Preparation and Reactions of Diphenylene.

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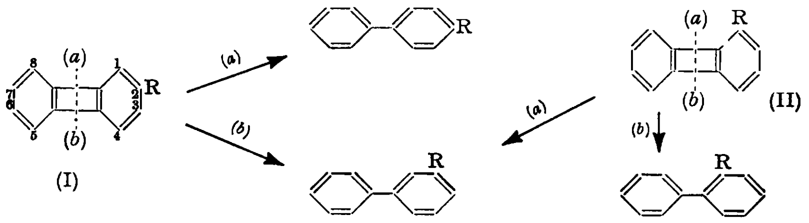
The synthesis of diphenylene (I; R = H) has been improved. With acetyl chloride and aluminium chloride it gives 2-acetyldiphenylene, in agreement with predictions based on wave-mechanics. The acetyl derivative has been converted *via* its oxime and the 2-acetamido-compound, into 2-aminodiphenylene, and into diphenylene-2-carboxylic acid by reaction with sodium hypochlorite. Reduction of 2-acetyldiphenylene by Raney nickel containing adsorbed hydrogen gives a mixture of 3- and 4-acetyldiphenyl, thus establishing the position of the acetyl group.

Diphenylene (I; R = H) was first prepared by Lothrop (*J. Amer. Chem. Soc.*, 1941, **63**, 1187) by distillation of 2 : 2′-dibromo- or better 2 : 2′-di-iodo-diphenyl with cuprous oxide, the yield from the di-iododiphenyl being 15%. It was later obtained from 2 : 2′-dibromodiphenyl in 4% yield by reaction with magnesium and anhydrous cupric chloride (Rapson, Shuttleworth, and van Niekerk, *J.*, 1943, 326). The early history of this hydrocarbon has been given by Lothrop (*loc. cit.*) and by Baker (*J.*, 1945, 258), and the latter has discussed the evidence confirming the structure (I; R = H). Lothrop (*loc. cit.*; *J. Amer. Chem. Soc.*, 1942, **64**, 1698) has prepared 1 : 8- and 2 : 7-dimethyldiphenylene and 2 : 7-dimethoxydiphenylene by the synthesis used for the parent compound.

Diphenylene is representative of the only known type of compound in which there is a four-membered ring fused to a benzene nucleus, and it may also be regarded as a derivative of the unknown *cyclo*butadiene, as shown in formula (I), which represents one of the five purely covalent canonical forms of the molecule. With the exception of preliminary experiments on its catalytic reduction, the chemical properties of diphenylene have not been previously investigated, and the present work was undertaken primarily with the object of studying substitution in the diphenylene nucleus. A further objective was the degradation of one of the benzene nuclei of diphenylene to give a derivative of benzo*cyclo*butene or of benzo*cyclo*butadiene.

The preparation of diphenylene from *o*-chloronitrobenzene *via* 2 : 2′-dinitrodiphenyl, 2 : 2′-diaminodiphenyl, and diphenyl-2 : 2′-iodonium iodide has been improved at each



stage, and special attention has been paid to the final distillation of the iodonium iodide (which first passes into 2 : 2′-di-iododiphenyl) with cuprous oxide, whereby in this last stage the rather variable yield has been raised to an average of 21%. The overall yield of diphenylene from *o*-chloronitrobenzene is now 6—9% (Lothrop, *ca.* 2%). We have been unable to prepare diphenylene (*a*) by heating *o*-di-iodobenzene with cuprous oxide, (*b*) by heating 2-*N*-nitrosoacetamidodiphenyl, (*c*) by electrolysis of aqueous sodium 2 : 2′-diphenate (cf. Weedon, *Quart. Reviews*, 1952, **6**, 380), or (*d*) by heating 2 : 2′-diphenic acid with cuprous oxide or copper chromite; the last reaction gave diphenyl, fluorenone, and the lactone of 2-carboxy-2′-hydroxydiphenyl.

Lothrop found that catalytic reduction of diphenylene over hot copper gave 30% of diphenyl, but an 85% yield is obtained in alcoholic solution in presence of Raney nickel (Baker, *loc. cit.*, p. 266; see Experimental). In presence of a palladium–charcoal catalyst, the reduction proceeds further (*ca.* 3 mols. of hydrogen are absorbed) owing to reduction of the diphenyl to phenyl*cyclo*-hexane and -hexenes. When diphenylene is reduced with sodium and liquid ammonia, a 30% yield of diphenyl is obtained, but reduction products of diphenyl are also obtained in quantity (for reduction of diphenyl with this reagent see Hückel and Bretschneider, *Annalen*, 1939, **540**, 157). Diphenylene is not reduced by amalgamated zinc and hydrochloric acid, or by *cyclo*hexadiene in presence of palladium (cf. Linstead, *Nature*, 1952, **169**, 100).

Diphenylene reacts with acetyl chloride (a large excess is required) and aluminium chloride in carbon disulphide to give 2-acetyldiphenylene (I; R = Ac; for proof of orientation see below) in 58% yield, and a diacetyldiphenylene, probably 2 : 6-diacetyldiphenylene, in 14% yield. The oxime of 2-acetyldiphenylene undergoes the Beckmann rearrangement, best with polyphosphoric acid (Horning and Stromberg, *J. Amer. Chem. Soc.*, 1952, **74**, 2680), and the resulting 2-acetamidodiphenylene is hydrolysed to 2-aminodiphenylene (I; R = NH_2). Oxidation of 2-acetyldiphenylene with sodium hypochlorite gives diphenylene-2-carboxylic acid (I; R = CO_2H), which has been converted into the methyl ester with diazomethane.

The orientation of the acetyldiphenylene depends on reductive cleavage of the 4-membered ring to give a derivative of diphenyl. A 1-substituted diphenylene (II) could give a 2- and a 3-substituted diphenyl as shown. A 2-substituted diphenylene (I) could similarly give a 3- and a 4-substituted diphenyl. Hence only the isolation of a 2- or a 4-substituted diphenyl could give conclusive evidence of orientation. Acetamidodiphenylene resisted hydrogenation in presence of nickel, palladium, or platinum catalysts. When diphenylenecarboxylic acid was warmed with sodium amalgam in aqueous dioxan, or with Raney nickel in ethanol, the yellow colour typical of the diphenylene system was discharged, but no diphenylcarboxylic acid could be isolated, and an examination of the ultra-violet absorption spectrum of the product in conjunction with the spectra of the three authentic diphenylcarboxylic acids (see Table 1) gave no conclusive information. When, however, acetyldiphenylene was warmed with Raney nickel in ethanol, a mixture of acetyldiphenyls was formed. Both chromatographic methods and ultra-violet absorption spectra (see Table 1) of the derived 2 : 4-dinitrophenylhydrazones showed conclusively

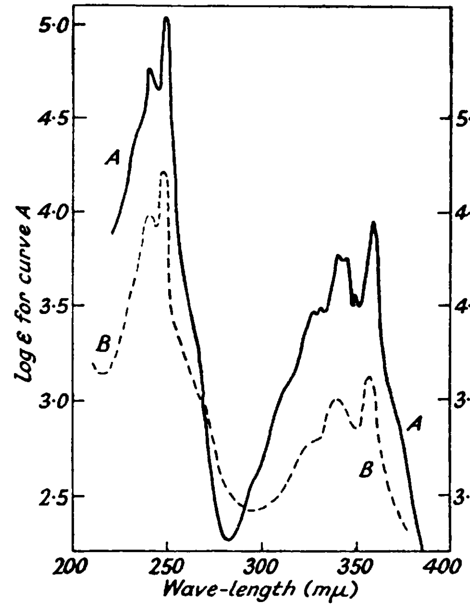
TABLE 1. *Ultra-violet absorption characteristics of diphenyl derivatives.*

Substituents *	Solvent	$\lambda_{max.}$ (mμ)	$\log_{10} \varepsilon_{max.}$	$\lambda_{min.}$ (mμ)	$\log_{10} \varepsilon_{min.}$
4-Acetyl	EtOH	282·5	4·39	239	3·40
2-Carboxylic acid	EtOH	245	4·07	235	4·07
3-Carboxylic acid	EtOH	250	4·22	241	4·21
4-Carboxylic acid	EtOH	264·5	4·42	228	3·73
D.N.P. of 2-acetyl	C_6H_6	369	4·34	310	3·55
D.N.P. of 3-acetyl	C_6H_6	376·5	4·37	316	3·55
D.N.P. of 4-acetyl	C_6H_6	299·5 384	4·12 4·40	282 327	4·06 3·73
D.N.P. of product from acetyldiphenylene	C_6H_6	296 381	4·03 4·39	324 —	3·72 —

* D.N.P. = 2 : 4-dinitrophenylhydrazone.

the presence of the 3- and the 4-substituted diphenyl. From this it follows that in the Friedel–Crafts reaction the acetyl group had entered the 2-position of the diphenylene nucleus.

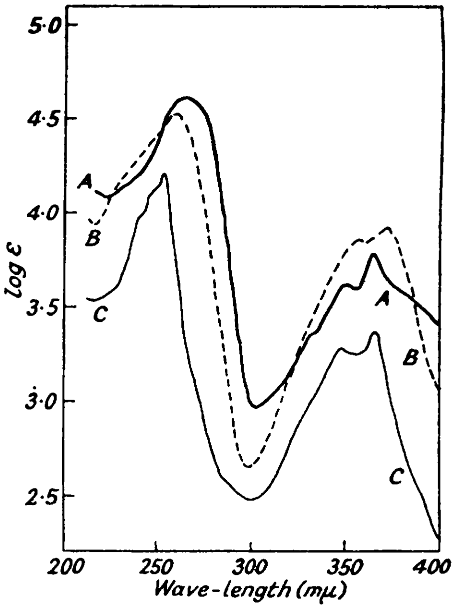
FIG. 1.



A, Diphenylene in ethanol.
B, 2-Aminodiphenylene in N-HCl.

Note. *The log ε scales for A and B are shown on the left- and right-hand sides respectively of the Figure.*

FIG. 2.



A, B, C, 2-Acetyl-, 2-amino-, and x-*hydroxy-diphenylene respectively.*

This orientation of the acetyldiphenylene (I; R = Ac) is in agreement with Brown's theoretical predictions (*Trans. Faraday Soc.*, 1949, **45**, 296; 1950, **46**, 146; see also Waser and Schomaker, *J. Amer. Chem. Soc.*, 1943, **65**, 1451) based on wave-mechanical calculations. The result cannot, however, be claimed as confirming the predictions, because Friedel–Crafts acylation may occur at different positions according to the reaction conditions (*e.g.*, in the case of naphthalene; see Thomas, " Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, 1941, pp. 271 *et seq.*).

Apart from nuclear acetylation, no other simple monosubstitution into the nucleus of diphenylene has been achieved. Bromination and nitration gave inseparable mixtures; sulphonation gave a disulphonic acid of unknown orientation. Ozonisation in carbon tetrachloride yielded a complex mixture of carbonyl compounds. With lead tetra-acetate in acetic acid diphenylene gave a 1·5% yield of a product which appears, from its ultra-violet absorption spectrum, to be a hydroxydiphenylene (see Fig. 2), and the similarity of the spectrum to that of 2-aminodiphenylene suggests further that the hydroxyl group is in position 2. 2-Acetyldiphenylene was not converted into 2-acetoxydiphenylene by hydrogen peroxide in acetic acid (cf. Ballio, *Gazzetta*, 1949, **79**, 924).

From the catalytic reduction of 2 : 2′-dinitrodiphenyl in presence of Raney nickel in ethanol–acetic acid at 30 atmospheres was isolated a crystalline complex of 2 mols. of 2 : 2′-diaminodiphenyl with 1 mol. of nickel acetate. This substance was also obtained under similar conditions from 2 : 2′-diaminodiphenyl and nickel acetate, the identity of the two specimens being established by *X*-ray powder photographs kindly taken by Dr. T. H. Bevan.

The ultra-violet absorption spectrum of diphenylene in hexane solution has been discussed by Carr, Pickett, and Voris (*J. Amer. Chem. Soc.*, 1941, **63**, 3231). The spectrum in ethanol is shown in Fig. 1 (see also Table 2); it agrees well with that obtained in hexane except for a slight shift in wave-length due to the change in solvent. The split peak in the region 330—400 mμ appears to be characteristic of simple diphenylene derivatives; it occurs in all the derivatives so far examined, except the 2 : 4-dinitrophenylhydrazone of 2-acetyldiphenylene where it is probably masked by the absorption of the dinitrophenylhydrazine residue (cf. Roberts and Green, *ibid.*, 1946, **68**, 214). The spectrum of 2-aminodiphenylene in hydrochloric acid (Fig. 1) closely resembles that of the parent hydrocarbon, but the spectrum of the free base in ethanol (Fig. 2) is much less complex; similar behaviour has been observed with other aromatic amines, *e.g.*, 4-aminopyrene (Jones, *ibid.*, 1945, **67**, 2127). The spectra of the oxime of 2-acetyldiphenylene, of 2-acetamido-, 2-carboxy-, and 2-methoxycarbonyl-diphenylene are very similar to that of the 2-acetyl compound (Fig. 2) and are not illustrated graphically.

TABLE 2. *Ultra-violet absorption characteristics of diphenylene derivatives.*

Substituents *	Solvent	λ(mμ)	$\log_{10} \varepsilon_{max.}$	λ(mμ)	$\log_{10} \varepsilon_{max.}$
None	EtOH	239	4·77	339	3·79
		248	5·05	343	3·76
		326	3·47	348	3·58
		330	3·49	358	3·97
2-Acetyl	EtOH	236	4·61	348	3·63
				363	3·80
Oxime of 2-acetyl	EtOH	237·5	4·40	355	4·86
		263	4·67	370	3·90
2-Acetamido	EtOH	237	4·36	349·5	3·97
		259	4·81	368	4·07
2-Amino	EtOH	258·5	4·53	357	3·85
				371	3·93
2-Amino	N-HCl	239·5	4·49	330·5	3·30
		248	4·73	339	3·53
				357	3·65
2-Carboxy	EtOH	256·5	4·87	347	3·75
				362	3·91
2-Methoxycarbonyl	EtOH	260	4·77	346	3·66
				360·5	3·83
D.N.P. of 2-acetyl	C_6H_6	295	4·20	375	4·31
				415	4·35
x-Hydroxy (?)	EtOH	253	4·70	346·5	3·78
				364	3·87

* D.N.P. = 2 : 4-dinitrophenylhydrazone.

EXPERIMENTAL

The temperatures recorded for sublimations are those of the heating baths.

Diphenylene.—The modifications of recorded methods are given in the following notes. (1) 2 : 2′-*Dinitrodiphenyl.* (*a*) See *Org. Synth.*, 1940, **20**, 45; the weight of copper bronze was reduced to 150 g. per 200 g. of *o*-chloronitrobenzene. The product (58% yield) was recrystallised twice before reduction. (*b*) See von Niementowsky, *Ber.*, 1901, **34**, 3325; copper bronze activated by iodine (Kleiderer and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4219) may replace the freshly precipitated copper powder. Pure 2 : 2′-dinitrodiphenyl is isolated directly in 44—53% yield. (2) 2 : 2′-*Diaminodiphenyl.* Catalytic reduction is more convenient than the use of tin and hydrochloric acid. Pure 2 : 2′-dinitrodiphenyl (60 g.) with Raney nickel (15 g.; Brown, *J. Soc. Chem. Ind.*, 1950, **69**, 353) suspended in ethanol (400 c.c.) and glacial acetic acid

(10 c.c.) in a steel bomb, was hydrogenated at 110°/30 atm. for 30—40 min. The considerable heat of reaction makes it desirable to interrupt the external heating for 1 hr., after which it is resumed for 4½ hr. The filtered solution was poured into water (2 l.) at 60° with vigorous stirring, and after cooling to 0° gave light brown, or colourless, crystals (36 g., 80%). (3) Diphenyl-2 : 2'-iodonium iodide was prepared from the diamine in 69% yield by Lothrop's method. (4) *Diphenylene.* Pyrolysis of the preceding compound was conducted in a short-necked, 150-c.c. flask fitted with an air-condenser having a pear-shaped bulb close to the ground joint attaching it to the flask. The apparatus was inclined at *ca.* 25° to the horizontal and rotated (*ca.* 100 rev./min.) by a motor attached co-axially to the top of the condenser. The flask dipped into a fusible metal-bath fitted with a lid, and the metal surface was covered with a thick layer of charcoal. The iodonium iodide (10 g.) was powdered with cuprous oxide (80 g.), the mixture heated for a few minutes at 100°/1 mm. in the reaction flask, which was then attached to the condenser and rotated in the metal-bath (pre-heated to 350—360°) for 4 min. The sublimed diphenylene was extracted into methanol (50 c.c.) and steam-distilled, giving diphenylene (1·055 g., 28%), m. p. 95—102°. Two recrystallisations from methanol raised the m. p. to 110—111°.

In a series of 12 runs, the yield of once recrystallised diphenylene, m. p. 106—109°, varied from 15 to 30% (average 21%). The mother-liquors yielded also diphenyl, 2-iododiphenyl, and carbazole. The dark yellow-green residue from the steam-distillation was collected and dissolved in methanol (50 c.c.) (charcoal), and the solution was filtered and concentrated (to *ca.* 20 c.c.), giving 2 : 2'-di-iododiphenyl (*ca.* 1·0 g. from a 10-g. run), m. p. 110°. Phenazone was also isolated as its picrate (cf. Lothrop, *loc. cit.*). The cuprous oxide may be used for at least five experiments without significant loss of activity. The *complex* of diphenylene with 2 : 4 : 7-trinitrofluorenone formed deep scarlet needles (from ethanol), m. p. 154° (decomp.) (Found: C, 64·1; H, 2·9; N, 9·2. $C_{12}H_8,C_{13}H_5O_7N_3$ requires C, 64·25; H, 2·8; N, 9·0%).

Complex of 2 : 2'-Diaminodiphenyl with Nickel Acetate.—In some of the reductions of 2 : 2'-dinitrodiphenyl the spent catalyst contained greenish-blue crystals. These were separated by shaking the mixture with chloroform: only the crystals floated. After several repetitions the compound was obtained in a fairly pure state. It was insoluble in the usual organic solvents, could not be recrystallised, and decomposed when boiled with water for 5 min., giving 2 : 2'-diaminodiphenyl (m. p. and mixed m. p. 78—80°) and a solution giving a strong positive reaction with dimethylglyoxime for nickel; the presence of acetate was revealed by the indigo test (Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publ. Co., New York, 1948). These and the analytical results suggested that the blue compound was a 2 : 1 *complex* of 2 : 2'-diaminodiphenyl with nickel acetate (Found, in material in which microscopical examination revealed the presence of traces of nickel: C, 60·8, 60·9; H, 5·4, 5·6; N, 10·9; Ni, 12·2. $C_{28}H_{30}O_4N_4Ni$ requires C, 61·7; H, 5·5; N, 10·3; Ni, 10·8%). The same complex was produced on heating ethanol–acetic acid solutions of nickel acetate and the diamine under pressure as in the catalytic reduction.

Catalytic Reduction of Diphenylene.—Ethanol (35 c.c.) and Raney nickel (0·25 g.) were saturated at room temperature and pressure with hydrogen. Diphenylene (0·5 g.) was then added from a side-arm and the hydrogenation continued (4 hr.) until one equivalent of hydrogen had been absorbed. The solution yielded crude diphenyl (0·43 g.; m. p. 56°), which, after two recrystallisations from aqueous methanol, had m. p. and mixed m. p. 70°.

Reduction by Sodium in Liquid Ammonia.—Liquid ammonia (*ca.* 100 c.c.) was added to a solution of diphenylene (0·30 g.) in ether (25 c.c.), followed by sodium (0·27 g.; 6 equivs.) in small portions. The solution changed in colour through yellow, purple, and deep blue to deep olive-green. Next day the residual solid was treated with water and extracted with ether. Removal of the ether and fractional sublimation yielded diphenyl (0·10 g., 30%), m. p. 66—67° (mixed m. p. with pure diphenyl, 69—70°). The lower- and higher-boiling fractions were unsaturated oils.

2-*Acetyl- and* 2 : 6(?)-*Diacetyl-diphenylene.*—Diphenylene (0·300 g.) was added to finely powdered aluminium chloride (0·300 g., 1·1 equivs.) and acetyl chloride (2·25 g., 10 equivs.) in pure, dry carbon disulphide (40 c.c.), and the mixture, which became deep red, was gently warmed on a water-bath for 1 hr. Next day dilute hydrochloric acid was added and, when the red crystalline aluminium chloride complex had decomposed, the mixture was filtered from the diacetyl derivative (0·066 g.). The filtrate was extracted with carbon disulphide and yielded a solid which was fractionally sublimed, giving diphenylene (collected at 100°/20 mm.) and 2-*acetyldiphenylene* (0·220 g.), m. p. 133—134° (collected at 130°/20 mm.). Recrystallisation from aqueous ethanol gave the pure compound as glistening yellow plates, m. p. 134—135°

(Found: C, 86·4; H, 5·1. $C_{14}H_{10}O$ requires C, 86·6; H, 5·2%). The 2 : 4-*dinitrophenylhydrazone* separated from acetic acid as bright red crystals, m. p. 257—258° (Found: C, 64·3; H, 3·7; N, 14·9. $C_{20}H_{14}O_4N_4$ requires C, 64·2; H, 3·75; N, 14·95%).

The 2 : 6(?)-*diacetyldiphenylene* mentioned above was recrystallised from ethanol and formed deep yellow needles, m. p. 247—248° (Found: C, 81·2; H, 5·0. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%).

2-Acetyldiphenylene gave an *oxime* as fine, pale yellow needles (from aqueous ethanol), m. p. 176° (Found: C, 80·2; H, 5·25; N, 6·8. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3; N, 6·7%).

2-*Acetamidodiphenylene*.—(a) *By use of polyphosphoric acid* (Horning and Stromberg, *loc. cit.*). The oxime (0·100 g.) was added to polyphosphoric acid (3·0 g.; *ca.* 84% P_4O_{10}), and the mixture kept at 100° for 10 min. The green, viscous solution was diluted and the solid extracted into ether–ethyl acetate (1 : 1), and sublimed. The 2-*acetamidodiphenylene* (0·060 g.; 60%) formed pale yellow plates, which after recrystallisation from aqueous ethanol had m. p. 146—147° (Found: C, 80·4; H, 5·1; N, 6·6. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3; N, 6·7%).

(b) *By use of phosphorus pentachloride.* Phosphorus pentachloride (0·100 g.) was added to the oxime (0·100 g.) in dry ether and, after 10 minutes' treatment with ice, extraction with ether–ethyl acetate and sublimation gave 2-acetamidodiphenylene (0·040 g.), m. p. 135—138°.

2-*Aminodiphenylene*.—2-Acetamidodiphenylene (0·05 g.) was heated with water (5 c.c.), concentrated hydrochloric acid (5 c.c.), and ethanol (1·0 c.c.) for 1 hr. On cooling, a hydrochloride separated. Addition of excess of dilute sodium hydroxide solution and extraction with ether gave 2-*aminodiphenylene*, which, after two sublimations, formed bright yellow needles (0·03 g.), m. p. 123—124° (Found: C, 86·2; H, 5·5; N, 8·6. $C_{12}H_9N$ requires C, 86·3; H, 5·4; N, 8·4%).

Diphenylene-2-*carboxylic Acid*.—Chlorine (0·7 g.) was passed into a cooled solution of sodium hydroxide (1·0 g.) in water (10 c.c.); of the resultant solution a portion (4 c.c.) was added to 2-acetyldiphenylene (0·100 g.) in dioxan (6 c.c.) at 70° and the mixture (2 layers) heated on a water-bath for ½ hr. Water was then added to give a homogeneous solution, followed by more sodium hypochlorite solution (2 c.c.), and the heating was continued for ¾ hr. The solution was concentrated under reduced pressure to remove the dioxan, and acidified with concentrated hydrochloric acid, giving a solid (0·090 mg.), m. p. 210—220°. Sublimation at 210°/20 mm., followed by recrystallisation from aqueous methanol, gave *diphenylene*-2-*carboxylic acid* as yellow prisms, m. p. 223—224° (Found: C, 79·5; H, 4·1. $C_{13}H_8O_2$ requires C, 79·6; H, 4·1%).

The *methyl ester*, prepared by diazomethane, sublimed at 130°/20 mm. as pale yellow plates (0·049 g.), m. p. 106—110°. Recrystallisation from aqueous methanol and a further sublimation raised the m. p. to 114—115° (Found: C, 79·7; H, 4·5. $C_{14}H_{10}O_2$ requires C, 80·1; H, 4·8%).

Orientation of the Acetyldiphenylene.—(1) *Action of Raney nickel on diphenylene.* Raney nickel (Brown, *loc. cit.*) (*ca.* 0·2 g.) was added gradually with shaking to a solution of the ketone (0·100 g.) in ethanol (10 c.c.) at 60° until the yellow colour was discharged. The filtered solution and washings were concentrated, excess of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid was added, and the mixture was boiled for several minutes. The dinitrophenylhydrazones were extracted into benzene, and the dried, concentrated extract passed through a column of alumina, which was eluted with benzene–ether (1 : 1), leaving some strongly adsorbed impurities at the top of the column. The eluate was evaporated and the residue crystallised from acetic acid, giving an orange-red product (0·070 g.), m. p. 170—210°.

(2) *Chromatography.* Chromatography of the 2 : 4-dinitrophenylhydrazones of 2-, 3-, and 4-acetyldiphenyl and of the preceding mixture was carried out on strips of Whatman No. 1 filter paper, the spots being detected by their colour in day-light and in ultra-violet light. On use of light petroleum (b. p. 80—100°) and ether (95 : 5), the R_F values of the 2-, 3-, and 4-isomers were 0·79, 0·45, and 0·35 respectively. The mixture gave spots of R_F value 0·45 and 0·35. The colour of the mixture (orange-red) also indicated that the product had this composition since the 2-, 3-, and 4-isomers are yellow, orange, and red respectively.

(3) *Reference compounds.* Samples of the 2 : 4-dinitrophenylhydrazones of 2-acetyldiphenyl (m. p. 169—170°) and 3-acetyldiphenyl (m. p. 191—192°) were kindly provided by Professor E. Campaigne of Indiana University. The 2 : 4-*dinitrophenylhydrazone* of 4-acetyldiphenyl (for preparation of 4-acetyldiphenyl see Gull and Turner, *J.*, 1929, 491) formed bright red plates, m. p. 238—239°, from acetic acid (Found: C, 64·1; H, 4·0; N, 15·0. $C_{20}H_{16}O_4N_4$ requires C, 63·9; H, 4·3; N, 14·9%).

Sulphonation of Diphenylene.—Diphenylene (0·200 g.) was dissolved in concentrated sulphuric acid (1·0 c.c.) and after 24 hr. the solution was poured into water (20 c.c.) and neutralised with barium carbonate. The filtered solution was evaporated almost to dryness (pale yellow crystals separated), dilute sulphuric acid added, the filtered solution again concentrated, *S*-benzylthiuronium hydrochloride added, and the solution heated to boiling and cooled in ice. The solid *salt* was collected and recrystallised several times from water, forming pale yellow needles, m. p. 248—249° (decomp.) (Found: C, 52·1; H, 4·4; N, 7·7. $C_{28}H_{28}O_6N_4S_4$ requires C, 52·2; H, 4·4; N, 8·7%).

Action of Lead Tetra-acetate on Diphenylene.—A solution of diphenylene (0·30 g.) and lead tetra-acetate (0·90 g.) in acetic acid (15 c.c.; distilled from potassium permanganate) was heated on the steam-bath for ½ hr., cooled, and poured into water. The orange solid was collected and heated on a steam-bath with 2N-sodium hydroxide for 40 min. Filtration removed diphenylene, and the dark brown filtrate was acidified with hydrochloric acid, giving a solid which sublimed at 140°/20 mm., giving a pale yellow product (0·005 g.), m. p. 139—140° [Found (on 1·3 mg.): C, 85·1; H, 5·6. $C_{12}H_8O$ requires C, 85·7; H, 4·8%]. The compound gave an intense red colour with alcoholic ferric chloride and is probably a *hydroxydiphenylene*.

We thank Professor D. H. Hey, D.Sc., for samples of diphenyl-2-, -3-, and -4-carboxylic acid, and the Department of Scientific and Industrial Research for a maintenance allowance awarded to M. P. V. B. We acknowledge also the help of Mr. J. W. Barton in preparing diphenylene, and in particular that of Dr. R. F. Curtis in developing the improved synthesis of diphenylene described in this paper.

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