Experimental

Two general methods were used in these preparations. In Method A, 0.017 mole of triphenylsilyl chloride was fused for four hours with 0.017 mole of urea and thiourea, respectively, in a 22 × 175 mm. test-tube fitted with a calcium chloride tube. The fused mass was removed, crushed and extracted with three 25-ml. portions of petroleum ether (b. p. 77–115°). The insoluble material proved to be ammonium chloride.

In Method B, double decomposition between triphenylsilyl chloride and sodium urethan, silver isocyanate, silver isothiocyanate, lead isothiocyanate, and ammonium isothiocyanate, respectively, was effected. In this method, the reactions were carried out in a round bottom flask provided with a condenser and a mechanical stirrer. The inert gas used was dry nitrogen. See Table I and accompanying footnotes for the results obtained by these two methods.

The results of the treatment of triphenylsilyl isocyanate and triphenylsilyl isothiocyanate with phenyllithium and phenylmagnesium bromide are given in Table II. In these reactions with the organometallic compounds, a three-necked flask provided with a condenser and a mechanical stirrer was used. The inert gas was dry nitrogen.

The melting point of a mixture of triphenylsilyl isocyanate (m. p., 100–101°) and triphenylsilyl isothiocyanate (m. p., 99–100.5°) was 80–85°.

Summary

Triphenylsilyl chloride was treated with urea and with sodium urethan to form triphenylsilyl isocyanate. When thiourea, lead isothiocyanate, and ammonium isothiocyanate, respectively, were used, triphenylsilyl isothiocyanate resulted. The products were shown to be identical with those obtained from the corresponding silver salts.

The reactions of triphenylsilyl isocyanate and triphenylsilyl isothiocyanate with phenylmagnesium bromide and phenyllithium were studied.

AMES, IOWA RECEIVED SEPTEMBER 6, 1949

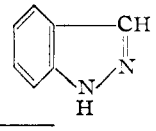
[CONTRIBUTION FROM NICHOLS LABORATORY, NEW YORK UNIVERSITY]

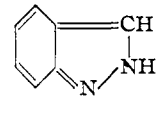
Structure and Ultraviolet Absorption Spectra of Indazole, 3-Substituted Indazole and Some of Their Derivatives[1]

BY V. ROUSSEAU[2] AND H. G. LINDWALL

The application of ultraviolet absorption spectra to the problem of the structure of indazole and 3-substituted indazole has been found to give results that are in agreement with those of von Auwers[3] based on the spectrochemical property of optical exaltation exhibited by indazoles.

von Auwers was enabled to report on the structure of indazole and 3-substituted indazole by comparing their specific exaltations, the surplus of the specific refraction over the theoretical, with those of their two isomeric series of N-alkyl and N-acyl derivatives. The specific exaltation of indazole, its 1-alkyl and 1-acyl derivatives were found to be of the same degree of magnitude but lower than those of the corresponding 2-alkyl and 2-acyl derivatives. The same observations were made when the specific exaltations of 3-substituted indazoles and 1,3-disubstituted indazoles were compared with those of the corresponding 2,3-disubstituted indazoles. Since the structure of the pairs of N-alkyl and N-acyl derivatives of indazole and 3-substituted indazoles employed had been established, it was reasonable to conclude that indazole and 3-substituted indazoles are built according to the pattern of their 1-alkyl derivatives, the benzenoid structure I. The desmotropic quinoid form II, whose existence had earlier been postulated, cannot be present in any appreciable amount.

I 

II 

A simpler and perhaps more convincing way of arriving at the ultimate structure lies in comparing the ultraviolet absorption spectrum of indazole with the spectra of 1-methyl- and 2-methylindazole. Of these three curves (Fig. 1) the one for indazole and the one for 1-methylindazole are very similar, but both differ markedly from the one for 2-methylindazole. Indazole then must be assigned the benzenoid structure, I, with the virtual exclusion of the quinoid structure, II. Comparison of the ultraviolet absorption spectra of 3-cyanoindazole and indazole-3-acid with those of their corresponding 1-methyl and 2-methyl derivatives (Fig. 2 and 3) also forces the assignment of the benzenoid structure to 3-substituted indazoles.

The preparation of 3-cyanoindazole by the diazotization of *o*-aminobenzyl cyanide at room temperature has previously been reported.[4] However, the synthesis of the intermediate *o*-aminobenzyl cyanide described here differs in some respects from earlier methods.[4,5] *o*-Nitrophenylpyruvic acid oxime was prepared from the condensation of *o*-nitrotoluene and diethyl oxalate followed by hydrolysis of the *o*-nitrophenylpyruvate formed before steam distillation of the unreacted *o*-nitrotoluene, since the pyruvate is also steam distillable.[6] The acid oxime was then isolated directly from the reaction mixture in 56% yield. The action of hot acetic anhydride on *o*-nitrophenylpyruvic acid oxime resulted in the

(1) Presented in part before the Organic Division of the American Chemical Society, Atlantic City, September, 1949.

(2) College of Mount St. Vincent, New York 63, N. Y.

(3) v. Auwers, Hugel and Ungemach, *Ann.*, **527**, 291 (1937).

(4) Pschorr and Hoppe, *Ber.*, **43**, 2543 (1910).

(5) Reissert, *ibid.*, **41**, 3810 (1908).

(6) Di Carlo, THIS JOURNAL, **66**, 1420 (1944).

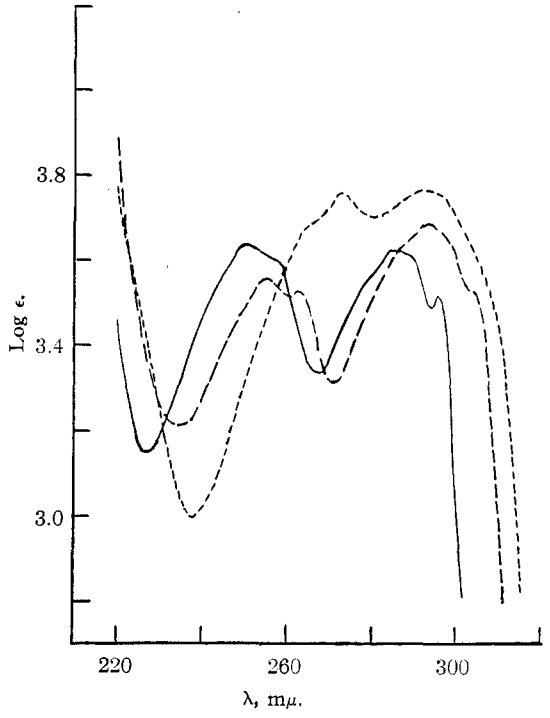


Fig. 1.—Ultraviolet absorption spectra of indazole, —; 1-methylindazole, — — —; 2-methylindazole, - - - -.

splitting off of carbon dioxide and water yielding *o*-nitrobenzyl cyanide (66%). Hydrogenation with palladium catalyst resulted in an 88% yield of *o*-aminobenzyl cyanide.

Indazole-3-acid was obtained by hydrolysis of 3-cyanoindazole in hot concentrated hydrochloric acid.[4] Thermal decarboxylation of indazole-3-acid yielded indazole which was obtained as a sublimate.[4,7] Some of the indazole, however, was obtained by the reduction of 3-cyanoindazole by means of sodium dropped into a refluxing solution of 3-cyanoindazole in absolute ethanol. The product, secured in 31% yield, was found to be identical with indazole procured by decarboxylation of indazole-3-acid.

N-Alkyl derivatives of 3-cyanoindazole have not previously been reported. The methylation of 3-cyanoindazole yielded 1-methyl or 2-methyl derivatives or a mixture of both, according to the procedure employed. The constitution of these two isomers was ascertained by hydrolysis of each to its corresponding acid, both of which are known.[8] These two acids when decarboxylated yielded the corresponding 1-methyl- and 2-methylindazole whose structures have been unequivocally proved.[9]

It has been found that indazole and 3-cyanoindazole will add smoothly to acrylonitrile to form stable N-cyanoethyl derivatives. The formation of pairs of isomers could not be detected. The products are formulated as 1-(2′-cyanoethyl)-indazole and 1-(2′-cyanoethyl)-3-cyanoindazole

(7) Schad, *Ber.*, **26**, 216 (1893).
(8) v. Auwers and Dereser, *ibid.*, **52**, 1340 (1919).
(9) v. Auwers and Duesberg, *ibid.*, **53**, 1179 (1920).

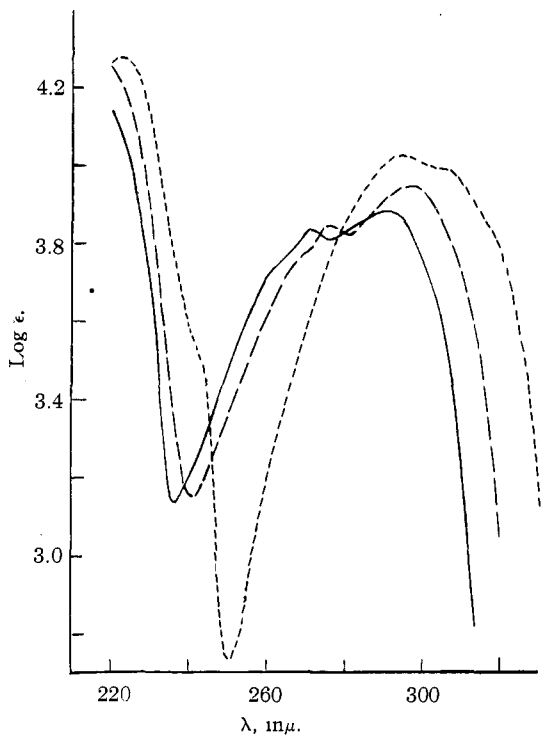


Fig. 2.—Ultraviolet absorption spectra of 3-cyanoindazole, —; 1-methyl-3-cyanoindazole, — — —; 2-methyl-3-cyanoindazole, - - - -.

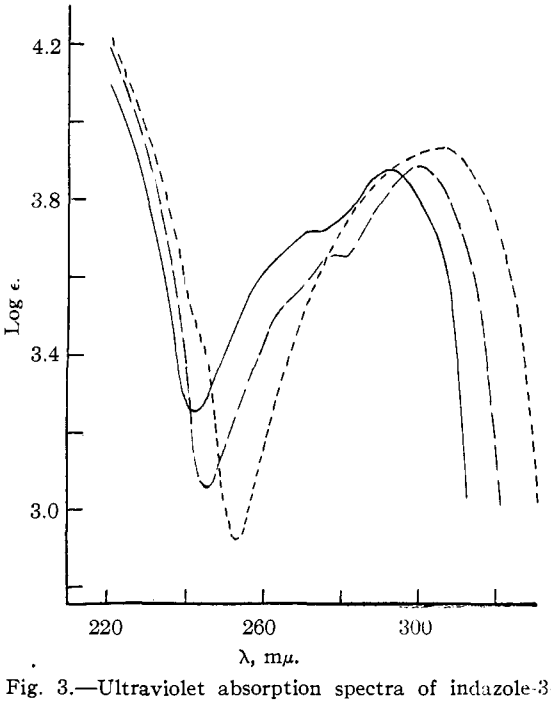


Fig. 3.—Ultraviolet absorption spectra of indazole-3-acid, —; 1-methylindazole-3-acid, — — —; 2-methylindazole-3-acid, - - - - -.

since their absorption curves are respectively nearly replicas of those of 1-methylindazole and 1-methyl-3-cyanoindazole (Figs. 4 and 5). These cyanoethyl addition compounds were hydrolyzed in strong acid to their corresponding acids, 1-(2′-carboxyethyl)-indazole[10] and 1-(2′-carboxyethyl)-indazole-3-acid.

Experimental[11]

o-Nitrophenylpyruvic Acid Oxime.—A mixture of 137 g. (1 mole) of *o*-nitrotoluene and 146 g. (1 mole) of diethyl oxalate was poured into a cooled solution of 23 g. of sodium in 400 ml. of absolute ethanol. The mixture was refluxed for 25 minutes. The ethyl *o*-nitrophenylpyruvate formed was then hydrolyzed by adding 100 ml. of water and refluxing for one hour. Unreacted *o*-nitrotoluene was then removed by steam distillation. The red solution of *o*-nitrophenylpyruvic acid was treated with activated charcoal and filtered. After cooling to 40–50°, 0.7 mole of hydroxylamine hydrochloride in 75 ml. of water was added. The excess acid was neutralized with 10% sodium hydroxide solution. After standing overnight, the solution was made acid to congo red with hydrochloric acid and refrigerated. The resulting oxime amounted to 125 g. (56%), m. p. 159–161°, including 5 g. secured by salting out the filtrate and cooling again.

o-Nitrobenzyl Cyanide.—*o*-Nitrophenylpyruvic acid oxime (120 g., 0.54 mole) was added in small portions and with occasional stirring to 120 ml. of acetic anhydride heated to 110°. The decarboxylation and dehydration proceeded vigorously. The solution was brought to the boiling point for a few minutes and then cooled. This was followed by the addition of 200 g. of ice, and after standing in the refrigerator overnight, the product was filtered and washed with water. A total of 70 g. of crude *o*-nitrobenzyl cyanide was thus obtained, including that procured on neutralization of the filtrate with sodium hydroxide solution. Successive recrystallizations from ethanol, ethyl acetate and ethanol with the aid of activated charcoal yielded 57 g. (66%) of *o*-nitrobenzyl cyanide, m. p. 82–84°, of sufficient purity to be reduced catalytically.

o-Aminobenzyl Cyanide.—The hydrogenation at room temperature of 50 g. (0.31 mole) of *o*-nitrobenzyl cyanide in 150 ml. of 95% ethanol under an initial pressure of 50 lb. per sq. in. was catalyzed by 1.5 g. of 5% palladium on charcoal. The reduction was allowed to proceed until 0.93 mole of hydrogen was consumed. The resulting amine was completely soluble in the ethanol. The catalyst was filtered, and the volume of the filtrate was doubled by the addition of water. Upon refrigeration 36 g. (88%) of *o*-aminobenzyl cyanide, m. p. 70–72°, crystallized. This was used without further purification for the preparation of 3-cyanoindazole.

3-Cyanoindazole.—It was synthesized by diazotizing *o*-aminobenzyl cyanide according to the procedure of Pschorr and Hoppe.[4]

Indazole-3-acid.—This was prepared by hydrolyzing 3-cyanoindazole in concentrated hydrochloric acid as described by Pschorr and Hoppe.[4]

Indazole. Method A.—Thermal decarboxylation of indazole-3-acid yielded indazole as Pschorr and Hoppe,[4] and Schad[7] have reported.

Method B.—Sodium (2 g.) in small pieces was added to a refluxing solution of 2 g. of 3-cyanoindazole in 25 ml. of absolute ethanol. At the end of the reaction, the solution was diluted with 50 ml. of water. The product was extracted with ether and dried over sodium sulfate. The ether was removed under reduced pressure, and the residue was taken up in 50 ml. of hot water and filtered. Indazole, 0.52 g. (31%), crystallized on cooling. One recrystallization from water gave colorless needles, m. p. 147–148°, identical with indazole prepared by the decarboxylation of indazole-3-acid; a mixed melting point determination showed no depression. Free cyanide ion was demonstrated to be present in the alkaline aqueous solution remaining after the extraction of the indazole by its conversion to Prussian Blue.

Anal. Calcd. for $C_7H_6N_2$: N, 23.7. Found: N, 23.7.

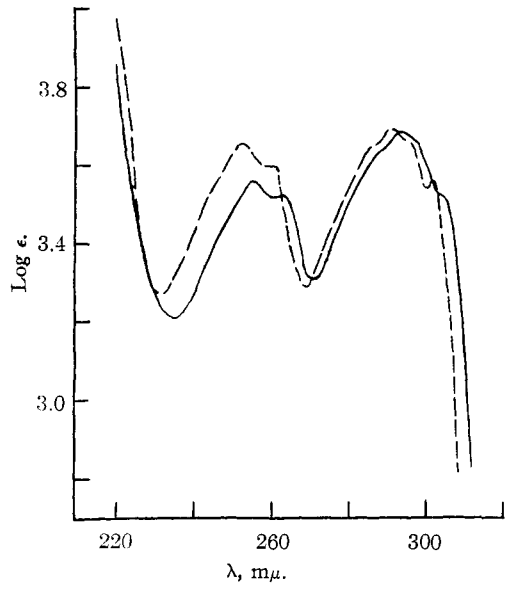


Fig. 4.—Ultraviolet absorption spectra of 1-methylindazole, —; 1-(2′-cyanoethyl)indazole, — — —.

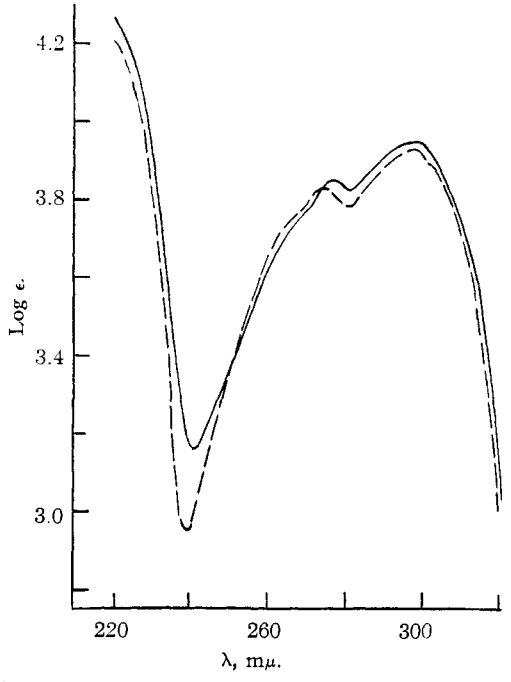


Fig. 5.—Ultraviolet absorption spectra of 1-methyl-3-cyanoindazole, ——; 1-(2′-cyanoethyl)-3-cyanoindazole, — — —.

(10) This acid is undoubtedly the same as the lower melting of two isomeric acids, m. p. 105.5–106.5° and 148–149°, obtained by v. Auwers and Kleiner, *J. prakt. Chem.*, **118**, 67 (1928), from the hydrolysis of two isomeric esters produced when indazole and β-chloropropionate were heated together in ethanolic sodium ethylate.

(11) All melting points are corrected and were taken with capillaries inserted in a metal block.

1-Methyl-3-cyanoindazole. Method A.—A mixture of 1.43 g. (0.01 mole) of 3-cyanoindazole and 6 g. (0.042 mole) of methyl iodide was heated in a sealed tube at 150° for four hours. The excess methyl iodide was removed under reduced pressure. The residue was dissolved in 20 ml. of hot ethanol and diluted with 20 ml. of hot water. Sufficient sodium bisulfite was added to reduce the iodine formed during the reaction. The light yellow solution was filtered while hot and further diluted with 10 ml. of 5% sodium hydroxide. The pale yellow methylated product which crystallized on cooling was washed with water and weighed 0.68 g. (43%); m. p. 67–70°. Two recrystallizations from 50% ethanol followed by one from petroleum ether yielded colorless needles; m. p. 72°.

Method B.—To a cooled solution of 3-cyanoindazole (2 g., 0.014 mole) in 20 ml. of 5% sodium hydroxide was added 1.75 g. (0.014 mole) of dimethyl sulfate. A precipitate occurred immediately. After standing in the refrigerator overnight, 1.68 g. (77%) of a mixture of 1-methyl- and 2-methyl-3-cyanoindazole was obtained; m. p. 54–60°. By fractional crystallization from petroleum ether it was possible to procure 0.48 g. of the less soluble 1-methyl-3-cyanoindazole, m. p. 70–71°, from 1.35 g. of the mixture.

Method C.—To an absolute ethanolic solution of sodium ethylate made from 0.16 g. of sodium in 5 ml. of ethanol was added 1 g. (0.007 mole) of 3-cyanoindazole and 1 g. (0.007 mole) of methyl iodide. The solution was refluxed for four hours and then diluted with water, causing the precipitation of 0.88 g. (80%) of a mixture of 1-methyl- and 2-methyl-3-cyanoindazole which melted at 54–60°. From this mixture some 1-methyl-3-cyanoindazole may be obtained by fractional crystallization as in method B.

Anal. Calcd. for $C_9H_7N_3$: C, 68.8; H, 4.5; N, 26.8. Found: C, 68.6; H, 4.7; N, 26.5.

2-Methyl-3-cyanoindazole. Method A.—A mixture of 1.43 g. (0.01 mole) of 3-cyanoindazole and 6 g. (0.042 mole) of methyl iodide was heated in a sealed tube at 100° for eight hours. The excess methyl iodide was evaporated. The residue was dissolved in 20 ml. of 95% ethanol and diluted with 20 ml. of hot water. Sufficient sodium bisulfite was added to reduce the iodine formed during the reaction. The light yellow solution was further diluted with 10 ml. of 5% sodium hydroxide. Refrigeration resulted in the crystallization of 0.35 g. (22%) of the methylated product; m. p. 100–103°. Successive recrystallizations from 50% ethanol and 95% ethanol yielded colorless needles melting at 105°.

Method B.—**Silver 3-cyanoindazole** was prepared by adding a solution of 1.7 g. (0.01 mole) of silver nitrate dissolved in 30 ml. of 50% aqueous ethanol to a stirred solution of 1.43 g. (0.01 mole) of 3-cyanoindazole and 0.8 ml. of concentrated ammonium hydroxide dissolved in 30 ml. of 50% aqueous ethanol. The silver salt precipitated immediately. It was washed with water, 95% ethanol, and ether. The white powder obtained weighed 2.42 g. (97%).

Anal. Calcd. for $C_8H_4N_3Ag$: Ag, 43.3. Found: Ag, 43.2.

One gram of the 3-cyanoindazole silver salt (0.004 mole) was suspended in 10 ml. of dry ether in which was dissolved 1 g. (0.007 mole) of methyl iodide. The mixture was refluxed and stirred for twelve hours. The cooled mixture was filtered, and the ethereal filtrate was allowed to evaporate. The residue was taken up in 10 ml. of 95% ethanol and diluted with 10 ml. of 0.5% sodium hydroxide solution. Refrigeration resulted in the crystallization of 0.103 g. of 2-methyl-3-cyanoindazole; m. p. 101–102°. The filtrate, diluted with 10 ml. of water and refrigerated, yielded 0.034 g. more of the product; m. p. 96–102°. A 22% yield was thus obtained. Recrystallization from 95% ethanol gave colorless needles; m. p. 105°.

Anal. Calcd. for $C_9H_7N_3$: C, 68.8; H, 4.5; N, 26.8. Found: C, 68.6; H, 4.7; N, 26.8.

1-Methylindazole-3-acid.—The hydrolysis of 0.5 g. of 1-methyl-3-cyanoindazole was accomplished by heating at just below the boiling point in 5 ml. of concentrated hydrochloric acid for two hours. Some of the acid crystallized on cooling, and this process was completed on the addition of 10 ml. of water, yielding 0.54 g. (98%) of slender, white needles which melted at 214–215° with slow evolution of carbon dioxide. Recrystallization from 10 ml. of 50% aqueous ethanol resulted in needles melting at 215–216°.

Anal. Calcd. for $C_9H_8O_2N_2$: N, 15.9. Found: N, 15.8.

2-Methylindazole-3-acid.—The hydrolysis of 0.29 g. of 2-methyl-3-cyanoindazole was performed by heating at just below the boiling point in 5 ml. of concentrated hydrochloric acid for two hours. The acid was made to crystallize on the addition of 10 ml. of water and cooling. The product, as white leaflets weighing 0.23 g. (71%), melted with rapid evolution of carbon dioxide at 221–223°. Recrystallization from 15 ml. of 70% ethanol gave leaflets melting at 224–225° when the temperature was raised at the rate of 3° per minute.

Anal. Calcd. for $C_9H_8O_2N_2$: N, 15.9. Found: N, 15.8.

1-Methylindazole was prepared by the decarboxylation of 1-methylindazole-3-acid.[9]

2-Methylindazole was prepared by decarboxylating 2-methylindazole-3-acid.[9]

1-(2′-Cyanoethyl)-indazole.—To 1 g. (0.0085 mole) of indazole dissolved in 10 ml. of anhydrous tertiary butyl alcohol was added 3 drops of trimethylbenzylammonium hydroxide and 0.45 g. (0.0085 mole) of acrylonitrile. The solution was maintained at 40° for two days and then diluted with 20 ml. of water and made acidic with acetic acid. Refrigeration resulted in crystallization of 1.29 g. (89%) of 1-(2′-cyanoethyl)-indazole, m. p. 83–84°. Recrystallization from 50% aqueous ethanol yielded slender, colorless needles, m. p. 84–85°.

Anal. Calcd. for $C_{10}H_9N_3$: C, 70.2; H, 5.3; N, 24.6. Found: C, 70.1; H, 5.5; N, 24.2.

1-(2′-Carboxyethyl)-indazole.—The hydrolysis of 1 g. of 1-(2′-cyanoethyl)-indazole was accomplished by refluxing slowly in 20 ml. of concentrated hydrochloric acid for one hour. The cooled solution was poured into four times its volume of water. The product crystallized from this solution weighed 1.01 g. (91%) and melted at 99–102°. Two recrystallizations from ligroin resulted in glistening, white leaflets, m. p. 108–109°.

Anal. Calcd. for $C_{10}H_{10}O_2N_2$: N, 14.7. Found: N, 14.4.

1-(2′-Cyanoethyl)-3-cyanoindazole.—To a solution of 3.0 g. (0.021 mole) of 3-cyanoindazole in 15 ml. of anhydrous tertiary butyl alcohol there was added 5 drops of 38% trimethylbenzylammonium hydroxide and 1.16 g. (0.022 mole) of acrylonitrile. After two hours, the red solution began to darken, and crystals started to fall out of solution. After twenty-four hours, the mixture was almost solid. The mixture was diluted with 30 ml. of water and acidified with acetic acid. After filtering and washing with water, 3.82 g. (93%) of crude product was obtained, m. p. 109–113°. Recrystallization from aqueous ethanol yielded 3.25 g., m. p. 113–114°. White needles melting at 114–114.5° were obtained on recrystallization from 95% ethanol.

Anal. Calcd. for $C_{11}H_8N_4$: C, 67.4; H, 4.1; N, 28.6. Found: C, 67.5; H, 4.2; N, 28.4.

1-(2′-Carboxyethyl)-indazole-3-acid.—The hydrolysis of 1.86 g. of 1-(2′-cyanoethyl)-3-cyanoindazole was performed in 40 ml. of refluxing, concentrated hydrochloric acid. At the end of two hours, the solution was cooled, and, on the addition of 150 ml. of water, the product began to crystallize slowly in small, well formed, white rosettes weighing 2.06 g. (93%), m. p. 205–210°. Recrystallization from water yielded white rosettes of needles which melted at 220–221° when the temperature was raised at the rate of 3° per minute. Recrystallization from glacial acetic acid did not change the melting point.

Anal. Calcd. for $C_{11}H_{10}O_4N_2$: N, 12.0. Found: N, 12.1.

Ultraviolet Absorption Measurements.—All determinations were made in aqueous solution. A Beckman quartz spectrophotometer was used. The spectrum was examined at 2 mμ intervals except near maxima and minima and there at 1 mμ intervals.

Summary

1. The benzenoid structure of indazole and 3-substituted indazole is confirmed on the basis of a comparison of their ultraviolet absorption spectra with those of their corresponding 1-methyl and 2-methyl derivatives.

2. Indazole and 3-cyanoindazole has been found to add to acrylonitrile to form 1-cyanoethyl derivatives exclusively.

3. The reduction of 3-cyanoindazole by means of sodium and ethanol has resulted in the cleavage of a carbon–carbon bond and the production of indazole.

4. The methylation of 3-cyanoindazole has been found to yield 1-methyl- or 2-methyl-3-cyanoindazole or a mixture of the two, depending on the procedure employed.

UNIVERSITY HEIGHTS
NEW YORK 53, N. Y. RECEIVED DECEMBER 10, 1949

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

The Nitration of Some 1,1,1-Trihalogeno-2,2-bisarylethanes

BY DAVID A. SHIRLEY AND THEODORE N. GOREAU

The high insecticidal activity of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (DDT) and certain related types has stimulated interest in the biological properties of compounds containing the 1,1,1-trichloro-2,2-bisarylethane structure. 1,1,1 - Trichloro - 2,2 - bis - (*p* - aminophenyl)-ethane has been reported[1,2] to have *in vitro* activity against *M. tuberculosis*. *In vivo* activity was also reported for this compound,[2] although more recent findings by Smith, Junge and McClosky[3] have indicated that the compound is of no value. 1,1,1 - Trichloro-2,2-bis-(*p* - nitrophenyl)-ethane has been reported to have chemotherapeutic activity against murine typhus[4] and *Rickettsia mooseri* in the mouse.[5]

We have been interested in the preparation and examination for biological activity of a number of 1,1,1-trihalogeno-2,2-bisarylethanes, particularly those containing nitro and amino groups.

In an earlier paper[6] were reported the nitration of 1,1,1-trichloro-2,2 - bis - (*p* - methoxyphenyl) - ethane (methoxychlor) and other transformations leading to several derivatives including an amino type. Nitration of methoxychlor gave a dinitro derivative. The positions of the nitro groups were shown by two independent methods of proof to be *ortho* to the methoxyl groups.

In the present work three additional types related to DDT and methoxychlor have been examined. These materials are 1,1,1-trichloro-2,2-bis-(*p*-bromophenyl)-ethane, 1,1,1-trichloro-2,2-bis-(*p*-tolyl)-ethane (II) and 1,1,1-tribromo-2,2-bis-(*p*-methoxyphenyl)-ethane. The reactions carried out on these compounds are summarized in Fig. 1 using 1,1,1-trichloro-2,2-bis-(*p*-tolyl)-ethane (II) as an example. The structures of the nitration products were proved by dehydrohalogenation to the corresponding ethylene compound (III) and oxidation to the known dinitrobenzophenone (V).

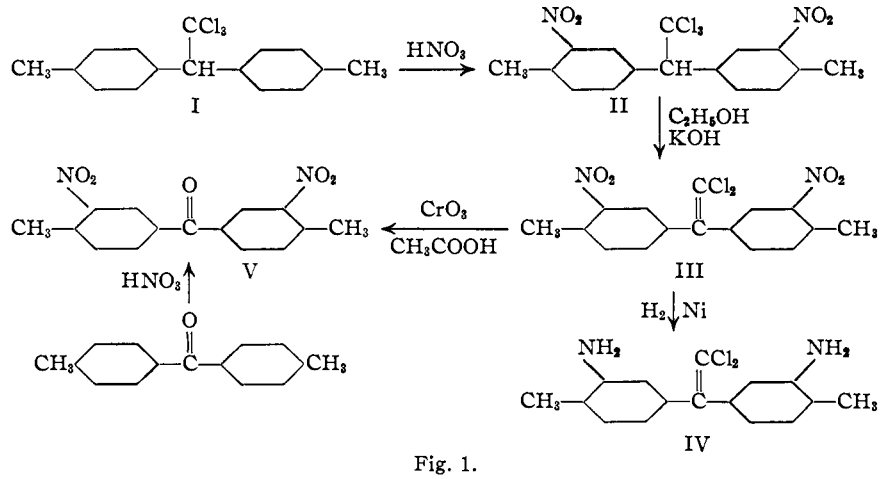


Fig. 1.

Experimental

1,1,1-Trichloro-2,2-bis-(3-nitro-4-methylphenyl)-ethane (II).—1,1,1-Trichloro-2,2-bis-(*p*-tolyl)-ethane (I),

(1) Burger, Graef and Bailey, THIS JOURNAL, **68**, 1725 (1946).

(2) Kirkwood and Phillips, *ibid.*, **69**, 934 (1947).

(3) Smith, Junge and McClosky, *J. Am. Pharm. Assoc. Sci. Ed.*, **37**, 461 (1948).

(4) Kikuth, Office of the Publication Board, Department of Commerce Report No. 248, p. 63.

(5) Lorenz, *Chem. Ber.*, **81**, 422 (1948) [*C. A.*, **43**, 4658 (1949)].

(6) Shirley, Goreau and Eiseman, THIS JOURNAL, **71**, 3173 (1949).