Electrophilic Catalysis in Nucleophilic Substitution and Elimination. V. Stereochemical Studies Involving Reactions of (+)-2-Octyl Bromide in Acetonitrile[1,2]

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When optically active 2-octyl bromide is heated in acetonitrile at 100.1° it racemizes at an initial rate which is larger than the rate of bromide ion production. The racemization is subject to strong autocatalysis by the bromide ions produced. In the presence of externally added AgBr, the initial rate of racemization of 2-octyl bromide remains unchanged but the autocatalyzed racemization is partially suppressed through the removal of Br^- by AgBr and the formation of $AgBr_2^-$. At 100.1° in acetonitrile, bromide ions are 26 times more nucleophilic toward 2-octyl bromide than nitrate ions; consequently, in the presence of nitrate ions, the polarimetric rate is subject to very strong autocatalysis arising from attack on optically active 2-octyl bromide by the bromide ions produced in the displacement reaction. The reaction between optically active 2-octyl bromide and silver nitrate in acetonitrile at 100.1° produces a mixture of alkenes (16.4%) and 2-octyl nitrate (83.6%), of inverted configuration with $87 \pm 3\%$ retention of optical purity, irrespective of the silver nitrate concentration or of the concentration of added Et_4NNO_3. The result is shown to be consistent with the formation of quadruple ion intermediates, $NO_3^-R^+Br^-Ag^+$ as proposed earlier.

Introduction

Considerable interest attaches to kinetic studies of silver-assisted substitutions in which solvolysis is excluded by the use of a sufficiently inert solvent.[1,4-6] In order to deduce the topological arrangement of the reactants in the product-determining step, it is mechanistically profitable to use anionic reagents which are more nucleophilic than the solvent, lead to essentially stable products, and do not complex[7] with Ag^+. The first, and simpler, stereochemical study of this type which we report here involves the reaction of 2-octyl

(1) Part IV: Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4771 (1965).

(2) Taken in part from the thesis presented by Dennis N. Kevill in partial fulfillment of the requirements for the Ph.D. Degree, University of London, Jan. 1960, and in part from a research report submitted by him during the tenure of a Temporary Assistant Lectureship at University College.

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(4) G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Am. Chem. Soc.*, **82**, 704 (1960), and references to earlier work quoted therein.

(5) Part III: Y. Pocker and D. N. Kevill, *ibid.*, **87**, 4760 (1965).

(6) In the *nucleophilic* solvent pyridine the reactions of primary and secondary alkyl halides with $AgNO_3$ are essentially direct nucleophilic displacements by pyridine assisted by silver ion (S_N2-Ag^+): J. A. Vona and J. Steigman, *ibid.*, **81**, 1095 (1959).

(7) Silver nitrite formally contains the powerfully nucleophilic ion NO_2^-; actually the concentration of free NO_2^- is low due to its complexing with $AgNO_2$ to produce $Ag(NO_2)_2^-$.[5] When optically active 2-octyl iodide is allowed to react with $AgNO_2$ in CH_3CN, the 2-nitrooctane and 2-octyl nitrite are of inverted configuration: N. Kornblum, D. E. Hardies, and W. J. Jones, unpublished observations quoted by N. Kornblum, *Org. Reactions*, 107 (1962).

bromide with $AgNO_3$ in CH_3CN[8] at 100.1°. The kinetic data for this system are best rationalized by a mechanism in which both silver cations and nitrate anions participate in the rate-determining step.[4,5] In problems of mechanism involving anion participation, illumination often follows from stereochemical studies carried out under kinetically controlled conditions, concurrently with parallel studies of the separate effects of solvent, of products, and of tetraalkylammonium salts containing the participating anion. We therefore felt it necessary to familiarize ourselves with the stereochemical behavior of optically active 2-octyl bromide in CH_3CN alone, as well as in CH_3CN containing AgBr, Et_4NBr, Et_4NNO_3, $AgNO_3$, and Et_4NNO_3-$AgNO_3$ mixtures, respectively.

Results

(1) Stability of (+)-2-Octyl Bromide in Acetonitrile. The production of bromide ions from 2-octyl bromide in acetonitrile solution at 100.1° is slow[5]; for instance, after 14 hr. at 100.1°, less than 1% of the bromine from a 0.160 M solution of 2-octyl bromide exists as free (titratable) bromide ions. The initial first-order rate coefficient of Br^- production is $k_1^i = 1.6 \times 10^{-7}$ sec.$^{-1}$. The rate of loss of optical activity from a 0.160 M solution of (+)-2-octyl bromide in acetonitrile at 100.1° is

Table I. The Racemization of (+)-2-Octyl Bromide in Acetonitrile at 100.1° [(+)-2-Octyl Bromide] = 0.160 M[a]

(a) In CH_3CN alone					
Time, hr.	0	2	6	22	46	70
Rotation[b]	2.34	2.31	2.22	1.36	0.21	0.03
$10^6 k_1^\alpha$		1.8	2.4	6.9	14.5	

Initial value $k_1^\alpha \sim 1.6 \times 10^{-6}$ sec.$^{-1}$

(b) AgBr present to the extent of 0.1 g./5-ml. aliquot of reaction mixture					
Time, hr.	0	2	6	22	46	70
Rotation[b]	2.34	2.31	2.22	1.80	1.08	0.41
$10^6 k_1^\alpha$		1.8	2.4	3.3	4.7	6.9

Initial value $k_1^\alpha \sim 1.6 \times 10^{-6}$ sec.$^{-1}$

(c) $[NEt_4Br] = 0.0100$ M[a]						
Time, min.	0	3	6	9	12	18	24
Rotation[b]	2.28	2.14	2.02	1.91	1.78	1.60	1.41
$10^2 k_2$		1.76	1.68	1.64	1.72	1.64	1.67

Mean value for k_2 1.69 $\times$ 10^{-2} l. mole^{-1} sec.$^{-1}$

[a] Concentration at room temperature. [b] Measurements at room temperature in 2-dm. polarimeter tube.

(8) Prior to our study, Kornblum and Hardies[9] reported that *concentrated* solutions of 2-octyl iodide and silver nitrate react to give 2-octyl nitrate of inverted configuration, a result which is compatible with a mechanism involving *rigidly oriented* ion pairs[4] or quadruple ions[5] as intermediates.

(9) N. Kornblum and D. E. Hardies, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1956, p. 2-O.

Table II. Changes in Optical Rotation and the Rates of Bromide Ion Production (k_2 in l. mole⁻¹ sec.⁻¹) in the Reaction of (+)-2-Octyl Bromide with Et₄NNO₃ in Acetonitrile at 100.1°

(A) [(+)-2-Oct.Br] = 0.160 M^a; [Et₄NNO₃] = 0.160 M^a; initial rotation = 2.32°ᵇ								
Time, min.	0	3	6	10	12	15	18	20	40
% reactionᶜ	1.1	2.8	4.6	6.8	8.1	9.4	11.8	12.9	21.0
% reduction in rotation	1.7	4.3	10.3	18.1	23.7	31.7	40.1	50.0	86.0
10⁴ $k_2{}^a$		6.1	6.4	6.5	6.8	6.5	6.9	6.8	6.5

Mean value for k_2 6.6 × 10⁻⁴ l. mole⁻¹ sec.⁻¹

(B) [(+)-2-Oct.Br] = 0.800 M^a; [Et₄NNO₃] = 0.240 M^a; initial rotation = 1.20°ᵇ							
Time, min.	0	4	8	12	17	22	28
% reactionᶜ	2.9	6.4	10.0	13.5	17.0	20.7	24.7
% reduction in rotation	4.2	10.8	19.2	30.0	41.6	52.5	64.2
10⁴$k_2{}^a$		6.5	6.8	6.9	6.8	6.7	6.6

Mean value for k_2 6.7 × 10⁻⁴ l. mole⁻¹ sec.⁻¹

ᵃ Quantities uncorrected for expansion of solvent from room temperature. ᵇ Rotations are measured in a 2-dm. tube at room temperature and initial rotations are taken prior to immersion in 100.1° thermostat. ᶜ Exprssed in terms of the 2-octyl bromide reacted.

appreciably faster and is subject to *strong* autocatalysis (Table Ia).

The initial rate of loss of optical activity in the presence of added AgBr is identical with that obtained in its absence (Table Ib), but during the later stages of reaction the presence of *silver bromide appears to suppress the autocatalyzed racemization by a significant amount.*

The symmetrical exchange reaction of (+)-2-octyl bromide with tetraethylammonium bromide in acetonitrile at 100.1° was followed in terms of loss in optical activity; the second-order coefficients (Table Ic) were calculated according to the formula, $k_2 = (2.303/2Bt) \log \alpha_0/\alpha_t$, where B is the concentration of NEt₄Br, t is the time of reaction, α_0 is the rotation of the (+)-2-octyl bromide at the time zero, and α_t is the rotation of the (+)-2-octyl bromide at time t.

(2) Reaction of (+)-2-Octyl Bromide with Tetraethylammonium Nitrate. The rate of loss of optical activity at 100.1° has been followed concurrently with the rate of chemical reaction as determined by bromide ion production from the (+)-2-octyl bromide. The rate of bromide ion production during the initial stages was found to be a second-order process, first order in 2-octyl bromide, and first order in tetraethylammonium nitrate; the reaction being a reversible S$_N$2 process (eq. 1).[5] It appears that even at 100.1° we are dealing

$$\text{2-Oct.Br} + \text{NEt}_4\text{NO}_3 \rightleftharpoons \text{2-Oct.ONO}_2 + \text{NEt}_4\text{Br} \quad (1)$$
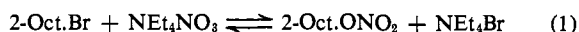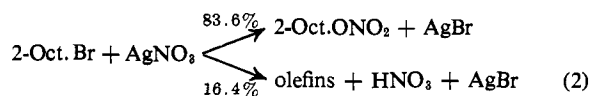
with a relatively clean substitution with little or no elimination accompanying it. The bimolecular displacement of bromide by nitrate ion in 2-octyl bromide would be expected to proceed with complete inversion. However, as the reaction proceeds, the bimolecular inversion relationship for the change in optical rotation breaks down because each molecular act of substitution by nitrate ions is accompanied by the production of bromide ions which in turn attack unreacted (+)-2-octyl bromide causing racemization. A comparison of the second-order rate coefficients for nucleophilic attack at 100.1° by bromide ions, 1.7 × 10⁻² l. mole⁻¹ sec.⁻¹, and by nitrate ions, 6.7 × 10⁻⁴ l. mole⁻¹ sec.⁻¹, shows that under our reaction conditions bromide ions are 26 times more nucleophilic towards 2-octyl bromide than nitrate ions. Consequently after quite small amounts of chemical reaction, a substantial proportion of the change in optical rotation of

the reaction mixture will be due to the racemization of (+)-2-octyl bromide by the bromide ions produced in the substitution reaction (Table II).

In principle the relative rotations of (+)-2-octyl bromide and (−)-2-octyl nitrate can be obtained by extrapolation to zero extent of reaction of a plot of (per cent loss of rotation/per cent extent of reaction) against per cent of reaction, but in practice the racemization caused by bromide ions, even at the early stages of substitution by NO₃⁻, is too great to permit an accurate extrapolation. Nevertheless if δ represents the rotation of (−)-2-octyl nitrate relative to (+)-2-octyl bromide, both possessing the same degree of optical purity, then a value for δ of *ca.* 0.3 can be estimated in the very initial stages of the reaction; this value accords with that expected for an essentially complete Walden inversion (see the Experimental Section).

(3) Reaction of (+)-2-Octyl Bromide with AgNO₃. The reaction of silver nitrate with (+)-2-octyl bromide in solvent acetonitrile at 100.1° has been found to proceed according to eq. 2.[5]

$$\text{2-Oct.Br} + \text{AgNO}_3 \underset{16.4\%}{\overset{83.6\%}{<}} \begin{array}{l} \text{2-Oct.ONO}_2 + \text{AgBr} \\ \text{olefins} + \text{HNO}_3 + \text{AgBr} \end{array} \quad (2)$$

The olefins formed will of course be inactive and any optical activity in the products must be due to the 2-octyl nitrate formed. At 100.1° it was shown by potentiometric titration of silver ion in solution, that with AgNO₃ concentrations in the range 0.08 to 0.24 M the reaction proceeded to completion within 2 hr. (+)-2-Octyl bromide was found to yield (−)-2-octyl nitrate, *i.e.,* an inversion of configuration occurred. In order to obtain the degree of optical purity in this inversion, experiments were performed under conditions such as to eliminate changes in rotation other than those occurring in the reaction of the (+)-2-octyl bromide with silver nitrate. It has been shown that a solution of (+)-2-octyl bromide in acetonitrile loses at 100.1° less than 1% of its optical activity during 2 hr., even in the presence of solid-phase silver bromide, and the (+)-2-octyl bromide can be considered as both chemically and optically stable over the period required for complete stoichiometric reaction with AgNO₃. Since it is known from independent studies that the molecular rotation of 2-octyl bromide is significantly

greater than that of 2-octyl nitrate possessing an identical degree of optical purity, errors will be minimized by using a concentration of silver nitrate equal to or in excess of that of the alkyl halide and directly measuring the rotation of the products. It was found that if excess silver nitrate over (+)-2-octyl bromide was used, and 2 hr. was allowed for the reaction to go to completion, that over a period of an additional 6 hr. at 100.1°, no additional change could be detected in the optical rotation of the products. The racemization of 2-octyl nitrate by nitrate ions in solvent acetonitrile at 100.1° must be an extremely slow reaction.

With a concentration of silver nitrate equal to or in excess of that of (+)-2-octyl bromide, the reaction in acetonitrile solution at 100.1° yields inactive olefins and (−)-2-octyl nitrate. The rotation of the (−)-2-octyl nitrate as formed in the reaction is obtained directly. It is found that the (−)-2-octyl nitrate is formed with a molecular rotation independent of the initial silver nitrate concentration and with 26% of the numerical value of the molecular rotation of the parent (+)-2-octyl bromide; and also that the addition of tetraethylammonium nitrate to the reaction of silver nitrate with (+)-2-octyl bromide, in acetonitrile at 100.1°, does not alter the optical rotation of the products formed (Table III).

Table III. Changes in Optical Rotation after Complete Reaction between (+)-2-Octyl Bromide and Silver Nitrate in Acetonitrile at 100.1°

[2-Oct.-Br],[a] M	[AgNO$_3$],[a] M	[Et$_4$N-NO$_3$],[a] M	Initial α,[b] degrees	Final α,[b] degrees	[M_{NO_3}]$_D$/[M_{Br}]$_D$[c]
0.0800	0.0800	...	+1.15	−0.26	0.27
0.0800	0.0800	0.0800	+1.15	−0.26	0.27
0.0800	0.0800	0.160	+1.15	−0.25	0.26
0.0800	0.160	...	+1.15	−0.24	0.25
0.160	0.160	...	+2.30	−0.47	0.25
0.0800	0.240	...	+1.15	−0.26	0.27

[a] Concentrations uncorrected for expansion of solvent from room temperature. [b] Measured at room temperature in 2-cm. polarimeter tube, the initial value being obtained from measurements on a 0.320 M solution of (+)-2-octyl bromide. [c] Comparison of the molecular rotation of the (−)-2-octyl nitrate, [M_{NO_3}]$_D$, with the molecular rotation of the parent (+)-2-octyl bromide, [M_{Br}], after correction for 16.4% olefin formation.

Discussion

When optically active 2-octyl bromide is heated in acetonitrile at 100.1° it is found to racemize at an initial rate, $k_1{}^\alpha = 1.6 \times 10^{-6}$ sec.$^{-1}$, which is roughly ten times greater than the initial rate of bromide ion production, $k_1{}^i = 1.6 \times 10^{-7}$ sec.$^{-1}$. This suggests a mechanism in which an intermediate is formed[10] which can as an alternative to product formation, revert to 2-octyl bromide with loss of optical activity but no net chemical reaction. A reaction mechanism involving ion pairs[11-13] is suggested: we associate $k_1{}^\alpha$ with ion-pair return after reorganization and $k_1{}^i$

(10) We are not able at present to exclude entirely the possibility that the relatively high value obtained for $k_1{}^\alpha$ is due in part to a bimolecular racemization process induced essentially by trace amounts of CH$_3$CNH$^+$Br$^-$ and CH$_3$CNH$^+$HBr$_2{}^-$ produced in the initial stages of reaction. To overcome this uncertainty, we have deduced $k_1{}^\alpha$ by extrapolating the polarimetric rate constant k_α to [Br$^-$] = 0.
(11) Y. Pocker, "Progress in Reaction Kinetics," Vol. 1, Pergamon Press, Inc., New York, N. Y., 1961, pp. 227, 228.
(12) A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **86**, 5010 (1964), and other references listed therein.

with solvent intervention leading to both elimination (84%) and substitution (16%). It appears that even for short-lived *sec*-alkyl cations, $k_1{}^\alpha$ may exceed $k_1{}^i$ by a significant amount when the capacity for solvent intervention either as a nucleophile or as a base is as low as that found in CH$_3$CN.[12]

That the autocatalytic loss of optical rotation in a reaction of (+)-2-octyl bromide in acetonitrile at 100.1° is due to racemization of remaining (+)-2-octyl bromide by bromide ions produced in the decomposition is confirmed by the addition of tetraethylammonium bromide when a second-order racemization is observed, presumably due to S$_N$2 attack of bromide ions upon the (+)-2-octyl bromide.

The bromide ion is found to be 26 times more nucleophilic than the nitrate ion as regards attack upon 2-octyl bromide in acetonitrile at 100.1°. Interpretation of optical measurements during attack by nitrate ions upon (+)-2-octyl bromide is consequently complex. Fortunately in the reaction of silver nitrate, the bromide ions formed are removed as silver bromide which has been shown, under the reaction conditions, not to racemize the remaining (+)-2-octyl bromide.

The partial suppression of the autocatalysis to the loss of optical activity in a solution of (+)-2-octyl bromide in acetonitrile at 100.1° by added silver bromide must be due to a removal of bromide ions, formed by the decomposition, from solution. This probably occurs through a formation of AgBr$_2{}^-$ complex ions.

The reaction of (+)-2-octyl bromide with silver nitrate was performed under controlled conditions such that the rotation observed in the products must be related to the rotation of the parent (+)-2-octyl bromide entirely through its reaction with silver nitrate. The (−)-2-octyl nitrate was formed with a molecular rotation 26% that of the parent (+)-2-octyl bromide, irrespective of the silver nitrate concentration or of the concentration of added tetraethylammonium nitrate. This constancy is additional evidence for the view already put forward on kinetic grounds[5] that the nitrate ion is involved to the same extent in each and every act of conversion.

The ratio of the molecular rotations for solutions of 2-octyl nitrate and 2-octyl bromide in acetonitrile possessing equal degrees of optical purity is

$$[M_{NO_3}]_D/[M_{Br}]_D = 1.37/4.55 = 0.30$$

In the conversion of (+)-2-octyl bromide to (−)-2-octyl nitrate in acetonitrile solution at 100.1 by means of silver nitrate, a factor of 0.26 ± 0.01 was obtained. It follows that the inversion takes place with 87 ± 3% retention of optical purity. If formation of rigidly oriented (NO$_3{}^-$...R$^+$) ion pairs or (NO$_3{}^-$ R$^+$ Br$^-$ Ag$^+$) quadruple ions are postulated as intermediates prior to product formation,[1,4,5] then it appears that some of them are nevertheless able to reorganize within this stage and prior to their collapse to give 2-octyl nitrate.

Experimental Section

Materials. The materials employed in this work have been purified and dried as described in the Experimental Section of part III in this series.[5]

(13) Y. Pocker, W. A. Mueller, F. Naso, and G. Tocchi, *ibid.*, **86**, 5011 (1964).

(−)-*2-Octanol.* The resolution of 2-octanol (B.D.H.) was carried out according to Kenyon[14]; the (−)-2-octanol used in this work had b.p. 88° (20 mm.), n^{25}D 1.4244, d^{25}_4 0.08202, $[\alpha]^{20}$D −9.9° (no solvent). (+)-2-Octyl bromide was prepared from (−)-2-octanol according to Kornblum, Lichtin, Patton, and Iffland,[15] b.p. 70° (10 mm.), n^{20}D 1.4500, d^{20}_4 1.090, $[\alpha]^{25}$D +33.3°.

Since all the experiments carried out in this investigation were performed at a temperature above the boiling point of acetonitrile, sealed bulbs containing 5-ml. aliquots of the reaction mixture were used throughout. Except where otherwise stated, optical rotations were measured at room temperature in a 2-dm. polarimeter tube; the tube was constructed so that the volume of liquid required to fill it was slightly less than 5 ml. Unless otherwise stated "the first" reading was taken after immersion in the thermostat for about 5 min. In several instances strictly initial values at zero extent of reaction were required and these were obtained prior to immersion in the thermostat. Points removed at subsequent intervals were stored in Dry Ice–alcohol slush and then allowed to warm up to room temperature just prior to the measurement of the optical rotation. When silver bromide was present the solution was filtered before filling the polarimeter tube. The reaction of (+)-2-octyl bromide with tetraethylammonium nitrate was followed as regards the rate of production of bromide ions by potentiometer titration of 2-ml. samples from each reaction tube against standard silver nitrate solution, after the optical rotation had been measured. Some reaction of (+)-2-octyl bromide with silver nitrate inevitably occurred during the "warm-up" period but this only slightly affected the olefin/nitrate ratio as was shown by determining the olefin at various percentages of reaction.

Relationship between Molecular Rotations in Acetonitrile Solution, of (+)-2-Octyl Bromide and (−)-2-Octyl Nitrate When Possessing Identical Degrees of Optical Purity. A sample of (+)-2-octyl nitrate was prepared from (+)-2-octanol by the method of Shriner and Parker[16] after purification by distillation under reduced pressure, n^{25}D 1.4238 and $\alpha^{24.5}$D +16.90° (1-dm. tube). Taking the value for the density d^{20} of 0.954 recorded by Shriner and Parker[16] $[\alpha]$D is 17.72°.

The (+)-2-octyl bromide used in the present investigation had $\alpha^{24.5}$D +36.56° (1-dm. tube), and taking the value for the density d^{25}_4 1.098 one obtains $[\alpha]$D 33.29°.

The rotations of 0.32 M solutions of both compounds in acetonitrile were measured in a 2-dm. polarimeter tube, (+)-2-octyl bromide, $\alpha^{24.5}$D 4.55°, and (+)-2-octyl nitrate, $\alpha^{24.5}$D 1.61°.

Brauns[17] has shown that for inversion of configuration with complete retention of optical purity, (+)-2-Oct.OH, $[\alpha]^{20}$D +9.93, corresponds to (−)-2-Oct.Br, $[\alpha]^{20}$D −40.64°.

Cristol, Franzus, and Shadan[18] have shown that with complete retention of optical purity, (−)-2-Oct.OH, $[\alpha]^{25}$D −9.52°, leads to (−)-2-Oct.NO$_3$, $[\alpha]^{25}$D −17.64°, so that (−)-2-Oct.OH, $[\alpha]$D −9.93°, corresponds to (−)-2-Oct.NO$_3$, $[\alpha]$D −18.40°.

It follows that for the pure liquids (−)-2-Oct.NO$_3$ of rotation $[\alpha]$D −18.40° has the same degree of optical purity as (−)-2-Oct.Br, $[\alpha]$D −40.64°.

The sample of (+)-2-octyl bromide used had $[\alpha]$D +33.29° and (−)-2-octyl nitrate with same degree of optical purity would have $[\alpha]$D −15.08°. The rotation of a 0.32 M solution of (−)-2-octyl nitrate, $[\alpha]$D −15.08°, in acetonitrile in a 2-dm. polarimeter would be (−15.08/17.72) × 1.61° = −1.37°.

The ratio of the molecular rotations for solutions of 2-octyl nitrate and 2-octyl bromide in acetonitrile possessing equal degrees of optical purity is $[M_{NO_3}]_D/[M_{Br}]_D$ = 1.37/4.55 = 0.30.

In the conversion of (+)-2-octyl bromide to (−)-2-octyl nitrate in acetonitrile solution at 100.1° by means of AgNO$_3$ in CH$_3$CN, a factor of 0.26 ± 0.01 was obtained indicating inversion with [(0.26 ± 0.01)/0.30] × 100 = 87 ± 3% retention of optical purity.

(14) J. Kenyon, "Organic Syntheses," Coll. Vol. 1, H. Gilman and A. H. Blatt, Ed., 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 418.

(15) N. Kornblum, N. N. Lichtin, J. T. Patton, and D. C. Iffland, *J. Am. Chem. Soc.*, **69**, 309 (1947).

(16) R. L. Shriner and E. A. Parker, *ibid.*, **55**, 766 (1933).

(17) H. Brauns, *Rec. trav. chim.*, **65**, 805 (1946).

(18) S. J. Cristol, B. Franzus, and A. Shadan, *J. Am. Chem. Soc.*, **77**, 2512 (1955).