

FINAL REPORT

PROJECT NO. A-296

METHYLENE RADICALS IN SOLUTION

By

JACK HINE, ARTHUR D. KETLEY, KOZO TANABE
and JAMES M. VAN DER VEEN



DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
CONTRACT NO. NONR-991(03)

16 JUNE 1959



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SUMMARY

The work carried out under this contract consisted largely of studies of reactions of alcohols and alkoxy and aryloxy anions with dihalomethylenes generated from haloforms and bases. Evidence was obtained that alkoxyhalomethylenes can be generated as reaction intermediates. The Reimer-Tiemann reaction was shown to proceed via a dihalomethylene intermediate. The reactions of dibromomethylene, dichloromethylene and chlorofluoromethylene with potassium isopropoxide in isopropyl alcohol were found to proceed by significantly different paths. From the nature of these paths valuable information about the chemistry of methylenes was obtained.

The work done under this contract consisted largely of studies of reactions of dihalomethylenes with oxygen-containing nucleophilic anions. The first study was an attempt to find evidence for the intermediacy of a methylene derivative other than a dihalomethylene. It was initially planned to attempt the α -dehydrohalogenation of a difluoromethyl ether in order to generate an alkoxyfluoromethylene..



It was found, however, that the isopropyl difluoromethyl ether, prepared by the action of potassium isopropoxide in isopropyl alcohol on chlorodifluoromethane at 0°, was inert to potassium isopropoxide, even at 50°. It was then realized that this inertness shows that the triisopropyl-orthoformate produced as a by-product in the reaction at 0° must have been formed via the intermediate, isopropoxyfluoromethylene. The evidence for this point was described briefly in Technical Report No. 1 (J. Am. Chem. Soc., 79, 2654 (1957).) and in greater detail in Technical Report No. 2 (J. Am. Chem. Soc., 80, 3002 (1958).). In the latter report quantitative measurements

are described that permitted certain more detailed conclusions to be drawn about the mechanistic nature and relative importance of various steps of the reaction. In the course of this investigation a method of drying and determining the water content of isopropyl alcohol was worked out and from the data obtained it was found possible to calculate the true second order rate constants for the hydrolysis of an ester by hydroxide ion in alcoholic solution (see Technical Report No. 3; J. Phys. Chem., 62, 1463 (1958).).

Since it seems probable that the Reimer-Tiemann reaction is an example of the reaction of an aryloxide ion with a dihalomethylene we studied this reaction. From the fact that sodium phenoxide, chloroform and sodium hydroxide react rapidly to give o - and p - hydroxybenzaldehyde under conditions where chloroform is relatively inert to the action of sodium phenoxide alone we have concluded that the Reimer-Tiemann reaction does indeed proceed by a dihalomethylene intermediate. This work is described in detail in Technical Report No. 4.

Since the course of the reaction of potassium isopropoxide with chlorodifluoromethane was so different from that previously reported for the reaction between other haloforms and alkali metal alkoxides, it was decided to study the reaction of potassium isopropoxide with other haloforms in some detail. These studies are described in Technical Report No. 5. Dichlorofluoromethane was found to give triisopropyl orthoformate in high yield. Chloroform and bromoform were found to give methylene halides, carbon monoxide, propylene, diisopropyl ether, and acetone, as well as the orthoester and under some conditions, dark colored products of high molecular weight. Mechanistic

explanations are given for these observations which shed considerable new light on the chemical behavior of methylene derivatives.

Respectfully submitted,

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Approved:

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