

Alkylations of Mono- and Dipotassio-2,3,3-triphenylpropionitrile. Equilibrium Factor in Benzhydrylations of 1,2-Dianions. Dehydrocyanation¹

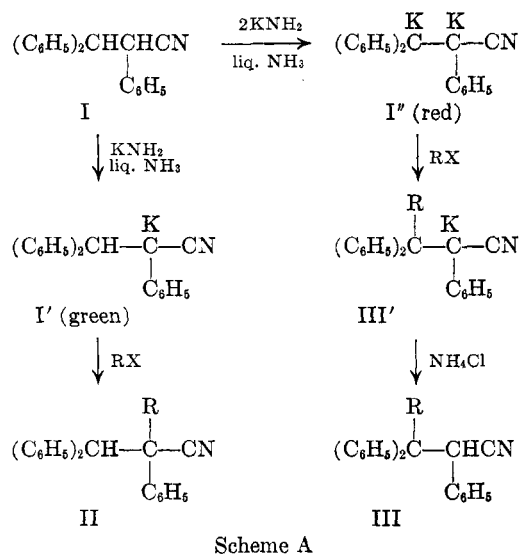
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Alkylations of 2,3,3-triphenylpropionitrile (I) through its monocarbanion to form the corresponding α -derivatives were effected with such diverse halides as *n*-butyl and benzhydryl halides in liquid ammonia. Alkylation of I through its dicarbanion to afford the β -derivative was realized with the butyl halide but not with the benzhydryl halide. The reaction with the latter halide gave mainly 2,3,3-triphenylacrylonitrile and tetraphenylethane. A related 1,2-dianion underwent a similar reaction with benzhydryl chloride. The α -butyl derivative of I underwent dehydrocyanation with potassium amide whereas the β -butyl derivative did not. Mechanisms are considered.

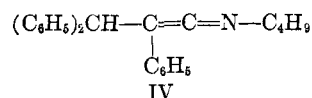
It has previously been observed³ that 2,3,3-triphenylpropionitrile (I) can be converted by one and two molecular equivalents of potassium amide in liquid ammonia to its mono and dipotassio salts, I' and I'' respectively. These salts were alkylated with benzyl chloride to form the α - and β -derivatives, II and III (R = benzyl), respectively (Scheme A).



It has now been found that these two modes of alkylation can be realized also with the more typical alkyl halide *n*-butyl bromide, which afforded II and III (R = *n*-butyl) in yields of 85 and 95%, respectively. It seems likely that other purely aliphatic alkyl halides would react similarly.

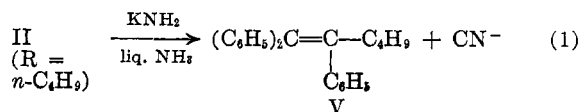
The structures of both products were supported by analysis and by infrared and n.m.r. spectra. The former spectra showed bands at 4.5 μ for the nitrile group⁴ and at 13–13.5 and 14.3–14.4 μ

for monosubstituted benzene rings,⁵ but not at (or near) 5 μ ,⁶ which might have been expected for the possible *N*-butyl derivative IV.



The n.m.r. spectra showed peaks for aromatic, benzylic and aliphatic protons, the relative areas under which were approximately 15:1:9 in agreement with structures II and III (R = *n*-butyl). These observed areas were considerably different from the calculated values of 14:4:7 for the possible ring-substituted derivatives. Moreover, the spectra showed single peaks for the benzylic protons, not double peaks for protons on adjacent carbon atoms, which would have been present in ring-substituted derivatives. Actually such a double peak was present in the spectrum of the original nitrile I, which has two such benzylic protons.⁷ Also, these spectra show that neither product was the possible dibutylation derivative, which would have no benzylic hydrogen.

These data show that the butylation products had structure II or III (R = *n*-butyl). That the one from the green monocarbanion I' was the α -derivative II was confirmed by dehydrocyanation with potassium amide in liquid ammonia to form olefinic hydrocarbon V and the cyanide ion in yields of 75 and 90%, respectively.



Such a dehydrocyanation has previously been observed with certain related nitriles having β -

(1) Supported in part by the National Science Foundation.

(2) Allied Chemical and Dye Corporation Fellow, 1958–1959.

(3) C. R. Hauser, T. M. Harris, and T. G. Ledford, *J. Am. Chem. Soc.*, **81**, 4099 (1959).

(4) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, 1958, p. 263.

(5) *Ibid.*, p. 64ff.

(6) This value has been reported for the ketenimine group in several compounds similar to IV; C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **75**, 657 (1953).

(7) See J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, 1959, p. 42.

hydrogen but no α -hydrogen.⁸ As the butylation product from the red dicarbanion I'' has an α -hydrogen but no β -hydrogen, it may be regarded as the β -derivative (III. R = *n*-butyl). This conclusion is further supported by analogy with the corresponding benzylation product III (R = benzyl), which was independently synthesized.⁸

Like the benzyl and butyl halides, benzhydryl bromide reacted with the monopotassium salt I' to give the corresponding α -derivative II (R = benzhydryl) (63%), though benzhydryl chloride failed to react appreciably with this salt even after longer treatment. The structure of the product was supported by its infrared spectrum and by dehydrocyanation with potassium amide (see equation 1).

However, unlike the benzyl and butyl halides, benzhydryl chloride or bromide reacted with dicarbanion I'' to give mainly unsaturated nitrile VI and the dimeric hydrocarbon VII. Whereas normal alkylation involved a molecular equivalent of the halide (see Scheme A), this reaction required two molecular equivalents of benzhydryl halide for maximum yields of VI and VII. The yields of these and other products under various conditions are summarized in Table I.



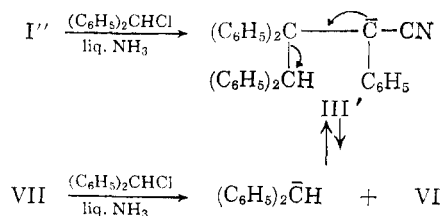
TABLE I

REACTIONS OF DIPOTASSIO SALT I'' WITH BENZHYDRYL CHLORIDE IN LIQUID AMMONIA

Halide, Mol. Equiv.	Hydrocarbon VII, % Yield	Diphenylmethane, % Yield	Unsat. Nitrile VI, % Yield	Nitrile I, % Recovered
1	51 ^a	29	56	24
1 ^b	40	18	57	33
1 ^c	53	.. ^d	42	22
1 ^{b,e}	52	.. ^d	50	.. ^d
2	69 ^f	..	79	..
2 ^{b,g}	49 ^h	..	80	..

^a The yield was 50% in a duplicate run. ^b Inverse neutralization procedure was employed. ^c Inverse addition procedure was employed. ^d An appreciable amount of this product was presumably produced. ^e Disodio salt of I was used. ^f An 82% yield of VII was isolated in another experiment. ^g Benzhydryl bromide was used. ^h This yield is probably not the maximum obtainable.

The formation of unsaturated nitrile VI and dimeric hydrocarbon VII may be accounted for on the reasonable assumption that normal alkylation of dicarbanion I'' occurred with the benzhydryl halide, but that the resulting monocarbanion III' underwent β -elimination accompanied by benzhydrylation of the resulting diphenylmethide ion (Scheme B). The latter alkylation to form VII is known to occur very rapidly.⁹



Scheme B

The possible benzhydrylation at the α -carbon of I'' followed by β -elimination of diphenylmethide ion evidently did not occur, as the resulting monocarbanion would have eliminated preferentially the cyanide ion (see equation 1).

Although the critical step in the above mechanism (Scheme B) is the β -elimination, the equilibrium of this step appears to be on the side of III', and the reaction proceeds as indicated only because the diphenylmethide ion is alkylated preferentially. That the equilibrium is on the side of III' was supported by treatment of red-orange diphenylmethide ion with an equivalent of unsaturated nitrile VI to produce a green color, which may be ascribed to III' or to a corresponding 1,2-addition product (imine). That the diphenylmethide ion undergoes preferential alkylation was supported by treatment of this green mixture with an equivalent of benzhydryl chloride to afford hydrocarbon VII and regenerated nitrile VI. Also there was obtained diphenylmethane, which presumably arose from unchanged III' (or 1,2-addition product) on neutralization (see below).

As the equilibrium in Scheme B appears to be on the side of anion III', the isolation of the nitrile III (R = benzhydryl) seemed possible. However, none of this compound was isolated when the reaction mixture from molecular equivalents of dicarbanion I'' and benzhydryl chloride was neutralized directly or inversely with ammonium chloride in liquid ammonia. Besides unsaturated nitrile VI and hydrocarbon VII, the starting nitrile I and diphenylmethane were obtained (see Table I). Nitrile I arose presumably from unchanged dicarbanion I'' on neutralization, but the red color of I'' must have been masked, as the reaction mixture before neutralization was blackish green. Possibly I'' had undergone conjugate- or 1,2-addition with VI, this reaction reversing on neutralization. The isolation of diphenylmethane in the above experiment indicated the presence in the reaction mixture of the corresponding amount of monocarbanion III' (or 1,2-addition product), which, on neutralization, would form this hydrocarbon and nitrile VI (see below).

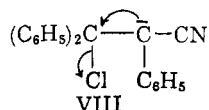
Neither was compound III (R = benzhydryl) isolated when diphenylmethide ion was treated with an equivalent of nitrile VI and the resulting green equilibrium mixture (containing anion III') neutralized directly or inversely with ammonium chloride. As diphenylmethane and nitrile VI

(8) C. R. Hauser and W. R. Brasen, *J. Am. Chem. Soc.*, **78**, 82 (1956).

(9) C. R. Hauser and P. J. Hamrick, *ibid.*, **79**, 3142 (1957).

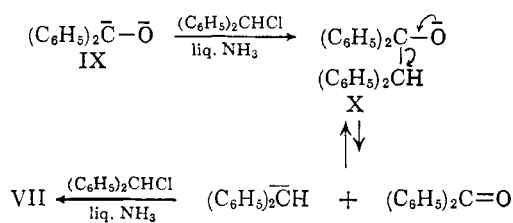
were regenerated, the diphenylmethide ion, in equilibrium with III', evidently underwent preferential neutralization even though it was present in relatively low concentration.

An alternative mechanism that would also account for the results in Table I would involve displacement on the halogen of benzhydryl halide by dicarbanion I'' to form, as intermediates, diphenylmethide ion and the chloroanion VIII (or the α -chloro derivative). The former intermediate would undergo benzhydrylation and the latter, β -elimination, to give hydrocarbon VII and unsaturated nitrile VI, respectively. Some of the diphenylmethide ion might add to nitrile VI to form, in equilibrium, monocarbanion III' (or the 1,2-addition product), from which diphenylmethane might be produced on neutralization (see Scheme B).



Such a displacement on halogen has been observed recently¹⁰ in liquid ammonia with the diphenylmethide ion and certain polyhalides, for example, carbon tetrachloride, though it appears not to have been demonstrated with benzhydryl chloride.

Of these two possible mechanisms for the reaction of dicarbanion I'' with the benzhydryl halide, that involving the initial alkylation (see Scheme B) seems more likely, especially as this type of mechanism was demonstrated in the corresponding reaction of the related 1,2-dianion IX with this halide (Scheme C). The intermediate monoanion X and the ketone in Scheme C correspond to intermediate monoanion III' and the unsaturated nitrile in Scheme B.



Scheme C

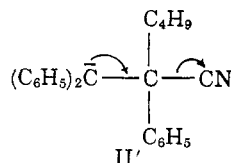
Similar to dicarbanion I'', dianion IX reacted with two molecular equivalents of benzhydryl chloride in liquid ammonia to give benzophenone, tetraphenylethane (VII), and diphenylmethane. These products must have arisen through the intermediate formation of monoanion X, as the carbinol corresponding to this anion has previously¹¹ been prepared by treatment of IX with one molecular

equivalent of benzhydryl chloride, followed by inverse neutralization of the reaction mixture. The failure to isolate the benzhydrylation product of dicarbanion I'' under such conditions (see above) is not surprising, as the equilibrium involving intermediate monoanion III' in Scheme B would presumably be further on the side of its elimination products than that of the corresponding intermediate X in Scheme C.

Also similar to the monoanion III' that was assumed to be formed when diphenylmethide ion was treated with unsaturated nitrile VI (see above), colorless monoanion X, prepared from red-orange diphenylmethide ion and benzophenone, reacted with benzhydryl chloride to give hydrocarbon VII, diphenylmethane, and benzophenone (see Scheme C). The corresponding reaction of X with benzyl chloride to afford triphenylethane was described previously.¹² That these reactions involved the intermediate formation of monoanion X was established by isolation of the corresponding carbinol employing inverse neutralization.¹³

Incidentally, in the reactions of the mono- and dianions shown in Scheme C, relatively more tetraphenylethane and relatively less diphenylmethane were obtained when the metallic cation was sodium than when it was potassium.

Further Consideration of Dehydrocyanation.—The β -elimination shown in equation 1 appears to involve the intermediate formation of carbanion II', as the reaction mixture acquires the dark red color characteristic of the diphenylmethide type of carbanion. When the solid nitrile II (R = *n*-butyl) was added to potassium amide in liquid ammonia, the red color was observed for about twenty minutes, but, when a solution of II in tetrahydrofuran was added, only a transient color appeared.



Attempts to alkylate the assumed intermediate carbanion II' to form a dialkylation product of I were unsuccessful. However, such a dialkylation product could presumably be prepared by further alkylation of carbanion III', which does not undergo dehydrocyanation under similar conditions (see Scheme A).

The dehydrocyanation (equation 1) furnishes the final step in a synthesis of such an olefin as V from phenylacetone nitrile, which has previously been benzhydrylated to form I in 99% yield.¹⁴ The yields in the α -butylation of I and dehydrocyana-

(10) C. R. Hauser, W. G. Kofron, W. R. Dunnivant, and W. F. Owens, *J. Org. Chem.*, **26**, 2627 (1961).

(11) P. J. Hamrick and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 493 (1959).

(12) P. J. Hamrick and C. R. Hauser, *ibid.*, **81**, 3144 (1959).

(13) P. J. Hamrick and C. R. Hauser, *ibid.*, **81**, 2096 (1959).

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

tion of the product were 85 and 89%, respectively. Earlier workers¹⁵ have prepared olefin V in unreported yield by butylation of deoxybenzoin, reaction of the resulting ketone with phenylmagnesium halide, and dehydration of the resulting carbinol.

Experimental¹⁶

Monopotassio Salt I'.—To a stirred solution of 0.025 mole of potassium amide in 250 ml. of commercial, anhydrous liquid ammonia was added 7.07 g. (0.025 mole) of solid 2,3,3-triphenylpropionitrile, and the resulting green solution was stirred for 15 min. This solution was considered to contain 0.025 mole of I'.³

Butylation of I' to Form α -Butyl Derivative II.—To a stirred solution of 0.025 mole of the monopotassio salt I' in 250 ml. of liquid ammonia was added 3.4 g. (0.025 mole) of butyl bromide in 15 ml. of dry ether. The green color of I' was discharged as the last of the bromide was added. The ammonia was evaporated as an equal volume of ether was added, and the resulting ethereal suspension was shaken with water. The ethereal layer was separated, dried over sodium sulfate, and the solvent removed. The solid residue was recrystallized twice from chloroform-methanol to give 7.2 g. (85%) of 2-diphenylmethyl-2-phenylhexanenitrile (II. R = *n*-butyl), m.p. 164.5–165°. Principal infrared bands were at 4.51, 13.4, and 14.3 μ .

Anal. Calcd. for C₂₅H₂₅N: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.63; H, 7.36; N, 4.24.

A sample of 3.4 g. (0.01 mole) of this nitrile was added to a stirred solution of 0.01 mole of potassium amide in 50 ml. of liquid ammonia. As the solid dissolved a deep red color developed, then gradually faded to tan within about 20 min. The ammonia was replaced with ether. The resulting ethereal suspension was shaken with water, and the two layers were separated. The aqueous layer gave a strong positive Prussian blue test for cyanide ion, the yield of which was 90% as determined by a standard procedure.¹⁷ The ethereal layer was combined with an ether extract of the aqueous layer and dried over sodium sulfate. The solvent was removed, and the residue was recrystallized from methanol to give 2.29 g. (75%) of 1,1,2-triphenylhexene (V), m.p. 88°. A 1.56-g. sample (5 mmoles) of this olefin was oxidized with chromium trioxide in glacial acetic acid¹⁸ to give benzophenone and valerophenone, which were identified by vapor phase chromatography by comparison of retention times with those of known samples.

When a solution of 6.8 g. (0.02 mole) of nitrile II (R = *n*-butyl) in 20 ml. of tetrahydrofuran was added to a stirred solution of 0.02 mole of potassium amide in 200 ml. of liquid ammonia, only a transient red color appeared as the reactants came into contact. The yields of olefin V and ammonia, only a transient red color appeared as the reactants came into contact. The yields of olefin V and cyanide ion were 89 and 70%, respectively.

Benzhydrylation of I' to Form α -Benzhydryl Derivative II.—To a stirred solution of 0.025 mole of I' in 250 ml. of liquid ammonia was added 6.2 g. (0.025 mole) of benzhydryl bromide in 30 ml. of dry ether. After 1 hr. ammonium chloride was added, and the ammonia replaced with an equal volume of ether. The resulting ethereal suspension was shaken with water, and the mixture was filtered. The solid was recrystallized from chloroform-methanol to give 7 g.

(63%) of 2,3,3,3',3'-pentaphenylisobutyronitrile (II. R = benzhydryl), m.p. 208–211° and at 212° after recrystallization from chloroform, reported m.p. 212–213°. This product was shown not to be the possible tetraphenylethane (VII, m.p. 212°) by mixed melting point (m.p. 188–192) with authentic VII and by the fact that it has previously been prepared by the benzydrylation of I' and analyzed.¹⁴ In the earlier procedure benzhydryl chloride was reported to give the product (m.p. 212–213°) in 33% yield after 2 hr. As we have been unable to isolate an appreciable yield of it with the chloride in the usual medium (see above) even after 3 hr., the earlier experiment apparently involved more drastic conditions or the use of the bromide.

The infrared spectrum of II (R = benzhydryl) showed bands at 4.5, 13.5, and 14.5 μ .

A 1-g. sample (2.2 mmoles) of this nitrile was added to a stirred solution of 5 mmoles of potassium amide in 60 ml. of liquid ammonia to give cyanide ion (35%)¹⁷ and presumably 1,1,2,3,3-pentaphenylpropene (not isolated). About half of the starting nitrile II (R = benzhydryl) was recovered.

Dipotassio Salt I''.—To a stirred solution of 0.05 mole of potassium amide in 250 ml. of liquid ammonia was added 7.07 g. (0.025 mole) of solid 2,3,3-triphenylpropionitrile, and the resulting deep red solution was stirred for 20 min. This solution was considered to contain 0.025 mole of I''.³

Butylation of I'' to Form β -Butyl Derivative III.—To a stirred solution of 0.05 mole of I'' in 250 ml. of liquid ammonia was added 7.6 g. (0.055 mole) of butyl bromide in 30 ml. of dry ether. After stirring for 90 min., the reaction mixture was neutralized with ammonium chloride, and the ammonia was evaporated. The residue was stirred with 100 ml. of hot ether, and the resulting mixture was filtered. This process was repeated twice, and the solvent was removed from the combined ethereal solution. The resulting solid residue was recrystallized twice from ethanol to give 13.3 g. (78%) of 2,3,3-triphenylheptanenitrile (III. R = *n*-butyl), m.p. 115–116°. More of the product, m.p. 114–116°, was isolated from the mother liquors; total yield 95%. The analytical sample melted at 116°. The infrared spectrum (KBr) had bands at 4.5, 13.1, and 14.1 μ .

Anal. Calcd. for C₂₅H₂₅N: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.67; H, 7.36; N, 4.19.

Reactions of I'' with Benzhydryl Chloride.—The results from these reactions under various conditions are summarized in Table I. Typical experiments employing 1 and 2 molecular equivalents of the halide are described below.

A. With 1 Equivalent of Halide.—To a stirred solution of 0.025 mole of I'' in 250 ml. of liquid ammonia was added 5.6 g. (0.025 mole) of benzhydryl chloride in 30 ml. of dry ether. The resulting blackish green mixture was stirred for 1 hr., and solid ammonium chloride was then added. The ammonia was evaporated, and the residue was stirred with 100 ml. of hot chloroform. The mixture was filtered, and an equal volume of methanol added to the filtrate. The solution was concentrated to approximately half its original volume, and chilled. The resulting cream-colored precipitate was recrystallized from chloroform-methanol to give 2.1 g. (51%) of tetraphenylethane (VII), m.p. and mixed m.p. 212°. The mother liquors were combined, and the solvent was evaporated. The residue (7 g., m.p. 94–144°) was separated into three fractions by crystallization from chloroform-methanol. The first fraction (3.5 g., 50%) was essentially pure 2,3,3-triphenylacrylonitrile (VI), m.p. and mixed m.p. 165°. The third fraction gave, after several recrystallizations from methanol, (1.63 g., 23%) of starting nitrile I, m.p. and mixed m.p. 104°. The middle fraction (0.5 g.) was shown by ultraviolet spectrometry to consist mainly (92%) of nitrile VI, the rest being nitrile I. The total yields of nitriles VI and I were estimated to be 56 and 24%, respectively. From the mother liquors was isolated diphenylmethane (29%), identified by its gas chromatographic retention time and its infrared spectrum, both identical with those of an authentic sample.

(15) N. P. Buu-Hoi, Hiong-Ki-Wei, A. Lacassagne, and J. Lecocq, *Compt. rend.*, **219**, 589 (1944).

(16) Melting points are uncorrected. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(17) F. Charlot and D. Bezier, "Quantitative Inorganic Analysis," trans. by R. C. Murray, John Wiley and Sons, Inc., New York, 1957, p. 380.

(18) See C. R. Hauser, P. S. Skell, R. D. Bright, and W. B. Renfrow, *J. Am. Chem. Soc.*, **69**, 589 (1947).

In another experiment the reaction mixture was poured into a solution of ammonium chloride in liquid ammonia (inverse neutralization procedure). The resulting mixture was worked up as described above (see Table I).

B. With 2 Equivalents of Halide.—To a stirred solution of 0.05 mole of I' in 250 ml. of liquid ammonia was added 20.3 g. (0.05 mole) of benzhydryl chloride in 60 ml. of dry ether. The resulting pale green mixture was stirred for 1 hr., neutralized with ammonium chloride, and worked up essentially as described under A. The cream-colored precipitate was recrystallized from chloroform to give 11.5 g. (69%) of tetraphenylethane, m.p. and mixed m.p. 212°. Evaporation of the remaining solvent and recrystallization of the residue from chloroform-methanol gave 11.1 g. (79%) of 2,3,3-triphenylacrylonitrile, (VI), m.p. and mixed m.p. 164.5–165°.

Reactions of Equilibrium Mixture from Nitrile VI and Diphenylmethide Ion. A. With Benzhydryl Chloride.—To a stirred, red-orange solution of 0.025 mole of potassium diphenylmethide¹⁰ in 200 ml. of liquid ammonia was added 7.07 g. (0.025 mole) of solid 2,3,3-triphenylacrylonitrile (VI). The color of the mixture gradually changed to green as the solid dissolved (1–2 hr.). To the resulting, stirred solution was added 5.63 g. (0.025 mole) of benzhydryl chloride in an equal volume of dry ether. After 1 hr., ammonium chloride was added, and the ammonia evaporated. Water was added to the residue, and the mixture was filtered. The solid was recrystallized from chloroform-methanol to give 2.2 g. (26%) of tetraphenylethane (VII), m.p. and mixed m.p. 212°. The mother liquors were concentrated and chilled to give, after recrystallization from methanol, starting nitrile VI, m.p. and mixed m.p. 164–165°. Also diphenylmethane was obtained in a yield estimated by vapor phase chromatography to be 66%.

Similarly, 0.021 mole of red-orange sodium diphenylmethide¹³ in 200 ml. of liquid ammonia was treated with 6 g. (0.021 mole) of nitrile VI in 15 ml. of tetrahydrofuran. After 30 min. the color had changed to purple-green. To the stirred solution was added 4.8 g. (0.021 mole) of benzhydryl chloride in some ether. After 2 hr. the reaction mixture was worked up as described above to give 3.2 g. (44%) of tetraphenylethane (VII), m.p. and mixed m.p. 212°, 4.5 g. (75%) of starting nitrile VI, m.p. and mixed m.p. 165°, and presumably some diphenylmethane.

B. With Ammonium Chloride.—The green equilibrium mixture from molecular equivalents of potassium diphenylmethide and nitrile VI was prepared in liquid ammonia as described above under (A), and poured into excess ammonium chloride in liquid ammonia. Diphenylmethane and nitrile VI were recovered.

Similarly the purple-green equilibrium mixture from molecular equivalents of sodium diphenylmethide and nitrile VI was prepared in liquid ammonia and tetrahydrofuran as described above and under (A), and poured into excess ammonium chloride in liquid ammonia. Diphenylmethane and nitrile VI were recovered.

Disodio and Dipotassio Salt IX.—To a stirred solution of 2.3 g. (0.1 g.-atom) of sodium in 250 ml. of anhydrous liquid ammonia was added 9.11 g. (0.05 mole) of benzophenone in 30 ml. of dry ether, and the resulting deep purple-black solution was stirred for 10 min. This solution was consid-

ered to contain 0.05 mole of disodiobenzophenone (IX).¹¹

Similarly 0.05 mole of benzophenone in ether was added to 4 g. (0.1 g.-atom) of potassium in liquid ammonia, and the resulting blue-black solution was stirred for 20 min. This solution was considered to contain 0.05 mole of dipotassiobenzophenone (IX).

Reaction of Dianion IX with Two Molecular Equivalents of Benzhydryl Chloride.—To a stirred solution of 0.05 mole of disodio salt IX in 250 ml. of liquid ammonia was added 20.3 g. (0.1 mole) of benzhydryl chloride in ether. The purple-black color of anion IX was discharged after slightly more than half of the halide had been added. The reaction mixture was stirred for 2 hr., and the ammonia and ether were evaporated. The residue was shaken with water and methylene chloride, and the resulting mixture was filtered. The methylene chloride layer of the filtrate was separated, dried over sodium sulfate, concentrated, and diluted with ether. The resulting precipitate was collected on a funnel and recrystallized from chloroform-methanol to give 5.22 g. (31%) of tetraphenylethane (VII), m.p. and mixed m.p. 212°. The ethereal filtrate obtained after removing VII was shown by vapor phase chromatography to contain 7 g. (77%) of benzophenone and 4.7 g. (28%) of diphenylmethane. This solution presumably also contained more tetraphenylethane (VII).

Similarly, a solution of 0.05 mole of dipotassio salt IX in liquid ammonia was treated with 0.1 mole of benzhydryl chloride in ether, the blue-black color of anion IX being discharged gradually as the first half of the halide was added. After stirring for 2 hr., the ammonia was evaporated, and the resulting ethereal suspension was poured into a stirred ethereal solution of acetic acid. Water was added, and the mixture was filtered. The solid on the funnel afforded 0.6 g. of tetraphenylethane (VII). The ether layer of the filtrate was worked up to give 1.3 g. more of VII; total yield isolated, 11%. Presumably more of VII was present in the reaction mixture but was not isolated. There was also obtained an oil, b.p. 92–122° at 0.4 mm., which was shown by vapor phase chromatography to consist of 8.6 g. (51%) of diphenylmethane and 7.46 g. (82%) of benzophenone.

Reactions of the Equilibrium Mixture from Benzophenone and Diphenylmethide Ion.—To a stirred red-orange solution of 0.05 mole of sodium diphenylmethide in 200 ml. of liquid ammonia was added 9.1 g. (0.05 mole) of benzophenone in 100 ml. of dry ether to form an essentially colorless mixture. After 10 min., 10.2 g. (0.05 mole) of benzhydryl chloride in 50 ml. of dry ether was added, and the ammonia and most of the ether were evaporated. The residue was stirred with chloroform, and the mixture filtered. The chloroform filtrate was concentrated and diluted with ethanol to precipitate 12.65 g. (76%) of tetraphenylethane (VII), m.p. and mixed m.p. 212°. The mother liquors were shown by vapor phase chromatography to contain 2.0 g. (24%) of diphenylmethane and 8.2 g. (90%) of benzophenone.

Similarly the colorless equilibrium mixture from molecular equivalents of red-orange potassium diphenylmethide and benzophenone in liquid ammonia and ether was treated with a molecular equivalent of benzhydryl chloride in ether and the reaction mixture was worked up essentially as described above. Diphenylmethane and benzophenone were largely recovered.