NOTES.

Preparation of 4 : 6-*Dimethoxytoluquinone.* By Albert E. Oxford.

THE methylating action of diacetyl peroxide on quinones (Fieser and Oxford, *J. Amer. Chem. Soc.*, 1942, **64**, in the press; Oxford, this vol., p. 577) provides a shorter route to 4 : 6-dimethoxytoluquinone than those starting from *o*-toluidine (Aulin and Erdtman, *Svensk Kemisk. Tids.*, 1938, **50**, 42; Anslow, Ashley, and Raistrick, J., 1938, 439).

Pyrogallol was methylated and oxidised to yield an equal weight of 2 : 6-dimethoxybenzoquinone by Baker's method (J., 1941, 665). To a solution of diacetyl peroxide (3·6 g.) (Gambarjan, *Ber.*, 1909, **42**, 4010) in glacial acetic acid (320 ml.), 2 : 6-dimethoxybenzoquinone (6·0 g.; 18% excess) was added, and the whole stirred at 80° until the quinone had dissolved and then maintained at 100° until evolution of carbon dioxide ceased (40 mins.). The cooled brown liquid was poured into water (1250 ml.) and extracted twenty-one times with light petroleum (about 300 ml. each time) and twice with carbon tetrachloride. The first seven light petroleum extracts were evaporated to dryness, and the residue crystallised from a very little carbon tetrachloride (at 3°) and then from ligroin (b. p. 80—100°) to yield 0·5 g., m. p. 123—125° (lit., 125°). The last fourteen light petroleum extracts were concentrated to very small volume; the product that crystallised was recrystallised from ligroin to yield 0·6 g., m. p. 121—125°. The carbon tetrachloride extracts were concentrated, chilled, and filtered from unchanged 2 : 6-dimethoxybenzoquinone, and the remainder of the solvent removed. The residue was collected, after trituration with methanol, and crystallised from ligroin to yield 0·2 g., m. p. 124—125°. The total yield was thus 1·3 g. of almost pure 4 : 6-dimethoxytoluquinone, *i.e.*, about 20% of the theoretical. A final crystallisation from methanol yielded 0·8 g. of the pure quinone, m. p. 125—126°.

The carbon tetrachloride mother-liquor from the crystallisation of the product from the first light petroleum extracts was evaporated to dryness, and the residue, after trituration with methanol, was crystallised successively from ligroin, aqueous methanol, and ligroin to yield 0·05 g. of pure 2 : 6-dimethoxy-3 : 5-dimethylbenzoquinone, m. p. 134° (see Oxford, *loc. cit.*). An impracticably large excess of 2 : 6-dimethoxybenzoquinone would evidently be required in order to suppress dimethylation entirely.—London School of Hygiene and Tropical Medicine, University of London. [*Received, July* 31*st*, 1942.]

Preparation of 2 : 3 : 5 : 6-*Tetrabromobenzoquinone.* By Herbert H. Hodgson and Clifford K. Foster.

2 : 6-Dibromo-4-nitrophenol (10 g.) in boiling 20% aqueous sodium hydroxide (50 c.c.) was treated with sodium hyposulphite (hydros) until the orange-red colour had almost vanished; on neutralisation, 2 : 6-dibromo-4-aminophenol separated as a white precipitate. This was immediately made into a paste with water (50 c.c.) and sulphuric acid (5 c.c., *d* 1·84) and treated at 5° with sodium nitrite (2·4 g. in the minimum quantity of water), 2 : 6-dibromo-4-diazobenzene-1-oxide (9 g.) separating (Found: Br, 57·8. Calc.: Br, 57·9%). The diazo-oxide (2 g.) was added slowly to bromine (2 c.c.) in glacial acetic acid (30 c.c.) at 80°, and the mixture heated at 100° until the excess of bromine had been removed. On cooling, yellow crystals (3 g.) of 2 : 3 : 5 : 6-tetrabromobenzoquinone separated, m. p., after recrystallisation from benzene, and mixed m. p. with an authentic specimen 300° (Found: Br, 75·5. Calc.: Br, 75·5%).

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Group) for gifts of chemicals.—Technical College, Huddersfield. [*Received, July* 11*th*, 1942.]

A Colour Test for Certain Carcinogenic Hydrocarbons. By E. B. Lisle.

Test papers prepared by steeping strips of pure filter-paper in a solution containing 4 g. of silver nitrate in 100 c.c. of water and 5 c.c. of a 0·08% solution of methylene-blue are dried and then soaked in a solution containing 2·8 g. of potassium bromide in 100 c.c. of water. The operations are carried out in a dark room, and the dried papers stored in a black glass airtight bottle. A drop of a solution containing 2 mg. of a hydrocarbon in 10 c.c. of pure toluene is placed on the almost white test paper, which is then illuminated with light, λ 4200—4400 A., for 5 minutes. In the presence of a carcinogenic hydrocarbon a blue-grey spot develops in many cases. 3 : 4-Benzpyrene, methylcholanthrene, cholanthrene, 5 : 6-*cyclo*penteno-1 : 2-benzanthracene, 1 : 2 : 5 : 6-dibenzfluorene, 9 : 10-dimethyl-1 : 2-benzanthracene, 1 : 2 : 5 : 6-dibenzanthracene afforded positive results. The non-carcinogenic compounds anthracene, chrysene, 1 : 2-benzanthracene, and faintly carcinogenic 9 : 10-dimethyl-1 : 2 : 5 : 6-dibenzanthracene gave negative results.—92, Durham Road, Blackhill, Co. Durham. [*Received, May 20th,* 1942.]

The Preparation of Certain 2-Thiolpyridine Derivatives. By Montague A. Phillips and Harry Shapiro.

The preparation of 2-thiolpyridine by the action of alcoholic potassium hydrosulphide on the corresponding chloro-derivative (Markwald, Klemm, and Trabert, *Ber.*, 1900, **33**, 1556) was considered inconvenient; the preparation of 5-nitro-2-thiolpyridine by this method, however, seems to be satisfactory (Rath, *Annalen*, 1931, **487**, 105; U.S. Pat., 1,753,658). Both these compounds have now been obtained by methods based on the work on alkyl *iso*thioureas by Johnson and Sprague (*J. Amer. Chem. Soc.*, 1936, **58**, 1348; 1937, **59**, 1837).

2-*Thiolpyridine*.—2-Bromopyridine (15·8 g.), thiourea (7·6 g.), and alcohol (50 c.c.) were refluxed for 1 hour; after cooling, aqueous ammonia (*d* 0·880; 30 c.c.) was added, the mixture kept for 5 days at room temperature, the alcohol removed under reduced pressure, and the residue acidified with acetic acid and extracted with chloroform. Removal of the solvent gave 2-thiolpyridine (7·5 g.), m. p. 116—120°, sufficiently pure for many purposes. Recrystallised from benzene it melted at 125° (yield, 5·3 g. or 47% of the theoretical).

5-*Nitro*-2-*thiolpyridine*.—2-Chloro-5-nitropyridine (Phillips, J., 1941, 12) (20 g.) was added to a solution of potassium hydrosulphide made by dissolving potassium hydroxide (15 g.) in methyl alcohol (300 c.c.) and saturating the solution with hydrogen sulphide. The mixture was refluxed for 1 hour, the alcohol removed under reduced pressure, and the residue dissolved in water (125 c.c.) and acidified (Congo-red) with hydrochloric acid. The precipitated thiol compound, dried in a vacuum, had m. p. 169°; Rath (*loc. cit.*) gives m. p. 171—172° (yield, 17·7 g. or 90%).

Both thiol compounds were identified and distinguished from the corresponding disulphides by the fact that they absorbed the theoretical amount of iodine to yield the latter, when dissolved in methanol.

2-(5-*Nitropyridyl*)iso*thiourea Hydrochloride*.—A solution of thiourea (7·6 g.) in alcohol (50 c.c.) containing 2-chloro-5-nitropyridine (15·8 g.) was refluxed for 1 hour and cooled. The crystalline solid obtained (18·0 g.; 77%) had m. p. 191° (decomp.), not raised by recrystallisation from alcohol (Found : N, 23·9; Cl, 15·0. $C_6H_6O_2N_4S,HCl$ * requires N, 23·8; Cl, 15·1%). Treatment of this water-soluble material, which is probably identical with the so-called "addition compound" of Surrey and Lindwall (*J. Amer. Chem. Soc.*, 1940, **62**, 1698) and from which they obtained 5 : 5′-dinitro-2 : 2′-dipyridyl disulphide, with excess of aqueous ammonia as described under 2-thiolpyridine gave a yield of 85% of 5-nitro-2-thiolpyridine.

2-(5-*Aminopyridyl*)iso*thiourea Dihydrochloride*.—The above nitro-compound (10 g.) was reduced by refluxing for 1 hour with stannous chloride (30 g.) and tin (18 g.) in concentrated hydrochloric acid (46 c.c.). After dilution with water (100 c.c.) and removal of tin as sulphide the filtrate was evaporated to dryness under reduced pressure. The residue, crystallised from alcohol, had m. p. 204° (decomp.) (yield, 5·0 g.) (Found : N, 21·5 : Cl, 27·1. $C_6H_8N_4S,2HCl,H_2O$ requires N, 21·6; Cl, 27·4%). The amino-group is diazotisable.—Research Laboratories, Messrs. May and Baker Ltd., Dagenham. [*Received, May 22nd,* 1942.]

The Interaction of Dimethylaniline and Nitric Acid. By Herbert H. Hodgson and Gerald Turner.

The investigation was undertaken to confirm, correlate, and where necessary amplify existing information on the reactions of dimethylaniline with nitric acid. Seven concentrations of acid were used, *d* 1·52, 1·42, 1·34, 1·254, 1·12, 1·046 and 1·024, the reactions were all carried out at 0° (and some at other temperatures), and the amount of acid was always in excess of that required for trinitration of the dimethylaniline, *e.g.*, dimethylaniline (5 g.) with 100 c.c. of the acid except at *d* 1·024, where 200 c.c. were used.

The results illustrate the variation with concentration of the dual action of nitric acid, *viz.*, nitration and oxidation. The latter is substantial only around *d* 1·12; the former not only becomes predominant with increasing acid density, but is accompanied by expulsion of a methyl group, a process which becomes more facile as the density of the acid or its temperature increases.

With nitric acid of *d* 1·52 at −5° to 0°, the product was entirely *N* : 2 : 4 : 6-tetranitromethylaniline. Van Romburgh (*Rec. Trav. chim.*, 1883, **2**, 108) used the nitric acid in 98% sulphuric acid at temperatures up to 55°.

At *d* 1·42, only 2 : 4 : 6-trinitromethylaniline was obtained at 0°. At room temperature initially, a violent reaction occurred with rise of temperature and deposition of 2 : 4-dinitromethyl- and 2 : 4-dinitrodimethyl-aniline. Similarly, 2 : 4 : 6-trinitromethylaniline was obtained from 2 : 4-dinitrodimethylaniline.

At *d* 1·34 and at *d* 1·254, practically pure 2 : 4-dinitrodimethylaniline was obtained in almost quantitative yield at 0° in 30—60 minutes. When the temperature was allowed to rise, a mixture of 2 : 4-dinitromethyl- with some 2 : 4-dinitrodimethyl-aniline was formed. If the reaction mixtures with nitric acid of *d* 1·34 and 1·254 were kept overnight, all the product became 2 : 4-dinitromethylaniline.

The oxidising action of nitric acid was greatest at *d* 1·12, about 40% of the total yield being the alcohol-insoluble 3 : 3′ : 5′ : 5′-tetranitrotetramethylbenzidine. Mertens (*Ber.*, 1886, **19**, 2125; cf. also van Romburgh, *Rec. Trav. chim.*, 1886, **5**, 243) gives m. p. 240—260°. If the product is crystallised from nitrobenzene, however, orange-red prisms are obtained, m. p. 273° (decomp. 275°) (Found : N, 20·2. Calc.: N, 20·0%). The remaining 60%, soluble in alcohol, was mostly 2 : 4-dinitrodimethylaniline.

Nitric acid of *d* 1·046 and 1·024 did not react with dimethylaniline at room temperature during a fortnight, but on gradual addition of sodium nitrite *p*-nitrosodimethylaniline nitrate was precipitated (cf. Earl and Mackney, *J. Proc. Roy. Soc. NS.W.*, 1933, **67**, 231) in amount almost equivalent to that of the sodium nitrite added, but always containing a small amount of *p*-nitrodimethylaniline (cf. Hodgson and Nicholson, J., 1941, 470). If excess of solid sodium nitrite was added fairly rapidly, small amounts of 3 : 3′-dinitrotetramethylbenzidine and *p*-nitromethylaniline accompanied the *p*-nitrosodimethylaniline.

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* Surrey and Lindwall erroneously give the formula as $C_6H_7O_2N_2SCl$.

In all cases, addition of sodium nitrite accelerated the reactions, and with acid of *d* 1·12 it produced a little *N*-nitroso-*p*-nitromethylaniline, while diminishing the yield of 3 : 3′ : 5 : 5′-tetranitrotetramethylbenzidine from *ca.* 40% to *ca.* 2·5%. With nitric acid of *d* 1·12 at 50°, only *ca.* 2·0% of the last-named compound was formed, almost pure 2 : 4-dinitrodimethylaniline being the main product in contrast to the much more contaminated product formed at 0°. Urea almost inhibited the reaction in acid of *d* 1·12 and delayed considerably the reactions in the more concentrated acids.

Nitric acid, *d* 1·42, expelled the methyl groups from 3 : 3′ : 5 : 5′-tetranitrodimethylbenzidine; the product crystallised rapidly from hot nitrobenzene in bright yellow, lenticular plates or slowly in rhomboidal plates, m. p. 227° (decomp.) (van Romburgh, *Rec. Trav. chim.*, 1886, **5**, 240, describes the compound as exploding above 220°) (Found : N, 23·4. Calc. : N, 23·2%). This behaviour is parallel with that of nitric acid on dimethylaniline, and on 2 : 4-dinitrodimethylaniline, both of which formed 2 : 4 : 6-trinitromethylaniline with acid of *d* 1·42 and *N* : 2 : 4 : 6-tetranitromethylaniline with acid of *d* 1·5.

p-Nitrosodimethylaniline, dissolved in acid of *d* 1·42, gave 2 : 4-dinitrodimethylaniline at 0° and 2 : 4-dinitromethylaniline when the temperature was allowed to rise.

The authors thank Imperial Chemical Industries (Dyestuffs) Ltd. for gifts of chemicals.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, May 20th,* 1942.]

Preparation of 1 : 2 : 4 : 5-*Tetraphenylbenzene from Benzylideneacetophenone.*

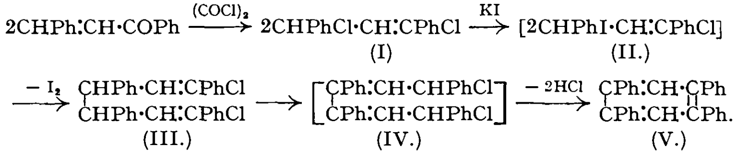
By ALEXANDER SCHÖNBERG and ABDEL FATTAH ALY ISMAIL.

STRAUS and EHRENSTEIN (*Annalen*, 1925, **442**, 105) showed that benzylideneacetophenone, when treated with phosphorus pentachloride, yielded the abnormal ketochloride *αγ*-dichloro-*αγ*-diphenylpropylene (I) (compare also Straus, *ibid.*, 1912, **393**, 238). The same substance was prepared more conveniently by means of oxalyl chloride (Staudinger, *Ber.*, 1909, **42**, 3975).

Straus and Ehrenstein (*loc. cit.*), by the action of phenylmagnesium bromide on (I), obtained a small amount of a substance, m. p. 152—154° (decomp.), believed to be *αζ*-dichloro-*αγδζ*-tetraphenyl-$\Delta^{\alpha\epsilon}$-hexadiene (III), as a by-product.

We treated (I) in dry acetone with potassium iodide; iodine was liberated and from the product (III) was obtained in good yield. This process proceeds probably in two stages : (1) one chlorine atom in (I), which is very reactive, is replaced by iodine with the formation of (II); (2) iodine is liberated and the two residues unite with the formation of (III). This reaction is similar to the formation of ethyl ethylenetetracarboxylate from ethyl dibromomalonate by means of sodium iodide (Finkelstein, *Ber.*, 1910, **43**, 1528).

When (III) is heated above its m. p., hydrogen chloride is evolved and 1 : 2 : 4 : 5-tetraphenylbenzene (V) formed almost quantitatively. It is assumed that (III) tautomerises to (IV), from which two molecules of hydrogen chloride are easily liberated. Substances (II) and (IV) are hypothetical intermediates. 1 : 2 : 4 : 5-Tetraphenylbenzene is thus now easily available.



$$2\mathrm{CHPh{:}CH{\cdot}COPh} \xrightarrow{(\mathrm{COCl})_2} \underset{\text{(I)}}{2\mathrm{CHPhCl{\cdot}CH{:}CPhCl}} \xrightarrow{\mathrm{KI}} \underset{\text{(II.)}}{[2\mathrm{CHPhI{\cdot}CH{:}CPhCl}]}$$

$$\xrightarrow{-\mathrm{I}_2} \underset{\text{(III.)}}{\begin{array}{l}\mathrm{CHPh{\cdot}CH{:}CPhCl}\\ |\\ \mathrm{CHPh{\cdot}CH{:}CPhCl}\end{array}} \longrightarrow \underset{\text{(IV.)}}{\left[\begin{array}{l}\mathrm{CPh{:}CH{\cdot}CHPhCl}\\ |\\ \mathrm{CPh{:}CH{\cdot}CHPhCl}\end{array}\right]} \xrightarrow{-2\mathrm{HCl}} \underset{\text{(V.)}}{\begin{array}{l}\mathrm{CPh{:}CH{\cdot}CPh}\\ |\qquad\quad\ \ \|\\ \mathrm{CPh{:}CH{\cdot}CPh.}\end{array}}$$

αζ-Dichloro-αγδζ-tetraphenyl-$\Delta^{\alpha\epsilon}$*-hexadiene* (III).—Benzylideneacetophenone (5 g.) was refluxed with oxalyl chloride (3·6 g.) for 10 hours (calcium chloride guard-tube) (Staudinger, *loc. cit.*), the excess of oxalyl chloride driven off, and the product (I) dissolved in acetone (50 c.c., free from water and alcohol). On addition of potassium iodide (9 g.) iodine was almost immediately liberated. After 7 hours' refluxing, the mixture was cooled in ice, and the precipitate (III) collected and washed with sulphurous acid. A further quantity was obtained from the acetone filtrate by concentration and cooling or by pouring in sulphurous acid and cooling. The precipitate separated from acetone, acetone–methyl alcohol, or chloroform–methyl alcohol (charcoal) in colourless crystals, m. p. 159—160° (decomp. and formation of a red liquid) (Found : C, 79·1; H, 5·3. Calc. for $C_{30}H_{24}Cl_2$: C, 79·1; H, 5·3%).

1 : 2 : 4 : 5-*Tetraphenylbenzene* (V).—1 G. of (III) was heated at about 200° (bath temp.) for 1 hour with occasional stirring, hydrogen chloride being evolved. The product separated from benzene–light petroleum (b. p. 70—80°) in long colourless needles, m. p. 264° (sublimation). not depressed by authentic 1 : 2 : 4 : 5-tetraphenylbenzene (Durand and Hsun, *Compt. rend.*, 1930, **191**, 1461; cf. Dilthey and Hurtig, *Ber.*, 1934, **67**, 2004) (Found : C, 94·4; H, 5·6. Calc. for $C_{30}H_{22}$: C, 94·3; H, 5·7%). The yield was almost quantitative.—FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, April 24th,* 1942.]