

The amine rapidly formed an amorphous carbonate, m.p. ca. 97–103°, on exposure to moist air.

The acetyl derivative, prepared with ether and acetic anhydride and recrystallized from heptane, had m.p. 131–132°, reported⁵ m.p. 124°.

endo-Norbornylurea, prepared from the amine hydrochloride and potassium cyanate, had m.p. 197–198° (from methanol), reported⁴ m.p. 196–197°.

Regeneration of pure *endo*-norbornylamine from the acetyl derivative was accomplished by 25 hours boiling with dilute sulfuric acid. Isolation in the usual manner and bulb-to-bulb distillation gave material of m.p. 75–85° (soft at 65°), reported⁴ m.p. 75–80°.

Anal. Calcd. for $C_7H_{13}N$: neut. equiv., 131. Found: neut. equiv., 131.

(+)-*endo*-Norbornylamine was prepared by the action of hydrazoic acid on (–)-*endo*-norbornanecarboxylic acid.² The acid used had m.p. 58–61°, $[\alpha]^{25}_D -10.7^\circ$ (*c* 2.7 in 95% ethanol, *l* 4) and was processed exactly as for the racemic acid (see **B** above) in three batches of 43 g. each, using proportional quantities of the other reagents. Distillation of the combined crude amine through a Vigreux column gave 62.0 g. (51%) of material, b.p. 87–88° (40 mm.), which set to a waxy solid, m.p. 73–80°, soft at 55°. A small sample removed for polarimetry showed $[\alpha]^{25}_D +7.58^\circ$ (*c* 2.7 in 95% ethanol, *l* 4). The exact magnitude of the rotation of the amine should be treated with reserve, since the large sample was optically impure and it was not re-melted to homogeneity before the polarimetric sample was removed.

Anal. Calcd. for $C_7H_{13}N$: neut. equiv., 131. Found: neut. equiv., 131.

Reaction of (+)-*endo*-Norbornylamine with Sodium Nitrite in Acetic Acid.—A solution of 61.5 g. of the above dextrorotatory amine in 430 ml. of glacial acetic acid was cooled, stirred, and treated portionwise with 61.5 g. of sodium nitrite during 1.5 hours. The mixture was kept cold an additional hour and then allowed to stand overnight at room temperature. More sodium nitrite (15.2 g.) was added during 15 minutes and the mixture, after being stirred one hour was diluted with 150 ml. of water and poured into 1500 ml. of ice-cold 20% sodium hydroxide. The mixture was extracted with ether, the ether layer was washed carefully with *N* hydrochloric acid and water, dried over calcium sulfate, and evaporated. Distillation of the residue through a Vigreux column gave (1) 2.0 g. of colorless liquid, b.p. 103° (38 mm.); (2) 53.4 g. of colorless liquid, b.p. 102° (36 mm.). The yield of crude acetate was thus 65%. This material had n^{25}_D 1.4601, $\alpha^{20}_D -0.772^\circ$ (neat, 1 dm.). It did not react with permanganate in acetone.

The infrared spectrum was virtually identical with that of pure *exo*-norbornyl acetate⁷ except for a strong, sharp band at 6.15 μ which is absent in the latter. This was attributable to the presence of a small amount of norbornyl nitrate.^{30,18} The nitrogen content (0.51%)³¹ indicated 5.8% contamination by nitrate. That the other most likely nitrogenous contaminant, norbornyl nitrite, was probably absent was suggested by the presence of only one extraneous band in the 6.0–6.2 μ region, rather than the two that would be expected for nitrite.³²

Twenty-five grams of the above crude acetate in 250 ml. of anhydrous ether were added dropwise during one hour to a stirred solution of 12.5 g. of lithium aluminum hydride in 350 ml. of ether. The mixture was boiled under reflux for 2.5 hours and then treated with 85 ml. of water. The resulting sludge was shaken with five 400-ml. portions of ether, the ether solutions were filtered, dried with calcium sulfate and evaporated under a Vigreux column, leaving 22.6 g. of crude *exo*-norboreol. This material was heated at reflux for 16 hours with 70 ml. of acetic anhydride and 220 ml. of glacial acetic acid, poured into ice-water, the mixture saturated with sodium chloride and extracted with ether. The ether extract was washed with dilute cold sodium hydroxide and with water, dried over calcium sulfate and evaporated under a Vigreux column, leaving 24.5 g. of crude acetate. Careful fractionation in a Vigreux column gave (1) a small fore-run of acetic anhydride, b.p. 40–55° (35 mm.); (2) 12.4 g. of colorless liquid, b.p. 95–98° (33 mm.), n^{25}_D 1.4558 (*exo*-norbornyl acetate containing ca. 1% acetic anhydride); (3) 9.2 g. of pure *exo*-norbornyl acetate, b.p. 96° (32 mm.), n^{26}_D 1.4560, n^{25}_D 1.4564, reported⁷ n^{25}_D 1.4565. Fraction 3 showed $\alpha^{25}_D -1.048^\circ$ (neat, 1 dm.); its infrared spectrum was identical in all details with that of authentic⁷ *exo*-norbornyl acetate.

A solution of a portion of fraction 3 in glacial acetic acid showed $[\alpha]^{25}_D -1.30^\circ$ (*c* 10.42, *l* 4). This polarimetry solution was used to make up to 10.00 ml. a sample of 1.4420 g. of *p*-toluenesulfonic acid monohydrate (0.759 *M*). After the resulting solution was heated at 75° for 3.4 hours, it was optically inactive, $\alpha^{25}_D +0.003 \pm 0.01^\circ$.

Acknowledgment.—We are indebted to the Office of Scientific Research, Air Research and Development Command, for financial support.

(30) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 251.

(31) Analysis by Dr. Adalbert Elek, Elek Microanalytical Laboratories.

(32) Reference 30, p. 253.

LOS ANGELES 7, CALIF.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Formation and Preferential β -Alkylation of the Dicarbocation of 2,3,3-Triphenylpropionitrile by Means of Potassium Amide in Liquid Ammonia^{1,2}

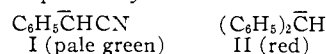
BY CHARLES R. HAUSER, THOMAS M. HARRIS³ AND T. GLENN LEDFORD⁴

RECEIVED SEPTEMBER 8, 1958

2,3,3-Triphenylpropionitrile was converted by one equivalent of potassium amide in liquid ammonia to the pale green monocarbocation, and by two equivalents of this base to the dark red dicarbocation. This twofold ionization involved the α - and β -hydrogens, respectively. The red dicarbocation reacted with an equivalent of benzyl chloride to give exclusively the β -benzyl derivative and with an equivalent of methylene chloride to produce apparently the corresponding cyclopropane derivative.

It is well known that the amide ion in liquid ammonia can effect the essentially complete ionization of a methylene hydrogen of phenylaceto-

nitrile or diphenylmethane to form the corresponding anions which may be formulated as carbocation I³ and II,⁶ respectively.



It therefore seemed possible that the amide ion could effect the essentially complete ionizations of

(5) See C. R. Hauser and W. R. Brasen, *THIS JOURNAL*, **78**, 494 (1956).

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

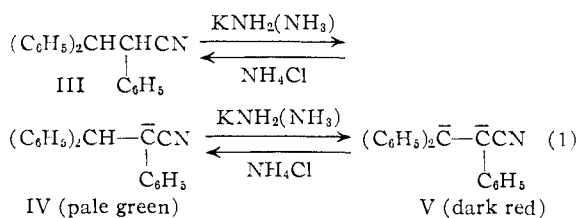
(1) Reported before the Southeastern Regional Meeting of the American Chemical Society at Durham, N. C., Nov. 14–16, 1957, and the 133rd National Meeting of the American Chemical Society at San Francisco, Calif., Apr. 13–18, 1958.

(2) Preliminary results were reported in a communication by C. R. Hauser and T. M. Harris, *THIS JOURNAL*, **79**, 6342 (1957).

(3) National Science Foundation Predoctoral Fellow, 1956–1958.

(4) Deceased; Eastman Kodak Co. Fellow, 1955–1958.

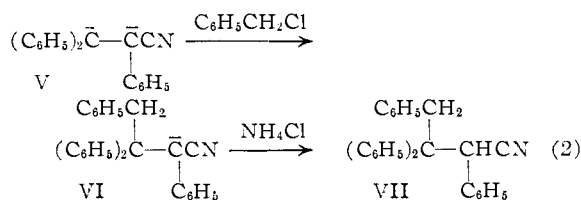
both the α - and β -hydrogens of 2,3,3-triphenylpropionitrile (III), which has the structural features of both phenylacetone and diphenylmethane. This twofold ionization of the nitrile III was evidently realized by means of two molecular equivalents of potassium amide in liquid ammonia employing an inverse-addition procedure. Thus, on adding this reagent to the nitrile there appeared immediately a pale green color which persisted until slightly more than an equivalent of the base had been introduced. Then the color changed to red which deepened as the remainder of the second equivalent of the potassium amide was added. The pale green color may be ascribed to the monocarbanion IV, and the red color to dicarbanion V (equation 1). Similar colors are known to be characteristic of the monocarbanions I⁵ and II,⁶ respectively.



As might be expected the primary ionization involves the hydrogen activated by a cyanide group and a phenyl group, and the secondary ionization by two phenyl groups.

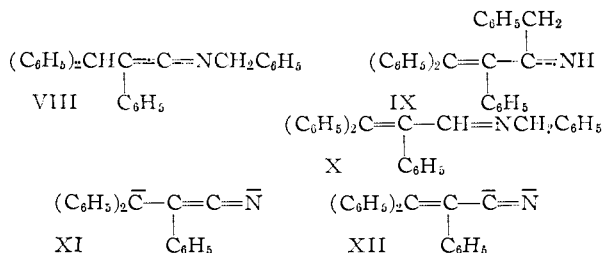
The opposite color changes were observed on neutralizing the reaction mixture with two molecular equivalents of solid ammonium chloride, the ammonium ion of which functions as an acid in liquid ammonia (see equation 1). Thus, the red color persisted until slightly more than one equivalent of this acid had been introduced. Then, the color became pale green which persisted until all of the second equivalent of the acid was added. The nitrile III was recovered quantitatively.

The dicarbanion V, which was prepared conveniently by the addition of nitrile III to two molecular equivalents of potassium amide in liquid ammonia (direct-addition procedure), was alkylated with a molecular equivalent of benzyl chloride to form presumably the intermediate monocarbanion VI. Acidification with ammonium chloride gave the β -benzyl derivative VII in 80% yield (equation 2).

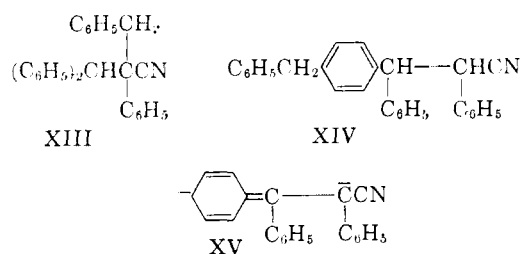


The product was shown to be a mono- and not a dibenzyl derivative by analysis and molecular weight determination. An infrared absorption spectrum of the product gave a band at 4.45 μ for the cyanide group.⁷ This presumably ruled out the possible alkylation products that were no longer nitriles such as the N-benzyl derivatives VIII and

X and the C-benzyl derivative IX. The first of these compounds might have arisen through the resonance form XI of the dicarbanion V, and the last two compounds through the resonance form XII.

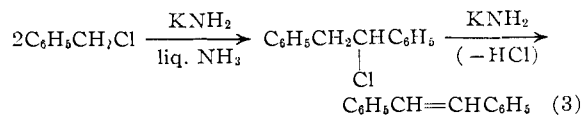


The possible alkylation products that were still nitriles included, besides the β -benzyl derivative VII represented in equation 2, the α -benzyl derivative XIII and the *o*- or *p*-benzyl derivatives of the α - or β -phenyl groups, for example, XIV. The latter compound might have arisen through resonance form XV of dicarbanion V.



The alkylation product was shown not to be the α -benzyl derivative XIII, which was readily prepared by the benzylation of the monocarbanion IV in the usual manner.

The product was indicated not to be such a ring substitution derivative as XIV by treatment with two equivalents of potassium amide in liquid ammonia and then by one equivalent of benzyl chloride. If the compound had structure XIV it should have been converted by the amide ion to the corresponding dicarbanion which would be expected to yield another benzyl derivative. However, no such benzyl derivative was produced. Instead, the compound was largely recovered and a good yield of stilbene was obtained. This result is accounted for on the basis that the compound is the β -benzyl derivative VII which has only one readily ionizable hydrogen, the α -hydrogen. Thus, this nitrile was converted by one equivalent of the amide ion to the monocarbanion VI leaving the second equivalent of this base to effect the self-condensation of the benzyl chloride leading to the formation of stilbene, a well established type of reaction (equation 3).⁸



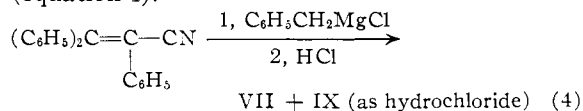
It is not surprising that the benzyl chloride reacted preferentially with the amide ion rather than

(7) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 223.

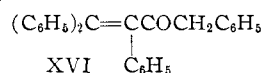
(8) See C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Factor and A. E. Brodhag, THIS JOURNAL, **78**, 1653 (1956).

with the monocarbanion VI, which was indicated to be difficult to alkylate by the failure of dicarbanion V to undergo dibenylation in liquid ammonia (see below).

The structure of the alkylation product of dicarbanion V was confirmed as VII by independent synthesis involving the conjugate addition of benzylmagnesium chloride to 2,3,3-triphenylacrylonitrile. This reaction was accompanied by 1,2-addition to form imine IX as its hydrochloride (equation 4).



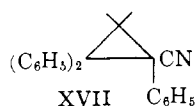
Although the main product was the imine hydrochloride, the desired nitrile VII was readily separated from the reaction mixture by its solubility in ether. The imine hydrochloride was identified by its infrared spectrum and by hydrolysis to the corresponding ketone XVI.



The fact that dicarbanion V underwent benzylation at the β -carbon was anticipated, since the carbanion at this position was expected to be more strongly nucleophilic than the one at the α -position.

The dicarbanion V also was treated with two equivalents of benzyl chloride in an attempt to effect dibenylation, but only the monobenzyl derivative VII was isolated. Thus, while dicarbanion V reacted rapidly with benzyl chloride, the resulting monocarbanion VI failed to undergo further benzylation in liquid ammonia within 9 hours. Incidentally in this experiment a second crystalline modification of VII was evidently obtained (see Experimental).

In a preliminary experiment with the dicarbanion V and a molecular equivalent of methylene chloride a compound was isolated that is tentatively assigned the cyclopropane structure XVII.



This structure was supported by analysis, molecular weight determination, and infrared spectrum, which showed absorption at 4.45μ for the cyanide group. Also in agreement with structure XVII the nuclear magnetic resonance spectrum showed bands attributable to both aromatic and aliphatic hydrogens.

It should be mentioned that like other highly hindered nitriles VII and XIII were found to be resistant to hydrolysis under normal conditions in acidic or basic media.⁹

Experimental¹⁰

2,3,3-Triphenylpropionitrile (III) was prepared in near quantitative yield by the benzydrylation of potassiophenyl-

(9) See C. R. Hauser and W. R. Brasen, *THIS JOURNAL*, **78**, 82 (1956).

(10) Melting points were taken on a Fisher-Johns melting point apparatus. Infrared spectra were produced with a Perkin-Elmer Infracord by the potassium bromide pellet method. Elemental

acetonitrile with benzhydryl chloride essentially as described previously.⁵ The product melted at $103\text{--}104^\circ$.

Twofold Ionization of Nitrile III by Amide Ion.—To a stirred suspension of 26 g. (0.092 mole) of nitrile III in 200 ml. of liquid ammonia was added slowly a solution of 0.184 mole of potassium amide in 300 ml. of liquid ammonia¹¹ by means of an inverse-addition flask. The nitrile was sufficiently soluble in the liquid ammonia so that the amide reacted rapidly to form the pale green color characteristic of the monocarbanion IV. The green color deepened somewhat until a molecular equivalent of amide ion had been added at which point the material in the flask was totally in solution. As slightly more potassium amide solution was added the reaction mixture took on a reddish cast which gradually changed to a definite dark red, deepening as the addition of the second equivalent of base progressed. The resulting dark red dicarbanion V appeared to be totally in solution.

After 10 minutes 5 g. (0.092 mole) of solid ammonium chloride was added, causing the red color of the solution to change back to green. Addition of another molecular equivalent (5 g.) of ammonium chloride dissipated all but a trace of the green color.

The ammonia was allowed to evaporate and the residual solid was washed copiously with water and collected on a Büchner funnel to give a quantitative return of starting nitrile, m.p. $100\text{--}101^\circ$, and $101\text{--}102^\circ$ after one recrystallization from ethanol. Admixture with an authentic sample of 2,3,3-triphenylpropionitrile⁵ did not depress the melting point.

Benylation of Dicarbanion V to Form β -Benzyl Derivative VII.—To a stirred solution of 0.1 mole of potassium amide in 300 ml. of liquid ammonia¹¹ was added 14.2 g. (0.05 mole) of solid 2,3,3-triphenylpropionitrile (III) by means of a powder funnel. The resulting dark red solution of dicarbanion V was stirred for 15 minutes, and 6.3 g. (0.05 mole) of benzyl chloride in an equal volume of ether was added. After stirring for 30 minutes longer, excess (5 g.) ammonium chloride was added, and the ammonia was evaporated on the steam-bath. Water was added and the slurry was poured onto a Büchner funnel. The solid was washed with water, dried, and washed with petroleum ether (b.p. $30\text{--}60^\circ$). The product was dissolved in hot ethanol and the solution was brought to saturation with water and allowed to crystallize. There was obtained 15.0 g. (80%) of 2,3,3,4-tetraphenylbutyronitrile (VII), m.p. $123.5\text{--}126^\circ$ (sintered at 122°). Two recrystallizations from ethanol raised the melting point to $125.5\text{--}128^\circ$. The infrared spectrum of the compound showed a nitrile band at 4.45μ and an absence of any band in the region of 6μ attributable to the imine group.⁷

Anal. Calcd. for $\text{C}_{28}\text{H}_{23}\text{N}$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.02; H, 6.25; N, 3.81.

In several other experiments the dicarbanion V was treated with two molecular equivalents of benzyl chloride. After reaction times ranging up to 9 hours in liquid ammonia the reactions were worked up as described above. Much benzyl chloride was recovered. There was obtained a white crystalline product, m.p. $138\text{--}139^\circ$, in yields of 33–47% after recrystallization from either ethanol or methanol. The compound gave satisfactory analyses for 2,3,3,4-tetraphenylbutyronitrile (VII).

Anal. Calcd. for $\text{C}_{28}\text{H}_{23}\text{N}$ (monobenzyl): C, 90.04; H, 6.21; N, 3.75; mol. wt., 373.5. Calcd. for $\text{C}_{36}\text{H}_{29}\text{N}$ (dibenzyl): C, 90.67; H, 6.31; N, 3.02; mol. wt., 463.6. Found: C, 90.04, 90.31; H, 6.25, 6.22; N, 3.55, 3.52; mol. wt., 341, 333, 328, 346.

The compound evidently was a second crystalline modification of the nitrile VII melting at $125.5\text{--}128^\circ$ described above. The infrared spectra of the two forms were superimposable.

A sample of the lower melting form was totally converted to the higher melting form by dissolving it in 95% ethanol and seeding the solution with a few small crystals of the latter form. A sample of the higher melting form was converted partially to the lower melting form by seeding

analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Molecular weights were determined by Dr. Carl Tiedcke, 705 George Street, Teaneck, N. J.

(11) See C. R. Hauser and T. M. Harris, *THIS JOURNAL*, **80**, 6360 (1958).

a 95% ethanol solution of it with a few crystals of the latter crystalline modification.

Treatment of Nitrile VII with Two Equivalents of Potassium Amide and One of Benzyl Chloride.—To a stirred solution of 0.2 mole of potassium amide in 300 ml. of liquid ammonia¹² was added 37.3 g. (0.1 mole) of 2,3,3,4-tetraphenylbutyronitrile (VII). The resulting green solution was stirred for 15 minutes, and 12.6 g. (0.1 mole) of benzyl chloride in a little ether then was added. The first few ml. of the halide solution produced a purple color which persisted until a few seconds after all of the halide had been added. After stirring for 5 minutes, excess (15 g.) ammonium chloride was added and the ammonia was evaporated as an equal volume of ether was added. The resulting ethereal suspension was shaken with water. The aqueous layer was extracted with ether containing some ethyl acetate and the extracts were combined with the ethereal layer. The ethereal ethyl acetate solution was dried and the solvents removed. The residue was taken up in hot benzene and about 800 ml. of petroleum ether (b.p. 30–60°) was added. The solution was cooled in an ice-bath to precipitate slowly 30.7 g. (83%) of recovered nitrile VII, m.p. 136–138°. The remaining liquors were concentrated to a small volume on the steam-bath and hot ethanol was added. Cooling produced 6.9 g. (77%) of stilbene, m.p. 110–112°, slightly contaminated with the nitrile. Recrystallization of the hydrocarbon from ethanol raised the melting point to 119–121°. Admixture with an authentic sample of stilbene, m.p. 122–124°, did not depress the melting point.

Independent Synthesis of β -Benzyl Derivative VII.—2,3,3-Triphenylacrylonitrile was prepared by the condensation of phenylacetonitrile with benzophenone in the presence of sodium amide.¹²

To a stirred ethereal solution of benzylmagnesium chloride prepared from 0.22 mole each of magnesium turnings and benzyl chloride was added 48.25 g. (0.172 mole) of 2,3,3-triphenylacrylonitrile. After stirring for 5 hours the reaction mixture was poured into iced hydrochloric acid. The ethereal layer was separated from the aqueous mixture containing the insoluble hydrochloride as imine IX, and dried for 12 hours over magnesium sulfate. During this time more of the imine hydrochloride precipitated. The ethereal solution was filtered and the solvent removed. Recrystallization of the residue from ethanol produced 2.8 g. (4.4%) of 2,3,3,4-tetraphenylbutyronitrile (VII), m.p. 137–138°. Admixture of this product with the benzylation product (m.p. 138–139°) of the dicarbanion of nitrile III did not depress the melting point, and their infrared spectra were superimposable.

The imine salt was converted to the corresponding ketone by boiling for one hour with 12 *M* hydrochloric acid. The water was decanted and the residue recrystallized from ethanol and acetone to give 22 g. (34%) of 1,3,4,4-tetraphenylbut-3-ene-2-one (XVI), m.p. 139–144°, yellow needles. Recrystallization from ethanol raised the melting point to 149–150°.

Anal. Calcd. for $C_{28}H_{20}O$: C, 89.80; H, 5.92. Found: C, 89.83; H, 6.06.

(12) *Org. Syntheses*, **31**, 52 (1951).

The infrared spectrum of the imine hydrochloride showed a broad band at 3.55 and a sharp band at 6.05 μ .⁷ These bands were absent in ketone XVI which had a well defined carbonyl band at 5.9 μ .¹³

Benylation of the Monocarbanion IV to form α -Benzyl Derivative XIII.—To a stirred solution of 0.05 mole of potassium amide in 300 ml. of liquid ammonia was added 14.2 g. (0.05 mole) of solid 2,3,3-triphenylpropionitrile (III) by means of a powder funnel. The resulting light green solution of monocarbanion IV was stirred for 15 minutes, and 6.3 g. (0.05 mole) of benzyl chloride in an equal volume of ether then was added. The reaction mixture was allowed to stir until the ammonia had evaporated completely. Water was added and the product collected on a Büchner funnel. The filter cake was washed with water, dried and washed with a little petroleum ether (b.p. 30–60°). There was obtained 18.14 g. (97%) of 2-benzyl-2,3,3-triphenylpropionitrile (XIII), m.p. 182–185°. Two recrystallizations from absolute ethanol raised the melting point to 185.5–187°. The infrared spectrum of this compound showed a band at 4.45 μ attributable to the cyanide group, but an absence of absorption about 6 μ , a region in which imines have been observed to absorb.⁷ This spectrum differed from that of 2,3,3,4-tetraphenylbutyronitrile (VII) in the fingerprint region.

Anal. Calcd. for $C_{25}H_{19}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.14; H, 6.33; N, 3.88.

Treatment of Dicarbanion V with Methylene Chloride.—To a stirred solution of 0.2 mole of potassium amide in 500 ml. of liquid ammonia was added 28.3 g. (0.1 mole) of 2,3,3-triphenylpropionitrile (III). The resulting red solution of dicarbanion V was stirred for 10 minutes, and 10.2 g. (0.12 mole) of methylene chloride in 50 ml. of ether then was added. After stirring for 1.5 hours (red color still present), the ammonia was replaced with ether. Water was added and the ethereal layer washed with 6 *M* hydrochloric acid, followed by water. The ethereal solution was dried and the solvent removed. The residue was taken up in hot methanol, and then treated with Norite to give on cooling 18.7 g. (64%) of apparently 1,2,2-triphenylcyclopropyl cyanide (XVII), m.p. 118–121°. Five recrystallizations from methanol raised the melting point to 131.5–132.5°.

Anal. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74; mol. wt., 295. Found: C, 89.69; H, 5.80; N, 4.73; mol. wt., 299, 286, 278, 291.

The infrared spectrum of the nitrile gave the following bands: 3.27, 4.45, 6.25, 6.30, 6.68, 6.88, 8.62, 9.26, 9.70, 9.85, 10.17, 12.68, 13.29, 14.15, 14.37 μ . The nuclear magnetic resonance spectrum of a saturated carbon disulfide solution of XVII indicated the presence of both aromatic and aliphatic hydrogens in the molecule.¹⁴ The aromatic absorption was much stronger and could be resolved into four distinct bands.

DURHAM, N. C.

(13) See ref. 7, p. 114.

(14) We are indebted to G. S. Paulett for the interpretation of the nuclear magnetic resonance spectrum which was determined in this Laboratory on a Varian N.M.R. Spectrometer, model V4300B.

[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

Derivatives of Aromatic Sulfinic Acids. III. Evidence for the Hydrogen Dichloride Ion from Epimerization Reactions¹

BY HARRY F. HERBRANDSON AND RICHARD T. DICKERSON, JR.

RECEIVED AUGUST 11, 1958

Asymmetric sulfinic esters, $ArS(O)OR$, epimerize at the sulfur atom when treated in nitrobenzene with hydrogen chloride and chloride ions as co-catalysts. The mechanism of the reaction is discussed, and the kinetics is interpreted as giving a value of 500–1000 l. mole⁻¹ for the association constant of the hydrogen dichloride ion in nitrobenzene at 25°: $Cl^- + H-Cl \rightleftharpoons ClHCl^-$.

The reactions of alkyl sulfites and alkyl arenesulfonates with thionyl chloride are very similar,² but

(1) This work was supported in part by the Office of Naval Research and in part by a grant from the R. P. I. Research Fund.

kinetic studies are complicated by the ease of hydrolysis of the thionyl chloride. Since these es-

(2) H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *This Journal*, **78**, 2576 (1956).