2,6-Indoledicarboxylic Acid (XI).—Ethyl 6-trifluoromethyl-2-indolecarboxylate (100 mg., 0.39 mmole) or an equimolar amount of the corresponding acid IX was warmed in a polyethylene test-tube with 10 ml. of 10 *N* sodium hydroxide by means of an oil-bath at 80–90°. The light yellow solution was diluted with 20 ml. of water and acidified with dilute hydrochloric acid. Cooling of the mixture yielded a brown powder which, after recrystallization from glacial acetic acid, was recovered as tan crystals which remained unmelted at 330°. This observation is in accord with that reported by Kermack[11] for his preparation of the dicarboxylic acid.

The hydrolysis may be carried out by boiling the reactants in a glass vessel for 10 minutes, but considerable etching occurs and as a result the product is difficult to purify.

2,4-Indoledicarboxylic Acid (X).—The hydrolysis of I or its corresponding acid VIII to X was carried out by the same procedure used with the 6-trifluoromethyl isomers. X was obtained in yields as high as 94% as colorless crystals from glacial acetic acid, m.p. 299–300° with darkening at 283°; calcd. neut. equiv. 102.6, found 102.1.

Diethyl 2,6-Indoledicarboxylate (XIII).—Into a solution of 110 mg. (0.536 mmole) of 2,6-indoledicarboxylic acid in 10 ml. of absolute ethanol at 70° was bubbled hydrogen chloride (2 bubbles per second) for 1 hr. The reaction mixture was cooled and poured onto cracked ice. The flocculent precipitate was collected and washed on the funnel with dilute potassium carbonate and water. Crystallization of the air-dried product successively from benzene-petroleum ether and aqueous ethanol gave 90 mg. (65%) of XIII as long, felted needles, m.p. 131–132°, which was found to be identical by means of m.p. and mixed m.p., as well as by comparison of the infrared spectrum, to an authentic sample of the diester prepared by the procedure of Kermack.[11]

Anal. Calcd. for $C_{14}H_{15}O_4N$: C, 64.35; H, 5.79. Found: C, 64.34; H, 5.90.

The esterification of XI to XIII was effected in almost quantitative yield when ethereal diazoethane was used.

Diethyl 2,4-Indoledicarboxylate (XII).—The conversion of 2,4-indoledicarboxylic acid to the corresponding diethyl ester XII was carried out with ethanolic hydrogen chloride and with ethereal diazoethane by the procedures described above for the 2,6-isomer; white needles, m.p. 143.4–144.2°, from aqueous ethanol.

Anal. Calcd. for $C_{14}H_{15}O_4N$: C, 64.35; H, 5.79. Found: C, 64.1; H, 5.7.

This compound was identical in m.p. with (no depression on admixture) and had the same infrared spectrum as an authentic specimen prepared from ethyl pyruvate *m*-carbethoxyphenylhydrazone by a modification of the method of Roder.[11] The fusion of the hydrazone with zinc chloride following the Roder procedure gave 1% of XII. The yields of XII were raised to 8% when the Fischer ring closure reaction was carried out in zinc chloride–acetic acid by the procedure used above for the preparation of I and II.

Treatment of *m*-Aminobenzotrifluoride with Boiling Aqueous Methanolic Potassium Hydroxide.—*m*-Aminobenzotrifluoride, 3.0 g., b.p. 189–190°, $n^{22}D$ 1.4811, was heated under reflux for 10.5 hr. with 15 ml. of a solution prepared from 20 g. of potassium hydroxide, 80 ml. of methanol and 40 ml. of water. The reaction mixture was protected by a soda-lime tube during the period of reflux. The amber solution was then cooled, diluted with 10 ml. of water and extracted with three 50-ml. portions of ether. The combined ethereal extract was washed with 15 ml. of water, which was added to the aqueous phase. The aqueous extract was concentrated to a volume of 12 ml., acidified with 1:1 hydrochloric acid and extracted three times with 50-ml. portions of ether. Evaporation of the ether yielded 20 mg. of tan needles which were obtained as a colorless solid by sublimation at 80° and 0.1 mm. Lack of material prevented its being identified and, although the substance was acidic to moist litmus, its m.p. of 189–190° ruled out *m*-aminobenzoic acid. The m.p. of an authentic sample of *m*-aminobenzoic acid, determined simultaneously with that of the unknown product, was 174–175°.

Removal of the ether from the extraction of the reaction mixture followed by distillation of the residue gave 2.7 g. (90%) of *m*-aminobenzotrifluoride, b.p. 189–191°, $n^{22}D$ 1.4802.

Repetition of the experiment under the same conditions, but with the time of reflux reduced to 2 hr., resulted in a 90% recovery of the amine; none of the acidic solid was observed.

CHESTNUT HILL 67, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

Spectrophotometric Relationships between Furoxanes and Nitroso Compounds[1]

BY J. H. BOYER, U. TOGGWEILER AND G. A. STONER

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Furoxanes, ψ- and normal nitroso aromatic compounds gave closely related infrared absorption patterns, 2–25 μ. Absorption in the ultraviolet at 255–285 mμ for furoxanes, at 265–310 mμ (two bands) for normal aromatic nitroso compounds and at 350–410 mμ for ψ-dinitrosoaromatic compounds was observed.

Furoxanes, ψ-dinitrosoaromatic compounds and normal nitroso compounds are closely related in certain chemical and physical properties. Significant differences between furoxanes and ψ-dinitrosoaromatic compounds have been described.[2] Characteristic properties in the absorption of light for certain members of the individual series have been recorded previously, but apparently their similarities and differences in this respect have not been discussed.

Seven absorption regions in the infrared between 1800 and 800 cm.$^{-1}$ characteristic of furoxanes were recently reported.[3] These included 1625–1600 cm.$^{-1}$ for the C=N bond; 1475–1410 cm.$^{-1}$ (doublet) for the O–N→O group; 1360–1300 cm.$^{-1}$ for the N–O bond; 1190–1150, 1030–1000 and 890–840 cm.$^{-1}$ for the furoxane ring; and 950–900 cm.$^{-1}$ (usually a doublet) for diaroylfuroxanes, their carbonyl derivatives and diarylfuroxanes. Bands characteristic of monomeric and dimeric aromatic nitroso compounds were found at *ca.* 1540–1500 (monomer) and 1500–1480 (dimer) cm.$^{-1}$ (C=C str. conjugated with the nitroso group), *ca.* 1380–1340 (monomer) and 1270–1260 (dimer) cm.$^{-1}$ (N=O str.), *ca.* 850–810 (monomer) and 855 (dimer) cm.$^{-1}$ (N=O bend).[4] The data recorded

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[1] Financial support of this work by the Office of Ordnance Research, U. S. Army, under Contract Nos. DA-01-009-ORD-331 and DA-01-009-ORD-428 is gratefully acknowledged.

[2] J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner and F. Sahhar, THIS JOURNAL, **77**, 5688 (1955).

[3] N. E. Boyer, G. M. Czerniak, H. S. Gutowsky and H. R. Snyder, *ibid.*, **77**, 4238 (1955).

[4] K. Nakamoto and R. E. Rundle, *ibid.*, **78**, 1113 (1956).

TABLE I

INFRARED ABSORPTION DATA (CM.$^{-1}$) FOR FUROXANES AND NITROSO COMPOUNDS FROM KBr DISKS

Compound	Absorption (1650–400 cm.$^{-1}$), [a] important bands are in italics.
Cyclohexenfuroxane (I)	*1623s*, *1517m*, *1475–1458s*, 1427s, *1346m*, 1276m, *1252w*, *1170s*, *1135s*, *1081w*, *1062w*, *1005s*, *959s*, *926s*, 905w, *847m*, *824s*, 723w, 668m, 649m, 494m, 453w, 436–434w, 420w
Octalin-2,3-furoxane (II)	*1634s*, *1515w*, *1479s*, *1468s*, 1429s, 1372w, *1355w*, 1330–1321w, 1304w, *1248w*, 1190w, *1161w*, *1114m*, *1094w*, *1072w*, 1054w, *998s*, 951w, *927w*, *915w*, *859w*, *834w*, 768w, 741w, 696m
3,4,5,6-Tetrabromocyclohexenfuroxane(III)	*1637s*, *1529w*, 1511w, *1473m*, *1326w*, *1256w*, 1232w, 1202w, *1179w*, 1166m, *1145w*, *1122w*, *1093w*, *1024m*, 1000w, *929w*, *860w*, *826m*, 796w, 755m, 715w, 688m, 648–647w, 610m, 601–598m, 575w, 568w, 540w, 530–529w, 467–462w, 450–447w, 419m
Diphenylfuroxane (IV)	*1595s*, 1580s, 1511s, *1479s*, *1460s*, 1447s, 1425s, *1332m* 1314s, 1285m, *1174m*, 1117s, 1075m, *1029w*, 1004m, 990m, 963s, *926–922m*, *837s*, *831s*, 774s, 731s, 717m, 710m, 694s, 654s, 618–616w, 593w, 551w, 542–540m, 505m, 492w, 458w, 439–437w, 420–419w
ψ-*o*-Dinitrosobenzene (V)	*1616s*, 1587s, 1538s, *1488s*, *1445s*, *1422s*, *1355s*, *1284s*, 1200s, 1148s, 1129s, 1049m, 1016s, 976m, 894s, *838s*, 759s, 746s, 736s, 674m, 577m, 564m, 553m, 520m, 481m, 479–473m, 435m, 420–419m
3,6-Dibromo-ψ-1,2-dinitrosobenzene (VI)	*1613s*, 1575m, 1522w, *1488m*, 1468w, *1368w*, *1307w*, 1242w, 1168w, 1042w, 927m, 897w, *837w*, 736w, 696w, 608w, 569–568w, 556w, 539–538w, 420.5–419w
ψ-1,2-Dinitrosonaphthalene (VII)	*1634m*, 1610s, 1592m, 1555m, 1524m, *1486m*, *1471m*, *1443m*, *1364w*, *1277m*, 1214w, 1164w, 1103w, 1082w, 971m, *829w*, 809–806m, 775m, 760m, 746m, 683w
ψ-9,10-Dinitrosophenanthrene (VIII)	*1634s*, 1618s, 1608s, 1585m, 1570m, 1529m, *1515s*, *1473s*, *1456s*, 1427m, *1368w*, 1321w, *1292m*, 1241w, 1205w, 1174w, 1120w, 1089m, 996w, 959m, *820w*, 757s, 723s, 693w, 680w
Nitrosobenzene (IX)	1595w, 1490m, 1462m, *1395s*, *1297w*, 1256w, 1192m, 1170m, 1157w, 1119w, 1074w, 1020w, 1004w, 952s, 924w, 779m, 762m, 689m, 666m, 615w, 590w, 564w, 529w, 489w
m-Dinitrosobenzene (X)	1605–1595m, 1543m, 1508m, 1479s, 1443s, *1364w*, *1282–1274s*, 1242s, 1217s, 1157m, 1121s, 1089s, 1004s, 951m, 928w, 890s, *823m*, 812s, 791m, 782s, 687s, 669s, 616m, 588m, 494–493m, 483m, 473w, 459–458w, 422–420m
ψ-*p*-Dinitrosobenzene (XI)	*1613s*, 1577–1558s, *1456*–1437s, 1408s, *1362s*, 1326s, *1280s*, 1267s, 1171s, 1160s, 1116s, 1104s, 1042–1026s, 957s, 886s, 866s, *822m*, 808s, 799s, 615s, 590m, 583m, 515m, 495s, 481s, 477s

in Table I for cyclohexenfuroxane (I), octalin-2,3-furoxane (II), 3,4,5,6-tetrabromocyclohexenfuroxane (III) and diphenylfuroxane (IV) supported the seven furoxane assignments. A strong C=N band was found in the region 1635–1600 cm.$^{-1}$. A weaker C=N band[2] at 1530–1515 cm.$^{-1}$ for I–III was in agreement with the static representation of the furoxane group. Interference absorption attributed to CH_2 (1485–1445 cm.$^{-1}$), CH (near 1340 cm.$^{-1}$) and the cyclohexane ring (1005–952 and 1055–1000 cm.$^{-1}$) was found as expected.[5] It was interesting to note that tetrabromocyclohexenfuroxane (III) did not show a doublet in the 1475–1410 cm.$^{-1}$ region. Each of the four furoxanes exhibited weak to moderate absorption in the 1300–1200 cm.$^{-1}$ region, and the alicyclic furoxanes (I-III) had a consistent value at 1250 cm.$^{-1}$, possibly exocyclic N→O str. (compare the stretching mode of the nitroso group in a dimer at 1265 cm.$^{-1}$).[4] Three bands between 1150 and 1060 cm.$^{-1}$ and a consistent weak to strong band at 930–924 cm.$^{-1}$ (in the region previously ascribed to those furoxanes with diaryl or diaroyl side-chains[3]) were characteristic of alicyclic furoxane systems. Each of these three furoxanes together with diphenylfuroxane also gave a weak to strong band in the region 835–825 cm.$^{-1}$, an extension of the lower limit of the previously assigned range of 890–840 cm.$^{-1}$.[3]

The assignment of bands 1616 (V), 1613 (VI and XI) and 1634 (VII and VIII) cm.$^{-1}$ to the azomethine linkage is less definite in these examples because of interference with aromatic unsaturation, 1625–1575 cm^{-1}.[6] Absorption, characteristic of ψ-*o*-dinitrosoaromatic compounds at 1540–1475 cm.$^{-1}$,[7] was assigned to C=C str. conjugated to nitroso groups[4] and it appeared that this band was shifted to near 1450 cm.$^{-1}$ for the highly conjugated ψ-*p*-dinitrosobenzene (XI). With the exception of compound VI, *o*-dinitrosoaromatic compounds showed doublet absorption at 1470–1420 cm.$^{-1}$, a property shared with furoxanes.[3] Each nitroso compound (V-XI) absorbed in the 1395–1355 (N=O str.[4]), 1310–1275 (possibly C–NO stretching[8]) and, with the exception of nitrosobenzene, 840–820 (N=O bend[4]) cm.$^{-1}$ regions; however, interference in the latter region from the *p*-disubstituted benzene (XI) was apparent.[9] A possible contribution from polymeric forms was demonstrated by bands at 1256 (IX) and 1274 (X) and 1267 (XI) cm.$^{-1}$.[4] Characteristic absorption in the regions 1225–950 and 860–730 cm.$^{-1}$ for substituted benzene rings[9] was found for IV, V, IX, X and XI.

Ultraviolet absorption values, Table II, provided a more reliable means for the differentiation of furoxanes, ψ- and normal nitroso compounds. Absorption near 282 and 304 mμ was reported for nitrosobenzene[10] and values of 266 and 300 mμ have now been observed for *m*-dinitrosobenzene. Limiting values, 350–410 mμ, for ψ-dinitrosoaromatic compounds were provided by ψ-9,10-dinitrosophen-

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(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 13, 29.

(6) Reference 5, p. 60.

(7) J. H. Boyer and W. Schoen, THIS JOURNAL, **78**, 423 (1956); J. H. Boyer, D. I. McCane, W. J. McCarville and A. T. Tweedie, *ibid.*, **75**, 5298 (1953).

(8) In their correlation of absorption of aromatic nitro compounds at 1300 cm.$^{-1}$ with $C–NO_2$ stretching vibration, R. D. Kross and V. A. Fassel, *ibid.*, **78**, 4225 (1956), recognized the partial double bond character of the C–N bond.

(9) Reference 5, p. 55.

(10) A. Schors, A. Kraaijeveld and E. Havinga, *Rec. trav. chim.*, **74**, 1243 (1955).

anthrene and ψ-*p*-dinitrosobenzene. Similar values for 3-phenyl-ψ-1,2-dinitrosobenzene and 4-nitro-6-phenyl-ψ-1,2-dinitrosobenzene were observed.[11] The characteristic furoxane absorption occurred in the region 255–285 mμ. As was to be expected, glyoximes absorbed in those regions which corresponded to their oxidation products, furoxanes or ψ-dinitrosoaromatic compounds.

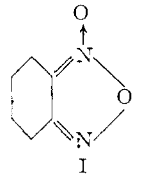
TABLE II

ULTRAVIOLET ABSORPTION DATA FROM A BECKMAN DK SPECTROPHOTOMETER FOR FUROXANES AND NITROSO COMPOUNDS IN ETHANOL

Compound	Concn., mmole	Wave length, mμ	ϵ
Cyclohexenfuroxane (I)	0.14	262–263	6700
Octalin-2,3-furoxane (II)	.14	262–263	6800
Tetrabromocyclohexenfuroxane (III)	.13	276–277	4700
Diphenylfuroxane (IV)	.10	283	5700
ψ-*o*-Dinitrosobenzene (V)	.10	355	6910
3,6-Dibromo-ψ-1,2-dinitrosobenzene (VI)	.05	382–384	8400
ψ-1,2-Dinitrosonaphthalene (VII)	.026	349–351	6700
		336–338	6500
		269–270	24000
		260–261	24000
ψ-9,10-Dinitrosophenanthrene (VIII)	.035	348–349	6000
		332–334	6200
		286–287	8900
		275–276	13700
Nitrosobenzene (IX)	.10	284, 308	6600, 3050
m-Dinitrosobenzene (X)	.10	268, 300	1000, 4490
ψ-*p*-Dinitrosobenzene (XI)	.05	305, 405	2140, 3580
ψ-1,2-Dinitroso-3,6-diphenylpyridazine (XII)	.033	397–399	13700
		263–265	8000
2-Methyl-2-nitrosopropane[a]	. .	300	100
4,5-Tetramethylene-ψ-1,2-dinitrosobenzene[b]	.05	370	6260
Dibenzoylfuroxane[c]	.077	261–263	3800
Dimethylfuroxane[d]	.04	258	7775
Dimethylglyoxime[a]	. .	226	17000
o-Benzoquinonedioxime	.10	385	3950
p-Benzoquinonedioxime	.01	323	19300

[a] Ref. 12, p. 166. [b] Ref. 7. [c] Ref. 3. [d] Ref. 15.

Bromination of ψ-*o*-dinitrosobenzene (V) brought about the formation of 3,4,5,6-tetrabromocyclohexenfuroxane (III).[12] This was apparently the only known direct transformation of a ψ-dinitrosoaromatic system into a furoxane. Two examples of the reverse process were found. Dehydrobromination[11] of III resulted in the formation of 3,6-dibromo-ψ-1,2-dinitrosobenzene, identified by nearly quantitative reduction to 3,6-dibromo-1,2-diaminobenzene. The other case consisted in the formation of azines of diacylfuroxanes, *e.g.*, dibenzoylfuroxane → 3,6-diphenyl-ψ-4,5-dinitrosopyridazine (XII).[3] The lower absorption at 263–265 mμ, log ϵ 3.90, for the latter compound was attributed to the *para*-polyaromatic system (compare 280 mμ, log ϵ 4.40, for *p*-terphenyl[13]). The present representation for compound XII, in contrast with its representation as an unsymmetrical furoxane,[3] predicts one form instead of two for 3,6-disubstituted-ψ-4,5-dinitrosopyridazines in which the subtituents at position 3 and 6 are different.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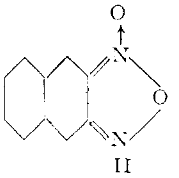
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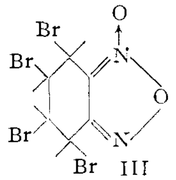
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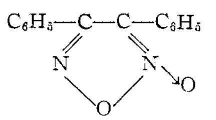
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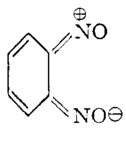
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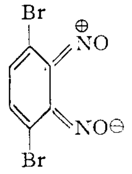
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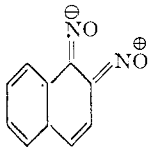
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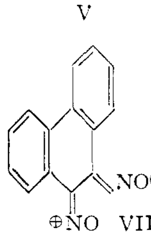
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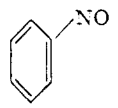
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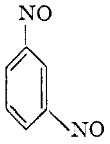
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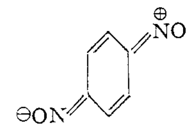
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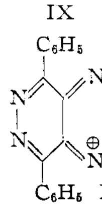
XII

Acknowledgment.—Frequent discussions of this problem with Mr. R. T. O'Connor of the Southern Regional Research Laboratory are gratefully acknowledged.

Experimental[14]

The furoxanes I, II and IV and ψ-9,10-dinitrosophenanthrene (VIII) were prepared previously.[15] Oxidation of 2-amino-1-nitronaphthalene with sodium hypochlorite produced ψ-1,2-dinitrosonaphthalene (VII).[16] Nitrosobenzene (IX), m.p. 66–68°, was commercially available from Fluka Inc., Buchs S. G., Switzerland.

An application of a method for the preparation of nitrosobenzene[17] was used for the preparation of *m*-dinitrosobenzene (X).[18] To 20 g. (0.12 mole) of *m*-dinitrobenzene and 15 g. (0.28 mole) of ammonium chloride dissolved in 500 ml. of water, 37 g. (0.52 mole) of zinc dust was added over a period of 5 minutes with vigorous stirring. After 5 minutes the temperature began to rise and reached 45° within 20 minutes, after which time the solution was filtered and the zinc oxide residue washed with 1 liter of hot water. The combined filtrates were then immediately cooled to 0° by addition of sufficient ice to leave at least 500 g. unmelted. To this cold solution 75 ml. of ice-cold sulfuric acid (sp.gr. 1.84) was added with rapid stirring. An ice-cold solution

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[11] P. A. S. Smith and B. B. Brown, This Journal, **73**, 2435 (1951).

[12] D. L. Hammick, W. A. M. Edwards and E. R. Steiner, *J. Chem. Soc.*, 3308 (1925).

[13] A. E. Gillam and D. H. Hey, *ibid.*, 1170 (1939).

[14] Elemental analyses by Micro-tech Laboratory, Skokie, Ill. Infrared spectra through the courtesy of Dr. J. Picard, Picatinny Arsenal, Dover, N. J., and Mr. R. T. O'Connor, Southern Regional Research Laboratory, New Orleans, La.

[15] J. H. Boyer and U. Toggweiler, This Journal, **79**, 895 (1957).

[16] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **111**, 612 (1917).

[17] G. H. Coleman, C. M. McCloskey and F. A. Stuart, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 668.

[18] K. Brandand and A. Modersohn, *J. prakt. Chem.*, **120**, 160 (1928), claimed that zinc and ammonium chloride were not useful in the reduction of *m*-dinitrobenzene to *m*-dinitrosobenzene.

containing 17 g. of technical sodium dichromate in 50 ml. of water was added as rapidly as possible with vigorous stirring. After 2 or 3 minutes, the mixture was filtered and the red-brown precipitate was washed with a liter of water and steam distilled. The yellow monomeric product, m.p. 144–145° (lit.[19] m.p. 146.5°), solidified from the steam distillate (51% yield).

Anal. Calcd. for $C_6H_4N_2O_2$: C, 52.94; H, 2.96; N, 20.58. Found: C, 52.98; H, 3.06; N, 20.80.

ψ-p-Dinitrosobenzene was prepared from phenol and nitrous acid.[20] Potassium bromide wafers of the initially formed rose colored, apparently polymeric product and the sublimed crystalline green monomer, m.p. 174–175° dec., gave identical absorption in the infrared, 2–16 μ.

The dioxime of *o*-benzquinone was obtained upon alkaline reduction of *ψ-o*-dinitrosobenzene with hydroxylamine.[21] The dioxime of *p*-benzquinone was commercially available.

The directions for the preparation of 3,4,5,6-tetrabromocyclohexenfuroxane (III) were modified.[12] To 150 ml. of carbon disulfide containing 7 g. (0.05 mole) of *ψ*-1,2-dinitrosobenzene, m.p. 71–72°, 17 g. (0.21 mole) of bromine in 30 ml. of carbon disulfide was added. The reaction mixture was irradiated for three hours with a 275-watt ultraviolet lamp. After evaporation of about half the solvent, 16 g. (70%) of tetrabromocyclohexenfuroxane was collected and washed with cold dilute alcohol. Upon recrystallization from 95% ethanol, the white needles melted at 172–173° (lit.[12] m.p. 170°). The dehydrobromination[12] was effected by adding 15% aqueous potassium hydroxide solution dropwise to 4.5 g. (0.01 mole) of tetrabromocyclohexenfuroxane in ethanol solution. At the end of the addition, the original yellow solution had turned brown. Evaporation of excess solvent permitted the separation of yellow crystals of 3,6-dibromo-*ψ*-1,2-dinitrosobenzene, 1.8 g. (60%) after recrystallization from ethanol, m.p. 132–133° (lit.[12] m.p. 132°).

3,6-Dibromo-*o*-phenylenediamine was prepared in two ways. The first consisted in adding a small excess of granular tin to a suspension of 0.8 g. (0.0025 mole) of 3,6-dibromo-*ψ*-1,2-dinitrosobenzene, m.p. 130–131°, in 25 ml. of 6 *N* hydrochloric acid. The reaction mixture was refluxed until reduction was complete (about 40 minutes) and the solution became colorless. Some additional 6 *N* hydrochloric acid was added to dissolve all the diamine hydrochloride. The hot solution was filtered to remove any excess tin and other impurities. Upon cooling, the amine hydrochloride, m.p. 150–155°, was recovered as fine white crystals (0.7 g.), 70% yield. Part of the amine salt was neutralized with a small excess of dilute sodium bicarbonate solution, in a suspension of dilute ethanol. More dilute ethanol was added to dissolve all the free amine, once the neutralization was completed. The diamine was once more recrystallized from dilute ethanol, and poorly defined white crystals, m.p. 95–96° (lit.[22] m.p. 94–95°), were recovered. This amine dissolved in concentrated nitric acid with dark red coloration.

The second method of preparation involved good stirring of a suspension of 0.6 g. (0.002 mole) of 3,6-dibromo-*ψ*-1,2-dinitrosobenzene in 15 ml. of hydriodic acid, kept at 110–120° for 20 minutes. No reduction occurred below 105–110°. At the end of this period, 20% aqueous sodium bisulfite solution was added slowly to the dark brown reaction mixture until all elemental iodine was reduced and the solution became colorless. After cooling in an ice-bath the yellow crystals of the amine hydroiodide separated and were filtered with suction. These yellow crystals were suspended in about 5 ml. of dilute alcohol, as a dilute solution of sodium bicarbonate was added until the solution became slightly alkaline. More dilute alcohol was added to dissolve all the free amine. After two additional recrystallizations, poorly defined white crystals, m.p. 93–94° were obtained, 0.1 g. (20%).

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[19] F. J. Alway and R. A. Gortner, *Ber.*, **38**, 1899 (1905), reported a reduction of *m*-dinitrobenzene with zinc and acetic acid to *m*-phenylenedihydroxylamine followed by oxidation with ferric chloride to *m*-dinitrosobenzene. In our hands this method gave very poor yields.

[20] P. Ruggli and C. Bartusch, *Helv. Chim. Acta*, **27**, 1371 (1944).

[21] T. Zincke and P. Schwarz, *Ann.*, **307**, 39 (1899).

[22] D. F. Calhane and P. M. Wheeler, *Am. Chem. J.*, **22**, 449 (1899).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF NEW MEXICO]

The Synthesis of 9-Methyl-3,4-benzpyrene and 8,9-Dimethyl-3,4-benzpyrene[1–3]

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3-Keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (I) underwent a Reformatsky reaction with ethyl bromoacetate, and dehydration of the resulting hydroxy ester followed by hydrolysis produced a mixture of isomeric acids in 83% yield from I. These acids were probably (1,11b-dihydro-7H-*meso*-benzanthrenyl-3-)-acetic acid (II), the predominant isomer, (1,2,3,11b-tetrahydro-7H-*meso*-benzanthrylidene-3)-acetic acid (III) and (4,5-dihydro-6H-*meso*-benzanthrenyl-3)-acetic acid (IV), an abnormal product. Catalytic reduction of II and III produced (1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-acetic acid (V) which underwent the Wilds modification of the Arndt–Eistert synthesis with diazoethane in 89% yield producing *β*-(1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-isobutyric acid (VI). Cyclization of VI in the presence of anhydrous hydrogen fluoride produced 8-keto-9-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (VII). The ketone VII was reduced by the Meerwein–Ponndorf method or methylated with methylmagnesium iodide producing carbinols which were dehydrated and dehydrogenated to 9-methyl-3,4-benzpyrene and 8,9-dimethyl-3,4-benzpyrene, respectively. This synthesis clarified the conflicting communications reporting the isolation of 9-methyl-3,4-benzpyrene. The new 3,4-benzpyrenes gave ultraviolet absorption spectra similar to the parent hydrocarbon, 3,4-benzpyrene. Samples of these new hydrocarbons will be evaluated for carcinogenic activity at the Northwestern University Medical School, Evanston, Ill.

The isolation of 9-methyl-3,4-benzpyrene (VIII) has been reported by Bergmann[5,6] and Fieser.[7] As part of a program directed toward completing the synthesis of the remaining unknown monomethyl-3,4-benzpyrenes,[8] it was of interest to investigate the conflicting properties reported for the 9-methyl isomer (Bergmann: m.p. 171–172.5°, picrate m.p.

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[2] This investigation was supported in part by a research grant (C-1595) from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

[3] Submitted for presentation before the Division of Organic Chemistry at the 131st Meeting of the American Chemical Society, Miami, Florida, April 7–12, 1957.

[4] Graduate Research Assistant, February, 1956, to September, 1956.

[5] E. Bergmann and O. Blum-Bergmann, THIS JOURNAL, **58**, 1678 (1936).

[6] E. Bergmann and F. Bergmann, *ibid.*, **60**, 1805 (1938).

[7] L. F. Fieser and F. C. Novello, *ibid.*, **62**, 1855 (1940).

[8] J. L. Adelfang and G. H. Daub, *ibid.*, **77**, 3297 (1955).