areas of hydrogens. In a separate run the peak corresponding to heptene-1 on g.l.p.c. was trapped and its mass spectrum was recorded. The parent peak appeared at m/e 98, consistent with nondeuterated heptene-1.[28]

After distillation of the low-boiling material, a pot residue was obtained (10.8 g.) whose infrared spectrum is consistent with a primary alcohol[28] and starting material.[8] G.l.p.c. comparison[29] of this mixture to authentic samples of hexyl allyl ether and *n*-hexyl alcohol[30] showed the mixture to consist of 87% *n*-hexyl alcohol and 13% starting material.[31]

In a separate run using dodecyl allyl ether (5.6 g., 0.025 mole) in 12 ml. of hexane, one-half the required amount of *n*-butyllithium (1.6 *N*, 8 ml., 0.012 mole) was added and the mixture was refluxed for 2 hr. The addition of 1 ml. of D_2O, after allowing the mixture to stand overnight, provided a high-boiling product (5.0 g.) which was 52% starting material and 48% dodecyl alcohol, by g.l.p.c. analysis. The n.m.r. spectrum showed no evidence for deuterium incorporation nor isomerization to dodecyl *cis*-propenyl ether, and the vinyl proton region was identical with that of the starting material.

Reaction of Octyl Allyl Ether with *n*-Butyllithium in Hexane at 30–40°.—Octyl allyl ether (1.0 g., 0.006 mole) was dissolved in 25 ml. of hexane and placed in a three-necked reaction flask which was surrounded with a water bath. Dropwise addition of 10 ml. of *n*-butyllithium in hexane (1.6 *N*) resulted in a 10° temperature rise (from 25 to 35°). After the addition was complete, the mixture was stirred for 1.25 hr. and then hydrolyzed by the addition of excess water. The organic layer was collected, dried with anhydrous magnesium sulfate, and filtered, and the low-boiling material was removed at aspirator pressure to give 0.8 g. of product whose infrared spectrum was consistent with a mixture of octyl *cis*-propenyl ether[8] and a primary alcohol.[27] G.l.p.c. comparison to authentic samples showed the mixture to consist of 77% *n*-octyl alcohol and 23% octyl *cis*-propenyl ether.

Reaction of Alkyl Allyl Ethers with *n*-Butyllithium at −33°.—Dodecyl allyl ether (5.0 g., 0.022 mole) was dissolved in 25 ml. of hexane, placed in a one-neck reaction flask, and cooled to −33° in a liquid ammonia bath. To this solution was added 5 ml. of *n*-butyllithium (1.6 *N*) in hexane. The resulting solution was allowed to stand for 6 hr. before the addition of 2 ml. of deuterium oxide. The mixture was dried with anhydrous magnesium sulfate and filtered, and the low-boiling material was removed to give a material (4.4 g.) which was predominantly octyl *cis*-propenyl ether by infrared and n.m.r. analysis.

Reaction of Alkyl Allyl Ether with *n*-Butyllithium in Excess Cyclohexene.—Dodecyl allyl ether (10 g., 0.044 mole) was dissolved in 50 ml. of cyclohexene and 38 ml. of *n*-butyllithium (1.6 *N*) was added dropwise. The reaction mixture was stirred overnight, hydrolyzed, and worked up as before. Distillation through a spinning-band column provided only heptene-1 as a new olefinic species. The n.m.r. spectrum of this material was entirely consistent with heptene-1 as was the mass spectrum,[28] indicating that norcarane derivatives could only have been formed in very low yield, if at all.

Attempted Reaction of Alkyl *cis*-Propenyl Ethers with *n*-Butyllithium.—Hexyl *cis*-propenyl ether (2.0 g., 0.014 mole) was dissolved in 50 ml. of hexane and 20 ml. of *n*-butyllithium (1.6 *N*) was added dropwise to the solution. The reaction mixture was allowed to stir overnight and then carbonated by pouring over excess Dry Ice through a syringe. The usual work-up of an acidic fraction provided an acid product (1.3 g., 38%) having an infrared spectrum identical with that of pentanoic acid. The neutral layer from this reaction (2.35 g.) had an infrared spectrum consistent with octyl *cis*-propenyl ether admixed with ketone. G.l.p.c. comparison to an authentic sample of dibutyl ketone indicated that carbonation provided ketones as well as acidic product. No evidence for the carbonation of an alkoxyallyl anionic species was obtained.

In a similar manner octyl *cis*-propenyl ether (1 g., 0.006 mole) was mixed with 10 ml. of *n*-butyllithium (1.6 *N*) and stirred for 1.25 hr. before addition of 2 ml. of deuterium oxide. The usual work-up provided a material (0.95 g.) having an n.m.r. spectrum identical with that of the starting compound. Thus, no significant incorporation of deuterium had occurred.

Additionally, to dodecyl *cis*-propenyl ether (5.6 g., 0.025 mole) in 12 ml. of hexane was added *n*-butyllithium (1.6 *N*, 16 ml.) and the resulting solution was refluxed for 2 hr. The addition of 1 ml. of D_2O and work-up provided a quantitative recovery of starting material which did *not* contain deuterium by n.m.r. analysis.

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(28) This data was obtained from a Bendix time-of-flight mass spectrometer to which was attached an Aerograph Model A-90P gas chromatograph. The author is indebted to Drs. J. C. Wootton and W. L. Courchene, of these laboratories, for this data.

(29) Using an Aerograph Model A-90P equipped with a 10-ft., 0.25-in. polyester column at an approximate flow rate of 60 cc./min.

(30) Obtained from Matheson Coleman and Bell.

(31) Percentages are taken directly from areas (peak height times width at half-height) and are not corrected for differences in thermal conductivity.

Mono- and Dialkylation of Phenylacetonitrile by Means of Sodamide and Sodium Hydride. Alkylation of Diphenylacetonitrile[1a]

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Monoalkylations of phenylacetonitrile with alkyl halides by means of sodamide in liquid ammonia or toluene were generally accompanied by dialkylation even though molecular equivalents of the reactants were employed. Toluene is preferable to liquid ammonia for certain monoalkylations, but the latter solvent is better for certain others. Also monoalkylation of phenylacetonitrile with *n*-butyl bromide by sodium hydride in 1,2-dimethoxyethane was accompanied by dialkylation. Further alkylation of the monobutyl derivative of phenylacetonitrile with benzyl chloride was effected by sodamide in liquid ammonia. Di-*n*-butylation of phenylacetonitrile was accomplished in excellent yield in a single operation with 4 molecular equiv. of *n*-butyl bromide and sodamide or sodium hydride. β-Phenylethylation of diphenylacetonitrile was realized in good yield by both reagents.

Many monoalkylations of phenylacetonitrile with alkyl halides have been reported.[2] Most of them were effected by sodamide in an inert solvent, but a few were done with this base in liquid ammonia.[3] Monomethylation and monobenzylation in the latter medium were shown[3] to be accompanied by considerable dialkylation even though phenylacetonitrile (I) was first converted to its sodio salt I′ by 1 molecular equiv. of sodamide, and the halide then added. Evidently equilibration between I′ and the monoalkyl derivative II occurred to regenerate I and form sodio salt II′ which underwent further alkylation to give dialkyl derivative III (Scheme I).

We have found, as would be expected,[3] that various monoalkylations by sodamide in liquid ammonia or even toluene are accompanied by some dialkylation. The results are summarized in Table I in which are

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(1) (a) Supported in part by the National Science Foundation. (b) Union Carbide and Carbon Chemicals Co. Fellow, 1962.

(2) A. C. Cope, H. L. Holmes and H. O. House, *Org. Reactions*, **9**, 107 (1957).

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

TABLE I

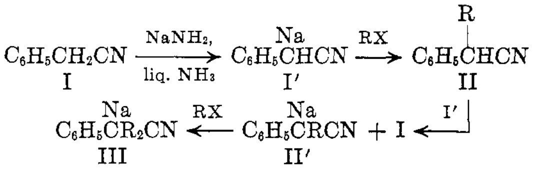
ALKYLATIONS OF PHENYLACETONITRILE WITH 1 MOLE EQUIV. OF ALKYL HALIDES AND SODAMIDE IN LIQUID AMMONIA OR TOLUENE[a]

	In liquid ammonia									In toluene				
Alkyl halide	Moles of reactants	Vol. of ammonia, ml.	Addition time, sec.	Reaction time, hr.	Products,[b] % II	III	I	V.p.c.[c] column	V.p.c. temp., ° C.	Moles of reactants	Vol. of toluene, ml.	Products,[d] % II	III	I
CH_3I	0.05	250	5–6	1	58	14	28	CW	200	0.5	500	62	16	21
n-C_3H_7Br	0.2	500	8–12	1	69	14	17	CW	200	...	...	...	...	...
i-C_3H_7Br	0.1	500	5–6	4	90	7	3	AL	Programmed	0.1	100	76	2	22
n-C_4H_9Br	0.05	250	5–6	2	73	10	17	SGR	Programmed	0.35	400	82	5	13
n-C_4H_9Br	0.05	250	180	1	60	13	12	CW	225	...	...	...	...	...
n-C_4H_9Br	0.1[e]	500	5–6	1	77[e]	5	18	CW	225	...	...	...	...	...
i-C_4H_9Br	0.05	250	5–6	1	46[f]	23	31	CW	200	...	...	...	...	...
s-C_4H_9Br	0.05	250	5–6	1	93	1	6	CW	200	...	...	58[g]	Some?[h]	Some?[h]
n-$C_5H_{11}Br$	0.1	500	5–6	1	81	8	11	AL	200	...	...	...	...	...
i-$C_5H_{11}Br$	0.2	500	8–12	1	70	8	22	CW	225	...	...	...	...	...
c-$C_6H_{11}Br$	0.1	500	5–6	2	37	4	59	SGR	Programmed	...	...	65–77[i,j]	Some?[h]	Some?[h]
n-$C_8H_{17}Br$	0.1	500	8–12	1	80	6	14	AL	275	...	...	...	...	...
$C_6H_5CH_2Cl$	...	...	...	...	33[i,k]	30[i,k]	31[i,k]	...	...	0.1	200	49	11	26
$C_6H_5CH_2CH_2Br$	0.05	250	180	5	61[l]	16[m]	...	SGR	Programmed	...	...	...	...	...

[a] For identification of the products, see ref. 2, 3, and those given in the notes to this table. [b] The yields of products were determined by v.p.c. except where noted. [c] CW = Carbowax 20M (5 ft.), AL = Apiezon L (5 ft.), SGR = silicone gum rubber (2 ft.). [d] The yields of products were determined by v.p.c. using the same columns indicated under liquid ammonia, except where noted. [e] Lithium amide was used instead of sodamide. [f] Reproduced to 1%. [g] Benzene used in place of toluene; Kali-Chemie A.-G., British Patent 748,064 (April 18, 1956); *Chem. Abstr.*, **52**, P12913*a* (1958). [h] Apparently no attempt was made to isolate this material. [i] Isolated by distillation. [j] Reference 6. [k] Reference 3. [l] B.p. 109–111° (0.05 mm.); P. G. Philpott and J. A. Barltrop [*J. Chem. Soc.*, 691 (1956)] reported b.p. 132° (0.16 mm.). [m] Isolated by crystallization from methanol, m.p. 75.5–76.5°. J. Jacques and H. B. Kagan [*Bull. soc. chim. France*, 128 (1956)] reported m.p. 75–76°.

included for comparison certain earlier results. Our yields of II, III, and I were determined by v.p.c. except where noted. The yields of products from the isobutylation in liquid ammonia were reproduced to within 1% by this method.

SCHEME I



$$\underset{\text{I}}{C_6H_5CH_2CN} \xrightarrow[\text{liq. NH}_3]{\text{NaNH}_2,} \underset{\text{I}'}{C_6H_5\overset{\text{Na}}{C}HCN} \xrightarrow{\text{RX}} \underset{\text{II}}{C_6H_5\overset{\text{R}}{C}HCN}$$

$$\underset{\text{III}}{C_6H_5\overset{\text{Na}}{C}R_2CN} \xleftarrow{\text{RX}} \underset{\text{II}'}{C_6H_5\overset{\text{Na}}{C}RCN} + \text{I} \xleftarrow{\text{I}'}$$

Table I shows that liquid ammonia generally afforded relatively more dialkylation than toluene even though the temperature at which the reaction occurred in the former solvent was much lower. Equilibration apparently occurred rapidly in liquid ammonia, since almost as much dialkylation was observed when n-butyl bromide was added within 5 sec. as when the halide was added during 3 min. (see Table I). However, equilibration seemed to be partly minimized by use of lithiophenylacetonitrile which underwent relatively less di-n-butylation than the sodio salt under similar conditions (see footnote e, Table I). Presumably, the lithionitrile would also be more satisfactory for certain other monoalkylations.

Table I further shows that the best yields of the monoalkyl derivatives II in liquid ammonia were obtained with the two secondary halides, isopropyl and *sec*-butyl bromides; similarly, the best yields (99%) of II reported previously[3] in this medium were realized with the relatively large secondary halides, benzhydryl and α-phenylethyl chlorides. Although equilibration may occur in such cases, further alkylation is apparently minimized by a steric factor.[4] Incidentally, monoalkylation of ethyl or t-butyl phenylacetate with primary alkyl halides[5] by sodamide in liquid ammonia is accompanied by much less dialkylation than that of phenylacetonitrile; this also may be ascribed to a steric factor as COOR is larger than CN.

It may be concluded that, although some dialkylation generally occurs, several of the monoalkylations can be realized in sufficiently good yield to be regarded as satisfactory for synthesis, especially when the monoalkyl derivative can be readily separated by distillation from the dialkyl III and regenerated I. Toluene is preferable to liquid ammonia for certain of the monoalkylations, for example, for the cyclohexylation,[6] but liquid ammonia is better for certain others such as benzhydrylation[3] which we have found unsatisfactory in toluene.

For comparison with the above results, two typical monoalkylations of phenylacetonitrile were effected by means of sodium hydride in refluxing 1,2-dimethoxyethane (monoglyme) employing molecular equivalents of the reactants. n-Butylation afforded II, III, and I in yields of 73, 9, and 12%, respectively; this result is comparable with that obtained with sodamide (see Table I). The corresponding benzylation by means of sodium hydride appeared to be more satisfactory than that with sodamide (see Experimental Section). Previously,[7] isobutylation of phenylacetonitrile was effected by sodium hydride in toluene in 66% yield; this result was similar to that obtained with sodamide in this solvent.[7]

Next, consideration was given to dialkylations of phenylacetonitrile (I). When the two alkyl groups to be introduced into I are the same, it is convenient to treat I with two or more molecular equivalents of an alkyl halide and reagent in a single operation. Such dialkylations have previously been effected by means of sodamide in ether or toluene, but the maximum yields were only 62–66%.[2] We have similarly obtained III (R = n-C_4H_9) in only 66% yield when slightly

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(4) A recent attempt to further alkylate II (R = benzhydryl) with benzhydryl chloride in liquid ammonia was unsuccessful, although the alkylation was realized with benzhydryl bromide: W. G. Kofron, W. R. Dunnavant, and C. R. Hauser, *J. Org. Chem.*, **27**, 2737 (1962).

(5) W. G. Kenyon, E. M. Kaiser, and C. R. Hauser, *ibid.*, **30**, 2937 (1965).

(6) E. M. Hancock and A. C. Cope, *Org. Syn.*, **25**, 25 (1945).

(7) G. L. Goerner, H. L. Muller, and J. L. Corbin, *J. Org. Chem.*, **24**, 1561 (1959).

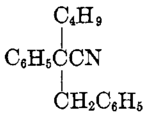
more than 2 molecular equiv. of *n*-butyl bromide and sodamide in liquid ammonia were used; also, 15% of the monoalkyl derivative II and 10% of unalkylated I were detected by v.p.c. Significantly, however, III (R = n-C_4H_9) was isolated in 92–95% yields when the dialkylation was effected with 4 molecular equiv. of the halide and sodamide in liquid ammonia or sodium hydride in refluxing monoglyme; in both cases, the product was pure by v.p.c. (eq. 1).

$$\text{I} \xrightarrow[\substack{\text{NaNH}_2\text{ in liq. NH}_3 \\ \text{or NaH in monoglyme}}]{\text{excess } n\text{-C}_4\text{H}_9\text{Br and}} \text{III (R} = n\text{-C}_4\text{H}_9) \qquad (1)$$

Interestingly, the success of the dialkylation with sodamide in liquid ammonia appears to be dependent on preferential reaction of the excess reagent with the halide rather than with the product III. Thus, in blank experiments, III (R = n-C_4H_9) was recovered unchanged after treatment with 2 molecular equiv. of the reagent and halide, but not after treatment with the reagent alone (see Experimental Section).

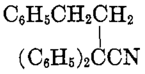
Although the present methods of dialkylation of I would presumably be successful also with other alkyl halides, the sodamide procedure was unsatisfactory with benzyl chloride, with which much stilbene was produced. The sodium hydride procedure was more satisfactory with this halide, III (R = $CH_2C_6H_5$) being obtained in 58% yield.

When the two groups to be introduced into I are different, consecutive operations with the two different halides appear to be required and, because the initial monoalkylation may be accompanied by dialkylation (see Table I), the desired dialkyl derivative may be difficult to prepare pure. Previously, further alkylations of intermediate monoalkylphenylacetonitriles have been effected in toluene by sodamide[2,8] or sodium hydride.[8] We have accomplished the further alkylation of II (R = n-C_4H_9) with benzyl chloride by means of sodamide in liquid ammonia to form IV in good yield.



$$\begin{array}{c} C_4H_9 \\ | \\ C_6H_5CCN \\ | \\ CH_2C_6H_5 \end{array}$$

IV



$$\begin{array}{c} C_6H_5CH_2CH_2 \\ | \\ (C_6H_5)_2CCN \end{array}$$

V

Finally, to supplement the various alkylations of diphenylacetonitrile described previously,[2,9] we have effected the β-phenylethylation of this nitrile by sodamide in liquid ammonia and by sodium hydride in monoglyme to form V in yields of 64 and 60%, respectively.

Experimental Section[10]

Monoalkylations of Phenylacetonitrile by Sodamide.—In Table I are summarized the results obtained from these alkylations in liquid ammonia and toluene. The details are described below under A and B.

A. In Liquid Ammonia.—To a stirred suspension of sodamide[11] in commercial, anhydrous liquid ammonia was added 1 molecular equiv. of phenylacetonitrile in 15–30 ml. of anhydrous ether. To the resulting sodiophenylacetonitrile was added, after 10–15 min., 1 molecular equiv. of the appropriate alkyl or aralkyl halide, in 10–20 ml. of anhydrous ether. After 1 hr. or longer (Dry Ice–acetone condenser), a slight excess of 1 molecular equiv. of ammonium chloride was added, and the ammonia was allowed to evaporate. Ether and water were added to the residue, and the layers were separated. The ethereal layer[12] was washed with saturated sodium chloride solution and combined with two additional ethereal extracts of the aqueous layer, treated in the same manner. After the ethereal solution was dried over anhydrous magnesium sulfate, the solvent was removed. The resulting crude product was subjected to v.p.c. analysis (employing appropriate columns), distilled, or recrystallized as indicated in Table I.

B. In Toluene.—To a stirred suspension of sodamide[11] in commercial, anhydrous liquid ammonia was added 1 molecular equiv. of phenylacetonitrile in some anhydrous ether. After 15 min., dry sulfur-free toluene containing some anhydrous ether was added dropwise. The solution was allowed to come to room temperature as the ammonia evaporated, and the flask was then warmed to distil out the remaining ammonia and ether. To the resulting suspension of sodiophenylacetonitrile in toluene was rapidly added 1 molecular equiv. of the appropriate halide. After refluxing for 2 hr., the reaction mixture was cooled and washed with water, and the toluene layer was combined with two benzene extracts of the aqueous layer.[12] The combined benzene and toluene layers were washed twice with water, and the solvents were removed by distillation. The resulting crude product was subjected to v.p.c. analysis, distilled, or recrystallized as indicated in Table I.

Monoalkylation of Phenylacetonitrile by Sodium Hydride. A. With *n*-Butyl Bromide.—To a stirred slurry of 4.37 g. (0.1 mole) of sodium hydride reagent[13] in 200 ml. of refluxing monoglyme, under dry nitrogen, was added a solution of 11.7 g. (0.1 mole) of phenylacetonitrile and 13.7 g. (0.1 mole) of *n*-butyl bromide in 100 ml. of monoglyme over a period of 22 min. Refluxing was continued for 3 hr., and most of the solvent was then removed under reduced pressure. The resulting paste was cooled in an ice bath, and 100 ml. of ether was added. After stirring the mixture, 100 ml. of water was added dropwise. The layers were separated, and the ethereal solution was extracted with two 100-ml. portions of water. The ethereal solution of the product was dried over anhydrous magnesium sulfate, and the solvent was removed. The residue was distilled and product was collected at 135–137° (10 mm.), lit.[14] b.p. 135–136° (10 mm.). Vapor phase chromatography (silicone gum rubber at 250°) of the distillate indicated that the product consisted of 12% recovered nitrile I, 73% α-*n*-butylphenylacetonitrile, and 9% α,α-di-*n*-butylphenylacetonitrile.

B. With Benzyl Chloride.—This reaction was effected as described for *n*-butyl bromide employing 11.7 g. (0.1 mole) of phenylacetonitrile, 12.65 g. (0.1 mole) of benzyl chloride, and 4.37 g. (0.1 mole) of sodium hydride reagent.[13] There was obtained 8.1 g. (39%) of 2,3-diphenylpropionitrile, b.p. 161–163° (3.8 min.), lit.[8] b.p. 134–150° (0.6 mm.); this was pure by v.p.c. Also, 50% of starting nitrile I and 35% of benzyl chloride were recovered.

Dialkylation of Phenylacetonitrile. A. By Sodamide.—To a stirred suspension of 0.4 mole of sodamide[11] in 300 ml. of anhydrous liquid ammonia was added, over 18 min., a solution of 11.7 g. (0.1 mole) of phenylacetonitrile and 54.8 g. (0.4 mole) of *n*-butyl bromide in 100 ml. of anhydrous ether. After stirring for 3 hr., slightly more than 4 molecular equiv. of solid ammonium chloride was added, and the ammonia was allowed to evaporate. The reaction mixture was worked up as described above for the monoalkylations of phenylacetonitrile by means of sodamide. Distillation of the crude product afforded 21.06 g. (92%) of α,α-di-*n*-butylphenylacetonitrile (III, R = n-C_4H_9),

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(8) G. L. Goerner and W. R. Workman, *J. Org. Chem.*, **19**, 37 (1954); G. L. Goerner and A. A. Holzschuh, *ibid.*, **23**, 1346 (1958).

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

(10) Analyses were by Dr. Ing. Schoeller, Kronach, West Germany. Melting points (Mel-Temp capillary melting point apparatus) and boiling points are uncorrected. An F and M Model 500 programmed-temperature gas chromatograph was used to produce the vapor phase chromatograms. The carrier gas was helium.

(11) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 122 (1954).

(12) The organic layer was washed initially with saturated sodium bisulfite solution when methyl iodide was employed as the alkylating agent.

(13) This reagent was obtained from Metal Hydrides, Inc., as an approximately 55% dispersion of sodium hydride in mineral oil, and was used as received.

(14) K. Mislow and C. M. Hamermesh, *J. Am. Chem. Soc.*, **77**, 1590 (1955).

b.p. 135–136° (3.5 mm.), lit.[15] b.p. 135–140° (1.5 mm.). The v.p.c. (silicone gum rubber at 100°) of both the crude and the distilled product showed one peak whose retention time was identical with that of an authentic sample.

In a blank experiment, a solution of 0.05 mole of nitrile III (R = n-C_4H_9) and 0.1 mole of n-butyl bromide in 25 ml. of ether was added to 0.1 mole of sodamide[11] in 150 ml. of liquid ammonia. After 3 hr., excess ammonium chloride was added, and the reaction mixture was worked up as described above. Distillation of the crude product afforded 9.99 g. (87%) of recovered starting nitrile, b.p. 135–136° (3.8 mm.),[15] which was indicated to be pure by v.p.c.

The blank experiment was repeated omitting the n-butyl bromide. After the ammonia was evaporated, water and ether were added. The solid was collected, dried, and recrystallized successively from 95% ethanol, methanol, and water to afford 5.21 g. of product, m.p. 226–230°, which appeared to be a mixture of α,α-di-n-butylphenylacetamidine and α,α-di-n-butylphenylacetamide. None of the original nitrile III was recovered. The infrared spectrum of the solid showed, besides aromatic and aliphatic absorptions, bands at 3500–3000 (NH) and 1725–1550 cm.$^{-1}$ ($C{=}N$ and $C{=}O$); nitrile absorption was absent. An analysis of the solid for nitrogen (9.23%) suggested a mixture of 56% amidine and 44% amide; however, neither compound was isolated.

B. By Sodium Hydride.—To a stirred slurry of 17.48 g. (0.4 mole) of sodium hydride reagent[13] in 200 ml. of refluxing monoglyme, under dry nitrogen, was added a solution of 11.7 g. (0.1 mole) of phenylacetonitrile and 54.8 g. (0.4 mole) of n-butyl bromide in 100 ml. of monoglyme over a period of 30 min. Refluxing was continued for 3 hr., and the reaction mixture was then worked up as described above for monoalkylations of phenylacetonitrile by means of sodium hydride. Distillation of the crude product yielded 21.8 g. (95%) of α,α-di-n-butylphenylacetonitrile (III, R = n-C_4H_9), b.p. 134–136° (3.5 mm.).[15] Both the crude and the distilled product were indicated to be pure by v.p.c. as in the corresponding experiment with sodamide.

The corresponding reaction with benzyl chloride was effected similarly. Fractionation of the resulting crude product afforded 8.48 g. (41%) of 2,3-diphenylpropionitrile, b.p. 160–163° (3.5 mm.),[3] and 17.22 g. (58%) of 1,2,3-triphenyl-2-cyanopropane, b.p. 215–218° (3.5 mm.), lit.[3] b.p. 185–186° (0.6 mm.). Each product exhibited one v.p.c. peak whose retention time was identical with that of an authentic sample.

Alkylation of 2-Phenylhexanenitrile with Benzyl Chloride.—To a stirred suspension of 0.05 mole of sodamide[11] in 250 ml. of anhydrous liquid ammonia was added a solution of 9.68 g. (0.05 mole) of 2-phenylhexanenitrile (II, R = n-C_4H_9)[16] in 15 ml. of anhydrous ether. After the reaction mixture had been stirred for 2 hr., it was worked up essentially as described above for monoalkylations of phenylacetonitrile by means of sodamide. The resulting residue was fractionated to afford 10.77 g. (82%) of crude 1,2-diphenyl-2-cyanohexane (IV), which was identified by v.p.c. using a 2-ft. silicone gum rubber column and indicated to consist of 91% of IV and 9% of II (R = n-C_4H_9). Redistillation afforded IV, b.p. 120–121° (0.07 mm.), which was indicated to be pure by v.p.c.

Anal. Calcd. for $C_{19}H_{21}N$: C, 86.64; H, 8.04; N, 5.32. Found: C, 86.69; H, 7.97; N, 5.45.

Alkylation of Diphenylacetonitrile with β-Phenylethyl Bromide. A. With Sodamide.—This reaction was performed essentially as described for phenylacetonitrile employing 0.05 mole of sodamide[11] in 250 ml. of liquid ammonia, 9.66 g. (0.05 mole) of diphenylacetonitrile, and 9.26 g. (0.05 mole) of β-phenylethyl bromide(reaction period, 4 hr.). After work-up, the crude residue was crystallized from methanol to afford 9.43 g. (64%) of 2,2,4-triphenylbutyronitrile (V), m.p. 100–101°.

Anal. Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.74; H, 6.44; N, 4.74.

B. With Sodium Hydride.—This reaction was accomplished essentially as described for phenylacetonitrile employing 9.66 g. (0.05 mole) of diphenylacetonitrile, 9.26 g. (0.05 mole) of β-phenylethyl bromide, and 2.19 g. (0.05 mole) of sodium hydride reagent.[13] Crystallization of the resulting oil from methanol afforded 8.95 g. (60%) of 2,2,4-triphenylbutyronitrile (V), m.p. 97.5–99.5°; 1.56 g. (16%) of starting nitrile was recovered.

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[15] N. Sperber, D. Papa, and E. Schwenk, *J. Am. Chem. Soc.*, **70**, 3091 (1948).

[16] The starting compound, which was prepared by n-butylation of sodiophenylacetonitrile in toluene and distilled, was indicated by v.p.c. to be 90% pure, being contaminated with 6% of I and 4% of III (R = n-C_4H_9). The 9.68 g. used contained 0.05 mole of II (R = n-C_4H_9).

Organometallic Chemistry. XII.[1] The Thermal Decomposition of n-Butyllithium, a Kinetic Study[2,3]

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The thermal decomposition of decane solutions of n-butyllithium to butene-1 and lithium hydride was observed to follow the first-order rate law for one to two half-lives. A linear correlation was evident between the first-order rate constant and the percentage of carbon-bound lithium, with k_1 doubling as the percentage of carbon-bound lithium was dropped from approximately 96 to 76% by the addition of increments of lithium butoxide. Extrapolation to 100% carbon-bound lithium at 130, 140, and 150° gave values for 10^3k of 2.2, 6.0, and 14.0 min.$^{-1}$. The ΔH^* and ΔS^* were calculated to be 31 kcal. mole^{-1} and -1 e.u., respectively, the rate increase brought about by the added alkoxide apparently being reflected in a more favorable entropy term. A kinetic isotope effect (k_H/k_D) in the range 3 to 4 was determined by measuring the decomposition rate for β,β-dideuteriobutyllithium. A transition state of the concerted, four-center type is proposed in which charge distribution and product stability play an important role.

While an enormous body of both theoretical and practical knowledge concerning numerous types of elimination reactions has been accumulated,[5] very little is known about the thermal elimination of alkali metal hydride from an organometallic substrate. Since this is, perhaps, the simplest reaction that these

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[1] Paper XI: R. A. Finnegan, *Trans. N. Y. Acad. Sci.*, **27**, 730 (1965).

[2] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of this work.

[3] (a) Preliminary announcement of this work has been made at the 149th National Meeting of the American Chemical Society, April 1965; Abstracts, p. 38P. See also footnotes 17–19 in ref. 3b. (b) R. A. Finnegan, *Chem. Ind.* (London), 895 (1962).

[4] Petroleum Research Fund Graduate Research Fellow, 1962–1964. This paper is based on a thesis submitted by H. W. Kutta to the Department of Chemistry, The Ohio State University, in partial fulfillment of the requirements for the degree of Master of Science, June 1964.

[5] (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII; (b) D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 6; (c) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, Chapter 12; (d) J. S. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; Chapter 8; (e) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., London, 1963.