3, 4-Benzotropolone and Related Compounds. IV.[1] Azo- and Hydroxy-3, 4-benzotropolones*

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There have been a few reports describing benzotropolones whose seven-membered ring carries an azo or hydroxy group, such as *x*-(*p*-tolylazo)-3,4-benzotropolone,[2] 3-(*p*-nitrophenylazo)-4, 5-benzotropolone,[3] its 7-phenyl derivative,[4] and 3-hydroxy-4,5-benzotropolone.[5] The present work is undertaken in order to obtain such a type of compound by means of azo-coupling and the hydroxylation of 3,4-benzotropolone (I) and its halogen derivatives (II, III and IV).

It has been found that monocyclic tropolones, like phenols, undergo azo-coupling with ease to give 5-arylazotropolones in fair yields.[6] On the other hand, I, II, III, and IV reacted sluggishly with diazotized amines to afford azo-compounds or rearrangement products, along with a considerable amount of tar, as is summarized in Table I. An attempted azo-coupling of I in an alkaline solution gave only a resinous product, no definite product being isolated. The azo-coupling of I with diazotized aniline was effected in an acetic acid solution in the presence of sodium acetate to yield phenylazo-3,4-benzotropolone (V), whose infrared absorption spectrum exhibited a carbonyl band in the region below 1650 cm^{-1} (Experimental), agreeing with a spectral feature of troponoid compounds.[7] V is either the 5- or the 7-phenylazo-compound, based upon the *o*, *p*-directing effect of its hydroxyl group; it seems more likely to be the former because its ultraviolet absorption spectrum resembles that of the 5-phenylazo-compound (VII, described below), as is shown in Fig. 1. The azo-coupling of I with diazotized aniline proceeded in a different mode when carried out in a pyridine solution; then it yielded an uncharacterized azo-compound (VI), the infrared absorption spectrum of which showed no carbonyl band (Experimental).

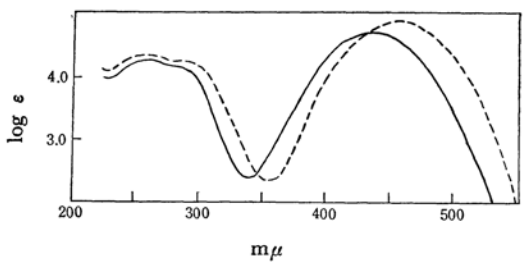


Fig. 1. Ultraviolet absorption spectra of 5-phenylazo-3, 4-benzotropolone (V, ——) and 5-phenylazo-7-bromo-3, 4-benzotropolone (VII, ----) in methanol.

The azo-coupling of 7-bromo-3,4-benzotropolone (IIa) with diazotized aniline in an acetic acid solution gave 5-phenylazo-7-bromo-3,4-benzotropolone (VII). However, when carried out in a pyridine solution, the same reaction resulted in the formation of rearrangement products, 2-phenyl-2*H*-benz[g]indazole-4,5-dione (VIIIa) and 2-phenylazo-1-naphthol (IX). Similarly, the azo-coupling of IIa with diazotized *p*-toluidine in a pyridine solution gave 2-(*p*-tolyl)-2*H*-benz[g]indazole-4,5-dione (VIIIb), but it did not produce an isolable amount of an azonaphthol. When the coupling component was *p*-methoxybenzenediazonium chloride, the products were 2-(*p*-anisylazo)- and 2,4-bis(*p*-anisylazo)-1-naphthols, no indazole derivative being produced. The azo-coupling of 7-chloro-3,4-benzotropolone (IIb) with diazotized aniline in a pyridine solution gave only IX, no indazole derivative again being isolated. The structure of VIII was established by the following reactions: (a) VIII was reduced to a leuco compound, which easily regenerated the original material on exposure to air; (b) VIII produced a diacetate (XII) on reductive acetylation and a quinoxaline derivative on treatment with *o*-phenylenediamine; (c) VIII was oxidized with peracetic acid to 1-phenyl- or 1-(*p*-tolyl)-3-(*o*-carboxyphenyl)pyrazole-4-carboxylic acid (XIIIa or XIIIb), and then XIIIa was decarboxylated by heating it with copper powder to give 1,3-diphenylpyrazole (XIV), whose melting point was undepressed on admixture with an authentic sample[8]; the infrared spectra of the two samples were also identical in all respects. Although it is not clear why the reaction of IIa with a diazotized amine gives rearrangement products

1) Part III: S. Ebine, This Bulletin, **35**, 122 (1962).

* Presented in part at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

2) T. Nozoe, Y. Kitahara and T. Ando, *Proc. Japan Acad.*, **27**, 107 (1951).

3) D. S. Tarbell and J. C. Bill, *J. Am. Chem. Soc.*, **74**, 1234 (1952).

4) W. Davey and H. Gottfried, *J. Org. Chem.*, **26**, 3707 (1961).

5) H. Fernholz, E. Hartwig and J.-C. Salfeld, *Ann.*, **576**, 137 (1952).

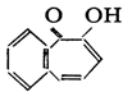
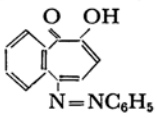
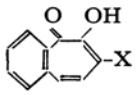
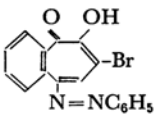
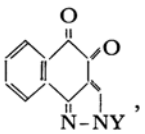
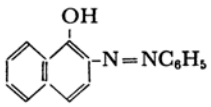
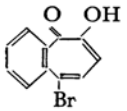
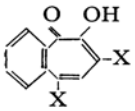
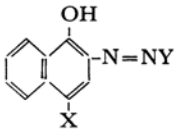
6) T. Nozoe, E. Sebe and S. Ebine, *Proc. Japan Acad.*, **26** (8), 24 (1950); W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **73**, 829 (1951).

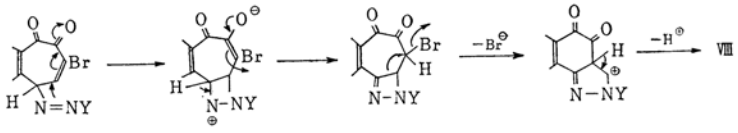
7) For the spectra of troponoid compounds, see M. Tsuboi, This Bulletin, **25**, 369 (1952); S. Kinumaki, K. Aida and Y. Ikegami, *Sci. Repts. Res. Inst. Tohoku Univ.*, **A-8**, 263 (1956); E. Kloster-Jensen, N. Tarkoy, A. Eschenmoser and E. Heilbronner, *Helv. Chim. Acta*, **39**, 780 (1956).

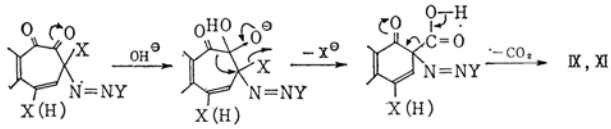
8) K. v. Awers and W. Schmidt, *Ber.*, **58**, 537 (1925).

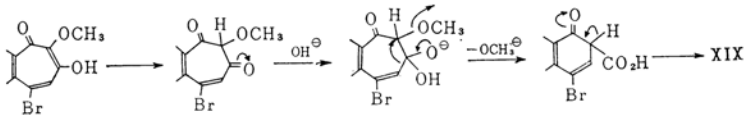
in a pyridine solution, whereas it gives a normal azo-coupling product in an acetic acid solution, possible courses for the formation of VIII and IX are tentatively illustrated by Schemes 1 and 2 respectively. III coupled with diazotized aniline to yield $C_{17}H_{11}O_2N_2Br$ (X), which showed an infrared absorption band at 1685 cm^{-1}, suggesting the presence of a non-troponoid carbonyl group. 5,7-Dibromo- and 5,7-dichloro-3,4-benzotropolones (IVa and IVb) reacted with diazotized aniline and *p*-toluidine, undergoing azo-coupling followed by rearrangement to the corresponding 2-arylazo-4-halogeno-1-naphthols (XI). This reaction is also illustrated by Scheme 2.

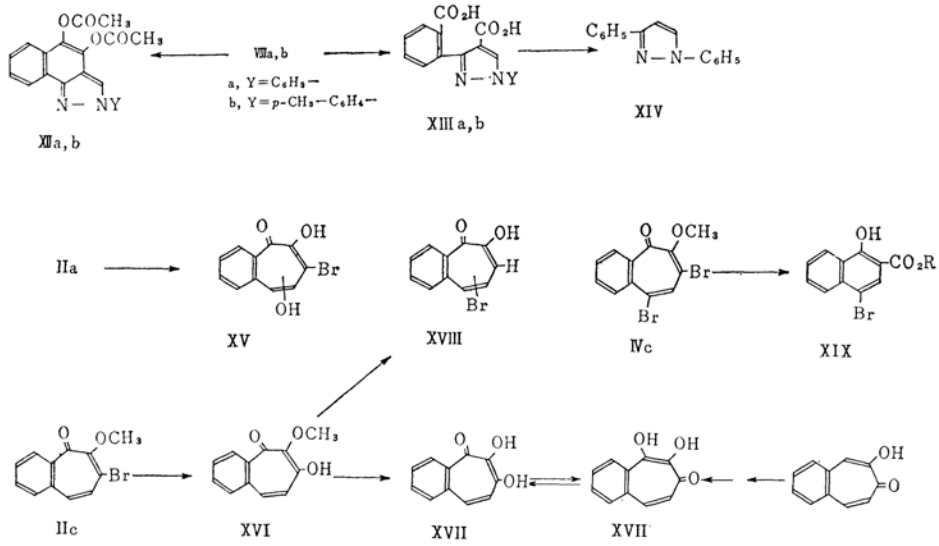
TABLE I. AZO-COUPLING PRODUCTS OF 3, 4-BENZOTROPOLONE AND ITS DERIVATIVES

3, 4-Benzotropolone and its derivative	Product (in acetic acid)	Product (in pyridine)
 I	 V	$C_{16}H_{12}ON_2$ VI
 IIa, X=Br IIb, X=Cl	 VII	 VIIIa, Y=C_6H_5 VIIIb, Y=*p*-$CH_3C_6H_4$	 IX
 III	$C_{17}H_{11}O_2N_2Br$ X	X
 IVa, X=Br IVb, X=Cl	 XIa, X=Br, Y=C_6H_5 XIb, X=Cl, Y=C_6H_5 XIc, X=Br, Y=*p*-$CH_3C_6H_4$	XI

Scheme 1, IIa $\xrightarrow{YN_2Cl}$  VIII

Scheme 2, II, IV $\xrightarrow{YN_2Cl}$  IX, XI

Scheme 3, IVc $\xrightarrow{KOH}$  XIX



Attempts were then made to obtain hydroxybenzotropolones. According to the method of hydroxylation of monocyclic tropolones,[9] I and IIa were subjected to persulfate oxidation; the former failed to give a definite product, but the latter furnished 5(?)-hydroxy-7-bromo-3,4-benzotropolone (XV). 7-Bromo-3,4-benzotropolone methyl ether (IIc) reacted with methanolic alkali, affording 6-hydroxy-7-methoxy-2,3-benzotropone (XVI). The treament of IIc with alkali results in the hydrolysis of the bromine atom, giving XVI, whereas monocyclic 2-methoxy-7-bromotropone with alkali results in the hydrolysis of the methoxyl group, giving 3-bromotropolone.[10] Such a difference has been pointed out previously.[11] The further hydrolysis of XVI with concentrated hydrochloric acid gave 6,7-dihydroxy-2,3-benzotropone (XVII), which was identical with Fernholz and his co-workers' 3-hydroxy-4,5-benzotropolone (XVII'),[5] obtained by the bromination and subsequent hydrolysis of 4,5-benzotropolone. The bromination of XVI yielded 4(?)-bromo-6,7-dihydroxy-2,3-benzotropone (XVIII) or its tautomer. 5,7-Dibromo-3,4-benzotropolone methyl ether (IVc), unlike IIc, reacted with methanolic alkali to yield rearrangement products, 1-hydroxy-4-bromo-2-naphthoic acid and its methyl ether (XIX). It is of interest that 3,4-benzotropolone and its derivatives have a tendency to undergo azo-coupling and other reactions, accompanied with rearrangement.

Experimental

The Azo-coupling of 3,4-Benzotropolone (I).—*5-Phenylazo-3,4-benzotropolone (V).*—A solution of 175 mg. of aniline in 2.3 ml. of 2.4 N hydrochloric acid was diazotized with 1.1 g. of 10% sodium nitrite. The benzenediazonium chloride solution was then dropped into an ice-cooled mixture of 250 mg. of I dissolved in 25 ml. of acetic acid and 4.5 g. of sodium acetate dissolved in 13.5 ml. of water. After the mixture had been stirred for 1 hr., the red precipitate was collected and crystallized from acetone to yield 120 mg. (30%) of V; red plates; m. p. 148—150°C; infrared spectrum in the 1800—1500 cm^{-1} region (KBr): 1622, 1587, 1560 cm^{-1}.

Found: C, 73.59; H, 4.19; N, 9.95. Calcd. for $C_{17}H_{12}O_2N_2$: C, 73.90; H, 4.38; N, 10.14%.

An Uncharacterized Azo-compound (VI).—Aniline (350 mg.) dissolved in 4.6 ml. of 2.4 N hydrochloric acid was diazotized with 2.2 g. of 10% sodium nitrite; the resulting solution was dropped into an ice-cooled solution of 500 mg. of I in 15 ml. of pyridine. After standing overnight in an ice-chest, the solution was concentrated below 30°C under reduced pressure to give a dark red, tarry residue. The residue was then dissolved in benzene and chromatographed on silica gel, affording 100 ml. (14%) of VI; brownish red needles; m. p. 171.5—172.5°C after recrystallization from ethanol; infrared spectrum (Nujol): 3333, 1595, 1580, 1536, 1511, 1429, 1319, 1163, 1020, 821, 757 cm^{-1}.

Found: C, 77.61; H, 4.64; N, 11.44. Calcd. for $C_{16}H_{12}ON_2$: C, 77.40; H, 4.87; N, 11.28%.

The Azo-coupling of 7-Bromo- and 7-Chloro-3,4-benzotropolones (IIa and IIb).—*5-Phenylazo-7-bromo-3,4-benzotropolone (VII).*—A solution of 200 mg. of IIa and 2.5 g. of sodium acetate in 80 ml. of acetic acid was treated with a benzenediazonium chloride solution prepared from 96 mg. of aniline in a manner described above. The product was recrystallized from petroleum ether to yield 80 mg. (28%) of VII as brownish orange needles; m. p. 168—169°C; infrared spectrum in the 1800—1500 cm^{-1} region (KBr): 1615, 1584, 1547, 1522 cm^{-1}.

9) T. Nozoe, S. Seto and S. Ito, *Proc. Japan Acad.*, **28**, 488 (1952); T. Nozoe, S. Seto, S. Ito, M. Sato and T. Katono, *Sci. Repts. Tohoku Univ., I*, **37**, 191 (1953).

10) T. Nozoe, Y. Kitahara and S. Masamune, *Proc. Japan Acad.*, **27**, 649 (1951).

11) S. Ebine, This Bulletin, **34**, 887 (1961).

Found: C, 57.55; H, 3.21; N, 7.62. Calcd. for $C_{17}H_{11}O_2N_2Br$: C, 57.48; H, 3.12; N, 7.89%.

2-Phenyl- and 2-(p-Tolyl)-2H-benz[g]indazole-4, 5-diones (VIIIa and VIIIb).—To an ice-cooled solution of 500 mg. of IIa in 15 ml. of pyridine there was added, drop by drop, a solution of benzenediazonium or *p*-toluenediazonium chloride prepared by the action of 1.4 g. of 10% sodium nitrite on 240 mg. of aniline or 280 mg. of *p*-toluidine dissolved in 3.2 ml. of 2.4 N hydrochloric acid. Dilution with an equal volume of water gave a precipitate, which was then filtered and recrystallized from ethanol to yield 160 mg. (29%) of VIIIa or 400 mg. (69%) of VIIIb, along with a 20% recovery of IIa. The pyridine filtrate contains azonaphthols as will be described below.

VIIIa; yellow needles; m. p. 251°C; infrared spectrum (Nujol): 3160, 1678, 1603, 1545, 1330, 1275, 1247, 910, 757, 700 cm^{-1}.

Found: C, 74.35; H, 3.85; N, 10.29. Calcd. for $C_{17}H_{10}O_2N_2$: C, 74.44; H, 3.68; N, 10.21%.

VIIIb; orangeish yellow needles; m. p. 273°C; infrared spectrum (Nujol): 3150, 1670, 1600, 1560, 1510, 1408, 1275, 1245, 1230, 957, 907, 863, 814, 772, 697 cm^{-1}.

Found: C, 74.78; H, 4.50; N, 9.98. Calcd. for $C_{18}H_{12}O_2N_2$: C, 74.99; H, 4.20; N, 9.72%.

Azonaphthols.—The pyridine filtrate obtained from VIIIa of the above experiment was concentrated under reduced pressure to a tarry residue; this was then dissolved in benzene and chromatographed on silica gel, yielding 45 mg. (9%) of 2-phenylazo-1-naphthol (IX). (Found: C, 77.59; H, 4.90; N, 11.44. Calcd. for $C_{16}H_{12}ON_2$: C, 77.40; H, 4.87; N, 11.28%; m. p. 134°C, the melting poing being undepressed on admixture with an authentic sample prepared by the condensation of 1, 2-naphthoquinone with phenylhydrazine.)

The pyridine filtrate from VIIIb, unlike that from VIIIa, gave no azonaphthol.

The azo-coupling of 500 mg. of IIa with a 1-mole equivalent of diazotized *p*-anisidine in a pyridine solution gave 65 mg. (12%) of 2-(*p*-anisylazo)-1-naphthol as red needles, m. p. 124°C (Found: C, 73.40; H, 4.99; N, 9.90. Calcd. for $C_{17}H_{14}O_2N_2$: C, 73.36; H, 5.07; N, 10.07%) and 30 mg. (3.6%) of 2, 4-bis(*p*-anisylazo)-1-naphthol as dark-brown fibrous needles, m. p. 182.5°C (Found: N, 13.40. Calcd. for $C_{24}H_{20}O_3N_4$: N, 13.59%), after the same work-up as above.

A pyridine solution of IIb (500 mg.) was coupled with benzenediazonium chloride in the same way as above, and the crude product was dissolved in benzene and chromatographed on silica gel to afford IX (85 mg., 14%), m. p. and mixed m. p. 134°C, with no benzindazoledione derivative.

Reaction of VIIIa and VIIIb.—*Hydrogenation.*—VIIIa or VIIIb (100 mg.) in 40 ml. of dioxane was hydrogenated over 50 mg. of 5% palladium-on-charcoal at atmospheric pressure until no further uptake of hydrogen was observed. The yellow solution faded during hydrogenation, but colored again on exposure to air. The removal of the catalyst and solvent left the original material (identified by a mixed melting point determination) in a quantitative recovery.

Reductive Acetylation.—A suspension of 100 mg. of VIIIa (or VIIIb) and 500 mg. of fused sodium acetate in 20 ml. of acetic anhydride was treated with 300 mg. of zinc powder. After the reaction mixture had become nearly colorless, the excess acetic anhydride was decomposed with water, the precipitate was extracted with boiling alcohol, the extract was concentrated, and the product was recrystallized from ethanol.

2-Phenyl-4, 5-diacetoxy-2*H*-benz[g]indazole (XIIa); colorless, fibrous needles; m. p. 191°C; yield 100 mg. (85%).

Found: C, 70.20; H, 4.20; N, 7.66. Calcd. for $C_{21}H_{16}O_4N_2$: C, 69.99; H, 4.48; N, 7.77%.

2-(*p*-Tolyl)-4, 5-diacetoxy-2*H*-benz[g]indazole (XIIb); colorless, fibrous needles; m. p. 167—168°C; yield 100 mg. (77%).

Found: C, 70.59; H, 4.95; N, 7.44. Calcd. for $C_{22}H_{18}O_4N_2$: C, 70.58; H, 4.85; N, 7.48%.

XIIa and XIIb underwent hydrolysis, followed by autoxidation, to regenerate VIIIa and VIIIb respectively when 10 mg. of the sample was heated in 1.5 ml. of ethanol containing 3 drops of concentrated hydrochloric acid.

Reaction with o-Phenylenediamine.—*o*-Phenylenediamine (120 mg.) and 80 mg. of VIIIa (or VIIIb) in 10 ml. of acetic acid were refluxed for 10 min.; the precipitate which separated on cooling was recrystallized from benzene.

Quinoxaline derivative of VIIIa; pale yellow needles; m. p. 233—234°C.

Found: C, 79.92; H, 3.90; N, 15.90. Calcd. for $C_{23}H_{14}N_4$: C, 79.75; H, 4.07; N, 16.18%.

Quinoxaline derivative of VIIIb; pale yellow needles; m. p. 252°C.

Found: C, 79.83; H, 4.52; N, 15.50. Calcd. for $C_{24}H_{16}N_4$: C, 79.98; H, 4.48; N, 15.55%.

Oxidation with Permanganate.—Aqueous potassium permanganate (10%, 15 ml.) was dropped into a solution of 200 mg. of VIIIa (or VIIIb) in 20 ml. of pyridine while the solution was being heated on a water bath. After 1 hr.'s heating, the pyridine was removed under reduced pressure, and the manganese dioxide was dissolved with sulfurous acid. The resulting solution was saturated with sodium chloride and extracted with ether. The evaporation of the solvent from the extract gave 90 mg. (74%) of phthalic acid, which was identified by converting it to phthalanil; m. p. and mixed m. p. 205—206°C.

Oxidation with Peracetic Acid.—To a solution of 200 mg. of VIIIa (or VIIIb) in 80 ml. of acetic acid containing 6 ml. of concentrated sulfuric acid there was added, drop by drop, 5 ml. of 30% hydrogen peroxide over a period of 1 hr. at 40°C. After being kept at the same temperature for another hour, the solution was concentrated to 10 ml. below 40°C under reduced pressure. Dilution with an equal volume of water gave a precipitate, which was then recrystallized from acetic acid.

1-Phenyl-3-(*o*-carboxyphenyl)pyrazole-4-carboxylic acid (XIIIa): colorless needles; m. p. 284—285°C (with decomposition); yield 180 mg. (80%).

Found: C, 66.34; H, 4.19; N, 9.09. Calcd. for $C_{17}H_{12}O_4N_2$: C, 66.23; H, 3.92; N, 9.09%.

1-(*p*-Tolyl)-3-(*o*-carboxyphenyl)pyrazole-4-carboxylic acid (XIIIb): colorless needles; m. p. 300—302°C (with decomposition); yield 160 mg. (71%).

Found: C, 66.94; H, 4.14; N, 8.80. Calcd. for $C_{18}H_{14}O_4N_2$: C, 67.07; H, 4.38; N, 8.69%.

The Decarboxylation of XIIIa.—A mixture of 200 mg. of XIIIa and 200 mg. of copper powder was heated at 285—295°C under 5-mmHg pressure for 10 min., the sublimate was then recrystallized from dilute ethanol to give 130 mg. (91%) of 1,3-diphenylpyrazole (XIV) melting at 84—84.5°C. (Found: C, 81.43; H, 5.70; N, 12.59. Calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72%.) The melting point was not depressed on admixture with an authentic sample, and infrared spectra of the two samples were superimposable.

The Azo-coupling of 5-Bromo-3,4-benzotropolone (III).—III (500 mg.) in acetic acid or pyridine was coupled with benzenediazonium chloride prepared from 240 mg. of aniline. After the same work-up as before, there was obtained an uncharacterized azo-compound (X) as red plates; m. p. 160—161°C; yields 150 mg. (21%) in an acetic acid solution and 110 mg. (16%) in a pyridine solution; infrared spectrum (KBr): 1685, 1614, 1587, 1506, 1459, 1384, 1192, 1168, 940, 758 cm^{-1}.

Found: C, 57.65; H, 2.99; N, 7.89. Calcd. for $C_{17}H_{11}O_2N_2Br$: C, 57.48; H, 3.12; N, 7.89%.

The Azo-coupling of 5,7-Dibromo- and 5,7-Dichloro-3,4-benzotropolones (IVa and IVb).—A solution of 500 mg. of IVa and 5 g. of sodium acetate in 75 ml. of acetic acid was treated with a diazonium chloride solution prepared from 185 mg. of aniline or 212 mg. of *p*-toluidine, and the azo-compound which resulted was recrystallized from ethanol. Azo-coupling carried out in a pyridine solution gave the same result. When IVb was substituted for IVa, the corresponding azo-compound was produced.

2-Phenylazo-4-bromo-1-naphthol (XIa); red needles; m. p. 178.5°C; yields 140 mg. (28%) in acetic acid, and 110 mg. (22%) in pyridine.

Found: C, 58.56; H, 3.43; N, 8.32. Calcd. for $C_{16}H_{11}ON_2Br$: C, 58.73; H, 3.39; N, 8.56%.

2-Phenylazo-4-chloro-1-naphthol (XIb): fibrous red needles; m. p. 160°C; yield 170 mg. (29%) in acetic acid.

Found: C, 68.04; H, 3.74; N, 9.50. Calcd. for $C_{16}H_{11}ON_2Cl$: C, 67.97; H, 3.92; N, 9.91%.

2-(*p*-Tolylazo)-4-bromo-1-naphthol (XIc): fibrous, reddish orange needles; m. p. 183—184°C; yield 150 mg. (29%) in a pyridine solution.

Found: C, 60.08; H, 3.97; N, 8.48. Calcd. for $C_{17}H_{13}ON_2Br$: C, 59.84; H, 3.84; N, 8.21%.

XIc showed no melting point depression on admixture with the sample (Found: C, 61.00; H, 4.05; N, 8.50%) prepared by the azo-coupling of 4-bromo-1-naphthol with *p*-toluenediazonium chloride in a pyridine solution.

The above azonaphthols were then subjected to reductive acetylation. To a suspension of 100 mg. of XIa or XIb and 500 mg. of fused sodium acetate in 3 ml. of acetic anhydride there was added 300 mg. of zinc powder in small portions. After the excess acetic anhydride had been decomposed with water, the precipitate was extracted with ethyl acetate. Upon cooling, the extrct gave the product, which was recrystallized from the same solvent.

1-Acetoxy-2-acetamino-4-bromonaphthalene: stout colorless needles; m. p. 232°C; yield 65 mg. (65%).

Found: C, 51.95; H, 3.85; N, 4.63. Calcd. for $C_{14}H_{12}O_3NBr$: C, 52.18; H, 3.75; N, 4.35%.

1-Acetoxy-2-acetamino-4-chloronaphthalene: fibrous colorless needles; m. p. 195—200°C; yield 67 mg. (68%).

Found: C, 60.20; H, 4.03; N, 4.70. Calcd. for $C_{14}H_{12}O_3NCl$: C, 60.55; H, 4.36; N, 5.04%.

5(?)-Hydroxy-7-bromo-3,4-benzotropolone (XV).—IIa (500 mg.) was dissolved in a mixture of 20 ml. of 0.4 N potassium hydroxide and 8 ml. of pyridine; to this there was added, drop by drop, a solution of 450 mg. of potassium persulfate in 15 ml. of water over a 2-hr. period with ice-cooling. After it had stood in an ice-chest for 3 days, the reaction mixture was strongly acidified with 100 ml. of concentrated hydrochloric acid to give a precipitate, whose recrystallization from ethanol gave 210 mg. of unchanged material (m. p. and mixed m. p. 147°C) and 150 mg. (28%) of XV; yellow needles; m. p. 317—320°C, with a darkening at 180°C; infrared spectrum in the 1800—1500 cm^{-1} region (Nujol): 1616, 1606, 1585 cm^{-1}.

Found: C, 49.67; H, 2.87. Calcd. for $C_{11}H_7O_3Br$: C, 49.46; H, 2.64%.

6-Hydroxy-7-methoxy-2,3-benzotropone (XVI).—7-Bromo-3,4-benzotropolone methyl ether (IIc) (300 mg.) was dissolved in methanolic alkali prepared from 15 ml. of methanol and 1.2 g. of 50% potassium hydroxide, and then allowed to stand at room temperature for 10 hr. The reaction mixture was acidified with dilute hydrochloric acid and concentrated; after the inorganic salt had been removed by washing the mixture with water, the precipitate was recrystallized from dilute ethanol to give 165 mg. (86%) of pale yellow scales; m. p. 103.5—104.5°C; infrared spectrum in the 1800—1500 cm^{-1} region (KBr): 1632, 1570, 1525 cm^{-1}; ultraviolet spectrum (MeOH): $m\mu$ (log ε), 260(4.55), 268(4.56), 350(3.90).

Found: C, 65.53; H, 5.56. Calcd. for $C_{12}H_{10}O_3 \cdot H_2O$: C, 65.44; H, 5.49%.

An anhydrous sample, m. p. 115—116°C, was obtained by drying over phosphorous pentoxide for 2 days at room temperature.

Found: C, 71.56; H, 5.06. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99%.

Benzylamine salt: pale yellow scales; m. p. 165—169°C.

Found: C, 73.88; H, 6.32; N, 4.82. Calcd. for $C_{12}H_{10}O_3 \cdot C_7H_9N$: C, 73.76; H, 6.19; N, 4.53%.

6,7-Dihydroxy-2,3-benzotropone (XVII).—A solution of 100 mg. of XVI in 2 ml. of concentrated hydrochloric acid was heated in a sealed tube at 135—140°C for 5 hr. Dilution with an equal volume of water and the recrystallization of the precipitate from water yielded 65 mg. (70%) of yellow needles; m. p. 133.5°C; infrared spectrum in the 1800—1500 cm^{-1} region (Nujol): 1640, 1595, 1522 cm^{-1}; ultraviolet spectrum (MeOH): $m\mu$ (log ε), 248(4.50), 270(4.56), 370(3.90); (Found: C, 70.07; H, 4.15. Calcd. for $C_{11}H_8O_3$: C, 70.21; H, 4.29%).

4(?)-Bromo-6,7-dihydroxy-2,3-benzotropone (XVIII).—Bromine (320 mg.) was dropped into a solution of 200 mg. of XVI in 2 ml. of acetic acid, whereupon a reddish-violet powder precipitated immediately. The whole was heated on a water bath for 1 hr. and then diluted with 20 ml. of water, giving 100 mg. (38%, after recrystallization from ethanol) of XVIII as yellow needles; m. p. 198.5°C; infrared spectrum in the 1800—1500 cm^{-1} region (Nujol): 1604, 1540, 1510

cm^{-1}: ultraviolet spectrum (MeOH): $m\mu$ (log ε), 280(4.74), 328(3.70), 380(3.74).

Found: C, 49.33; H, 2.71. Calcd. for $C_{11}H_7O_3Br$: C, 49.46; H, 2.64%.

The reddish-violet powder described above was an intermediate product which regenerated XVI upon being heated with water.

Dimethyl ether: colorless needles from methanol; m. p. 73—75°C.

Found: C, 53.15; H, 3.75. Calcd. for $C_{13}H_{11}O_3Br$: C, 52.91; H, 3.76%.

The Action of Alkali on 5, 7-Dibromo-3, 4-benzotropolone Methyl Ether (IVc).—A solution of 300 mg. of IVc in 60 ml. of methanol containing 1.2 g. of 50% of potassium hydroxide was set aside overnight at room temperature. After acidification with dilute hydrochloric acid, the solvent was distilled, and the residue was then recrystallized from methanol to give 180 mg. (73%) of methyl 1-hydroxy-4-bromo-2-naphthoate (XIX, R=CH_3) (m. p. 120—121°C) (Found: C, 51.08; H, 3.42. Calcd. for $C_{12}H_9O_3Br$: C, 51.27; H, 3.23%); when treated with diazomethane, this gave methyl 1-methoxy-4-bromo-2-naphthoate, (m. p. 94°C) (Found: C, 53.09; H, 3.71. Calcd. for $C_{13}H_{11}O_3Br$: C, 52.90; H, 3.76%). When carried out under reflux, this reaction gave 1-hydroxy-4-bromo-2-naphthoic acid (XIX, R=H) (m. p. and mixed m. p. 237°C with decomposition).

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