[CONTRIBUTION FROM SYNTHETIC FUELS RESEARCH BRANCH, BUREAU OF MINES]

The Reduction of Simple Olefins with Sodium and Methanol in Liquid Ammonia[1]

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1-Hexene and 2-cyclopropyl-1-pentene are unaffected by sodium in liquid ammonia and by sodium and ammonium bromide in liquid ammonia; however, they are reduced by sodium and methanol in liquid ammonia to hexane and 2-cyclopropylpentane, respectively. 2-Hexene is unaffected by sodium and methanol in liquid ammonia.

It has been proposed that a conjugated cyclopropylalkene behaves like a conjugated diene toward catalytic hydrogenation, and can add hydrogen by either a 1,2- or a 1,4-mechanism.[3]

Our interest in the mechanism of homogeneous hydrogenation[4] prompted the study of the reduction of cyclopropylalkenes by sodium in liquid ammonia. Conjugated dienes are reduced by this reagent, whereas simple monoölefins are unaffected.[5] The reduction of methyl cyclopropyl ketone by sodium and ammonium sulfate in liquid ammonia yields 2-pentanone and 2-pentanol exclusively.[3b] This reaction presumably involves a conjugate type of reduction.

In the present study it was found that 2-cyclopropyl-1-pentene was unaffected by sodium in liquid ammonia and by sodium and ammonium bromide in liquid ammonia, but was reduced by sodium and methanol in liquid ammonia to 2-cyclopropylpentane. No other product, except the starting olefin, was obtained.

Although the literature[5] contains numerous examples of the inertness of simple monoölefins to sodium in liquid ammonia, there is no example of the reaction of a simple olefin with sodium and liquid ammonia in the presence of a hydrolytic agent. The successful reduction of the cyclopropylalkene prompted us to extend the study to 1-hexene and 2-hexene.

1-Hexene gave a 41% yield of hexane with sodium and methanol in liquid ammonia when the theoretical amount of sodium was used. The remainder of the product was unreacted 1-hexene. 2-Hexene was unaffected under the same conditions. No reaction took place with 1-hexene when ammonium bromide was employed as the hydrolytic agent instead of methanol.

Experimental

All reactions were run in a clear Dewar vessel which was fitted with a sealed stirrer, an addition tube, and a Dry Ice condenser with a sodium hydroxide drying tube.

Reaction of 1-Hexene with Sodium and Ammonium Bromide in Liquid Ammonia.—To a mixture of 8.4 g. (0.10 mole) of 1-hexene (Phillips Petroleum Co., pure grade) and 150 ml. of a liquid ammonia solution containing 39.2 g. (0.40 mole) ammonium bromide was added 4.6 g. (0.20 mole) sodium over a period of 40 minutes. The reaction mixture never acquired more than a pale blue color, indicating that the sodium was reacting very rapidly after it had dissolved in the liquid ammonia. Stirring was continued for 30 minutes and the reaction mixture was then diluted with cold water. The infrared spectrum of the organic layer indicated that it was pure 1-hexene. Apparently the sodium had reacted only with ammonium ion.

Reaction of 1-Hexene with Sodium and Methanol in Liquid Ammonia.—A mixture of 21.0 g. (0.25 mole) of 1-hexene and 32 g. (1.0 mole) of methanol was diluted with liquid ammonia to a total volume of about 300 ml., and 11.5 g. (0.50 mole) of sodium was added over a period of 100 minutes. Stirring was continued for 60 minutes, and the white reaction mixture was then diluted with cold water. The infrared spectrum of the organic layer showed it to be a mixture of 1-hexene and hexane. Mass spectrographic analysis indicated that 41% of the mixture consisted of hexane.

Reaction of 2-Hexene with Sodium and Methanol in Liquid Ammonia.—A mixture of 21.0 g. (0.25 mole) of 2-hexene (Phillips Petroleum Co., technical grade) and 32 g. (1.0 mole) of methanol was diluted with liquid ammonia to a total volume of about 300 ml., and 11.5 g. (0.50 mole) sodium was added over a period of 85 minutes. Stirring was continued for 40 minutes, and the white reaction mixture was then diluted with cold water. Infrared and mass spectrographic analysis of the organic layer indicated the formation of a maximum of 0.5% of hexane, some or all of which may have been derived from impurities in the 2-hexene.

Reaction of 2-Cyclopropyl-1-pentene with Sodium and Liquid Ammonia.—To a mixture of 10.1 g. (0.09 mole) of 2-cyclopropyl-1-pentene and 200 ml. of liquid ammonia was added 0.24 g. (0.01 mole) of sodium. Stirring was continued for 4 hours, at the end of which time the reaction mixture still had the deep blue color characteristic of solutions of sodium in liquid ammonia. The sodium was treated with ammonium bromide and the reaction mixture diluted with cold water. The infrared spectrum of the organic layer indicated that it was pure 2-cyclopropyl-1-pentene.

Reaction of 2-Cyclopropyl-1-pentene with Sodium and Ammonium Bromide in Liquid Ammonia.—To a mixture of 11.1 g. (0.10 mole) of 2-cyclopropyl-1-pentene and a solution of 44.1 g. (0.45 mole) of ammonium bromide in 200 ml. of liquid ammonia was added 9.2 g. (0.40 mole) of sodium over a period of one hour. Stirring was continued for 3 hours, and the white reaction mixture was then diluted with cold water. The infrared spectrum of the organic layer indicated that it was pure 2-cyclopropyl-1-pentene.

Reaction of 2-Cyclopropyl-1-pentene with Sodium and Methanol in Liquid Ammonia.—To a mixture of 22.2 g. (0.20 mole) of 2-cyclopropyl-1-pentene, 60 ml. (*ca.* 1.5 moles) of methanol and 100 ml. of liquid ammonia was added 18.5 g. (0.80 mole) of sodium over a period of 3 hours. Stirring was continued for 1.5 hours and the white reaction mixture diluted with cold water. Infrared analysis of the organic layer indicated that *ca.* 40% of the 2-cyclopropyl-1-pentene had been reduced to 2-cyclopropylpentane, and that no other products had been formed.

Discussion

In 1951, King reported the only example of the chemical reduction of a carbon–carbon double bond that was not conjugated with another unsaturated center.[6] He found that three allyl-

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(1) Presented at the Meeting in Miniature of the Pittsburgh Section of the American Chemical Society on June 11, 1953.

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(3) (a) R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **71**, 172 (1949); (b) **71**, 3595 (1949); (c) V. A. Slabey and P. H. Wise, *ibid.*, **74**, 3887 (1952).

(4) (a) I. Wender, R. Levine and M. Orchin, *ibid.*, **72**, 4375 (1950); (b) I. Wender, M. Orchin and H. H. Storch, *ibid.*, **72**, 4842 (1950); (c) I. Wender, H. Greenfield and M. Orchin, *ibid.*, **73**, 2656 (1951); (d) M. Orchin, in "Advances in Catalysis," **5**, edited by W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Academic Press, Inc., New York, N. Y., 1953.

(5) For excellent reviews see (a) A. J. Birch, *Quart. Rev.*, **4**, 69 (1950); (b) G. W. Watt, *Chem. Revs.*, **46**, 317 (1950).

(6) T. J. King, *J. Chem. Soc.*, 898 (1951).

amines, N-allylpiperidine, N-2-methylallylpiperidine and diethyl-2-methylallylamine, were reduced by sodium and methanol in liquid ammonia to the corresponding saturated amines, while N-crotylpiperidine, N-2-*t*-butylallylpiperidine, N-cyclohex-2-enylpiperidine and N-2,3,4,5-tetrahydrobenzylpiperidine were unaffected by the same reagent. In no case was a non-terminal olefin reduced.

The successful reduction of 1-hexene invalidates the generally held opinion that isolated carbon–carbon double bonds are inert in metal–liquid ammonia systems. Failure to obtain reduction of 2-hexene is consistent with King's observation[6] that reduction of non-conjugated olefins under these conditions is confined to terminal double bonds. A satisfactory interpretation of these results must await further experimental data.

The reduction of 2-cyclopropyl-1-pentene by sodium and methanol in liquid ammonia does not appear to proceed more readily than the similar reduction of 1-hexene and gives no ring-opening products. The reduction of the cyclopropyl olefin would thus indicate that the conjugation between the cyclopropyl group and the ethylenic linkage is not a first-order conjugation. This result is in agreement with considerable spectroscopic evidence that the conjugation of the cyclopropyl group with an unsaturated center is a second-order conjugation, that is, hyperconjugation.[7]

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(7) For leading references, see R. P. Mariella and R. R. Raube, This Journal, **74**, 518 (1952).

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[Contribution from the Department of Chemistry of the University of Kansas]

Reaction of Propylene Oxide with Hydrogen Halides

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Extent of attack on the secondary carbon by halide ion on propylene oxide in ring-opening reactions with hydrogen chloride, hydrogen bromide and with hydrogen iodide has been found to decrease in the order Cl > Br > I and to increase with increase in temperature. Entropies and enthalpies of activation have been calculated and the differences are rationalized by consideration of transition state structures. Significant solvent effects in the reactions also have been observed. Addition of positive halogen 3,5-dinitrobenzoates to propylene has been found to afford largely the secondary ester, with an increase in primary ester formation accompanying an increase in temperature. Analysis of isomeric content of reaction products was accomplished largely by infrared spectrophotometric methods.

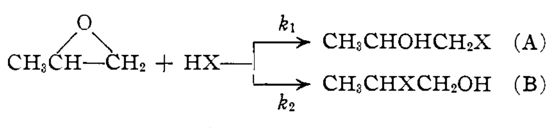
As part of a general study of factors affecting the direction of ring opening in unsymmetrically substituted ethylene oxides, a comparison has been made of the reactions of the simplest of these compounds, propylene oxide, with hydrochloric, with hydrobromic and with hydriodic acid. The choice of propylene oxide as a substrate for such a study was dictated by the following considerations: (1) the reaction of propylene oxide with hydrochloric acid is known[1] to give a mixture of isomers; (2) from the data of Levene and Walti,[2] it may be assumed that reaction at either carbon takes place with Walden inversion and that the kinetics for both reactions are presumably the same; (3) the smaller the molecule, the greater are the expected differences in the properties of the primary and secondary alcohol products, since the functional group is a correspondingly greater part of the molecule; and (4) the propylene chlorohydrins have already been prepared and characterized.[3]

Smith and Skyle[1] reported that both hydrochloric and hydrobromic acids gave 90% of attack of halogen at the primary carbon of glycidol, while 1,2-epoxybutane has been found[4] to give increasingly greater attack in the primary position as the size of the halogen increases. In this connection, it is significant that Swain[5] has provided quantitative evidence for the long accepted generalization that the base strengths toward carbon of the halide ions are in the same order as the size of the ions, that is, chloride < bromide < iodide.

From the theory of absolute reaction rates, the relative rates of formation of two isomers from the same reactants may be related by the equation[6]

$$\ln \frac{k_1}{k_2} = \frac{\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger}}{R} - \frac{\Delta H_1^{\ddagger} - \Delta H_2^{\ddagger}}{RT} \qquad (1)$$

If k_1 and k_2 are constants for the reactions



$$CH_3CH\overset{O}{—}CH_2 + HX \begin{cases} \xrightarrow{k_1} CH_3CHOHCH_2X & (A) \\ \xrightarrow{k_2} CH_3CHXCH_2OH & (B) \end{cases}$$

then from a plot of the reciprocal temperature *versus* the logarithmic ratio of product A to product B obtained in the reaction, it should be possible to evaluate the differences in entropy and enthalpy of activation from the intercept and slope of the straight line predicted from the equation 1. If the differences between chloride, bromide, and iodide are due only to steric effects, one might expect that the en-

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