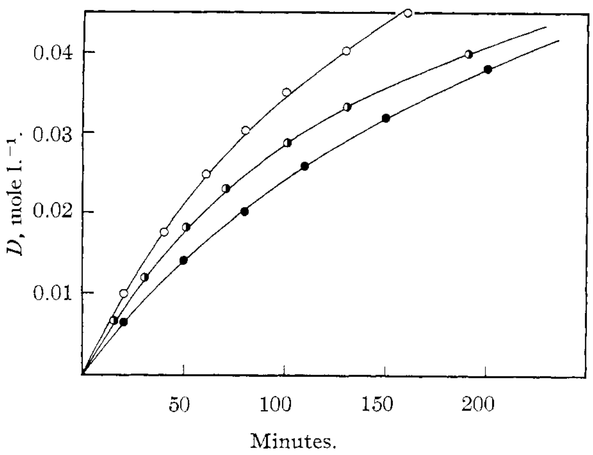

Fig. 3.—D *vs.* t curves for the reaction of 2,4-dinitrochlorobenzene and allylamine in 2-phenylethanol at 24.8 ± 0.1°: ○, A_0 = 0.3948 M, B_0 = 0.1283 M; ◑, A_0 = 0.05127 M, B_0 = 0.6589 M; ●, A_0 = 0.2477 M, B_0 = 0.129 M.

where $\beta = k_1 + k_3B_0 + k_4A_0$, and

$$\gamma = k_5 - 2k_3 - k_4$$

The ability of eq. 5 to fit the experimental data was tested by the methods described previously.[1] Preliminary values for k_1, k_3 and k_4 were obtained from plots of k_2 *vs.* B_0 at constant A_0 and k_2 *vs.* A_0 at constant B_0. An initial value for k_5 was obtained from the experiment in Table IV in which N-allyl-2,4-dinitroaniline, D, was added. These values were: $k_1 = 1.37 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$, $k_3 = 1.11 \times 10^{-4}$ l.^{2}mole^{-2}sec.$^{-1}$, $k_4 = 0.74 \times 10^{-4}$l.^{2}mole^{-2}sec.$^{-1}$, $k_5 = 1.4 \times 10^{-4}$l^2 mole^{-2}sec.$^{-1}$.

The above rate constants and eq. 5 were used to calculate D *vs.* t curves for comparison with the experimental curves. The values of the rate constants were then varied by a trial and error process to obtain optimum coincidence of calculated and experimental D *vs.* t curves. The rate constants that finally resulted were: $k_1 = 1.35 \times 10^{-4}$ l.mole^{-1}sec.$^{-1}$, $k_3 = 1.2 \times 10^{-4}$ l.^{2} mole^{-2}sec.$^{-1}$, $k_4 = 0.7 \times 10^{-4}$l.^{2}mole^{-2}sec.$^{-1}$, $k_5 = 1.3 \times 10^{-4}$ l.^{2}mole^{-2}sec.$^{-1}$.

These rate constants give excellent agreement between calculated and experimental D *vs.* t curves for all eight experiments in Table III. Six of these comparisons are shown in Figs. 2 and 3. The smooth lines are the calculated curves, and the circles represent experimental points. These experiments cover an almost eightfold variation in B_0 and more than a fivefold variation in A_0. There is no combination of two rate constants, k_1 and k_3, that will give satisfactory fits over this range of initial concentrations. It is possible that simultaneous variation of two or more of the rate constants can be made to yield a new set of values which will give satisfactory fits, but our experience in fitting these curves suggests limits of less than 10% for any of the four rate constants.

A reaction mechanism consistent with this complex kinetic pattern has been presented previously[1] and need not be repeated here. The fact that the present data obtained in 2-phenylethanol are explained by the considerations applied previously to the chloroform case lends further support and generality to the mechanism. It seems reasonable that this mechanism should be considered in all solvents, although it is clear that in some solvents, *e.g.*, ethanol, some of the rate constants may be negligible in magnitude or totally absent.

A still further element of generality is added to this mechanism by the results in Table IV, which make it clear that this reaction can be promoted by compounds other than those containing the amino or nitro function. The carbonyl groups in benzil and the sulfoxide and sulfone linkages are all groups which are capable of participating as hydrogen bond acceptors and are all effective in accelerating the rate of reaction of 2,4-dinitrochlorobenzene with allylamine in 2-phenylethanol. In the quantities involved in the experiments of Table IV, it seems improbable that these compounds are functioning by altering the characteristics of the reaction medium. A more probable explanation is that previously offered for the accelerating effect of the nitro group.[1] Benzotrifluoride might also have been expected to catalyze the reaction. The reason for its failure to do so is not clear, but possible complicating factors lie in the difference between N—H···F and N—H···O hydrogen bonds and in steric considerations relating to the trifluoromethyl group.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 21, N. Y.]

C *versus* O Alkylation in the Case of a Stable Cation

BY MALCOLM BERSOHN

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The sodium salt of 2-nitropropane converted 3-bromocyclohexene to cyclohexenone whereas a C-alkylated product was obtained with tropylium bromide. It is suggested that the C-alkylation of the stable cycloheptatrienylium ion involves a reversible dissociation to give the equilibrium product.

The researches of Kornblum and co-workers[1] have led to the useful generalization postulated by him that in graded S_N1-S_N2 displacement reactions involving ambident anions, for a particular anion, the greater the S_N1 character of the transition state, the more predominant is bond formation by the most electronegative atom of the ambient

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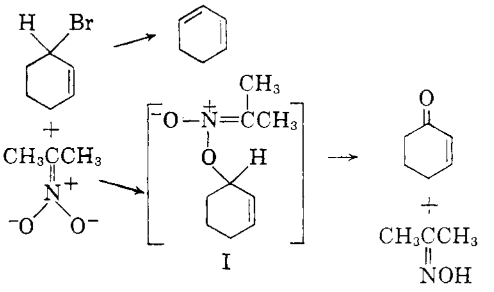
[1] (a) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955); (b) N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

anion, which is the atom bearing the greatest negative charge in the ground state. As pointed out by Kornblum and Lurie,[1b] with carbonium ions, cognizance must be taken of the greater or lesser non-selectivity which is a characteristic of such highly energetic species.

The 2-nitropropane anion was first allowed to react with 3-bromocyclohexene, the reaction leading partially to dehydrohalogenation and partially (44%) to Δ^2-cyclohexenone and a roughly corresponding quantity of acetone oxime.[2] The assumed intermediate nitronic ester I is not stable enough to be isolated at room temperature.[3] In that part of the bromide which underwent displacement, O-alkylation clearly predominated as no C-alkylated product was isolated. We see here that allylic halides, even as virtually all benzylic halides, on undergoing a displacement reaction with 2-nitropropane form a bond to oxygen rather than to carbon. Hass and Bender[3] showed that in the case of benzyl halides the displacement is kinetically second order.

When the 2-nitropropane anion was treated under identical conditions with Doering's cycloheptatrienylium ion in the form of tropylium bromide,[4] the isolated product (68% yield) was a crystalline compound with infrared absorption peaks at 6.51 and 7.41 μ corresponding to a tertiary nitro compound and ultraviolet absorption λ_{max} in 95% ethanol 259 mμ, log ε 3.61, which is similar to that of reported cycloheptatriene derivatives.[5] Hydrogenation removed the ultraviolet absorption and gave an amine whose acetyl derivative gave an analysis in agreement with expectation for III. The product then is II and O-alkylation evidently predominates. No tropone was detected by infrared examination of the crude product, nor was any acetone oxime found.

The kinetic product to be expected from this reaction is the O-alkylation product. This is because *charge neutralization is important at distances where covalent bonding energies are negligible.*[6] Thus two hydrogen atoms coming from infinite separation to a distance of 4 Å. lose negligible amounts of energy[7] either on account of overlap of their charge distributions or van der Waals effects, whereas if the separation between a hydride ion and a proton in methanol is decreased from infinity to 4 Å. the loss of potential energy due to charge neutralization is about 2.5 kcal. per mole. (The calculation assumes Coulombic point charges.) Even in going from 4 to 3 Å. separation the decrease in energy in the ionic case is 0.8 kcal., whereas in the atomic case the decrease in energy (increase in bonding energy) is only 0.4 kcal. Solvation reduces the magnitude of this effect but by no means eliminates it, for solvated ions still behave like charged bodies. This effect will increase the probability that an ambident anion will approach a carbon atom bearing a positive charge with its most negatively charged atom rather than with the atom which might form a stronger covalent bond but has less negative charge. The carbon of the enolate anion and the nitroalkane ion and the nitrogen of the nitrite ion should form stronger bonds than oxygen because their bond formation leaves intact the carbonyl or nitro group resonance stabilization. The O-alkylation product is thus presumed to be rate determined and less stable.



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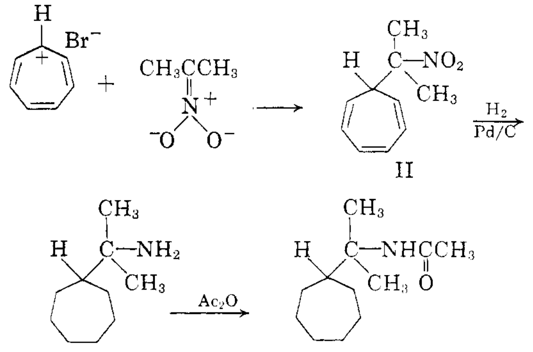

II

III

The unexpected experimental result is plausibly rationalized by assuming that the dissociation of the less stable O-alkylation product back into the two stable ions which formed it is much more rapid than the elimination of acetone oxime. Hence the more stable C-alkylated product can steadily accumulate, although in this view it is formed more slowly.

Experimental[8]

2-Cyclohexenone.—Sodium 782 mg., was dissolved in 40 ml. of anhydrous methanol which had been distilled twice from calcium hydride. To this solution was added at room temperature under nitrogen 3.94 g. (44 mmoles) of 2-nitropropane which had been dried over Drierite and then 5.5 g. (34 mmoles) of 3-bromocyclohexene. After 20 hours the methanol and cyclohexadiene were distilled at atmospheric pressure and collected. The distillate mixture had ultraviolet absorption with λ_{max} at 256 mμ. The residue was dissolved in water and ether. The ethereal extract was washed twice with 10% sodium hydroxide solution to remove the excess 2-nitropropane, then once with saturated sodium chloride solution. The ether solution was next dried over magnesium sulfate and the ether was removed by evaporation. The residue boiled at 70–75° at water-pump pressure. The yield of distilled colorless product was 1.43 g. (44%); 1.00 g. of the product formed 2.64 g. (93%) of twice recrystallized 2,4-dinitrophenylhydrazone of 2-cyclohexenone, m.p. 162–163°. Acidification and continuous ether extraction of the aqueous layers gave 963 mg. of acetone oxime.

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(2) This type of reaction has been reported for a number of allylic halides by M. Montavon, *et al., Helv. Chim. Acta*, **40**, 1250 (1957).

(3 H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949).

(4) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 3205 (1957).

(5) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 352 (1954).

(6) For a graphical depiction of this principle *vide* W. J. Moore, "Physical Chemistry," Prentice Hall, Inc. New York, N. Y., 1956 pp. 296, 297.

(7) *I.e.* about 0.05 kcal. per mole, interpolated from J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 132 (1950), Table II.

(8) Melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., and Microtech Laboratories, Skokie, Ill.

1-(Dimethylnitromethyl)-2,4,6-cycloheptatriene (II).—Sodium (360 mg., 15.7 mmoles) was dissolved in 27 ml. of methanol which had been distilled twice from calcium hydride. To this solution was added at room temperature under nitrogen 1.84 g. (21 mmoles) of 2-nitropropane which had been dried over Drierite. To the mixture was added all at once 2.65 g. (15.5 mmoles) of cycloheptatrienylium bromide with continuous stirring. The stirring was continued for 16 hours. At the end of this time the methanol was removed below room temperature by the water-pump. The residue was extracted with several portions of ether and then evaporated at room temperature with a stream of nitrogen. The crystalline residue remaining had no infrared absorption maxima between 5.86 and 6.35 μ. It had strong sharp maxima at 6.51 and 7.41μ. The product formed star-shaped crystals with a pleasant odor, instantly soluble in methanol or pentane. It was sublimed at 70° under water-pump pressure to give 1.98 g. (69%) of colorless and analytically pure product, m.p. 41.5°.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.22; H, 7.55; N, 7.95.

Heating at 120° in a sealed tube under nitrogen did not affect the infrared spectrum of a sample of II. Heating for one hour at 200° resulted in charring.

2-Acetamido-2-cycloheptylpropane (III).—Compound II (950 mg., 5.3 mmoles), 500 mg. of 5% palladium-on-charcoal and 20 ml. of ethyl acetate were stirred under one atmosphere of hydrogen; 781 ml. (33 mmoles) was consumed by II. After 10 hours, the catalyst was removed by filtration. The resulting solution was transparent in the ultraviolet. Acetic anhydride (30 ml.) was added to the solution and the mixture was refluxed for 3 hours. The liquids were removed by distillation on the steam-bath under reduced pressure. The residue was recrystallized three times from ethanol–pentane. The yield was 650 mg. (62%) of III, m.p. 111–111.6°, with no absorption in the ultraviolet.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 73.04; H, 11.75. Found: C, 73.36; H, 11.47.

Acknowledgments.[9]—The author is deeply indebted to Professor G. Stork, whose suggestions made a major contribution to this work. Grateful acknowledgment is also made of the experimental advice of Dr. S. D. Darling. Professor N. Kornblum has most kindly and helpfully criticized some of the discussion.

[9] This work was supported in part by a fellowship from 1957 to 1959 from the National Science Foundation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

Cyclopropanes. VIII.[1] Rates of Ring Opening of Substituted Cyclopropyl Ketones and Carbinols[2]

BY H. M. WALBORSKY AND L. PLONSKER[3]

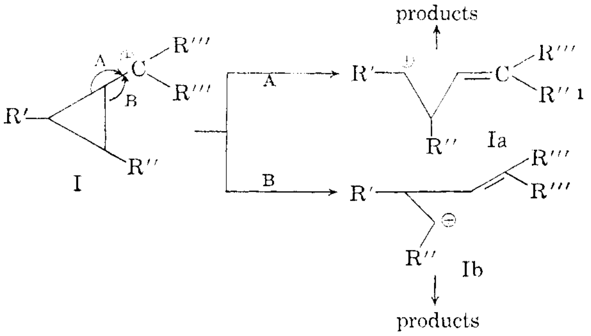
RECEIVED NOVEMBER 23, 1960

A series of optically active cyclopropyl ketones and carbinols has been prepared in which substituents were varied in the 1- and 2-positions of the ring and on the carbinyl carbon. The rates of acid-catalyzed ring opening have been determined polarimetrically and in some instances by infrared spectroscopy. The effect of geometric isomerism as well as the effect of the substituents on the rates of ring opening is discussed. In certain cases the polarimetric rate was found to be faster than the rate measured by infrared spectroscopy. The implication of this observation on the mechanism of this reaction is discussed.

Examples of the cyclopropylcarbinyl rearrangement can be found in the acid-catalyzed dehydration of cyclopropylcarbinols,[4] solvolysis of certain cyclopropylcarbinyl esters and halides,[5] deamination of cyclopropylcarbinyl amines[6] and the acid-catalyzed rearrangement of cyclopropyl ketones.[7]

Although the rearrangement of unsubstituted cyclopropylcarbinyl derivatives has been studied kinetically[8] no systematic kinetic studies on substituted compounds have been carried out.

Chemical evidence shows that, in general,[9] when the cyclopropylcarbinyl cation I is generated, ring opening will occur toward that carbon atom that can best delocalize a positive charge.



The choice between the intermediates Ia or Ib will depend upon the relative abilities of R′ and R″ to delocalize a positive charge.

The rearrangement products of substituted cyclopropyl ketones can be explained in an analogous manner. In these cases the cyclopropyl-

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[1] For paper VII of this series, see H. M. Walborsky, T. Sugita, M. Ohno and Y. Inouye, *J. Am. Chem. Soc.*, **82**, 5255 (1960).

[2] This work was supported by a grant from the National Science Foundation, which is gratefully acknowledged.

[3] Ethyl Corporation Fellowship, 1959–1960.

[4] (a) R. Stoermer, F. Schenk and H. Buchman, *Ber.*, **61**, 2312 (1928); (b) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6396 (1955); (c) H. M. Walborsky and J. F. Pendleton, *ibid.*, **82**, 1405 (1960).

[5] (a) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951); (b) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952); (c) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959).

[6] (a) N. J. Demjanow, *Ber.*, **40**, 4393 (1907); (b) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951).

[7] (a) R. C. Fuson and F. N. Baumgartner, *ibid.*, **70**, 3255 (1948); (b) E. P. Kohler and W. N. Jones, *ibid.*, **41**, 1249 (1919); (c) E. G. Ford, P. N. Chakravorty and E. S. Willis, *ibid.*, **60**, 413 (1938).

[8] As a leading reference see R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[9] See, however, S. Julia, M. Julia and C. Huynh, *Bull. soc. chim. France*, 174 (1960); this work indicates that stereochemical factors may also be playing an important role.