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The Reaction of Tropolones with Phosphorus Oxychloride. The Rearrangement Reaction of 5-Arylazo-2-chlorotropones to 2-Aryl-4, 5-dichloroindazoles

Katsuo KIKUCHI, Masaki YAGI*1 and Kunio TAKADA*2

Department of Chemistry, Faculty of Liberal Arts and Science, Yamagata University, Koshirakawa-cho, Yamagata

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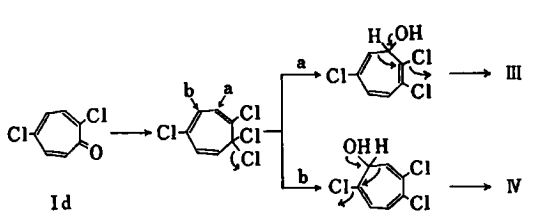
The reaction of tropolone and phosphorus oxychloride gave 2-chlorotropone. Similarly, 5-cyano-, 5-nitro, and 5-chlorotropolones afforded the corresponding 2-chlorotropone derivatives in moderate yields. 3-Cyanotropolone gave 2-chloro-7-cyanotropone, while 3-phenyltropolone afforded only 2-chloro-3-phenylbenzaldehyde. When 3-bromotropolone and 5-bromotropolone were treated similarly, 2, 7-dichloro- and 2, 5-dichlorotropones were obtained respectively, with a facile halogen exchange. The further treatment of 2, 5-dichlorotropone with phosphorus oxychloride afforded 2, 5-dichloro- and 3, 4-dichlorobenzaldehydes. The reaction of 5-*p*-tolylazo-, 5-phenylazo-, and 5-*p*-nitrophenylazotropolones with phosphorus oxychloride gave the corresponding 5-arylazo-2-chlorotropones, which, on further treatment with an excess of the reagent, gave 2-aryl-4, 5-dichloroindazoles.

2-Chlorotropone derivatives, important intermediates for the preparation of many kinds of 2- (or 7-) substituted tropones, azulenes and seven-membered aromatic compounds fused with several kinds of heterocyclic rings, have generally been prepared (a) by the copper sulfate-catalyzed decomposition of 2-hydrazinotropones with concentrated hydrochloric acid,[1-3] and (b) by the reaction of thionyl chloride on appropriate tropolones.[2,4-6]

We have found that the reaction of tropolone derivatives with phosphorus oxychloride also gave 2-chlorotropones with moderate yields, and that the 5-arylazo-2-chlorotropones thus obtained were, by an excess of the reagent, rearranged to 2-aryl-4, 5-dichloroindazoles; these results will be described in this paper.

When tropolone in dimethylformamide was treated with phosphorus oxychloride at room temperature for about 4 hr, 2-chlorotropone (Ia) was obtained in about a 40% yield. When the reaction was carried out in benzene or chloroform under reflux, however, no detectable amount of Ia was isolated; only a colorless crystalline powder (II) was obtained. The compound (II), because of its sparing solubility in usual organic solvents, could not be purified. II was decomposed gradually with hot water to regenerate tropolone, and reacted with alcoholic methylamine to give 2-methylaminotropone and tropolone.

A similar reaction carried out with 5-cyanotropolone and 5-nitrotropolone gave 2-chloro-5-cyanotropone (Ib) in a 73% yield and 2-chloro-5-nitrotropone (Ic) in a 90% yield respectively. The reaction of 5-chlorotropolone with an equimolar amount of the reagent gave 2, 5-dichlorotropone (Id) in about a 50% yield. However, when an excess of the reagent was applied to 5-chlorotropolone or to Id, 2, 5-dichlorobenzaldehyde (III) and 3, 4-dichlorobenzaldehyde (IV) were isolated. Such a type of rearrangement had already been observed in the reaction of tropolone with thionyl chloride to give 2-chlorobenzaldehyde.[4] In the present reaction, these dichlorobenzaldehydes are thought to be formed through a tetrachloro compound. The attack of water on the intermediate, followed by rearrangement, will give the final products depicted below, though such an intermediate has not actually been isolated.



*1 Present address: Adeka Argus Chemical Co., Ltd., Higashiogu, Arakawa-ku, Tokyo.

*2 Present address: The Research Institute for Iron, Steel and Other Metals, Tohoku University, Katahira-cho, Sendai.

1) S. Seto, *Sci. Repts. Tohoku Univ., Ser. I*, **37**, 275, 286, 297 (1953).
2) T. Sato, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **80**, 1167, 1171, 1342 (1959).
3) T. Nozoe, Y. Kitahara, K. Takase and I. Murata, This Bulletin, **37**, 1292 (1964).
4) B. J. Abadir, J. W. Cook, J. D. Loudon and D. K. V. Steel, *J. Chem. Soc.*, **1952**, 2350.
5) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **74**, 5683 (1952).
6) T. Mukai, This Bulletin, **32**, 272 (1959).

The reaction of 5-bromotropolone and phosphorus oxychloride also afforded Id, with a facile halogen exchange.

The reaction of 3-substituted tropolones with phosphorus oxychloride should give two isomeric products, *i. e.*, 2-chloro-3-substituted and 2-chloro-7-substituted tropones; actually, however, only one of the two was isolated. Thus, the reaction of 3-cyanotropolone and 3-bromotropolone with phosphorus oxychloride gave 2-chloro-7-cyanotropone (Ie)[3] in a 70% yield and 2, 7-dichlorotropone (If) in a 45% yield respectively. Contrary to the above two cases, the reaction of 3-phenyltropolone afforded colorless crystals (V), $C_{13}H_9OCl$, instead of the expected 2-chloro-phenyltropone, even when some of the reactant was recovered unchanged. The infrared spectrum of V exhibited an absorption band at 1683 cm^{-1}, and the oxidation of V with potassium permanganate afforded a monocarboxylic acid (VI), $C_{13}H_9O_2Cl$. The treatment of the acid with concentrated sulfuric acid did not afford a fluorenone derivative, suggesting that the carboxyl group is not adjacent to the phenyl group. V is thought to be 2-chloro-3-phenylbenzaldehyde formed in a manner similar to that in the formation of III from 5-chlorotropolone. In accordance with the postulated formula, the NMR spectrum[7] of V exhibited, besides the signals characteristic of an aldehyde proton (−0.40, singlet) and aromatic protons (2.35—2.8, multiplet, phenyl, C_4 and C_5 protons), an additional low-field quartet at 2.06 τ (J=6.7 and 2.8 cps, intensity one proton). The chemical shift and splitting indicate that this signal is generated by the C_6 proton coupled with the C_5 and C_4 protons. The ultraviolet spectrum of V in alcohol [λ_{max}, 241 and 307 mμ (log ε, 4.29 and 3.18)] is similar to that of 3-phenylbenzaldehyde,[8] and quite different from that of 4-phenylbenzaldehyde.[9]

We then turned our attention to the preparation of 5-arylazo-2-chlorotropones. When 5-*p*-tolylazotropolone in dimethylformamide was treated with an equimolar quantity of phosphorus oxychloride under ice-cooling, brownish-orange crystals (VIIa) and colorless crystals (VIIIa) were obtained in 78 and 6% yields respectively. VIIIa was also obtained in about a 50% yield when VIIa was treated with an excess of the reagent. The reaction of 5-*p*-tolylazotropolone with thionyl chloride in benzene also gave VIIa. The ultraviolet spectrum of VIIa exhibits absorption maxima at 300—315 and 385 mμ (log ε, 3.96 and 4.44), and the infrared spectrum shows a carbonyl band in the region below 1650 cm^{-1}, a spectral feature agreeing with that of troponoid compounds.[10] These data and the analytical values show that VIIa is 2-chloro-5-*p*-tolylazotropone.

The compound (VIIIa), $C_{14}H_{10}N_2Cl_2$, is stable toward dilute alkali and acids, and is not oxidized by potassium permanganate in acetone at room temperature. The ultraviolet spectrum of VIIIa is shown in Fig. 1. The NMR spectrum of VIIIa exhibits signals at 7.62 (3H, singlet), 2.15—2.85 (6H, multiplet) and 1.66 τ (1H, singlet), suggesting that VIIIa is an aromatic compound with a pyrazole or a similar heteroaromatic ring system.

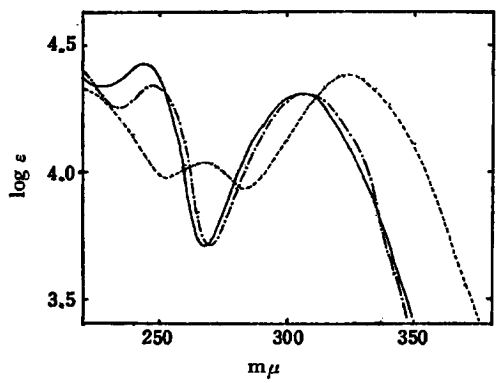
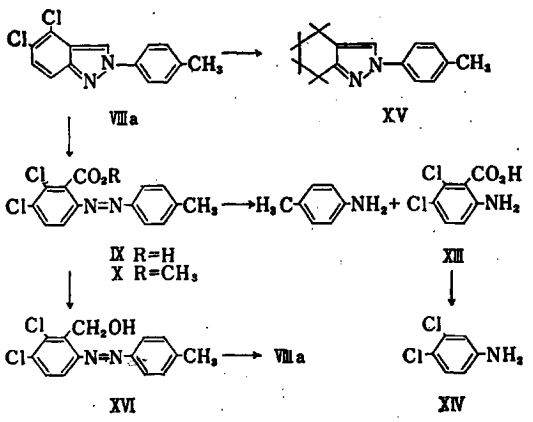


Fig. 1. Ultraviolet spectra of VIIIa (—·—·—) VIIIb (——) and VIIIc (----) in ethanol.

VIIIa was oxidized with chromic acid to give an acid (IX), $C_{14}H_{10}O_2N_2Cl_2$, and with nitric acid to give the same acid (IX), plus two mononitro compounds (XI and XII). The ultraviolet spectrum of the methyl ester (X) of IX exhibits maxima at 342 and 430—440 mμ, resembling those of azobenzene derivatives. The catalytic reduction of IX gave *p*-toluidine and 2-amino-5, 6-dichlorobenzoic acid (XIII), which decomposed above its melting point (175°C) to give 3, 4-dichloroaniline (XIV). The acid (IX) is, therefore, 3, 4-dichloro-4'-methylazobenzene-2-carboxylic acid. It is known that 2-phenylindazole, on oxidation with chromic acid, gives azobenzene-2-carboxylic acid;[11] the results obtained above can be explained on the assumption that VIIIa is 4, 5-dichloro-2-*p*-tolylindazole. This structure was confirmed by the following results. The catalytic reduction of VIIIa gave 2-*p*-tolyl-4, 5, 6, 7-tetrahydroindazole (XV). The NMR spectrum of XV exhibits signals at 8.25 (C_5- and C_6-methylene protons, multiplet), 7.68 (methyl protons, singlet), 7.40 (C_4- and C_7-methylene protons, multiplet) and 2.5-3.0 τ

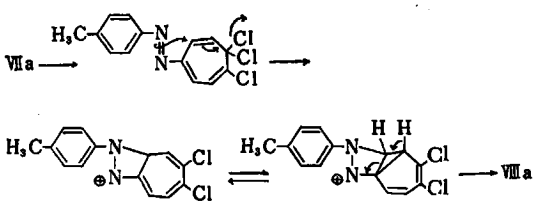
7) The NMR spectra were measured in deuteriochloroform, using tetramethylsilane as an internal standard, on a Varian A-60 spectrometer.
8) J. J. Godfroid, *Compt. rend.*, **257**, 2296 (1963).
9) H. Suzuki, This Bulletin, **33**, 613 (1960).
10) For the spectra of troponoid compounds, see M. Tsuboi, This Bulletin, **25**, 369 (1952); S. Kinumaki, K. Aida and Y. Ikegami, *Sci. Repts, Res. Inst. Tohoku Univ.*, **A-8**, 263 (1956); E. Kloster-Jensen, N. Tarkoy, A. Eschenmoser and E. Heilbronner, *Helv. Chim. Acta*, **39**, 780 (1956).
11) J. D. Loudon, "Chemistry of Carbon Compounds, A Modern Comprehensive Treatise," Vol. IV, Part A, ed. by E. H. Rodd. Elsevier Publishing Co., Amsterdam (1957), p. 278.



benzene-ring protons and C_3-proton, multiplet). The reduction of the ester (X) with lithium aluminum hydride gave a 2-hydroxymethylazobenzene derivative (XVI) and a 2-hydroxymethylhydrazobenzene derivative (XVII). The oxidation of XVII with bromine afforded XVI. The heating of XVI with 75% sulfuric acid afforded the original indazole (VIIIa), as expected.[11]

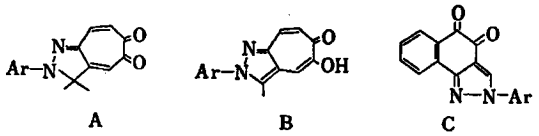
The bromination of VIIIa afforded 3-bromo-4, 5-dichloro-2-*p*-tolylindazole (XVIII); the position of the bromine atom was confirmed by the nitric acid oxidation aimed at giving IX. The position of the nitro group in XI and XII is not clear.

The reaction of 2-methoxy-5-*p*-tolylazotropone[12] and phosphorus oxychloride gave the same indazole (VIIIa) in about a 57% yield. The mechanism of the formation of VIIIa from VIIa is assumed to be as follows:



The reaction of 5-phenylazotropolone and phosphorus oxychloride gave 2-chloro-5-phenylazotropone (VIIb) and 4, 5-dichloro-2-phenylindazole (VIIIb). Similarly, 5-*p*-nitrophenylazotropolone afforded 2-chloro-5-*p*-nitrophenylazotropone (VIIc) and 4, 5-dichloro-2-*p*-nitrophenylindazole (VIIIc). The ultraviolet spectra of VIIIb and VIIIc are shown in Fig. 1.

It is known that 5-arylazotropolone with isopropyl, ethyl and acetamidoethyl groups on the 4-position undergo cyclization to give a cyclohepta[*c*]pyrazole-5, 6-dione derivative (A)[13] and a 5-hydroxycyclohepta[*c*]pyrazole-6-one derivative (B),[14,15] and that 7-bromo-3, 4-benzotropolone, upon an azo-coupling reaction, directly affords a benz[*g*]indazole-4, 5-dione derivative (C).[16] The formation of VIIIa-VIIIc is another interesting example of the rearrangement reaction of 5-arylazotropone derivatives.



Experimental

The Reaction of Tropolone and Phosphorus Oxychloride. a) To a solution of 2.0 g of tropolone in 8 m*l* of dimethylformamide, 3.0 g of phosphorus oxychloride was added; the mixture was then left to stand for about 4 hr. The mixture was diluted with water and extracted with chloroform. The chloroform solution was washed with water, and the solvent was evaporated under reduced pressure. The crystalline residue was recrystallized from cyclohexane to give 920 mg of colorless crystals, mp 59—62°C, not depressed on admixture with an authentic sample of 2-chlorotropone (Ia).

b) To a solution of 3.00 g of tropolone in 20 m*l* of dry benzene, 4.50 g of phosphorus oxychloride was added, after which the mixture was refluxed on a water bath for 5 hr. The crystalline solid that separated was filtered and washed successively with benzene and ether to give 4.57 g of white powder (II). It is insoluble in usual organic solvent, such as chloroform, benzene, acetonitrile, and dimethylformamide, and has no distinct melting point. The filtrate from II afforded 35 mg of a dark oil which could not be crystallized.

The Reaction of II and Methylamine. A 1.00-g sample of the II obtained above was suspended in 3.0 m*l* of ethanol, and then 2.0 m*l* of ethanol saturated with methylamine was added under ice cooling and stirring. After 30 min, the solvent was evaporated under reduced pressure. A dilute sodium carbonate solution was then added to the residue, and the mixture was extracted with chloroform. The chloroform solution was washed with water, and the solvent was evaporated to give reddish-orange crystals, mp 65—75°C. Chromatographic separation on an alumina column, followed by recrystallization from cyclohexane, afforded 310 mg of yellow crystals, mp 75—79°C, not depressed on admixture with an authentic sample of 2-methylaminotropone.[17] The alkaline solution was acidified with dilute hydrochloric acid and extracted with chloroform. The chloroform solution afforded 220 mg of tropolone, mp 46—50°C.

12) T. Nozoe, K. Takase and H. Matsumura, "Dai Yuki Kagaku," Vol. 13, Asakura Shoten, Tokyo (1960), p. 287.
13) T. Nozoe, T. Ikemi and T. Ozeki, *Proc. Japan Acad.*, **31**, 455 (1955), and the references cited therein.
14) T. Nozoe, K. Takase and K. Umino, This Bulletin, **38**, 358 (1965).
15) T. Nozoe, K. Takase and K. Suzuki, *ibid.*, **38**, 362 (1965).
16) S. Ebine, *ibid.*, **38**, 2029 (1965).
17) T. Nozoe, S. Seto, H. Takeda, S. Morosawa and K. Matsumoto, *Sci. Repts. Tohoku Univ., Ser. I*, **36**, 126 (1952).

The Reaction of II and Water. A 1.00-g sample of II was suspended in 20 m*l* of water and then left at room temperature for about 5 hr, but no appreciable change was observed. When the mixture was heated at about 70°C, it gradually dissolved to give a pale brown solution. After it had stood overnight, the solution was extracted with chloroform to give 400 mg of tropolone.

2-Chloro-5-cyanotropone (Ib). To a solution of 100 mg of 5-cyanotropolone in 1.0 m*l* of dimethylformamide, 200 mg of phosphorus oxychloride was added under ice cooling. After it had stood for 1.5 hr, the mixture was poured into 10 m*l* of water. The crystals that separated were collected and washed with water to give 82 mg (73%) of pale brown crystals, mp 140—144°C, not depressed on admixture with an authentic sample of Ib.[18]

2-Chloro-5-nitrotropone (Ic). a) The similar treatment of a mixture of 200 mg of 5-nitrotropolone and 300 mg of phosphorus oxychloride in 1.0 m*l* of dimethylformamide gave 202 mg of Ic as pale yellow needles, mp 135—140°C. Recrystallization from a mixture of benzene and cyclohexane raised the melting point to 138—140°C. IR (KBr): 1632, 1602 cm^{-1} (C=C and C=O).

Found: C, 45.60; H, 2.28; N, 7.65%. Calcd for $C_7H_4O_3NCl$; C, 45.31; H, 2.17; N, 7.55%.

b) A mixture of 300 mg of 5-nitrotropolone and 900 mg of thionyl chloride in 10 m*l* of dry benzene was refluxed for 6 hr and then left to stand overnight. The evaporation of the solvent and an excess of thionyl chloride under reduced pressure afforded 330 mg of yellowish-orange crystals, mp 120—134°C. Recrystallization from benzene gave 245 mg of Ic, mp 133—138°C, not depressed on admixture with the sample obtained above.

2, 5-Dichlorotropone (Id) and Its Rearranged Products. *a) The Reaction of 5-Chlorotropolone and Phosphorus Oxychloride.* A mixture of 400 mg of 5-chlorotropolone and 400 mg of phosphorus oxychloride in 3.0 m*l* of dimethylformamide was left to stand at room temperature for 2.5 hr, and then diluted with 50 m*l* of water to give 246 mg of crystals, mp 90—98°C. Recrystallization from ethanol afforded 2, 5-dichlorotropone (Id), mg 95—97°C, not depressed on admixture with an authentic sample of Id.[2]

b) The Reaction of 5-Bromotropolone and Phosphorus Oxychloride. The similar treatment of 500 mg of 5-bromotropolone and 400 mg of phosphorus oxychloride in 4.0 m*l* of dimethylformamide gave 280 mg of crystals, mp 60—75°C. Recrystallization from ethanol afforded 143 mg of crystals, mp 91—95°C. Further recrystallization afforded Id as colorless crystals, mp 95—97°C, not depressed on admixture with the sample obtained above.

c) The Reaction of 5-Chlorotropolone with an Excess of Phosphorus Oxychloride. A solution of 400 mg of 5-chlorotropolone and 1.00 g of phosphorus oxychloride in 2.0 m*l* of dimethylformamide was left to stand overnight. The subsequent dilution of the mixture with water separated a viscous oil which gradually solidified. It was collected, washed with water, dissolved in cyclohexane, and passed through a silica gel column. The fraction eluted with cyclohexane afforded 158 mg (35%) of pale yellow crystals, mp 54—56°C. Recrystallization from aqueous ethanol afforded 2, 5-dichlorobenzaldehyde (III) as colorless needles, mp 55—56°C (Found: C, 47.59; H, 2.72%), which were identified by converting them to 2, 5-dichlorobenzoic acid; mp and mixed mp 152—154°C.

The fraction eluted with a mixture of benzene and cyclohexane (1 : 1) gave 58 mg of pale yellow crystals, mp 39—42°C. Recrystallization from aqueous ethanol afforded colorless crystals, mp 43—44°C, not depressed on admixture with an authentic sample of 3, 4-dichlorobenzaldehyde (IV).

d) The Reaction of 2, 5-Dichlorotropone and Phosphorus Oxychloride. The similar treatment of 350 mg of Id with 930 mg of phosphorus oxychloride gave 153 mg of III and 50 mg of IV.

2-Chloro-7-cyanotropone (Ie). The similar treatment of a mixture of 600 mg of 3-cyanotropolone and 960 mg of phosphorus oxychloride in 3.0 m*l* of dimethylformamide gave 532 mg of colorless crystals, mp 155—160°C. Recrystallization from benzene afforded Ie as colorless crystals, mp 159—161°C, not depressed on admixture with an authentic sample.[3]

2, 7-Dichlorotropone (If) from 3-Bromotropolone. The similar treatment of 3-bromotropolone with phosphorus oxychloride afforded If, mp 128—130°C, in about a 40% yield; no other pure substance was isolated.

The Reaction of 3-Phenyltropolone and Phosphorus Oxychloride. A solution of 600 mg of 3-phenyltropolone and 1.40 g of phosphorus oxychloride in 6 m*l* of dimethylformamide was left to stand for 6 hr and then diluted with water. The crystals, which separated at first as an oil, were collected, dissolved in benzene, and washed with dilute sodium hydroxide and water. The alkaline solution, on acidification with hydrochloric acid, gave 145 mg of 3-phenyltropolone. The benzene solution, after the evaporation of the solvent, left a crystalline residue which was dissolved in a mixture of benzene and petroleum ether (1 : 1) and passed through a silica gel column. The fraction eluted with the same solvent mixture gave 320 mg of 2-chloro-3-phenylbenzaldehyde (V) as colorless prisms, mp 104—106°C. Recrystallization from ethanol raised the melting point to 106—107°C.

Found: C, 72.24; H, 4.16%. Calcd for $C_{13}H_9OCl$: C, 72.40; H, 4.21%.

When an equimolar quantity of the reagent was used (6 hr, at room temperature), only 3-phenyltropolone was isolated unchanged.

The oxidation of V with potassium permanganate in acetone afforded 2-chloro-3-phenylbenzoic acid (VI) as colorless plates, mp 156—158°C (after recrystallization from ethanol).

Found: C, 67.13; H, 3.63%. Calcd for $C_{13}H_9O_2Cl$: C, 67.11; H, 3.90%.

2-Chloro-5-*p*-tolylazotropone (VIIa) and 4, 5-Dichloro-2-*p*-tolylindazole (VIIIa). a) To a suspension of 240 mg of 5-*p*-tolylazotropolone in 1.2 m*l* of dimethylformamide, 170 mg of phosphorus oxychloride was added under ice cooling. After the crystals were dissolved, 2-chloro-5-*p*-tolylazotropone (VIIa) gradually separated out. After the mixture had stood for 4.5 hr, these crystals were collected and washed with water. Recrystallization from benzene gave 155 mg of VIIa as brownish-orange plates, mp 161—163°C.

18) K. Kikuchi, This Bulletin, **40**, 355 (1967).

The filtrate was diluted with water, and the yellow crystals that separated out were collected and washed with water. These crystals, combined with the residue obtained by the evaporation of the mother liquor from the above recrystallization, were dissolved in a mixture of benzene and cyclohexane (1 : 1) and chromatographed on 1.5 g of silica gel. The fraction eluted with the same solvent mixture gave 16 mg of 4, 5-dichloro-2-*p*-tolylindazole (VIIIa), mp 130—134°C. The fraction eluted with benzene gave 48 mg of VIIa, mp 160—162°C.

An analytical sample of VIIa was recrystallized from ethanol to give brownish-orange plates, mp 162—163°C. IR (KBr): 1624, 1593 cm^{-1} (C=C and C=O).

Found: C, 65.15; H, 4.38; N, 10.56%. Calcd for $C_{14}H_{11}ON_2Cl$: C, 65.00; H, 4.25; N, 10.87%.

An analytical sample of VIIIa was recrystallized from ethanol to give colorless microcrystals, mp 136.5—137°C.

Found: C, 60.43; H, 3.55; N, 10.34%. Calcd for $C_{14}H_{10}N_2Cl_2$: C, 60.67; H, 3.64; N, 10.11%.

VIIIa was stable toward alkali and acids, and did not give a picrate.

b) To a solution of 240 mg of 5-*p*-tolylazotropolone in 2.5 m*l* of benzene, 130 mg of thionyl chloride was added; the solution was then refluxed for 2.5 hr. The evaporation of the solvent and an excess of the reagent left a dark brown crystalline residue, which was dissolved in benzene and passed through an alumina column. The fractions eluted with benzene and a mixture of benzene and chloroform (1 : 1) afforded 105 mg of VIIa, mp 157—159°C, undepressed on admixture with the sample obtained above.

The Reaction of 5-Phenylazotropolone (and 5-*p*-Nitrophenylazotropolone) with Phosphorus Oxychloride. a) A solution of 300 mg of 5-phenylazotropolone and 240 mg of phosphorus oxychloride in 1.2 m*l* of dimethylformamide was treated in the manner described above to give 200 mg of 2-chloro-5-phenylazotropone (VIIb), mp 127—129°C, and 32 mg of 4, 5-dichloro-2-phenylindazole (VIIIb), mp 90—92°C.

The recrystallization of VIIb from a mixture of benzene and cyclohexane gave reddish-orange plates, mp 128—129°C. IR (KBr): 1630, 1597 cm^{-1} (C=C and C=O).

Found: C, 64.69; H, 3.86; N, 11.11%. Calcd for $C_{13}H_9ON_2Cl$: C, 63.77; H, 3.70; N, 11.49%.

The recrystallization of VIIIb from methanol gave colorless needles, mp 93—94°C.

Found: C, 59.23; H, 3.18; N, 10.48%. Calcd for $C_{13}H_8N_2Cl_2$: C, 59.37; H, 3.06; N, 10.65%.

b) The similar treatment of 200 mg of 5-*p*-nitrophenylazotropolone and 120 mg of phosphorus oxychloride in 1.0 m*l* of dimethylformamide gave 118 mg of 2-chloro-5-*p*-nitrophenylazotropone (VIIc), mp 200—205°C (decomp.), and several milligrams of 4, 5-dichloro-2-*p*-nitrophenylindazole (VIIIc), mp 207—212°C.

The recrystallization of VIIc from dioxane afforded deep reddish-brown prisms, mp 205°C (decomp.). IR (KBr): 1630, 1598 cm^{-1} (C=C and C=O).

Found: C, 53.88; H, 2.87; N, 14.52%. Calcd for $C_{13}H_8O_3N_3Cl$: C, 53.90; H, 2.79; N, 14.51%.

The recrystallization of VIIIc from dioxane afforded yellow microcrystals, mp 212—213°C.

Found: C, 50.72; H, 2.91%. Calcd for $C_{13}H_7O_2N_3Cl_2$: C, 50.67; H, 2.29%.

The Formation of VIIIa from VIIa or 2-Methoxy-5-*p*-tolylazotropone. a) To a solution of 1.22 g of VIIa in 10 m*l* of dimethylformamide, 1.10 g of phosphorus oxychloride was added, after which the mixture was allowed to stand at room temperature overnight. The solution was then diluted with water, and the crystals were collected. The chromatographic separation of these crystals on an alumina column, followed by recrystallization from a mixture of benzene and cyclohexane, gave 615 mg of VIIIa, mp 135—137°C.

b) The addition of 300 mg of phosphorus oxychloride to a suspension of 200 mg of 2-methoxy-5-*p*-tolylazotropone in 3.0 m*l* of dimethylformamide gave a clear, deep red solution. After standing for 4 hr, the mixture was treated similarly to give 125 mg of VIIIa, mp 134—136°C.

The Formation of VIIIb (and VIIIc) from VIIb (and VIIc). a) The similar treatment of 1.00 g of VIIb gave pale brown crystals, mp 85—105°C. Distillation under reduced pressure (2 mmHg; bath temperature 100—125°C), followed by recrystallization from methanol, afforded 250 mg of VIIIb, mp 92—95°C.

b) The similar treatment of 200 mg of VIIc gave 90 mg of VIIIc as pale yellow crystals, mp 207—209°C.

Oxidation of 4, 5-Dichloro-2-*p*-tolylindazole (VIIIa). *a) Chromic Acid Oxidation.* To a solution of 133 mg of chromic anhydride in 0.2 m*l* of water and 2.0 m*l* of acetic acid, 140 mg of VIIIa was added; the mixture was then heated on a water bath for 4 hr. The mixture was diluted with water, and the crystals that separated out were collected and washed with water to give 110 mg of brownish-orange crystals, mp 210—225°C (decomp.). The separation of the acidic part with a dilute sodium hydroxide solution gave 44 mg of 3, 4-dichloro-4'-methylazobenzene-2-carboxylic acid (IX), mp 229—233°C (decomp.). An analytical sample was recrystallized from acetic acid to give reddish-orange prisms, mp 236—238°C (decomp.).

Found: C, 54.10; H, 3.03; N, 9.21%. Calcd for $C_{14}H_{10}O_2N_2Cl_2$: C, 54.39; H, 3.26; N, 9.06%.

Methyl Ester (X). Obtained by the addition of ethereal diazomethane to IX. Recrystallization from methanol gave X as orange plates, mp 95—96°C.

Found: C, 55.63; H, 3.80; N, 8.45%. Calcd for $C_{15}H_{12}O_2N_2Cl_2$: C, 55.74; H, 3.74; N, 8.67%.

b) Nitric Acid Oxidation. To a solution of 300 mg of VIIIa in a mixture of 3.0 m*l* of acetic acid and 0.3 m*l* of acetic anhydride, 300 mg of nitric acid (sp. gr., 1.50) was added; the mixture was then warmed at 85°C for 1 hr. The crystals that separated out were collected and washed with water to give 100 mg of IX, mp 228—235°C (decomp.). The filtrate was diluted with water, and extracted with chloroform, and the chloroform solution was treated with a dilute sodium hydroxide solution. The alkaline solution was acidified to give 60 mg of the second crop of IX, mp 232—236°C (decomp.).

The chloroform solution was washed with water, and dried, and the solvent was evaporated to give yellow crystals. These crystals were dissolved in a mixture of benzene and cyclohexane (1 : 1) and chromatographed on 1.5 g of silica gel. The first fraction, eluted with the same solvent mixture, gave 30 mg of 4, 5-dichloro-

x-nitro-2-p-tolylindazole (XI), mp 168—172°C. The third and fourth fractions, eluted with the same solvent mixture and with benzene, gave 27 mg of 4, 5-dichloro-x'-nitro-2-p-tolylindazole (XII), mp 189—192°C.

The recrystallization of XI from acetic acid gave fine yellow needles, mp 173—174°C.

Found: C, 52.36; H, 2.92; N, 12.72%. Calcd for $C_{14}H_9O_2N_3Cl_2$: C, 52.19; H, 2.82; N, 13.04%.

The recrystallization of XII from acetic acid gave yellow needles, mp 193—194°C.

Found: C, 52.19; H, 3.06; N, 12.31%. Calcd for $C_{14}H_9O_2N_3Cl_2$: C, 52.19; H, 2.82; N, 13.04%.

Catalytic Reduction of the Acid (IX). A 300 mg sample of IX in 60 ml of ethanol was catalytically hydrogenated in the presence of Adam's catalyst. The uptake of hydrogen was about 80 ml at an ordinary pressure and temperature. The removal of the solvent under reduced pressure afforded a brown oil. The benzene solution of this oil was shaken with a dilute sodium hydroxide solution, and the alkaline solution was acidified with acetic acid. The extraction of the solution with ether and the evaporation of the solvent gave 95 mg of colorless crystals, mp 160—168°C (decomp.). Several recrystallizations from aqueous ethanol afforded 2-amino-5, 6-dichlorobenzoic acid (XIII) as colorless needles, mp 173—175°C (decomp.) (Found: C, 41.08; H, 2.53; N, 6.75%).

The acid (XIII) was heated above its melting point for 5 min, and the product was recrystallized from cyclohexane to give colorless crystals, mp 69—71°C, not depressed on admixture with an authentic sample of 3, 4-dichloroaniline (XIV).

The benzene solution was washed with water, and the solvent was evaporated to give a dark red oil. Acetylation of this oil with acetic anhydride afforded 25 mg of acet-p-toluidide, mp 143—145°C.

Catalytic Reduction of 4, 5-Dichloro-2-p-tolylindazole (VIIIa). A solution of 400 mg of VIIIa and 250 mg of sodium acetate in 50 ml of ethanol was catalytically hydrogenated in the presence of 100 mg of Adam's catalyst. The removal of the catalyst and the evaporation of the solvent gave colorless crystals. Recrystallization from petroleum ether gave 125 mg of colorless crystals, mp 65—70°C. Purification through its picrate, followed by the recrystallization of the regenerated product from aqueous ethanol, gave 2-p-tolyl-4, 5, 6, 7-tetrahydroindazole (XV) as colorless prisms, mp 71—72.5°C.

Found: C, 79.64; H, 8.03; N, 13.00%. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20%.

Reduction of the Ester (X) with Lithium Aluminum Hydride. To a solution of 380 mg of X in 5 ml of absolute ether, a solution of 45 mg of lithium aluminum hydride in 3 ml of absolute ether was added; the solution was then refluxed for 3.5 hr. The excess of the reagent was decomposed with water, the precipitate was filtered off, and the filtrate was washed with water. The solvent was removed, and the residue was dissolved in a mixture of benzene and cyclohexane (1 : 1) and passed through an alumina column (5 g). A fraction eluted with the same solvent mixture gave 130 mg of the unchanged ester (X), while a fraction eluted with a mixture of benzene and chloroform (1 : 1) gave 52 mg of reddish-orange crystals, mp 100—107°C. Recrystallization from ethanol afforded 3, 4-dichloro-2-hydroxymethyl-4'-methylazobenzene (XVI) as organge needles, mp 103—105°C (sintered at about 100°C).

Found: C, 56.94; H, 3.96; N, 9.24%. Calcd for $C_{14}H_{12}ON_2Cl_2$: C, 56.96; H, 4.10; N, 9.49%.

The fraction eluted with a mixture of chloroform and methanol gave 15 mg of pale brown crystals, mp 145—150°C. Recrystallization from benzene afforded 3, 4-dichloro-2-hydroxymethyl-4'-methylhydrazobenzene (XVII) as colorless crystals, mp 159—160°C.

Found: C, 56.78; H, 4.63; N, 9.12%. Calcd for $C_{14}H_{14}ON_2Cl_2$: C, 56.58; H, 4.75; N, 9.43%.

When about two molecular equivalents of lithium aluminum hydride were applied, XVII was isolated in about a 75% yield.

The Formation of XVI from XVII. To a solution of 240 mg of XVII in 6.0 ml of ethanol, a solution of 200 mg of bromine in 1.0 ml of ethanol was added. After the mixture had then stood for 30 min, the solvent was evaporated under reduced pressure and the residue was diluted with water. The crystals thereby obtained were dissolved in benzene and passed through an alumina column. The fraction eluted with a mixture of benzene and chloroform gave orange crystals, mp 92—105°C; yield, 130 mg. Recrystallization from ethanol gave XVI as orange needles, mp 95—105°C.

The Formation of VIIIa from XVI. A 30 mg sample of XVI in 0.4 ml of 75% sulfuric acid was heated at 90°C for 20 hr; the crystals thereby separated were then filtered and washed several times with water to give 15 mg of pale brown crystals, mp 134—136°C. These crystals showed no depression of the melting point on admixture with a sample of VIIIa, and the infrared spectrum was also identical with that of VIIIa.

Bromination of VIIIa. To a solution of 50 mg of VIIIa in 1.0 ml of acetic acid, 35 mg of bromine was added. After the mixture had been heated for about 15 min at 85°C, the crystals that separated out were filtered and washed with water to give 52 mg of crystals, mp 183—184.5°C. Recrystallization from acetic acid gave 3-bromo-4, 5-dichloro-2-p-tolylindazole (XVIII) as fine, colorless needles, mp 184.5—185.5°C.

Found: C, 47.06; H, 2.28; N, 7.61%. Calcd for $C_{14}H_9N_2BrCl_2$: C, 47.22; H, 2.55; N, 7.87%.

Oxidation of XVIII with Nitric Acid. A 80 mg sample of XVIII was treated with 100 mg of nitric acid (sp. gr., 1.50), as in the case of the oxidation of VIIIa, to give 9 mg of orange crystals, mp 236—238°C (decomp.). The infrared spectrum of these crystals was identical with that of IX.