

TABLE III
 2-ALKOXYETHYL PHENYL KETONES R—O—CH₂CH₂COC₆H₅

—R	Yield, %	n _D ²⁰	d ₄ ²⁰	Molec. refrac.		Carbon, %		Hydrogen, %	
				Σ	Calcd.	Calcd.	Found	Calcd.	Found
CH ₃ ^a	90	1.5250	1.0602	46.96	47.46	73.14	73.12	7.37	7.36
C ₂ H ₅ ^b	82	1.5190	1.0356	51.57	52.23	74.13	73.93	7.92	7.73
C ₃ H ₇	82	1.5193	1.0300	56.19	56.68	74.97	74.30	8.39	7.83
CH(CH ₃) ₂	89	1.5083	1.0108	56.19	56.73	74.97	74.39	8.39	8.30
C ₄ H ₉	91	1.5036	0.9976	60.81	61.19	75.69	74.98	8.80	8.78

^a Straus and Berkow (ref. 7, p. 144) reported b. p. 125–126° (16 mm.), *d*₄¹⁵, 1.020. ^b Kohler (ref. 6, p. 388), who obtained this ketone as a by-product in the preparation of phenyl vinyl ketone from α,β-dibromopropiophenone, reported b. p. 135° (18 mm.), m. p. about 12°.

These alkoxyethyl phenyl ketones readily formed 2,4-dinitrophenylhydrazones; the melting points of the latter are given in sequence to the appropriate alkyl group: CH₃, 175.5–176.5°; C₂H₅, 161.0–161.5°; C₃H₇, 158.0–158.5°; CH(CH₃)₂, 174.5–175.0°; C₄H₉, 152.5–153.0°.

In one instance, the impure 2-(1-methylethoxy)-ethyl phenyl ketone, obtained by distillation as described above, was redistilled through a six-inch column from an oil-bath at 140–155°. Several fractions of constant refractive index were removed at 106–107° (18 mm.)^{6,7} and were found to possess the following physical properties: n_D²⁰ 1.5440; *d*₄²⁰ 1.0350; Σ *MR*⁸ 40.35; *MR* calcd. 40.31. The product, acrylophenone, formed (a) a 2,4-dinitrophenylhydrazone derivative [or 1-(2,4-dinitrophenyl)-3-phenyl-Δ²-pyrazoline], m. p. 155–156° and (b) a phenylhydrazone deriva-

tive [or 1,3-diphenyl-Δ²-pyrazoline],^{9,10,11} m. p. 153°.

Summary

1. Certain β-alkoxypropionitriles, obtained by the interaction of acrylonitrile and various alcohols, were hydrolyzed to yield β-alkoxypropionic acids which, in turn, were converted into the corresponding acid chlorides.

2. The β-alkoxypropionyl chlorides reacted with diphenylcadmium to yield 2-alkoxyethyl phenyl ketones, three of which have not previously been reported. These ketones tend to be unstable upon distillation and decompose to produce acrylophenone.

(9) Straus and Berkow, ref. 7, reported m. p. 152°.

(10) Schafer and Tollens, *Ber.*, **39**, 2181 (1906), reported m. p. 152–153°.

(11) Young and Roberts, *THIS JOURNAL*, **68**, 649 (1946), reported m. p. 154–155°.

(6) Kohler, *Am. Chem. J.*, **42**, 375 (1909), reported b. p. 118° (18 mm.).

(7) Straus and Berkow, *Ann.*, **401**, 121 (1913), reported b. p. 115° (18 mm.).

(8) Includes 0.65 correction for exaltation of C₆H₅CO- compounds; cf. Auwers, *Ber.*, **45**, 2765 (1912).

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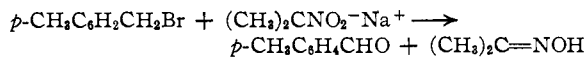
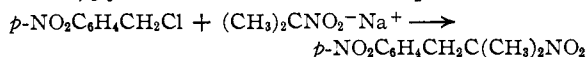
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

A Proposed Mechanism of the Alkylation of Benzyl Halides with Nitro Paraffin Salts¹

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It was shown in the preceding paper⁴ that, of nine para-substituted benzyl halides, only *p*-nitrobenzyl chloride gave carbon-alkylation with sodium 2-propanenitronate whereas the other eight benzyl halides gave oxygen-alkylation in 68–77% yield as illustrated in the equations



These facts led us to seek some explanation for the anomalous behavior of *p*-nitrobenzyl chloride in this reaction.

(1) An abstract of a thesis by Myron L. Bender, submitted to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1948. Presented before the Division of Organic Chemistry, 114th American Chemical Society meeting, St. Louis, Missouri, September 6, 1948.

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(4) Hass and Bender, *THIS JOURNAL*, **71**, 1767 (1949).

The anions of nitroparaffin salts have been represented as resonance hybrids involving forms with the negative charge on oxygen or on carbon.⁵ Carbon-alkylation may then be considered⁶ to involve a nucleophilic displacement by the resonating anion at carbon while oxygen-alkylation may be considered to involve a displacement by the resonating anion at oxygen. The compounds resulting from oxygen-alkylation, nitronic esters, have been isolated in several cases similar to the present work⁷ and have been prepared by a different synthesis⁸; they are thermally unstable and decompose spontaneously even at room temperature into carbonyl compounds and oximes. While the mechanisms discussed above account for the possibility of the two modes of alkylation, they furnish no basis of explaining the anomalous behavior of *p*-nitrobenzyl chloride.

(5) Kornblum, Lichtin, Patton and Iffand, *ibid.*, **69**, 307 (1947).

(6) Hauser, *ibid.*, **60**, 1957 (1938).

(7) Thurston and Shriner, *J. Org. Chem.*, **2**, 183, 560 (1937–1938); Weister and Helmkamp, *THIS JOURNAL*, **67**, 1167 (1945), and other references cited therein.

(8) Arndt and Rose, *J. Chem. Soc.*, **1** (1935).

The second-order rates of the four alkylation reactions involving lithium 2-propanenitronate and *o*-nitrobenzyl chloride, *m*-nitrobenzyl chloride, *p*-nitrobenzyl chloride and benzyl chloride have been determined at $30 \pm 0.3^\circ$; the experimental results are shown in Fig. 1. The relative rates of these four halides in this reaction are compared in Table I with the relative rates of the

TABLE I
COMPARISON BETWEEN RATES OF ALKYLATION AND POTASSIUM IODIDE REACTIONS

Halide	Alkylation ^a	Lithium 2-propanenitronate in ethanol at 30°		
		$k_2 \times 10^4$ (l./mole sec.)	Relative k_2	KI in acetone ^{9,10} at 50° Relative k_2
<i>o</i> -Nitrobenzyl chloride	C(46%) + O(30%)	1.37	9.2	9.2
<i>p</i> -Nitrobenzyl chloride	C(83%) + O(1%)	1.05	7.1	7.0
<i>m</i> -Nitrobenzyl chloride	O(73%)	0.64	4.3	4.0
Benzyl chloride	O(73%)	0.29	1.9	1.0

^a See Table III for experimental evidence.

halides in another second-order reaction, the reaction with potassium iodide in acetone. The correlation between the rates of these two reactions implies that the rate-determining step is the same for all four halides in the reaction with lithium 2-propanenitronate (as it is assumed to be in the potassium iodide reaction). Previous evidence indicates that the rate-determining

TABLE II
PARALLELISM BETWEEN CARBON-ALKYLATION AND STILBENE FORMATION

Benzyl halide	Alkylation: alcoholic sodium 2-propanenitronate		Williamson reaction: alcoholic sodium hydroxide or sodium alkoxide		Reference
	Carbon	Oxygen	Stilbene	Ether	
<i>p</i> -CH ₃		X		X	^a
<i>p</i> -Br		X		X	^b
Unsubstituted		X		X	^c
<i>p</i> -CO ₂ CH ₃		X		X	^h
<i>p</i> -COCH ₃		X		X	ⁱ
<i>p</i> -CN		X		X	³
<i>m</i> -NO ₂		X		X	^d
<i>p</i> -CF ₃		X		X	ⁱ
<i>o</i> -NO ₂	X	X	X	X	^e
<i>p</i> -NO ₂	X	X	X	X	^f
2,4-DiNO ₂	X	X	X	X	^g

^a Radziewski and Wispek, *Ber.*, **15**, 1745 (1882).
^b Errera, *Gazz. chim. ital.*, **17**, 203 (1887). ^c Cannizzaro, "Jahresbericht über die Fortschritte der Chemie," 1856, p. 581. ^d Errera, *Gazz. chim. ital.*, **18**, 234 (1888).
^e Bischoff, *Ber.*, **21**, 2072 (1888). ^f Romeo, *Gazz. chim. ital.*, **35**, I, 111 (1905). ^g Krassuski, *J. Russ. Phys.-Chem. Soc.*, **27**, 339 (1895). ^h Methyl ether: b. p. 95-96° (2.5 mm.); n_D^{20} 1.5217. *Anal.* Calcd. for C₁₀H₁₂O₂: C, 66.66; H, 6.75. Found: C, 66.4; H, 6.61. ⁱ Methyl ether: b. p. 104-106° (3 mm.); n_D^{20} 1.5274; lit. b. p. 107-109° (3.5 mm.); n_D^{20} 1.5287. ^j Ethyl ether: b. p. 59-61° (5 mm.); n_D^{20} 1.4380. *Anal.* Calcd. for C₁₀H₁₄F₃O: C, 58.78; H, 5.43. Found: C, 58.5; H, 5.47.

(9) Bennett and Jones, *J. Chem. Soc.*, 1815 (1935).

(10) Conant, Kirner and Hussey, *THIS JOURNAL*, **47**, 488 (1925).

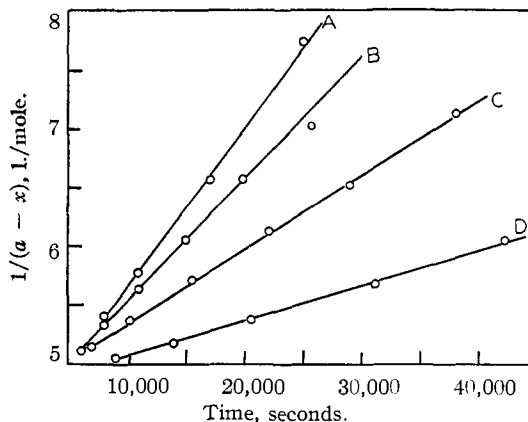


Fig. 1.—Reaction of lithium 2-propanenitronate with benzyl halides at $30 \pm 0.3^\circ$, $a = a' = 0.200 M$: (A) *o*-nitrobenzyl chloride; (B) *p*-nitrobenzyl chloride; (C) *m*-nitrobenzyl chloride; (D) benzyl chloride. Each line represents one run.

step in oxygen-alkylation is the formation of a nitronic ester.^{8,7} Since the four halides illustrate both oxygen- and carbon-alkylation, this study leads to the conclusion that the rate-determining step in both oxygen- and carbon-alkylation is the formation of a nitronic ester intermediate.

The reactions of *o*-nitro-, *m*-nitro-, *p*-nitro- and 2,4-dinitrobenzyl chlorides with sodium 2-propanenitronate compiled in Table III show that carbon-alkylation occurs with both *o*- and *p*-nitrobenzyl chlorides but not with *m*-nitrobenzyl chloride.

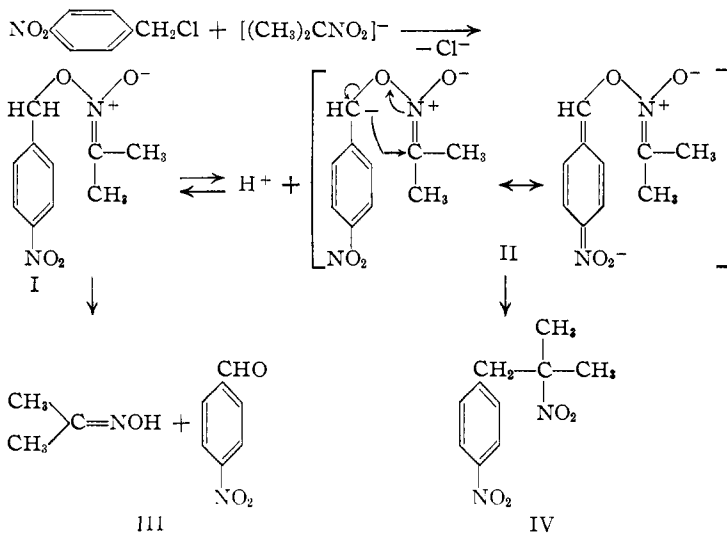
Table II presents a parallelism between those benzyl halides showing carbon-alkylation with sodium 2-propanenitronate and those exhibiting stilbene formation in the Williamson reaction. The mechanism proposed for stilbene formation¹⁰ involves the ready removal of a benzylic hydrogen facilitated by the presence of an ortho- or para-nitro group.

It is therefore proposed that the ease of removal of a benzylic hydrogen is an important factor in the production of carbon-alkylation. The following experiments substantiate this conclusion. The effect of a methyl group on the carbon alpha to the benzene ring would be to reduce the ionization of the benzylic hydrogen and, therefore, to favor oxygen-alkylation. This has been borne out by experiment: 1-(α -bromoethyl)-4-nitrobenzene gave a 60% yield of *p*-nitroacetophenone. The effect of increasing the acidity of the medium would be to hinder the ionization of the benzylic hydrogen and, therefore, to favor oxygen-alkylation. Two parallel runs were made with *p*-nitrobenzyl chloride and sodium 2-propanenitronate except that in one run an additional equivalent amount of 2-nitropropane was added. This increased the acidity of the medium (as

(11) Plisov, *Ukrainsku. Khim. Zhur.*, **4**, Sci. 1't., 241 (1929); Kleucker, *Ber.*, **62**, 2587 (1929); Kharasch, Nudenberg and Fields, *THIS JOURNAL*, **66**, 1276 (1944).

any acid would) and increased the oxygen-alkylation from 1% (no free nitroparaffin) to 6% (with free nitroparaffin).

The mechanism shown is suggested to explain the foregoing experiments.



The first step in both oxygen- and carbon-alkylation is the formation of the nitronic ester, I. When oxygen-alkylation occurs, *p*-nitrobenzaldehyde and acetoxime, III, are produced by thermal cleavage of the nitronic ester, I, at (a) together with a hydrogen shift. When carbon-alkylation occurs, the resonance-stabilized carbanion, II, is formed by the ionization of a benzylic hydrogen of I. Following the ionization, an internal nucleophilic displacement reaction by II occurs, producing the carbon-alkylation product, IV. An examination of the Fischer-Hirschfelder model of II shows that the spatial requirements for this rearrangement are satisfied since the two carbon atoms forming a new bond are adjacent to each other. Thus, there are two competing reactions of a nitronic ester such as I. The relative amounts of the final products are determined by the relative rates of the competing cleavage and ionization reactions. Since the rate of the ionization reaction is a function of the position of the ionization equilibrium, those factors in the structure of the reactants and in the reaction medium which shift the equilibrium of the ionization reaction will shift the direction of alkylation.

That the foregoing mechanism is not the only one possible in the alkylation of nitroparaffin salts is illustrated by the reaction of 1-(β -bromoethyl)-4-nitrobenzene with sodium 2-propanenitronate to produce 3-methyl-3-nitro-1-(*p*-nitrophenyl)-butane. By the preparation of a possible intermediate, *p*-nitrostyrene, and its conversion to the final product under the original reaction conditions, this reaction seems to proceed in two steps. The first step is dehydrobromination effected by the 2-propanenitronate ion acting as a

base. The second step is a Michael addition catalyzed by the basic reaction conditions.

Experimental¹²

1-(α -Bromoethyl)-4-nitrobenzene.—Seven-hundredths mole of 1-ethyl-4-nitrobenzene (n_D^{20} 1.5454) was brominated in carbon tetrachloride. A procedure of Cumming, Hopper and Wheeler¹³ was followed. A 92% yield of 1-(α -bromoethyl)-4-nitrobenzene was obtained; b. p. 152–153° (5 mm.); n_D^{20} 1.6028.

Anal. Calcd. for $\text{C}_9\text{H}_8\text{BrNO}_2$: N, 6.09. Found: N, 6.27.

Reaction of Halides and Sodium 2-Propanenitronate.—These alkylations which were run as described in a previous paper³ are summarized in Table III.

Preparation of *p*-Nitrostyrene.—1-(β -Bromoethyl)-4-nitrobenzene (m. p. 67–68°) was converted to *p*-nitrostyrene according to the method of Strassburg, Gregg and Walling¹⁴; m. p. 19–20°; lit. m. p. 21°.¹⁴

Condensation of *p*-Nitrostyrene and 2-Nitropropane.—*p*-Nitrostyrene (2.0 g., 0.013 mole), 2-nitropropane (1.2 g., 0.013 mole), and 10 drops of methanolic sodium methoxide dissolved in 10 ml. of methanol were refluxed for forty hours; after cooling the crystals were filtered. A 72% yield of 3-methyl-3-nitro-1-(*p*-nitrophenyl)-butane was obtained; m. p. 81–82°.

Proof of Structure of 2-Methyl-2-nitro-1-(*o*-nitrophenyl)-propane. **a. Reduction.**—2-Methyl-2-nitro-1-(*o*-nitrophenyl)-propane was reduced with Raney nickel and hydrogen as described by Hass, Berry and Bender.¹⁵ An 82% yield of 1-(*o*-aminophenyl)-2-methyl-2-propylamine was obtained; b. p. 107–109° (3.5 mm.); n_D^{20} 1.5577.

Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{N}_2$: N, 17.05. Found: N, 17.11.

(b) Selective Deamination.—1-(*o*-Aminophenyl)-2-methyl-2-propylamine was treated with 50% hypophosphorous acid according to the method of Kornblum and Iffland,¹⁶ to produce 2-methyl-1-phenyl-2-propylamine in 85% yield; b. p. 80° (15 mm.); n_D^{20} 1.5122; benzoyl derivative, m. p. 112–113°; lit. b. p. 94° (15 mm.); n_D^{20} 1.5132; benzoyl derivative, m. p. 112.5–113°.¹⁶

Proof of Structure of 3-Methyl-3-nitro-1-(*p*-nitrophenyl)-butane. **a. Reduction.**—3-Methyl-3-nitro-1-(*p*-nitrophenyl)-butane was reduced with Raney nickel and hydrogen as described by Hass, Berry and Bender.¹⁵ A 79% yield of 1-(*p*-aminophenyl)-3-methyl-3-butylamine was obtained; b. p. 120–122° (1 mm.); m. p. 36–37°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{18}\text{N}_2$: N, 15.72. Found: N, 15.7.

(b) Selective Deamination.—4-(*p*-Aminophenyl)-2-methyl-2-butylamine was treated with 50% hypophosphorous acid according to Kornblum and Iffland¹⁶ to produce 2-methyl-4-phenyl-2-butylamine in 72% yield; b. p. 98–100° (10 mm.); n_D^{20} 1.5061.

Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{N}$: C, 80.93; H, 10.50; N, 8.58. Found: C, 80.8; H, 10.8; N, 8.55.

(c) Exhaustive Methylation.—2-Methyl-4-phenyl-2-butylamine was converted to the corresponding methiodide with methyl iodide and potassium hydroxide in 73% yield using the directions of Plattner¹⁷; m. p. 202° dec.

(12) All melting points are corrected. Microanalyses by Mr. H. Galbraith and Miss L. Roth.

(13) Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," Constable & Co., Ltd., London, England, 1937, p. 351.

(14) Strassburg, Gregg and Walling, *THIS JOURNAL*, **69**, 2142 (1947).

(15) Hass, Berry and Bender, *ibid.*, **71**, 2290 (1949).

(16) Kornblum and Iffland, *ibid.*, **71**, 2137 (1949).

(17) Plattner, *Helv. Chim. Acta*, **27**, 229 (1944).

TABLE III
 REACTION OF HALIDES WITH SODIUM 2-PROPANENITRONATE

Halide	Moles of halide	Moles of sodium 2-propanenitronate	Time, hours	Temp., °C.	Product	M. p. of product °C.	Yield %
<i>o</i> -Nitrobenzyl chloride ^a	0.19	0.2	18	25	2-Methyl-2-nitro-1-(<i>o</i> -nitrophenyl)-propane ⁱ	54-55	46
					<i>o</i> -Nitrobenzaldehyde ^f	41-42	30
<i>m</i> -Nitrobenzyl chloride ^b	.05	.05	0.25	80	<i>m</i> -Nitrobenzaldehyde ^g	55-57	73
<i>p</i> -Nitrobenzyl chloride ^c	.059	.059	1	80	2-Methyl-2-nitro-1-(<i>p</i> -nitrophenyl)-propane	64-66	83
					<i>p</i> -Nitrobenzaldehyde ^h	104-106	1
<i>p</i> -Nitrobenzyl chloride ^c	.059	.059 ^m	1	80	2-Methyl-2-nitro-1-(<i>p</i> -nitrophenyl)-propane	64-66	76
					<i>p</i> -Nitrobenzaldehyde ^h	104-106	6
1-(α -Bromoethyl)-4-nitrobenzene	.03	.03	15	25	<i>p</i> -Nitroacetophenone ⁱ	79-80	60
1-(β -Bromoethyl)-4-nitrobenzene ^d	.05	.05	3	80	3-Methyl-3-nitro-1-(<i>p</i> -nitrophenyl)-butane ^k	81-82	54
2,4-Dinitrobenzyl chloride ^e	.05	.05 ^e	15	25	1-(2,4-Dinitrophenyl)-2-methyl-2-nitropropane ^l	68-69	33

^a M. p. 47-49°. ^b M. p. 45-46°. ^c M. p. 70-71°. ^d M. p. 67-68°. ^e M. p. 33-34°. ^f Phenylhydrazone, m. p. 154°. ^g Semicarbazone, m. p. 240°. ^h Semicarbazone, m. p. 220°; the aldehyde was separated by sodium bisulfite extraction. ⁱ Phenylhydrazone, m. p. 132°. ^j Calcd. for C₁₀H₉O₄: C, 53.56; H, 5.40; N, 12.49. Found: C, 53.5; H, 5.44; N, 12.49. ^k Calcd. for C₁₁H₁₁N₂O₄: C, 55.45; H, 5.92; N, 11.76. Found: C, 55.6; H, 6.04; N, 11.70. ^l Calcd. for C₁₀H₁₁N₂O₆: C, 44.61; H, 4.12; N, 15.61. Found: C, 44.4; H, 4.27; N, 15.8. ^m 0.059 mole of 2-nitropropane added to increase the acidity. This experiment was reproduced three times.

Anal. Calcd. for C₁₄H₂₁IN: C, 50.45; H, 7.26; N, 4.20. Found: C, 50.5; H, 7.25; N, 4.28.

The methiodide was converted to 3-methyl-2-phenyl-2-butene according to the procedure of Cope and Overberger¹⁸ in 78% yield; b. p. 85-86° (16 mm.); *n*_D²⁰ 1.5060.

(d) **Preparation of Isoamylbenzene.**—3-Methyl-1-phenyl-2-butene in ethanol solution was treated with Raney nickel and hydrogen at 50 p. s. i. and 25° for twenty hours. A 78% yield of isoamylbenzene was obtained; b. p. 83-84° (16 mm.); *n*_D²⁰ 1.4862; lit. b. p. 84° (16 mm.); *n*_D²⁰ 1.4835.¹⁹ 2,4-Diacetaminoisoamylbenzene was prepared according to method of Ipatieff and Schmerling¹⁹; m. p. 212-213°. The melting point of a mixture of this sample and an authentic sample showed no depression.

Rate Study. Materials.—Commercial absolute ethanol was used as solvent. 2-Nitropropane (*n*_D²⁰ 1.3940) was a re-rectified Commercial Solvents Corp. product. *p*-Nitrobenzyl chloride (m. p. 70-70.5°) was a recrystallized Eastman Kodak Co. product. *m*-Nitrobenzyl chloride (m. p. 45-46°) and *o*-nitrobenzyl chloride (m. p. 47-49°) have been described previously.⁸ Benzyl chloride was a Baker C. p. product.

Method.—Fifty ml. of an ethanolic solution containing 0.02 mole of lithium 2-propanenitronate²⁰ was placed in the reaction vessel and equilibrated in the constant-temperature bath. A fifty-ml. portion of an ethanolic solution containing 0.02 mole of halide was equilibrated in the constant-temperature bath and then pipetted into the reaction vessel. The reaction mixture was shaken and the timer was started.

The rates of reaction were determined by titration of the free chloride ion by the Volhard method. Ten-ml. aliquots were removed from the reaction mixture at intervals and drowned in ice-cold dilute nitric acid in a glass-stoppered bottle. An excess of standard silver nitrate

solution and a few ml. of nitrobenzene was added, and the mixture was vigorously shaken. The excess silver nitrate was then titrated against standard potassium thiocyanate solution using ferric alum as indicator. This modification of the Volhard procedure gave reproducible results accurate to within 3% when tested on known synthetic reaction mixtures.²¹

Results.—Figure 1 gives the experimental results of these rate studies. Since the initial concentrations of the reacting substances in these second-order reactions were the same, the rate expression may be written as $k_2t = [1/(a-x)] - (1/a)$ so that the plot of $1/(a-x)$ against t should be linear, the slope being equal to k_2 . Table I gives the values of the second-order rate constant calculated in this manner.

Acknowledgment.—Several stimulating discussions with Drs. Herbert C. Brown and Nathan Kornblum on various phases of this theory are gratefully acknowledged.

Summary

A kinetic study of the reactions of four benzyl halides with lithium 2-propanenitronate indicates that the rate-determining step in both oxygen- and carbon-alkylation is the formation of a nitronic ester intermediate. A comparison of the alkylation and Williamson reactions of benzyl halides indicates that the ease of removal of a benzylic hydrogen by a base is an important factor in determining the direction of the alkylation reaction. A mechanism is suggested to explain these results.

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(18) Cope and Overberger, *THIS JOURNAL*, **70**, 1433 (1948).

(19) Ipatieff and Schmerling, *ibid.*, **60**, 1476 (1938).

(20) The lithium salt was used since a homogeneous reaction mixture was needed.

(21) This method is essentially that of Beste and Hammett, *THIS JOURNAL*, **62**, 2482 (1940).