[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Alkylations of Certain Carbanions with 1-Chloro-1,2-diphenylethane. β-Eliminations with Other Bases.[1]

CHARLES R. HAUSER, CHARLES F. HAUSER, AND PHILLIP J. HAMRICK, JR.

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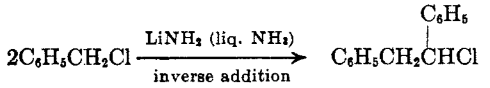
1-Chloro-1,2-diphenylethane underwent the substitution type of reaction with sodium diphenylmethide and sodio- or potassiophenylacetonitrile in liquid ammonia to form the corresponding alkylation products in high yields. However, this halide exhibited β-elimination with disodiophenylacetic acid and sodium ethoxide under similar conditions.

1-Chloro-1,2-diphenylethane (I) has recently[2] been prepared in good yield through the self-alkylation of benzyl chloride by means of lithium amide or sodium amide in liquid ammonia (Equation 1).

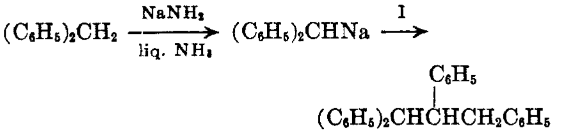


$$2C_6H_5CH_2Cl \xrightarrow[\text{inverse addition}]{LiNH_2\text{ (liq. }NH_3)} C_6H_5CH_2\overset{C_6H_5}{\overset{|}{C}}HCl \qquad (1)$$

I

The success of this preparation is dependent on the use of the inverse addition procedure, since halide I readily undergoes dehydrohalogenation (β-elimination) in the presence of excess of the amide ion to form stilbene.[2]

In spite of its tendency to undergo β-elimination,[3] halide I has now been found to enter into the substitution type of reaction with certain carbanions in liquid ammonia. Thus, sodium diphenylmethide underwent alkylation with halide I to form hydrocarbon II in 93% yield (Equation 2).

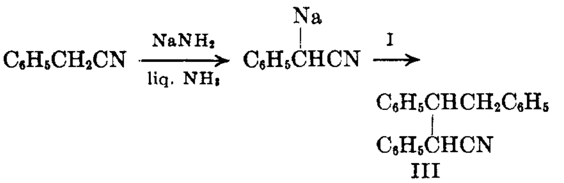


$$(C_6H_5)_2CH_2 \xrightarrow[\text{liq. }NH_3]{NaNH_2} (C_6H_5)_2CHNa \xrightarrow{I} (C_6H_5)_2CH\overset{C_6H_5}{\overset{|}{C}}HCH_2C_6H_5 \qquad (2)$$

II

Analogous alkylations of sodium diphenylmethide with various halides including β-phenylethyl chloride have previously been described.[4]

Similarly sodio- or potassiophenylacetonitrile underwent alkylation with halide I to form nitrile III in 80–81% yield (Equation 3).



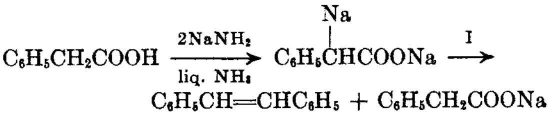
$$C_6H_5CH_2CN \xrightarrow[\text{liq. }NH_3]{NaNH_2} C_6H_5\overset{Na}{\overset{|}{C}}HCN \xrightarrow{I} \begin{array}{l} C_6H_5CHCH_2C_6H_5 \\ \quad | \\ C_6H_5CHCN \end{array} \qquad (3)$$

III

The product from this reaction consisted of only one of the two possible diastereoisomers of nitrile III. The analogous alkylation of sodio- or potassiophenylacetonitrile with α-phenylethyl chloride[5] has been shown[6] to produce the erythro isomer of 2,3-diphenylbutyronitrile in 99% yield.

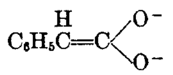
The reaction represented by Equation 3 has furnished a convenient starting point for a subsequent study[7] of the influence of stereochemistry on the acid-catalyzed five- versus six-carbon ring cyclizations of the corresponding carbóxylic acid.

However, disodiophenylacetic acid failed to undergo appreciable alkylation with halide I. Instead, β-elimination occurred to form stilbene (75%) and monosodiophenylacetic acid which was isolated as the free acid (73%) (Equation 4).



$$C_6H_5CH_2COOH \xrightarrow[\text{liq. }NH_3]{2NaNH_2} C_6H_5\overset{Na}{\overset{|}{C}}HCOONa \xrightarrow{I} C_6H_5CH{=}CHC_6H_5 + C_6H_5CH_2COONa \qquad (4)$$

This result might suggest that the dianion of phenylacetic acid functions more like an oxygen base as in resonance structure IV than a carbanion, although this carbanion has been alkylated with certain other halides.[8]



(IV)

Also halide I underwent β-elimination with sodium ethoxide to form stilbene (92%); none of the corresponding substitution product was found.

In Table I are summarized the types of reaction exhibited by halide I with the anions of these sodio

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[1] Supported by the Office of Ordnance Research, U.S. Army.

[2] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

[3] It should be mentioned that halide I was kept in the refrigerator for several months without apparent decomposition.

[4] C. R. Hauser and P. J. Hamrick, Jr., *J. Am. Chem. Soc.*, **79**, 3142 (1957).

[5] C. R. Hauser and W. R. Brasen, *J. Am. Chem. Soc.*, **78**, 494 (1956).

[6] W. R. Brasen and C. R. Hauser, *J. Am. Chem. Soc.*, **79**, 395 (1957).

[7] D. Lednicer and C. R. Hauser, *J. Am. Chem. Soc.*, **80**, 3409 (1958).

[8] C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.* **78**, 4942 (1956).

bases or, in certain cases, potassio bases[9] in liquid ammonia at −33°.

TABLE I

Types of Reaction of Halide I with Anions in Liq. NH_3 at −33°

Substitution	β-Elimination
$(C_6H_5)_2\bar{C}H$	$\bar{N}H_2$
$C_6H_5\bar{C}HCN$	$C_6H_5\bar{C}HCO\bar{O}$
	OC_2H_5

Since halide I undergoes β-elimination with ethoxide ion but the substitution type of reaction with the more strongly basic diphenylmethide ion, the well known generalization[10] that the former reaction is favored by an increase in basic strength is not applicable to these two anions. The generalization was based mostly on studies of a series of oxygen bases such as the acetate, phenoxide, and hydroxide ions[10]; it might possibly be applicable also to a series of carbanions when considered alone.

EXPERIMENTAL[11]

Alkylation of sodium diphenylmethide with halide I to form hydrocarbon II. To a stirred suspension of 0.05 mole of sodium amide in 200 ml. of liquid ammonia[12] there was added a solution of 8.80 g. (0.05 mole) of diphenylmethane in 200 ml. of anhydrous ether, followed after 5 min. by a solution of 10.8 g. (0.05 mole) of 1-chloro-1,2-diphenylethane (I)[2] in 50 ml. of anhydrous ether. The red color of the diphenylmethide ion was discharged within a few minutes to produce a yellow mixture. After stirring for 0.5 hr., the liquid ammonia was evaporated on the steam bath as an equal volume of ether was added. The resulting ethereal suspension was shaken with water, and the two layers were separated. The ethereal layer was dried over Drierite, and, after filtering, the solvent was removed. The residue was recrystallized twice from methanol to give 16.2 g. (93%) of 1,1,2,3-tetraphenylpropane (II), m.p. 82–83°.

Anal. Calcd. for $C_{27}H_{24}$: C, 93.05; H, 6.94. Found: C, 93.31; H, 6.77.

Alkylation of alkali phenylacetonitriles with halide I to form nitrile III. To a stirred suspension of 0.05 mole of sodium amide in 200 ml. of liquid ammonia[12] there was added a solution of 5.85 g. (0.05 mole) of phenylacetonitrile in 50 ml. of anhydrous ether, followed after 5 minutes by a solution of 10.8 g. (0.05 mole) of 1-chloro-1,2-diphenylethane (I) in 50 ml. of anhydrous ether. The mixture was stirred for several hours (Dry Ice-acetone condenser), and the liquid ammonia was then replaced by ether. The resulting suspension was shaken with water, and the layers were separated. The ethereal layer was washed with water, dilute hydrochloric acid, and sodium bicarbonate solution. After drying over Drierite, the solvent was removed, and the residue was recrystallized from petroleum ether (b.p. 30–60°) to give several crops of crystals of 2,3,4-triphenylbutyronitrile (III). The total yield was 11.8 g. (80%), m.p. 131–132°; reported m.p. 129–131°.[13]

Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.71; H, 6.55; N, 4.63.

Similarly a solution of 0.10 mole of potassium amide in 200 ml. of liquid ammonia was treated with a solution of 12.87 g. (0.11 mole) of phenylacetonitrile in 50 ml. of ether. The resulting green solution of potassiophenylacetonitrile was stirred for 15 min., and then treated during 5 min. with a solution of 21.65 g. (0.10 mole) of halide I in 50 ml. of ether. The color was discharged within 45 min. A little ammonium chloride was added, and the suspension was taken to dryness on the steam bath. The residue was washed well with water, and recrystallized from ethanol to give 23.2 g. (81%, needles) of nitrile III, m.p. 131–132°.

Reaction of disodiophenylacetic acid with halide I (β-Elimination). To a stirred suspension of 0.1 mole of sodium amide in 200 ml. of liquid ammonia[12] was added a solution of 6.80 g. (0.05 mole) of phenylacetic acid in 50 ml. of dry ether, followed after 5 min. by a solution of 10.80 g. (0.05 mole) of 1-chloro-1,2-diphenylethane (I) in 50 ml. of ether. A purple color appeared immediately. After 25 min., the liquid ammonia was replaced by ether (steam bath), and the resulting ethereal suspension was extracted with two 50 ml. portions of water. The combined aqueous solution (after heating to remove dissolved ether) was cooled and acidified to precipitate 5.0 (73%) of phenylacetic acid, m.p. and mixed m.p. 75–76°. The ethereal solution was dried over Drierite, and the solvent was removed. The yellow residue (9.0 g.) melted at 119–125°. Recrystallization from methanol-chloroform solution (ratio 4:1) gave 6.7 g. (75%) of stilbene, m.p. and mixed m.p. 126–127°.

Reaction of sodium ethoxide with halide I (β-elimination). To a solution of 1.6 g. (0.07 mole) of sodium metal in 300 ml. of liquid ammonia there was added 3.5 g. (0.0701 mole) of absolute ethanol (blue color discharged). The resulting solution of sodium ethoxide (0.07 mole) was stirred, and a solution of 15 g. (0.069 mole) of 1-chloro-1,2-diphenylethane (I) in 50 ml. of ether was added. After 5 hr. (Dry Ice–acetone condenser), solid ammonium chloride (10 g.) was added, and the liquid ammonia was replaced by ether (200 ml.). Water was added, and the two layers separated. The ethereal layer was evaporated (steam bath) to leave a solid residue which was taken up in 25 ml. of hot benzene. Petroleum ether (b.p. 30–60°) was added to precipitate 10.2 g. (82%) of stilbene, m.p. and mixed m.p. 124–125°. More (1.3 g.) of stilbene was isolated from the mother liquor; total yield 92%. No other product was found.

DURHAM, N. C.

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(9) Although the metallic cation appears to have no significant influence on the ratio of the substitution and elimination products from a halide with ethoxide ion in ethanol (see M. S. Newman and F. J. Evans, *J. Am. Chem. Soc.*, 76, 4187 (1954)), such an influence has been observed with certain stronger bases. Thus, β-phenylethyl chloride reacts with sodium diphenylmethide in liquid ammonia to form almost exclusively the substitution product, whereas this halide undergoes appreciable (18%) β-elimination with potassium diphenylmethide, which effectively functions as the stronger base; see ref. 4.

(10) See C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 451–2; E. E. Royals, *Advanced Organic Chemistry*, Prentice-Hall, Inc., New York, N. Y., 1954, p. 299.

(11) Melting points were taken on a Fisher-Johns melting point apparatus. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(12) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, *VIII*, 122 (1954).

(13) Y. De Schuttenbach, *Ann. chim.* (11), 6, 90 (1936).