set of irradiations, 7.0 cm filter paper discs were irradiated through a quartz window on a vacuum stage. The system was sealed with a rubber O-ring which was also subject to irradiation. The clearance between the window and the paper was ca. 2 mm. In this set, sizing was observed only in a ring consisting of the outer 1 cm of the paper (i.e., the part closest to the O-ring). The mean free path for diffusion of molecules the size of oxygen at this pressure is ca. 2 mm. In a modification of this experiment, two pieces of an O-ring ca. 1 cm long were placed 1 cm apart near the center of the paper. In this case, the entire sheet was sized.

In a third set of irradiations, a 7.0 cm filter paper disc was rolled up inside the quartz test tube, sealed with the rubber stopper and irradiated under vacuum for one hour. In this case, the irradiated surface was held tightly against the tube by the coiled paper. No sizing was observed.

DISCUSSION

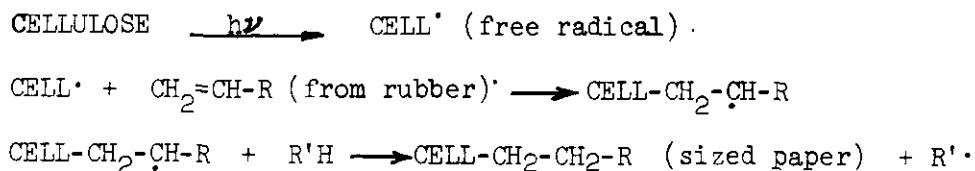
These results, taken together, constitute fairly strong evidence that the sizing effect requires a volatile component from rubber. When a relatively large space around the paper was available (test tube) the volatile component was able to migrate to all parts of the paper. When a small space was available (vacuum stage), the volatile component was trapped in the first 1 cm of paper it encountered. When essentially no space was available (rolled paper in test tube), the volatile component did not reach the exposed surface of the paper in sufficient quantity.

Exposure of the paper to ultraviolet light appears to be a requirement for the effect. The back side of the paper was never sized, even in the case

of the rolled up sheet where the volatile component would have much greater access to the unexposed side. Exposure of the rubber component may or may not be required. In the case of the O-ring, it was always exposed. In the case of the rubber stopper, it was shielded from direct rays but received considerable stray radiation on that portion inside the tube. Appreciable sticking of the rubber to the quartz was noted in both cases, indicating decomposition. These observations are indicative but do not prove that irradiation of the rubber is required.

One can conjecture as to the mechanism. One reasonable mechanism which is consistent with the results to date is shown in the Scheme. Free radicals are known to be formed on cellulose upon irradiation.

Scheme. Possible mechanism for photosizing



Olefins are reasonable decomposition products or volatile components in rubber. Olefins react with free radicals, forming a chemical bond as shown in the Scheme. Since olefins are hydrophobic, sizing would result from this hypothetical process.

Other work done in the Division indicated that sizing materials which are properly distributed (e.g., vacuum transport) and chemically bonded to paper can give sizing even when present in very small amounts. Hence, it would not require very much material from the rubber to give the observed results.

The vacuum was previously shown to be necessary to obtain sizing (1,2). The role of the vacuum could be two fold. First, it could be a mobilizing factor, increasing the rate of evaporation and mean free path of the volatile component. Secondly, it could serve to stabilize free radicals formed on cellulose by removing oxygen. Although Desai and Shields (1) claimed an inert atmosphere was insufficient, they did not say whether a vacuum degassing procedure was used to completely remove oxygen. Evidence to date does not allow one to say whether either or both of these roles are active.

The last unanswered question which comes to mind is that of how the present results fit in with the report by Desai and Shields (1). In an earlier report (3) on the volatile components formed upon irradiating cellulose, they used quartz tubes with rubber septa at both ends. "These ends were covered with filter paper to protect the rubber septa from any undue exposure to the radiation from the lamp." However, it is questionable whether this was adequate for the 24 hr exposures used. The volatile products reported all contained methyl groups and are easier to rationalize as rubber oxidation products than as cellulose-derived products.

In their report on photochemical sizing (1), they mention a new, aluminum apparatus but do not give details of construction. In view of the fact that they did not exclude rubber in their previous work, it may not be unfair to assume, lacking evidence to the contrary, that rubber or some other hydrophobic sealing material (e.g., vacuum grease) was used in their photosizing work. Therefore, it is possible that they too were observing sizing due to material external to the paper.

EXPERIMENTAL

All irradiations described herein were done with a Hanovia 450 watt medium-pressure mercury lamp mounted horizontally in the air inside an asbestos enclosure. This is not the same light source used by Nagel (2), but is similar to the one used by Desai and Shields (1,3). The sample to lamp distance was ca. 9 cm, and varied slightly from apparatus to apparatus. Test tubes were placed parallel to the axis of the lamp. All samples were evacuated until the pressure was less than 0.07 mm before starting the lamp and the pressure decreased to 0.03 mm during the irradiation. All irradiations described here were for 60 min.

A freshly opened box of Whatman No. 1 filter paper was used for all experiments. Some yellowing was observed due to irradiation. The test tubes and vacuum stage were equipment which was on hand. As such, the thickness of the quartz and perhaps the transmission characteristics at short wavelengths were somewhat different.

Sizing was determined by placing small (2-3 microliters) drops of water on the paper. On samples which were considered sized, the drops remained on the surface for at least two minutes--often until evaporation. On samples which were considered unsized, the droplets were absorbed almost immediately. It was difficult to distinguish the behavior from that of untreated filter paper. All such determinations were qualitative, but it was generally easy to tell whether a sample or portion of a sample was "sized" or "not sized."

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THE INSTITUTE OF PAPER CHEMISTRY

QUARTERLY RESEARCH REPORT

DIVISION: Natural Materials and Systems

DATE: October 2, 1974

✓ PROJECT NO.: 3134 "A Fundamental Study of the Photochemistry of Carbohydrates, Cellulose, and Related Compounds" (Institute Project) (FE)

Project Leader: R. D. McKelvey

OBJECTIVE:

1. Investigate the ultraviolet spectra of carbohydrates and related model compounds.
2. Mechanistic and exploratory studies on the photochemistry of carbohydrates and related models.
3. Extension into cellulose systems. Examine uses related to the modification and stabilization of cellulose.

BUDGET:

\$42,400 (2 years)

SCHEDULE: Original schedule---October 20, 1972 - October 24, 1974

Due to the general, exploratory nature of the project, no firm schedule was established. Objective 1 was completed. Work on objective 2 has centered on the acetal group. Little work has been done on objective 3.

This work was interrupted for about 6 months while work on photochemical decolorization of effluents (Project 1102-32) was carried out. Therefore, it is behind schedule as far as the budget is concerned. Spending through August 1974 accounted for 65% of the budget. Five reports were written and one manuscript was submitted to the Research Bulletin and Carbohydrate Research.

SUMMARY OF RESULTS AND PLANS FOR FUTURE WORK:

Studies of the ultraviolet spectra of carbohydrates did much to dispel the idea, which is common in the literature, of the "acetal chromophore." By careful purification of the compounds, it was possible to attribute the absorbance at ca. 275 nm to impurities. It is hoped that molecular orbital calculations can be done through the academic program to substantiate this conclusion.

PROJECT NO.: 3134

DATE: October 2, 1974

Model studies on the acetal group have centered around two reactions, a ring opening process and a chain cleavage process. These reactions help to explain the products observed in carbohydrate photochemistry. Preliminary results indicate that the relative importance of the two reactions might be sensitive to conformational effects. This could lead to the conclusion that cellulose and starch should have different photochemistry.

Present work involves the study of these conformational effects. It is hoped that this aspect can be completed soon and that work on cellulose modification can begin. There are several applications in the area of the photochemical attachment of sizing agents onto cellulose and light-initiated graft polymerization onto cellulose which should be tried. The photochemical technique adds the further dimension of imaging to our current technology.

If any of the above applications look promising, a project proposal could be written concerning further development. This would be dependent on the results obtained and the extent of interest in the techniques.

Several fundamental, mechanistic problems have been turned up by this work. It is anticipated that these will be of interest to students and that some will be examined through our academic research program.

Objectives for Next Quarter

1. Complete the work on the conformational effects which might control the ring opening and chain cleavage reactions.
2. Initiate work on the photochemical grafting or graft polymerization of olefins onto cellulose. This is envisioned as a feasibility study. If, as the work develops, the method looks promising, it is anticipated that a new project would be proposed.

Prepared by R. D. McKelvey

THE INSTITUTE OF PAPER CHEMISTRY

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Prepared by: R. D. McKelvey

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SIGNED Ronald D. McKelvey
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A FUNDAMENTAL STUDY OF THE PHOTOCHEMISTRY OF CARBOHYDRATES,
CELLULOSE, AND RELATED COMPOUNDS

The attached manuscript summarizes the work to date on ketone initiated hydrogen abstraction reactions of 2-methoxytetrahydropyran. The results help explain some of the reactions of carbohydrates in the literature. The manuscript is being submitted to the Research Bulletin of The Institute of Paper Chemistry and to Carbohydrate Research for publication.

PHOTOCHEMISTRY OF CARBOHYDRATE MODEL COMPOUNDS. I.
KETONE INITIATED HYDROGEN ABSTRACTION REACTIONS
OF 2-METHOXYTETRAHYDROPYRAN

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ABSTRACT

The reaction of 2-methoxytetrahydropyran with ketones under the influence of ultraviolet light was studied as a model for carbohydrate degradation. The two major "carbohydrate" products were methyl valerate and δ -valerolactone. With benzophenone in benzene, methyl 5-phenylvalerate was also formed. Two mechanistic pathways involving the 2-methoxytetrahydropyran-2-yl radical can account for the products. The relative importance of the two pathways was found to be a function of the ketone and solvent. An explanation based on conformational effects on a concerted, carbon-oxygen bond cleavage accompanying hydrogen abstraction is offered.

INTRODUCTION

The study of the photochemical reactions of carbohydrates is complicated by several factors. Most of the compounds have little or no absorbance in the accessible ultraviolet. This leads to the possibility of sensitized reactions originating from chromophoric impurities. The polyfunctionality of these materials gives rise to a large number of sites of comparable reactivity, giving complex product mixtures. In addition, many of the photoproducts absorb light more strongly than the starting materials and, therefore, secondary reactions can obscure primary processes.¹

Further frustrating efforts to understand the basic processes taking place is the fact that a wide variety of conditions have been employed in work reported in the literature.² Researchers interested in textiles are concerned with the effect of dyes on the photochemistry of cellulose.³ Others have studied the effects of inorganic additives on carbohydrate photochemistry.⁴ In most cases, oxygen is present in the system, which promotes more rapid reaction, but also leads to extensive degradation, in some cases all the way to carbon dioxide.¹

In many instances, authors report working with materials which show a weak absorption maximum at 260-280 nm.⁵ This has been ascribed to both the open chain, carbonyl form of the compounds⁶ and also to an absorption band of the "acetal chromophore" itself.⁷ Our experience has been that most commercial samples of carbohydrates show absorption in this region but, in most cases, careful recrystallization can completely remove the absorbing impurities. One might infer from this that impure samples have been used occasionally in the past. This conclusion was also reached by Bos.⁸

The most reasonable impurities would be carbonyl compounds, the absorption being due to the $n \rightarrow \pi^*$ transition. Such groups are almost certainly present as irregularities in cellulose.⁸ It was with these considerations in mind that we decided to examine the photochemistry of 2-methoxytetrahydropyran (MeOTHP), a model for a glycoside, in the presence of ketones.

A previous report⁹ of the reaction of MeOTHP, benzophenone, and benzene in the presence of ultraviolet light gave the major products as δ -valerolactone and methyl valerate (Eq. 1), formed in a ratio of 16:1 and a total yield, based on starting material consumed, of 41%. This product ratio seemed surprising since one would expect that the loss of methyl radical (path A, Eq. 2) from the proposed intermediate 2-methoxytetrahydropyran-2-yl radical would be less favorable

than the loss of the primary alkyl radical (path B) based on relative radical stabilities whereas the reported product ratio indicated the opposite. Further- more, di-t-butyl peroxide was reported to give methyl valerate as the major, volatile product in a thermal reaction and no valerolactone was found.¹⁰

[Cut 1 and 2 here]

In this paper, we would like to report: 1) the finding of another, major photoproduct in the above benzophenone, benzene system which indicates that path B is the major pathway; 2) a solvent effect in going to t-butyl alcohol favoring path A; 3) a change in product distribution in changing from benzophenone to acetone; and 4) a discussion based on concerted loss of alkyl radical during hydrogen abstraction.

RESULTS

Irradiation of MeOTHP in the presence of acetone or benzophenone and in the absence of oxygen led to the production of δ -valerolactone and methyl valerate. In addition, with benzophenone in benzene, methyl 5-phenylvalerate was a major product. This product was not identified in the previous report.⁹ The results (Table I) indicate that the product distribution is a function of both the solvent and the ketone.

[Table I here]

The products were identified by comparison of v.p.c. retention times on at least two different columns and infrared or n.m.r. spectra of samples collected from the v.p.c. column with those of authentic materials. Quantitative results were obtained by v.p.c. and assumed a molar flame ionization response proportional to molecular weight.

In addition to these major products, several other, minor products showed up in the chromatograms but, with the exception of biphenyl in Irradiation 4, were not identified. Biphenyl was identified only by retention time on two columns. Also, some relatively nonvolatile products must have formed in some cases, since not all of the starting material could be accounted for by the observed products. These minor products varied, both in amount and retention time, with the reaction conditions.

The difference in major product ratio might a priori be attributed to a lack of stability of methyl valerate and/or δ -valerolactone in the benzophenone and acetone systems, respectively. However, in control experiments these products were found to decompose to the extent of only 15% or less, even when irradiated for the full time of the MeOTHP irradiations. Since these products were gradually formed during the MeOTHP irradiations, the average exposure to the reaction conditions would have been less than in the control experiments. Therefore, product instability cannot account for the difference.

DISCUSSION

The mechanism previously proposed^{9,11} and shown in part in Eq. 2, accounts for δ -valerolactone and methyl valerate. In addition, the methyl 5-phenylvalerate found in Irradiation 4 can be accommodated by the mechanism by reaction of the methyl valer-5-ylate radical with the benzene solvent as shown in Eq. 3.

[Cut 3 here]

Thus, methyl valerate and methyl 5-phenylvalerate both derive from the ring opening path B shown in Eq. 2. Path B, therefore, accounts for 78% of the identified products in Irradiation 1 and 67% in Irradiation 4. In Irradiation 3, however, path B accounts for only 30% of the observed products.

No explanation of the lack of reaction in the acetone-benzene system (Irradiation 2) comes to mind. Benzene is known to be ineffective in quenching the triplet state of acetone in the gas phase.¹²

Comparison of Irradiations 1 and 3 indicates that the ketone can have an effect on the product distribution. Comparison of Irradiations 3 and 4 indicates that the solvent can also influence the reaction. There are two possible explanations for these effects.

The first rationale involves interaction with solvent and/or ketone (or an intermediate derived therefrom: e.g., ketyl radical) after the initial, hydrogen abstraction step. One possibility would be the formation of relatively nonvolatile products.

Irradiation 3 gave the largest amount of nonvolatile products (Table I). A side reaction of the initial, cyclic radical would consume starting material but should not change the relative importance of paths A and B. Therefore, this could not account for the change in product ratio. Loss of the methyl group results in the formation of δ -valerolactone and determines the amount of product observed by path A. This leaves side reactions of the ring-opened methyl valer-5-ylate radical to account for the differences.

Possible side reactions include radical couplings. Dimethyl sebacate, the product of dimerization of the open chain radical, was not formed in amounts greater than 1% in these irradiations, as shown by v.p.c. Therefore, the possibility of coupling with the ketyl radical formed from benzophenone (Eq. 4) remains. One might expect this reaction to be more important with benzophenone than with acetone due to the greater stability of the delocalized ketyl radical. Furthermore, in *t*-butyl alcohol, the route to methyl 5-phenylvalerate is not available. Therefore, one would expect the reaction shown in Eq. 4 to be most important in Irradiation 3.

[Cut 4 here]

The second rationale involves interaction of solvent and/or ketone during the initial, hydrogen abstraction step. In order for such interaction to influence the product distribution, the product determining step, i.e., loss of alkyl radical, must be concerted with hydrogen abstraction. The transition state would have the carbon-oxygen bond partially broken while the ketone was breaking the carbon-hydrogen bond. Such a transition state, with two bonds partially broken, would be energetically favorable only if compensated for by the partial formation of the carbonyl double bond. Therefore, appreciable overlap between the orbitals being "liberated" by the bond breaking process must develop in the transition state. This is illustrated in Fig. 1.

[Fig. 1 here]

In order for significant overlap to develop in the transition state, the two bonds being broken must be parallel. Steric considerations would favor an anti elimination over a syn elimination. This transition state is analogous to the anti-periplanar transition state favored in E2 eliminations.

Figure 1 shows that those conformations of MeOTHP in which the methoxy group is axial (equatorial H) have the C6-O bond (tetrahydropyran numbering) parallel to the C2-H bond. The continuous increase in carbonyl orbital overlap would result in ring cleavage, giving the open chain radical. Conformation 2, in which the methoxy group is axial and the methyl group is anti in relation to the C2-H, would have available in addition a second mode of reaction in which the methyl-oxygen bond is broken, giving valerolactone and methyl radical.

Figure 1 also shows that the conformations of MeOTHP in which the methoxy group is equatorial cannot undergo ring cleavage in concert with hydrogen abstraction and develop significant orbital overlap between the orbitals being

formed on carbon and oxygen. The angle between these orbitals would be ca. 60 degrees. Furthermore, only Conformation 3 could give valerolactone in a concerted fashion.

MeOTHP has been shown by n.m.r. to exist as a mixture of 72% axial methoxy and 28% equatorial methoxy at 38° as the neat liquid.¹³ Using the same method, values of 86% axial and 69% axial were found in benzene and tertiary butyl alcohol, respectively (see Experimental). This is consistent with the anomeric effect and its dependence on solvent dielectric constant.

This difference in conformational population is in the right direction but not of sufficient magnitude to account for the difference between Irradiations 3 and 4. Other steric effects involving solvent and/or ketone are necessary to account for all of the results. Different degrees of solvation of the various conformations and different steric requirements for hydrogen abstraction by the two ketones could account for the product distributions observed.

The implication of this mechanistic reasoning, if it is shown to be correct, is that α -glycosides which are conformationally mobile with respect to movement of the aglycone should have both ring opening and oxidative deglycosylation paths available to them whereas β -glycosides should have only the deglycosylation path available. For polysaccharides, the ring opening process would not reduce the molecular weight directly whereas deglycosylation would give chain cleavage.

Although a variety of results have been reported for cellulose,¹⁴ a common observation is a reduction in molecular weight. At least one author¹⁵ has suggested a mechanism involving hydrogen abstraction at the anomeric carbon by excited oxygen leading to chain cleavage and lactone formation. Although light absorption by oxygen at 254 nm seems insignificant¹⁶ (extinction coefficient ca. $10^{-5} \text{ cm}^{-1} \text{ atm}^{-1}$), the mechanism was, otherwise, similar to that suggested here.

We are presently looking at conformationally rigid model systems in an attempt to test the concertedness of the reaction.

EXPERIMENTAL

Starting materials

Reagent-grade benzene was stirred with sulfuric acid and distilled. Tertiary butyl alcohol was refluxed with and distilled from calcium hydride. Acetone was distilled from potassium permanganate. Benzophenone was recrystallized twice from 95% ethanol. 2-Methoxytetrahydropyran was prepared by the method of Woods and Kramer.¹⁷ No impurities were detected by n.m.r. or v.p.c.

Irradiations

Irradiations were carried out in a Rayonet Photochemical Reactor (Southern New England Ultraviolet) with RPR 3000 lamps using pyrex tubes as filters. This assured that only ketones were absorbing light. Dilute solutions (see Table II) were deoxygenated by bubbling nitrogen through the solution for 20-30 min prior to and during irradiation or by at least three freeze-pump-thaw cycles followed by sealing the tube in vacuo.

[Table II here]

Control experiments

Two solutions were prepared, degassed by three freeze-pump-thaw cycles, sealed in vacuo, and irradiated as above for 21 hr. The first solution, composed of 0.180 g of valerolactone, 1.6 g of acetone, and 18 ml of t-butyl alcohol, showed 84% of the original valerolactone concentration and no new peaks in the gas chromatogram after irradiation. The second solution consisted of 0.089 g of methyl valerate, 0.184 g of benzophenone, and 20 ml of benzene and showed 88% of the original methyl valerate concentration and a new peak corresponding to 12% of the original methyl valerate concentration.

Product analysis

Products were identified by preparative v.p.c. followed by spectral comparison with known samples. Methyl valerate was identified by n.m.r. spectroscopy while δ -valerolactone and methyl 5-phenylvalerate were identified by infrared. All compounds showed retention times identical to authentic samples on two or more v.p.c. columns. Biphenyl was identified in Irradiation 4 by retention time only.

Quantitative analysis was carried out by v.p.c. A molar response proportional to molecular weight was assumed for the flame ionization detector for the identified products. Unidentified, minor products were assumed to have a response equal to that of MeOTHP. Columns used were: 10% Carbowax 20M on 60/80 Chromosorb W, 1/8" x 6'; 20% Carbowax 1500 on 100/120 Gas Chrom Q, 1/8" x 20'; 3% OV-17 on 100/120 Gas Chrom Q, 1/8" x 4'. Preparative v.p.c. was done on 5% SE-30 on 60/70 Anakrom ABS, 1/4" x 5'.

N.m.r. analysis of the conformation of 2-methoxytetrahydropyran

N.m.r. spectra of MeOTHP were run in benzene and *t*-butyl alcohol. The signal for H-2 ("anomeric proton") was then used to determine the axial: equatorial ratio according to the method of Pierson and Runquist,¹³ who determined the ratio for neat MeOTHP. The distance between the outer peaks (shoulders) of the broad triplet was 5.5 ± 0.5 Hz in benzene and 6.5 ± 0.5 Hz in *t*-butyl alcohol. These values correspond to $86 \pm 10\%$ and $69 \pm 10\%$ axial methoxy, respectively. Pierson and Runquist found a value of 72% for the neat liquid.

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TABLE I

COMPOSITION OF SOLUTIONS AFTER IRRADIATION^a

Irradiation ^b	Sensitizer	Solvent	MeOTHP	MeVal ^c	Val ^d	MePhVal ^e	Minor ^f
1	Acetone	<u>t</u> -BuOH	53	18	5	--	14
2	Acetone	benzene	100	0	0	0	0
3	Benzophenone	<u>t</u> -BuOH	64	3	7	—	0
4	Benzophenone	benzene	58	7	14	22	10 ^g

^aV.p.c. analysis of products at least as volatile as benzophenone (mole percent of original MeOTHP concentration).

^bSee Table II for details.

^cMeVal = methyl valerate.

^dVal = δ -valerolactone.

^eMePhVal = methyl 5-phenylvalerate.

^fMinor products not identified; yield based on original MeOTHP concentration.

^gIncludes 3% biphenyl.

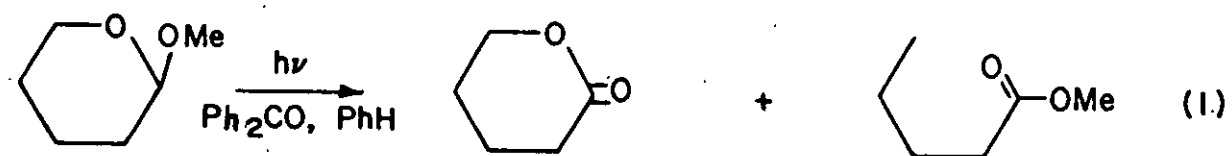
TABLE II

IRRADIATIONS

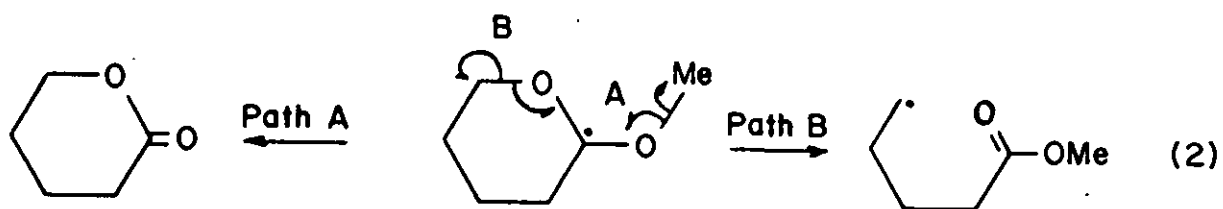
Irradiation	Solvent (ml)	Ketone (g)	MeOTHP (g)	Time (hr)
1	<u>t</u> -BuOH (18)	Acetone (1.6)	0.628	21
2	Benzene (18)	Acetone (2.4)	0.585	36
3	<u>t</u> -BuOH (20)	Benzophenone (0.185)	0.122	16
4	Benzene (20)	Benzophenone (0.188)	0.118	19

Figure Caption

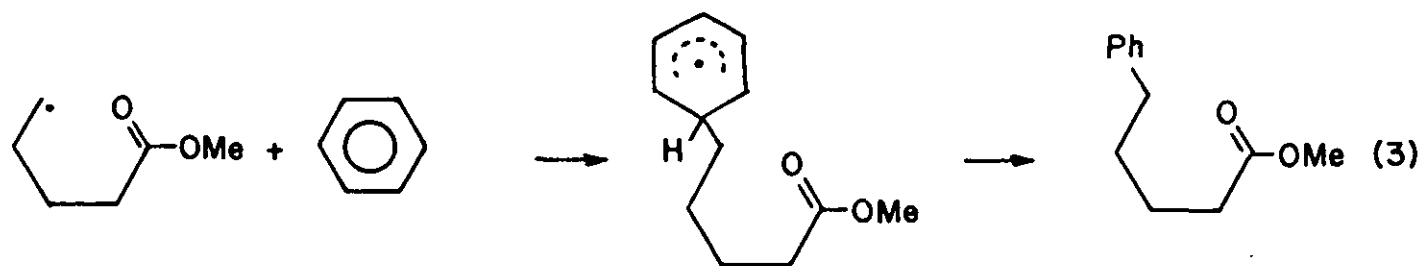
Figure 1. Orbital Overlap for Concerted Elimination



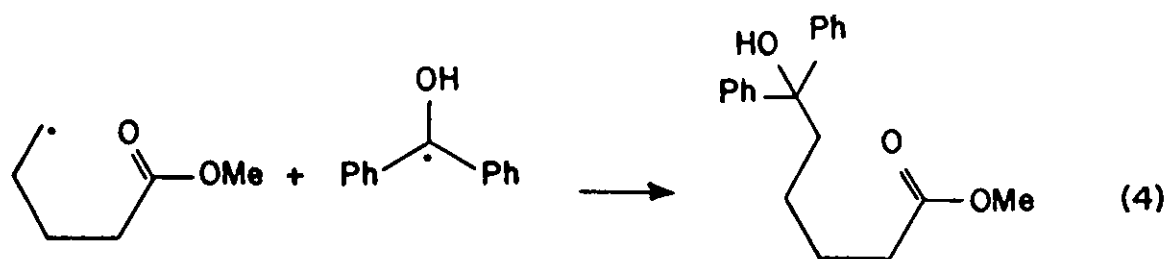
Cut 1



Cut 2



Cut 3



Cut 4

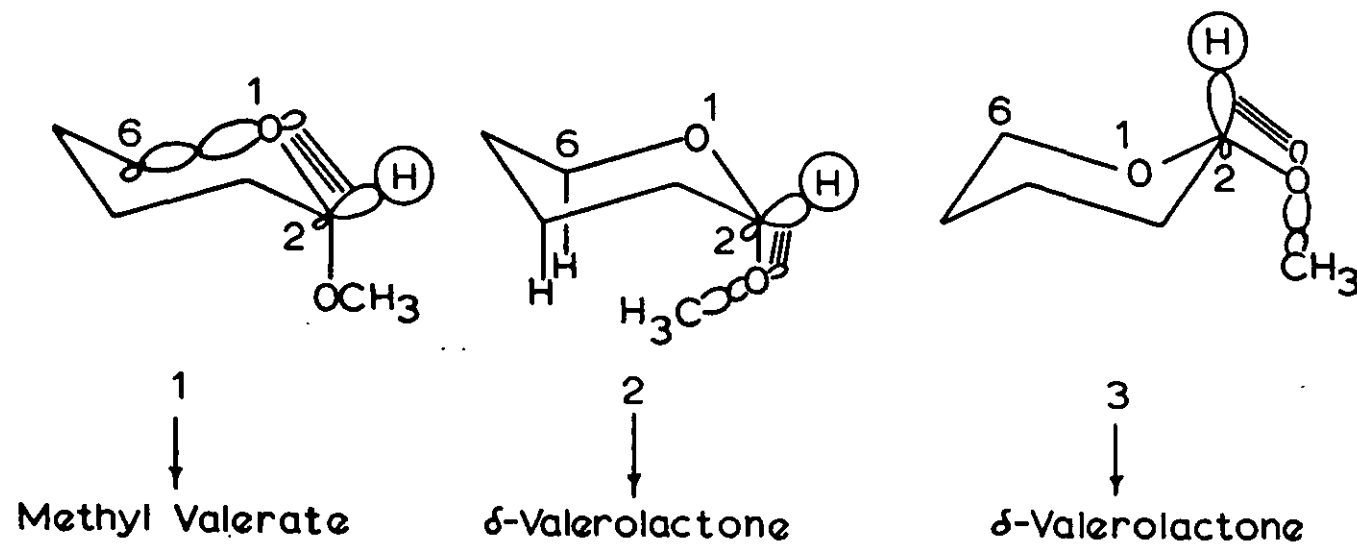


Figure 1. Orbital Overlap for Concerted Elimination