[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Alkylations of Diphenylacetonitrile with Certain Halides by Potassium Amide in Liquid Ammonia. Dehydrocyanations of Polyphenyl Nitriles to Form Olefins[1]

BY CHARLES R. HAUSER AND WALLACE R. BRASEN[2]

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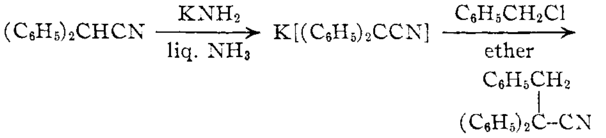
Alkylations of diphenylacetonitrile with benzyl, α-phenylethyl and benzhydryl chlorides were effected in excellent yields by means of potassium amide in liquid ammonia. The resulting polyphenyl nitriles underwent dehydrocyanation (β-elimination) to form olefins on further treatment with this base. This type of reaction is apparently new for nitriles.

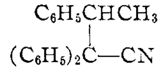
The benzylation of diphenylacetonitrile with benzyl chloride to form I previously has been effected in 83% yield by sodium ethoxide in ethanol,[3] in 67% yield by methylmagnesium iodide in ether,[4] and in unreported yield by sodium amide in ether.[5] We have realized this alkylation in 96% yield by potassium amide in a mixture of liquid ammonia and ether. An equally good yield probably could be obtained with sodium amide in this medium.



$$(C_6H_5)_2CHCN \xrightarrow[\text{liq. }NH_3]{KNH_2} K[(C_6H_5)_2CCN] \xrightarrow[\text{ether}]{C_6H_5CH_2Cl} (C_6H_5)_2\overset{C_6H_5CH_2}{\overset{|}{C}}\text{—}CN$$

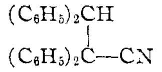
I

The corresponding alkylations of this nitrile with α-phenyl-ethyl and benzhydryl chlorides were effected similarly to form II and III in yields of 88 and 96%, respectively. These two alkylations apparently have not been reported previously.



$$(C_6H_5)_2\overset{C_6H_5CHCH_3}{\overset{|}{C}}\text{—}CN$$

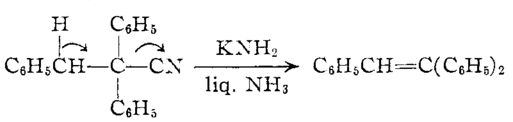
II



$$(C_6H_5)_2\overset{(C_6H_5)_2CH}{\overset{|}{C}}\text{—}CN$$

III

These polyphenyl nitriles resulting from alkylations were found to undergo an apparently new type of reaction with potassium amide in liquid ammonia. This involved dehydrocyanation to form the corresponding olefin. For example, nitrile I gave triphenylethylene in 94% yield. Presumably a β-hydrogen is removed as a proton by the amide ion and the cyano group is released as an anion (β-elimination).



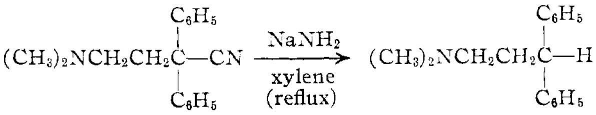
$$C_6H_5\overset{H}{\overset{|}{C}}H\text{—}\underset{C_6H_5}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}\text{—}CN \xrightarrow[\text{liq. }NH_3]{KNH_2} C_6H_5CH{=}C(C_6H_5)_2$$

I

Similarly nitriles II and III underwent dehydrocyanation to form 1,1,2-triphenylpropene-1 and tetraphenylethylene in yields of 80 and 44%, respectively. In the latter case about 75% dehydrocyanation apparently occurred but much of the olefin was lost during purification.

It is to be noted that nitriles I, II and III, with which the β-eliminations were realized, have a relatively hindered cyano group and no α-hydrogen. Moreover, the β-hydrogen is activated by at least one phenyl group.

These dehydrocyanations are to be distinguished from decyanations[6] such as that of IV to form V which have generally been realized with sodium amide at relatively high temperatures. In contrast to I, II and III, in which the β-hydrogen is activated by a phenyl group, nitrile IV has no such activated β-hydrogen.



$$(CH_3)_2NCH_2CH_2\underset{C_6H_5}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}\text{—}CN \xrightarrow[\substack{\text{xylene}\\ \text{(reflux)}}]{NaNH_2} (CH_3)_2NCH_2CH_2\underset{C_6H_5}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}\text{—}H$$

IV V

It should be mentioned that like other highly hindered nitriles, I, II and III were found to be resistant to hydrolysis in acidic or basic medium.

Experimental[7]

Benzylation of Diphenylacetonitrile to Form I.—A solution of 0.25 mole of potassium amide in 500 ml. of liquid ammonia was prepared from 0.25 g. atom of potassium.[8] To the stirred solution was added 48.3 g. (0.25 mole) of solid diphenylacetonitrile.[9] To the resulting greenish-brown solution was added during 10 minutes a solution of 33 g. (0.255 mole) of benzyl chloride in 100 ml. of anhydrous ether, and the mixture stirred for one hour. More ether (300 ml.) was then added, and the ammonia evaporated on the steam-bath. After adding water, the ether was removed, and the aqueous mixture filtered. The solid was recrystallized from methanol (cooled in the refrigerator) to give 70.8 g. (99%) of α,α,β-triphenylpropionitrile (I), m.p. 126.5–127.5°, reported m.p. 126°.[4]

Dehydrocyanation of I.—To a stirred solution of 0.115 mole of potassium amide in 500 ml. of liquid ammonia was added 32 g. (0.113 mole) of solid I, followed by 200 ml. of ether, and the stirring continued for one hour. After removing the ammonia, water was added, and the two layers were separated. The ether layer was shaken with water, 2 *M* hydrochloric acid, and, finally, 10% sodium bicarbonate solution. After drying over calcium chloride the ether was removed leaving an oil which was crystallized from a mixture of methanol and acetone (cooled in the refrigerator) to give 27 g. (93.5%) of triphenylethylene (IV), m.p. 68.5–69.5°. A mixed melting point with an authentic sample of IV, m.p. 68.5–69.5°, was the same.

Oxidation of the product with chromic acid in acetic acid yielded benzophenone, m.p. 48–49°, and benzoic acid, m.p. 120.5–121.5°, which were confirmed by the mixed melting point method.

2,2,3-Triphenylbutyronitrile (II).—This product, m.p. 103–104°, was obtained in 89% yield by the alkylation of diphenylacetonitrile with α-phenylethyl chloride essentially as described for the benzylation. A sample, recrystallized from methanol (89% recovery), melted at 103.5–104.5°.

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[1] Supported in part by the National Science Foundation.

[2] Carbide and Carbon Chemicals Co. Fellow, 1953–1954.

[3] V. Meyer and K. Neure, *Ann. Chem. Justus Liebigs*, **250**, 140 (1888).

[4] K. Sisido, N. Nozaki and O. Kurihara, THIS JOURNAL, **72**, 2270 (1950).

[5] P. Ramart, *Bull. soc. chim. France*, [4] **35**, 196 (1924).

[6] See R. Levine and W. C. Fernelius, *Chem. Revs.*, **54**, 520 (1954).

[7] Melting points and boiling points are uncorrected. Analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

[8] See R. S. Yost and C. R. Hauser, THIS JOURNAL, **69**, 2325 (1947).

[9] We are indebted to the Dow Chemical Co. for a generous sample of this compound.

Anal. Calcd. for $C_{22}H_{19}N$: C, 88.90; H, 6.40; N, 4.70. Found: C, 89.21; H, 6.30; N, 4.79.

Dehydrocyanation of II, conducted as described for I, gave an 80% yield of 1,1,2-triphenylpropene-1 (V), m.p. 86–87°; reported m.p. 86–87°[10] and 89–90°.[11]

2,2,3,3-Tetraphenylpropionitrile (III).—This compound was prepared by the alkylation of diphenylacetonitrile with either benzhydryl chloride or bromide essentially as described for the benzylation. The crude product was crystallized from ethylene glycol diether to give a 96% yield of III melting at 242° dec.

Anal. Calcd. for $C_{27}H_{21}N$: C, 90.21; H, 5.89; N, 3.90. Found: C, 90.36; H, 6.06; N, 4.09.

Dehydrocyanation of III was carried out as described for I except that the liquid ammonia–ether reaction solution was stirred for two hours. The ammonia was then removed and water added. After removal of the ether the aqueous mixture was filtered, and the solid recrystallized three times from a mixture of benzene and methanol to yield 44% of tetraphenylethylene, m.p. and mixed m.p. 220–221°. Titration of the aqueous filtrate with silver nitrate[12] accounted for 37% of the cyanide ion. Since a blank experiment employing potassium cyanide showed that only 47% of the original cyanide ion would have remained in the aqueous filtrate, it may be concluded that about 75% of nitrile III was dehydrocyanated.

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[10] K. Ziegler, H. Grabbe and F. Ulrich, *Ber.*, **57B**, 1983 (1924).

[11] J. Levy, *Bull. soc. chim. France*, [4] **29**, 878 (1921).

[12] W. C. Pierce and E. L. Haenisch, "Qualitative Analysis," John Wiley and Sons, Inc., New York, N. Y., p. 305.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON COLLEGE]

The Synthesis of α-Amino-o-tolualdehyde Diethylacetal and its Attempted Conversion to Pseudoisoindole

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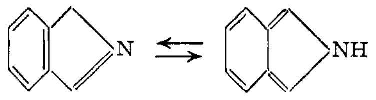
A number of attempts to prepare pseudoisoindole (I) by the acid-catalyzed pyrolysis of α-amino-o-tolualdehyde diethylacetal (III) has given only resinous substances. The starting compound for the synthesis of III, α-phthalimido-o-toluic acid (IV), was obtained by the condensation of phthalide with potassium phthalimide in dimethylformamide followed by acidification. The structure of the acid IV was established by an independent, but less direct, Gabriel phthalimide synthesis, and also by degradation. Treatment of IV with thionyl chloride followed by a Rosenmund–Zetzsche reduction of the resulting α-phthalimido-o-toluyl chloride (V) produced α-phthalimido-o-tolualdehyde (VI). The aldehyde VI afforded α-phthalimido-o-tolualdehyde diethylacetal (VII) on treatment with ethyl orthoformate. Cleavage of VII by hydrazine yielded the amino acetal III. The average over-all yield of III in four preparations was *ca.* 25%.

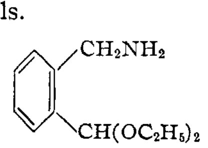
In connection with studies on the aromatic character of heterocyclic compounds, we undertook the preparation of pseudoisoindole (I), the tautomer of the hypothetical compound, isoindole (II).[2]

Since Barber and co-workers[3] were able to prepare Schiff bases by the pyrolysis of mixtures of ketals and primary amines in the presence of catalytic amounts of ammonium chloride, this method was chosen as the most promising route to pseudoisoindole, a cyclic Schiff base.



I II

Accordingly the amino acetal necessary for the attempted synthesis of I, α-amino-o-tolualdehyde diethylacetal (III), was prepared in consistently good yield by a convenient five-step process employing phthalide and potassium phthalimide as the starting materials.



III

Condensation of phthalide with potassium phthalimide in dimethylformamide at reflux temperature followed by acidification of the reaction mixture afforded, after purification, 60% yields of α-phthalimido-o-toluic acid (IV). The structure of the acid was proved by comparison with a sample of IV obtained from ethyl α-phthalimido-o-toluate (IVa) by acidolysis with formic acid containing catalytic amounts of concentrated sulfuric acid, since treatment of IVa with even mildly alkaline reagents invariably opened the ring of the phthalimido substituent. The ethyl ester IVa was obtained by treating ethyl α-bromo-o-toluate[4] with potassium phthalimide in dimethylformamide. In addition to having identical melting points (not depressed on admixture), both specimens of IV yielded the same dibasic acid, α-(o-carboxybenzamido)-o-toluic acid (IVb), on solution in aqueous sodium hydroxide followed by precipitation with dilute hydrochloric acid. Heating of the dicarboxylic acid IVb in glacial acetic acid for eight hours re-formed the monobasic acid IV. It was of interest to note that the direct heating of IVb in the absence of a solvent at temperatures slightly above its melting point not only yielded the expected acid IV, but also a sublimate of phthalic anhydride, indicating that some cleavage of IVb had occurred. Cleavage of a sample of IVb (from IV prepared by the phthalide–potassium phthalimide procedure) by hydrochloric acid yielded the expected products, phthalic acid and phthalimidine, both characterized by com-

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[1] Abstracted in part from the M.S. theses of Stanley F. Bedell, Paul E. Drummond and Clement L. Kosloski.

[2] *Cf.* R. C. Elderfield and T. N. Dodd, Jr., in R. C. Elderfield, "Heterocyclic Compounds," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 275, for a summary of the historical background of isoindole.

[3] H. J. Barber and W. R. Wragg, *J. Chem. Soc.*, 610 (1946); H. J. Barber, D. H. O. John and W. R. Wragg, THIS JOURNAL, **70**, 2282 (1948).

[4] W. Davies and W. H. Perkin, *J. Chem. Soc.*, **121**, 2022 (1922); J. C. Sheehan and W. A. Bolhofer, THIS JOURNAL, **72**, 2786 (1950).