and the solution refluxed for two hours. Acidification with concentrated hydrochloric acid precipitated the disulfide which was collected by filtration and recrystallized from water.

Anal. Calcd. for $C_8H_6N_4O_4S_2$: C, 33.5; H, 2.11; N, 19.6; S, 22.4. Found: C, 33.9; H, 2.54; N, 19.3; S, 21.5.

Ultraviolet Absorption Spectra.—One mg. per cc. stock solutions of the compounds were prepared; 5-mercaptouracil and 5-uracilyl disulfide were dissolved in 0.1 *N* sodium hydroxide, uracil-5-isothiouronium chloride was dissolved in water. These stock solutions were diluted 100-fold with 0.1 *N* hydrochloric acid and 0.1 *N* sodium hydroxide, respectively, to obtain the compounds in 10 γ/cc. final concentration, at *p*H 1 and 13. The corresponding solvent "blanks" were prepared the same way without the compounds. Beckman model DU spectrophotometer was used. The following absorption maxima and molar extinctions were obtained.

	*p*H 1		*p*H 13	
	λ_{max}	ϵ	λ_{max}	ϵ
5-Mercaptouracil	274	7,300	291	8,800
5-Uracilyl disulfide	272	15,000	290	19,000
Uracil-5-isothiouronium chloride	268	8,400	290	7,800

CHICAGO 9, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Some Pyrroles, Phenols and Pyridines Contained in a Gilsonite Distillate

BY JAMES M. SUGIHARA AND DAVID P. SORENSEN

RECEIVED SEPTEMBER 7, 1954

The pyrolysis of Gilsonite yielded a distillate, from which pyrroles and phenols were separated in the form of potassium salts. Pyridines then were extracted with aqueous phosphoric acid. Small amounts of each of these fractions were separated conveniently by chromatographic methods. The identification of pyrrole, 2-methylpyrrole, phenol, *o*-cresol, 3,5-dimethylphenol, 1-naphthol, 4-picoline, 2,6-lutidine, 3,4 lutidine, 2,5-lutidine, 3,5-lutidine and 2,3,5-trimethylpyridine is described.

The pyrolysis of Gilsonite, an asphaltite,[1] yields a distillate in an amount of about 55%. Saturated and unsaturated hydrocarbons as well as basic nitrogen compounds have been reported[2] to be present in this distillate. The probable absence of aromatic hydrocarbons also was indicated.[2a] Evidence for the presence of 3-ethylpyridine and 2,3,5-trimethylpyridine in the basic fraction has been derived.[3]

In the work herein described the procedure developed permitted the processing of relatively small amounts of materials. The distillate A, derived in the pyrolysis of Gilsonite, was subjected to a distillation to obtain 6.5% of a low-boiling fraction B (b.p. 35–120°) and 31% of a fraction C (b.p. 60–150°, 13 mm.). Fraction B did not contain any nitrogen- or sulfur-containing compounds, as shown by analyses. The separation of basic and acidic compounds from C by conventional methods using aqueous acids and bases was attended with much tar formation and concomitant loss of the desired fractions. Any pyrroles contained might be expected to be degraded to a considerable extent upon contact with mineral acids. For these reasons pyrroles and phenols were first removed from C by reaction with potassium metal.[4] The solid mixture of salts was treated with water to hydrolyze pyrrole salts. The pyrroles then were extracted with ether, leaving the salts of phenols in the aqueous phase, which could be acidified and ether-extracted to obtain a phenol fraction. Basic compounds were separated by extraction with an aqueous solution of phosphoric acid.

Pyridine and alkylpyridines are reported[5] to yield dipyridyls by condensation with sodium in the presence of air. The comparable reaction with potassium[6] proceeds much more slowly. The extent of condensation of pyridine and its alkyl derivatives during the initial separation procedure with potassium, whereupon phenols and pyrroles were converted into salts, would undoubtedly be limited. When pyridine was added to the neutral fraction, obtained after phenols, pyrroles and pyridines were removed, 92% of a chromatographically homogeneous fraction was recovered. This fraction was demonstrated to be unchanged pyridine.

The separation of relatively small amounts of each of the fractions was accomplished by a chromatographic procedure. Pyrroles were located on the absorbent using *p*-dimethylaminobenzaldehyde[7] as a streak indicator. The location of phenols was effected with an alkaline solution of potassium permanganate and of pyridines with tetraiodophenolphthalein. Pyridine compounds were found to react rapidly with the sodium salt of tetraiodophenolphthalein to yield a colorless solution. The colored form of the indicator was presumed to form a complex of the type indicated by I. Dilute mineral acids could readily regenerate the violet color of the indicator.

From the pyrrole fraction, pyrrole and 2-methylpyrrole were isolated. Tetraiodopyrrole, pyrrole picrate, 1-pyrroleacetic acid, 1-pyrroleacetamide, 2-pyrrolecarboxanilide and the condensation product of pyrrole and phthalic anhydride were prepared and compared with authentic samples. 5-Methyl-2-pyrrolecarboxanilide, 1-*p*-nitrobenzoyl-2-methylpyrrole and the condensation product of

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(1) H. Abraham, "Asphalts and Allied Substances," 5th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1944, p. 250.

(2) (a) W. C. Day, *J. Franklin Inst.*, **140**, 221 (1895); (b) C. F. Mabery, THIS JOURNAL, **39**, 2015 (1917).

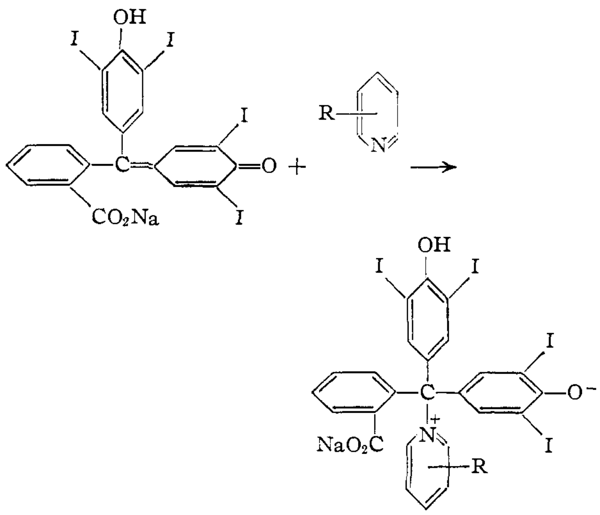
(3) R. E. Reusser, Master's thesis, University of Utah, 1949.

(4) A. G. Janssen, E. R. Scherz, R. Van Meter and John S. Ball, THIS JOURNAL, **73**, 4040 (1951), extracted pyrroles from shale-oil naphtha with solid potassium hydroxide.

(5) C. R. Smith, *ibid.*, **46**, 414 (1924), and earlier references, which are therein cited.

(6) B. Emmert, *Ber.*, **49**, 1060 (1916).

(7) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. I, Academische Verlagsgesellschaft, G.m.b.H., Leipzig, 1934, p. 66.



I

2-methylpyrrole and phthalic anhydride were synthesized and also compared with authentic samples. Evidence for other pyrrole compounds was obtained, but amounts available did not permit identification. Phenol, *o*-cresol, 3,5-dimethylphenol and 1-naphthol were separated from the phenolic fraction. Identification was realized by the preparation of the derivatives listed in Table I and comparison with authentic samples.

TABLE I

DERIVATIVES OF PHENOLS

Chromatographic fraction	Compound	M.p., °C. Aryloxyacetic acid Found	Lit.[a,b]	Bromo Found	Lit.[a]	3,5-Dinitrobenzoate Found	Lit.[b]
G-1-1	Phenol	98–100[c]	99	92–95	95(tri)	144–146	145.8
G-2-1	*o*-Cresol	149–152	152	53–55	56(di)		
G-3-1	3,5-Dimethylphenol			162–164	166(tri)	192–194.5	195.4
G-5-1	1-Naphthol	188–191	193.5	102–103.5	105(di)		

[a] R. L. Shriner and R. C. Fuson, "The Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 271. [b] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 380. [c] Neutral equivalent, 148; calcd., 152.

TABLE II

DERIVATIVES OF ALKYLPYRIDINES

Chromatographic fraction	Compound	M.p., °C., of addition compounds with Picric acid Found	Lit.[a]	Styphnic acid Found	Mercuric chloride Found	Lit.[a]	Chloroplatinic acid Found	Lit.[a]
H-1-1	2,6-Lutidine	155–158	161 (168)	172–173[b]	189–191	191		
H-1-2	4-Picoline[c]	167–168	167	184–185[d]	126–128	130		
H-4-1	2,3,5-Trimethylpyridine	181–183	184		106–108	110	208–210	212 (227)
H-4-2	3,4-Lutidine	161–164	163		146–148	146–148	202–203 d.	205 d.
H-5-1	2,5-Lutidine	149–151	151–152 (167)		160–163	164	187–193 d.	191 d.
H-5-2	3,5-Lutidine	226–231	228–230 (238)		169–171	172–173		

[a] Beilstein, "Handbuch der Organischen Chemie," 4 ed., Vol. XX, 1935. [b] Prepared by the general procedure of R. H. F. Manske, L. Marion and F. Leger, *Can. J. Research*, **20B**, 133 (1942). *Anal.* Calcd. for $C_{13}H_{12}O_8N_4$: C, 44.32: H, 3.43. Found: C, 44.10; H, 3.19. [c] The addition compound with 2,4,6-trinitro-*m*-cresol was also prepared by the procedure given in ref. *b*. *Anal.* Calcd. for $C_{13}H_{12}O_7N_4$: C, 46.43; H, 3.60. Found: C, 46.59; H, 3.67. [d] Prepared by the procedure given in ref. *b*. *Anal.* Calcd. for $C_{12}H_{10}O_8N_4$: C, 42.61; H, 2.98. Found: C, 42.87; H, 2.63.

The separation and identification of 4-picoline, 2,6-lutidine, 3,4-lutidine, 2,5-lutidine, 3,5-lutidine and 2,3,5-trimethylpyridine were realized as summarized in Table II. Crystalline addition compounds of 4-picoline and 2,6-lutidine with styphnic acid and of 4-picoline with 2,4,6-trinitro-*m*-cresol are reported. The chromatographic separation of a synthetic mixture of 2-, 3- and 4-picolines and 2,3-lutidine was demonstrated to be efficient with near quantitative recovery of each compound.

Acknowledgment.—This investigation was supported by a research grant from the American Gilsonite Company, and in part by a Frederick Gardner Cottrell grant from Research Corporation.

Experimental[8]

Preparation of Gilsonite Coker-distillate and Separation of Pyrrole (F), Phenol (G) and Pyridine Fractions (H).—Five thousand grams of commercial Gilsonite[9] derived from the Bonanza vein was placed in a cast-iron retort, fitted with a metal, water-cooled condenser, and heated externally by a battery of gas burners. Heating was conducted at such a rate as to provide a uniform flow of distillate but with no entrainment of undegraded solids. The yields of Gilsonite coker-distillate (A) and of coke were 2750 and 1500 g., respectively.

Anal. Distillate A: C, 84.7; H, 12.0; N, 1.99; S, 0.54. Coke: C, 86.0; H, 6.1; N, 1.42; S, 0.95.

The distillation of 2750 g. of A provided a fraction B, 180 g., b.p. 35–120°, and a fraction C, 850 g., b.p. 60–150° (13 mm.).

Anal. Fraction B: C, 85.4; H, 14.1; N, 0.00; S, 0.00. Fraction C: C, 85.4; H, 12.9; N, 1.60; S, 0.60.

Fraction C (1000 g.) and 20 g. of potassium were heated at 100° for 4 hours. The resulting mixture was cooled to 0°, and the solid formed and unreacted potassium were filtered off, leaving the neutral and basic compounds in the filtrate D. The solid was washed four times with 250 ml. of petroleum ether (b.p. 35–60°), and then treated in succession with 50 ml. of 95% ethanol and 250 ml. of water. The resulting solution was extracted four times with 250-ml. portions of ether, leaving an aqueous solution E. The ether solution was dried over anhydrous calcium sulfate. Removal of ether left 6 g. of a pyrrole fraction F, b.p. 50–95° (15 mm.).

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(8) All melting points are corrected. Boiling points are uncorrected and as recorded at prevailing atmospheric pressure, about 640 mm., unless otherwise specified. Carbon, hydrogen and sulfur analyses were made by Dr. G. Weiler and Dr. F. B. Strauss, Oxford, England; nitrogen was determined by the Kjeldahl method.

(9) Supplied by the American Gilsonite Co., Salt Lake City, Utah.

Anal. C, 78.2; H, 8.0; N, 11.2; S, 1.03.

Solution E was acidified with 3 *N* sulfuric acid, and the resulting solution was extracted four times with 250-ml. portions of ether. The ether solution was dried over anhydrous calcium sulfate. Removal of ether left 9 g. of a phenol fraction G.

Anal. C, 69.7; H, 8.2; N, 1.56; S, 1.90.

Solution D was extracted with 500 ml. of 40% aqueous phosphoric acid, leaving the neutral compounds in fraction I. The acid solution was treated with sufficient solid sodium hydroxide until the resulting solution was basic. The latter was then extracted four times with 250-ml. portions of ether. The ether solution was dried over anhydrous calcium sulfate. Removal of ether left 6 g. of a pyridine fraction H, b.p. 160–220°.

Anal. C, 77.5; H, 9.5; N, 1; S, 0.62.

To 1000 g. of the neutral fraction I were added chromatographically homogeneous 1-naphthol, *o*-cresol and pyridine in amounts of 1.0, 1.0 and 5.0 g., respectively. This solution was treated with potassium in the same manner as described for fraction C. After chromatography 0.74 g. of 1-naphthol, 0.91 g. of *o*-cresol and 4.6 g. of pyridine were recovered.

Chromatographic Resolution of F, G and H.—Twelve grams of F, dissolved in 100-ml. of petroleum ether (b.p. 35–70°), was placed on a column (250 × 80 mm., diam.) of Magnesol[10]–Celite[11] (5:1 by wt.) using 1500 ml. of petroleum ether (b.p. 35–70°) as the developer. After the column was extruded and streaked with an indicator (*p*-dimethylaminobenzaldehyde:85% phosphoric acid:water, 1:5:45, by wt.), two red bands, which were distinctly separated by an interzone, were observed near the bottom of the column and a wide red band over the central portion of the column. Dark-colored materials were strongly adsorbed at the top. With an ultraviolet light the central portion appeared to consist of eight discrete zones but with incomplete separation. The column was sectioned into three parts, discarding the top fifth. Elution was effected with acetone. Removal of acetone left 4 g. (F-1) from the bottom zone, 1.5 g. (F-2) from the second zone, and 5 g. (F-3) from the central area. Upon rechromatographing F-3, further separation was indicated, but amounts of fractions derived were so small that characterization of individual components was not possible.

Fraction G (56 g.) was distilled at 15 mm. to collect G-1, b.p. 160–180°, 7 g.; G-2, b.p. 180–190°, 8 g.; G-3, b.p. 190–200°, 7 g.; G-4, b.p. 200–220°, 6 g.; and G-5, undistilled solids. Two grams of G-1 was dissolved in 10 ml. of petroleum ether (b.p. 35–70°) and placed on a column (160 × 20 mm., diam.) of Magnesol–Celite (5:1 by wt.). Development was effected with 250 ml. of petroleum ether (b.p. 35–70°) containing 1% *t*-butyl alcohol (by vol.). The column was extruded and streaked with a solution containing 1% potassium permanganate in 10% aqueous sodium hydroxide.[12] Three zones were observed to reduce the indicator with well-defined interzones. The column was sectioned, and each of the portions of the adsorbent was eluted with acetone. After solvent removal the components originally contained in the bottom two zones were found not to exhibit typical phenolic properties. Removal of petroleum ether from the effluent provided a further amount of non-phenolic compounds. The top zone yielded 0.5 g. of material. Two grams of the latter was rechromatographed in the same manner. The resulting column was observed to contain a single zone, as indicated by the permanganate streak indicator. Upon elution with acetone and removal of the eluting solvent, 1.3 g. of G-1-1 was obtained.

Fraction G-2 was processed in a similar way. Of the three fractions derived by chromatography of 2 g. of this fraction, that contained in the leading zone (G-2-1) was obtained in an amount of 0.5 g. Much smaller quantities were derived from the other two fractions. Chromatographically homogeneous materials were derived likewise from the remaining fractions as follows: 0.75 g. of G-3-1 from 7 g. of G-3 and 0.5 g. of G-5-1 from 18 g. of G-5. Fraction G-4 was found to contain but very small amounts of phenolic compounds.

Fraction H (150 g.) was fractionally distilled to collect H-1, b.p. 160–165°, 5 g.; H-2, b.p. 165–170°, 4 g.; H-3, b.p. 170–175°, 4 g.; H-4, b.p. 175–180°, 5 g.; H-5, b.p. 180–185°, 5.5 g.; and higher boiling fractions. Three grams of H-1, dissolved in 10 ml. of petroleum ether (b.p. 35–60°), was placed on a column (160 × 20 mm., diam.) of Magnesol–Celite (5:1 by wt.). Development was effected with 150 ml. of petroleum ether (b.p. 35–60°). Three fluorescent bands were visible with ultraviolet light, with clear-defined interzones. The column was extruded and streaked with an indicator (2 g. of sodium salt of tetraiodophenolphthalein in 500 ml. of 20% ethanol). The indicator in the areas corresponding to the upper two zones, visible with ultraviolet light, became colorless. The column was sectioned, and the adsorbent was eluted with acetone. Removal of the solvent left 0.25 g. of H-1-1 from the lower zone and 0.5 g. of H-1-2 from the upper zone. A similar chromatographic separation of H-2 and H-3 indicated a high degree of resolution, but chromatographically homogeneous fractions were, in no case, obtained in sufficient quantities to permit identification. The chromatography of 2.5 g. of H-4 permitted the separation of 0.25 g. of H-4-1 from the leading zone. A mixture of compounds, consisting of seven or more components as indicated by observation of the chromatogram with ultraviolet light, was obtained from the upper portions of this column. This mixture was purified by a procedure[13] in which an exchange in salt types was carried out as follows: mercuric chloride salts to picrates to mercuric chloride salts to picrates. The picrates thus derived were dissolved in 10 ml. of petroleum ether (b.p. 35–60°) and placed on a column packed with Magnesol–Celite. The picrates were decomposed by the adsorbent, and upon development with petroleum ether the pyridine compounds were separated. The principal zone yielded 0.75 g. of H-4-2. Fraction H-5 was processed in the same manner as H-4. From 7 g. of H-5, 1 g. of H-5-1 and 1 g. of H-5-2 were obtained. The application of these procedures to the higher-boiling fractions did not permit the isolation of any compounds in sufficient quantities such that identification was possible.

The efficiency of the chromatographic separation procedure was determined by treating a mixture of 2-picoline, 4-picoline, 3-picoline and 2,3-lutidine in amounts of 2.0 g. each. Chromatography was effected as described for H-1. The compounds appeared on the column from bottom to top in the order given above, with discrete interzones between each of the zones. Amounts recovered were 2.0 g. of 2-picoline, 1.9 g. of 4-picoline, 1.7 g. of 3-picoline and 1.9 g. of 2,3-lutidine. Picrates of each were prepared and compared with authentic samples.

Derivatives of Pyrroles.—Chromatographic fraction F-1, b.p. 160–163°, yielded the following pyrrole derivatives using procedures described in the literature: tetraiodopyrrole, m.p. 145–148° dec. (reported[14] 149° dec.); pyrrole picrate, m.p. 65–67° (reported[15] 69°); 1-pyrroleacetic acid, m.p. 87–89° (reported[16] 91°); 1-pyrroleacetamide, m.p. 165–168° (reported[16] 169°); 2-pyrrolecarboxanilide, m.p. 150–151.5° (reported[17] 153°); and a condensation product[18] with phthalic anhydride, m.p. 236–239 (reported[19] 240–241°). In each instance the melting point of the derivative admixed with an authentic sample was not depressed. Chromatographic fraction F-2 was characterized as 2-methylpyrrole by preparing the following derivatives by procedures described in the literature: 5-methyl-2-pyrrolecarboxanilide, m.p. 171–173° (reported[17] 173°); 1-*p*-nitrobenzoyl-2-methylpyrrole, m.p. 196–197.5° (reported[20] 198°); and a condensation product[18] with phthalic anhydride, m.p. 212–214° (reported[21] 215°). These compounds did not depress the melting points of authentic samples.

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(10) A product of Westvaco Chlorine Products Co., South Charleston, West Virginia.

(11) A siliceous filter-aid produced by the Johns-Manville Co., New York, N. Y.

(12) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

(13) A. C. Bratton and J. R. Bailey, *ibid.*, **59**, 175 (1937).

(14) G. Ciamician and M. Dennstedt, *Ber.*, **16**, 2582 (1883).

(15) A. Treibs and P. Dieter, *Ann.*, **513**, 65 (1934).

(16) G. R. Clemo and G. R. Ramage, *J. Chem. Soc.*, 49 (1931).

(17) A. Treibs and W. Ott, *Ann.*, **577**, 119 (1952).

(18) H. Fischer and H. Orth, *ibid.*, **502**, 237 (1933), considered this compound to be a pyrroleninephthalide.

(19) G. Ciamician and M. Dennstedt, *Ber.*, **17**, 2957 (1884).

(20) A. Treibs and K.-H. Michl, *Ann.*, **577**, 115 (1952).

(21) G. Ciamician and M. Dennstedt, *Ber.*, **19**, 2201 (1886).

Derivatives of Phenols and Pyridines.—The compounds listed in Tables I and II were prepared by the usual methods. Melting points of all derivatives of phenols and of 4-picoline and 2,6-lutidine were not depressed when admixed with authentic samples.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

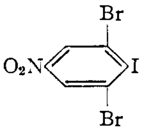
Anomalous Ullmann Reactions. The Unsymmetrical Coupling of 2,6-Dibromo-4-nitroiodobenzene[1]

BY ROBERT B. CARLIN AND EDWARD A. SWAKON[2]

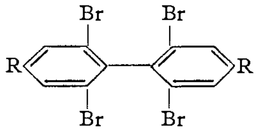
RECEIVED AUGUST 11, 1954

When 2,6-dibromo-4-nitroiodobenzene (I) was treated with copper at 180–220°, four products were isolated and characterized: the "normal" product, 2,2′,6,6′-tetrabromo-4,4′-dinitrobiphenyl (II); plus the by-products 2,3′,6-tribromo-2′-iodo-4,5′-dinitrobiphenyl (IV), 2,6-bis-(2,6-dibromo-4-nitrophenyl)-4-nitroiodobenzene (V), and 3,5-dibromonitrobenzene (VI). The structures of II, IV and V were established by degradations to known compounds or to compounds which were synthesized by other methods. The formation of IV must be the result of an unsymmetrical Ullmann coupling of I, in which one of the two coupling I molecules undergoes displacement of a bromine atom rather than of the normally more active iodine atom, which in this case is further activated by a *p*-nitro group. The interaction of I and IV undoubtedly accounts for the formation of V. The hydrogenolysis of the carbon–iodine bond of I yields VI; reactions of this type have been observed by other investigators.

During an investigation of the benzidine rearrangement of 3,3′,5,5′-tetrabromohydrazobenzene,[3] an independent synthesis of 2,2′,6,6′-tetrabromobenzidine (III) appeared desirable. A synthetic route starting with 2,6-dibromo-4-nitroiodobenzene (I) offered some promise; the Ullmann transformation of I should yield the tetranitrobiphenyl II, which should be reducible to III.



I

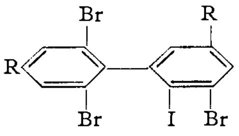


II, R = NO_2
III, R = NH_2
VII, R = NHAc

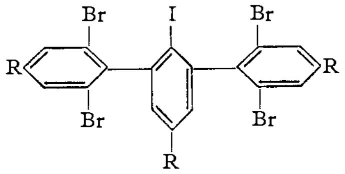
Known behavior of the halogenated benzenes in the Ullmann reaction suggested that the iodine atom of I should be far more readily displaced than the bromine atoms in the coupling by copper, for iodobenzenes are in general more active than bromobenzenes, and nitro groups *para* to halogen exert a pronounced activating effect whereas *meta* nitro groups have little influence.[4]

The synthesis I → II → III has now been accomplished, but an investigation of the action of copper on I disclosed that other products than II were formed. The by-products proved to be 2,3′,6-tribromo-2′-iodo-4,5′-dinitrobiphenyl (IV), 2,6-bis-(2,6-dibromo-4-nitrophenyl)-4-nitroiodobenzene (V) and 3,5-dibromoaniline (VI). This report is concerned with the isolation of the products from the Ullmann mixture, the characterization and proof of structure of each product and something of its mode of formation.

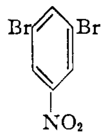
After I was mixed with sand and heated with copper–bronze powder at 180–220° for about a half hour, II, IV, V and VI were isolated in 30, 20, 4 and 5% yields, respectively; I was recovered unchanged in 10% yield, and a glassy resin accounted for an additional 15% of the weight of the starting material. No appreciable changes in the nature or ratio of products were effected by using nitrobenzene or mesitylene as solvents, by "activating" the copper powder,[5] by excluding atmospheric moisture from the mixture or by carrying out the reaction in a nitrogen atmosphere. The components of the reaction mixture were separated by solvent extraction and fractionation, steam distillation and high-vacuum sublimation. Such were the properties of IV and V that they were isolated from the mixture more easily than was II. Indeed, despite the fact that more II is formed than IV or V, the presence of II among the products was not discovered until long after both IV and V had been found. The operational details of the separation are described in the Experimental Section.



IV, R = NO_2
VIII, R = NH_2
IX, R = NHAc
X, R = H



V, R = NO_2
XV, R = NH_2
XVI, R = NHAc



VI

Proof of Structure of II.—The symmetrical tetrabromodinitrobiphenyl II could be obtained in either of two apparently dimorphic modifications; one, m.p. 174–175°, crystallized from methanol, but this form gave the second one, m.p. 184–185°, when subjected to high-vacuum sublimation. Analysis showed the two forms to be isomeric.

The structure of II was established on the basis of the following evidence. Treatment of a solution of II in ethanol with hydrogen in the presence of Raney nickel gave benzidine identified by com-

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(1) From the D. Sc. Thesis by Edward A. Swakon.

(2) Institute Graduate Fellow in Organic Chemistry, 1950–1951.

(3) R. B. Carlin and W. O. Forshey, Jr., THIS JOURNAL, **72**, 793 (1950).

(4) (a) *Cf.* P. E. Fanta, *Chem. Revs.*, **38**, 139 (1946); (b) W. Davey and R. W. Lattner, *J. Chem. Soc.*, **264** (1948).

(5) E. C. Kleiderer and R. Adams, THIS JOURNAL, **55**, 4219 (1933).