NOTES.

Preparation of Some p-*Alkylsulphonylbenzylammonium Chlorides.* By J. CYMERMAN, A. KOEBNER, and W. F. SHORT.

THE *p*-alkylsulphonylbenzylammonium chlorides described in Table I were prepared in 1944—1945 by the following methods :

(A) $p\text{-Cl}\cdot SO_2\cdot C_6H_4\cdot CN \longrightarrow H\cdot SO_2\cdot C_6H_4\cdot CN \longrightarrow R\cdot SO_2\cdot C_6H_4\cdot CN \longrightarrow R\cdot SO_2\cdot C_6H_4\cdot CH_2\cdot NH_3\}Cl$

(B) $p\text{-Cl}\cdot SO_2\cdot C_6H_4\cdot CH_2\cdot NHAc \longrightarrow H\cdot SO_2\cdot C_6H_4\cdot CH_2\cdot NHAc \longrightarrow R\cdot SO_2\cdot C_6H_4\cdot CH_2\cdot NHAc$

The reduction of *p*-cyanobenzenesulphonyl chloride to *p*-cyanobenzenesulphinic acid is described by Walker (B.P. 580,884; 26.1.1944), Andrewes, King, and Walker (*Proc. Roy. Soc.*, 1946, *B*, **133**, 51), and Fuller, Tonkin, and Walker (*J.*, 1945, 636), who also alkylated the sulphinic acid and reduced two of the resulting *p*-alkylsulphonylphenyl cyanides to *p*-alkylsulphonylbenzylammonium chlorides. In method

(B), we have improved the yield of *p*-acetamidomethylbenzenesulphonyl chloride (Bergeim and Braker, *J. Amer. Chem. Soc.*, 1944, **66**, 1459). Jensen and Schmith (*Z. physiol. Chem.*, 1944, **280**, 37) describe the reduction of this chloride to *p*-acetamidomethylbenzenesulphinic acid and conversion into *p*-methylsulphonylbenzylammonium chloride but an abstract of this paper was not available until long after we had completed our experiments. The reduction of the sulphonyl chloride has since been described by Dewing (*J.*, 1946, 467) and by Carter and Hey (this vol., p. 147).

TABLE I.

p-Alkylsulphonylbenzylammonium chlorides.

p-R·SO$_2$·C$_6$H$_4$·CH$_2$·NH$_3$}Cl; R =	Method.	Yield, %.*	M. p.	Formula.	Found, N, %.	Calc. or reqd., N, %.
(1) Methyl	A and B	*ca.* 100 and 32	275—278°	$C_8H_{12}O_2NClS$	6·4	6·3
(2) Ethyl	A	85	230	$C_9H_{14}O_2NClS$	6·0	5·95
(3) n-*Propyl*	B	—	238—240	$C_{10}H_{16}O_2NClS$	5·6	5·6
(4) iso*Propyl*	A	95	221—222	$C_{10}H_{16}O_2NClS$	5·6	5·6
(5) n-*Butyl*	B	—	267—268	$C_{11}H_{18}O_2NClS$	5·5	5·3
(6) sec.-*Butyl*	A	96	201—202	$C_{11}H_{18}O_2NClS$	5·5	5·3
(7) n-*Amyl*	A	87	265—266	$C_{12}H_{20}O_2NClS$	5·05	5·05
(8) n-*Hexyl*	A	86	263—265	$C_{13}H_{22}O_2NClS$	5·0	4·8
(9) n-*Heptyl*	A	95	260—261	$C_{14}H_{24}O_2NClS$	4·7	4·6
(10) n-*Octyl*	A	90	261·5—262	$C_{15}H_{26}O_2NClS$	4·55	4·4
(11) n-*Hexadecyl*	B	—	235—245	$C_{23}H_{42}O_2NClS$	3·4	3·2
(12) *Benzyl*	B	—	265—270	$C_{14}H_{16}O_2NClS$	4·8	4·7
(13) *Phenyl*	A	45	258—260	$C_{13}H_{14}O_2NClS$	4·9	4·9

* Yields by method (A) are expressed as percentage of theoretical calculated on the cyanide used. In method (B) the yield is calculated on the acetobenzylamide.

(1) Jensen and Schmith (*loc. cit.*) prepared this compound by method (B) and record m. p. 265°. Fuller, Tonkin, and Walker (*loc. cit.*) obtained an 86% yield, m. p. 279—280°, by reduction in 10% ethanolic ammonia at 15—70°/95 atmospheres.

(2) Preparation by Dr. T. D. Robson. The *p*-ethylsulphonylphenyl cyanide was prepared as described by Oxley, Partridge, Robson, and Short (*J.*, 1946, 763). Fuller, Tonkin, and Walker (*loc. cit.*) obtained *p*-ethylsulphonylbenzylammonium chloride, m. p. 222°, in 73% yield, by reduction in saturated ethanolic ammonia at 70 lbs./sq. in.

(13) p-*Cyanodiphenyl sulphone*, m. p. 117—118° (Found: N, 5·8. $C_{13}H_9O_2NS$ requires N, 5·8%), was obtained in 74% yield by heating the corresponding acid (Meyer, *Annalen*, 1923, **433**, 338) and benzenesulphonamide (2 mols.) at 225—230° for 2 hours (cf. Oxley *et al.*, *loc. cit.*).

p-*Cyanobenzenesulphinic Acid.*—A solution of *p*-cyanobenzenesulphonyl chloride (20 g.) (Remsen, Hartman, and Muckenfuss, *Amer. Chem. J.*, 1896, **18**, 156) in hot acetone (30 c.c.) was added during 30 minutes to a well-stirred solution of sodium sulphite heptahydrate (50 g.; 2 mols.) in water (100 c.c.) at 75—80°, the solution being kept alkaline to litmus throughout by periodical addition of sodium carbonate. Heating and stirring were continued for a further 1½ hours, and the sulphinic acid (14 g.; 84·5%), precipitated at 0° by acidification with concentrated hydrochloric acid and collected in ethyl acetate, crystallised from hot water in prismatic plates, m. p. 121—122° (Found: N, 8·55; S, 19·3. Calc. for $C_7H_5O_2NS$: N, 8·4; S, 19·2%). Andrewes, King, and Walker (*loc. cit.*) record m. p. 126—127°, and Fuller, Tonkin, and Walker (*loc. cit.*), m. p. 128—129°. If extraction of the acid solution with ethyl acetate was delayed, a solid separated, and crystallisation from aqueous ethanol gave needles of *bis*-p-*cyanophenyl disulphoxide*, m. p. 158—159° (Found: C, 55·85; H, 2·6; N, 9·45. $C_{14}H_8O_2N_2S_2$ requires C, 56·0; H, 2·7; N, 9·35%).

Alkylation of p-*Cyanobenzenesulphinic Acid.*—A solution of the sodium salt in 50% aqueous ethanol was refluxed with the alkyl halide (1·1—1·2 mols.) for 4—24 hours (see Table II). The *p*-alkylsulphonylphenyl cyanides, precipitated by adding water and crystallised from aqueous alcohol, had the properties recorded in Table II.

Reduction of p-*Alkylsulphonylphenyl Cyanides.**—An approx. 5% solution of the *p*-alkylsulphonylphenyl cyanide in 15% (w/w) methanolic ammonia was shaken with Raney nickel (*ca.* 0·5 g. per g. of cyanide) at 25° in an atmosphere of hydrogen at an initial pressure of 50 lbs./sq. in. When 5 g. of cyanide were used reduction was complete in 1—3 hours. The catalyst was removed by filtration, and the filtrate concentrated to a small volume, saturated with dry hydrogen chloride, and evaporated to dryness. The residue of *p*-alkylsulphonylbenzylammonium chloride was purified by crystallisation from methanol and had the properties recorded in Table I.

p-*Acetamidomethylbenzenesulphonyl Chloride.*—The method of Bergeim and Braker (*loc. cit.*), which gives a 45% yield, was slightly modified. Acetobenzylamide (100 g.) was added during 45 minutes to chlorosulphonic acid (300 c.c.) so that the temperature remained below 15°. The mixture was stirred for an hour at room temperature and then for an hour at 50—60°. The solution was cooled and poured on crushed ice, and the oil which separated solidified when triturated with water containing 2% of ether. After being washed with water and dried in a vacuum the sulphonyl chloride (100 g.; 60%) had m. p. 96—98°. Bergeim and Braker (*loc. cit.*) stated that the pure chloride has m. p. 95—97°.

p-*Acetamidomethylbenzenesulphinic Acid.*†—The preceding sulphonyl chloride (248 g.) and a solution

* See also Boots Pure Drug Co., Koebner, Robson, and Short, B.P. 583,585 (6.10.1944).

† See also Boots Pure Drug Co. Ltd., Koebner and Short, B.P. 584,584 (5.1.1945).

TABLE II.

p-*Alkylsulphonylphenyl cyanides from* p-*cyanobenzenesulphinic acid.*

p-R·SO_2·C_6H_4·CN; R =	Yield, %.*	Time, hrs.	M. p.	Formula.	Found, N, %.	Calc. or reqd., N, %.
(1) Methyl	80	4	142·5—143·5°	$C_8H_7O_2NS$	—	—
(2) *n*-Propyl	75	6	84—85	$C_{10}H_{11}O_2NS$	6·8	6·7
(3) iso*Propyl*	36	15	102	$C_{10}H_{11}O_2NS$	6·6	6·7
(4) *n*-Butyl	80	20	79—80	$C_{11}H_{13}O_2NS$	6·45	6·3
(5) sec.-*Butyl*	50	18	71—72	$C_{11}H_{13}O_2NS$	6·4	6·3
(6) n-*Amyl*	85	19	90—91	$C_{12}H_{15}O_2NS$	5·95	5·9
(7) n-*Hexyl*	90	18	87—88	$C_{13}H_{17}O_2NS$	5·7	5·6
(8) n-*Heptyl*	85	20	96—97	$C_{14}H_{19}O_2NS$	5·5	5·3
(9) n-*Octyl*	75	20	97—97·5	$C_{15}H_{21}O_2NS$	5·15	5·0
(10) n-*Hexadecyl*	95	24	111·5—112	$C_{23}H_{37}O_2NS$	3·7	3·6
(11) Benzyl	95	21	195·5—196	$C_{14}H_{11}O_2NS$	5·55	5·45

* Overall yield from *p*-cyanobenzenesulphonyl chloride.

(1) Prepared from *p*-methylsulphonylaniline in 65% yield by Walker (*loc. cit.*) and by Fuller, Tonkin, and Walker (*loc. cit.*), who record m. p. 141°. Oxley *et al.* (*loc. cit.*) obtained the cyanide, m. p. 142—143°, in 75% yield from *p*-methylsulphonylbenzoic acid and benzenesulphonamide.

(2) Obtained in 80% yield by reduction of the corresponding allyl compound by Fuller *et al.* (*loc. cit.*), who record m. p. 84—85°, and in 64% yield from *p*-*n*-propylsulphonylbenzoic acid and benzenesulphonamide by Oxley *et al.* (*loc. cit.*) who give m. p. 83—84°.

(4) Prepared from sodium *p*-cyanobenzenesulphinate in 69% yield by Fuller *et al.* (*loc. cit.*) who record m. p. 75—76°.

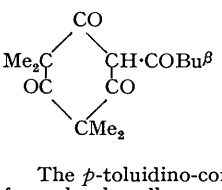
(11) Fuller *et al.* (*loc. cit.*) record m. p. 194—195° for a preparation obtained from the sulphinate in 79% yield.

of sodium sulphite heptahydrate (378 g.; 1 mol.) in water (750 c.c.) were stirred at room temperature, and sodium hydrogen carbonate (170 g.; 2 mols.) was added in portions so that the mixture remained alkaline to litmus throughout. Reduction was complete in 2 hours, and the solution was saturated with sodium chloride to precipitate the rest of the sodium *p*-acetamidomethylbenzenesulphinate. Careful acidification of a solution of this salt at 0° afforded the sulphinic acid, which separated from water in colourless plates, m. p. 139—140° (Found: N, 6·5. Calc. for $C_9H_{11}O_3NS$: N, 6·6%); yield, *ca.* 75%. Jensen and Schmith (*loc. cit.*) record m. p. 137—138°, Dewing (*loc. cit.*) m. p. 148°, and Carter and Hey (*loc. cit.*) m. p. 138°.

p-*Alkylsulphonylbenzylammonium Chloride from* p-*Acetamidomethylbenzenesulphinic Acid.*—A solution of crude sodium *p*-acetamidomethylbenzenesulphinate in 50% aqueous ethanol was refluxed for 3 hours with the alkyl iodide (1·2 mols.), and the solution was then evaporated almost to dryness in a vacuum. The residue was triturated with cold 5% aqueous sodium thiosulphate, the solid was collected, washed with a little ice-water, and hydrolysed by refluxing for 2 hours with 2·5N-hydrochloric adid. The solution was then concentrated to a small volume, and the crude *p*-alkylsulphonylbenzylammonium chloride was collected and purified by crystallisation from alcohol. The yield of *p*-methylsulphonylbenzylammonium chloride was 71%, but the analogues (Nos. 3, 5, 11 and 12 in Table I) were obtained in small yield.—RESEARCH LABORATORIES, MESSRS. BOOTS PURE DRUG CO. LTD., NOTTINGHAM. [*Received, April 10th*, 1947.]

A Synthesis of Leptospermone. By L. H. BRIGGS, C. H. HASSALL, and W. I. TAYLOR.

THE formula shown, suggested by Briggs, Penfold, and Short (*J.*, 1938, 1193) for leptospermone, a constituent of the essential oil of *Leptospermum scoparium*, was recently substantiated by degradative methods (Briggs, Hassall, and Short, *J.*, 1945, 706). Its structure has now been confirmed synthetically by the methylation of phlor*iso*valerophenone.



A solution of phlor*iso*valerophenone (2 g.) (Kenney and Robertson, *J.*, 1939, 1601) in potassium hydroxide solution (2·15 g. in 10 c.c.) and methyl iodide (5·4 g.) were heated electrically in a sealed tube to 70° and shaken for 3 days. After cooling, the heavy brown insoluble layer was dried and distilled at 10 mm., yielding a fraction, 0·788 g., $n_D^{23°}$ 1·492—1·513 (bath temp. 120—140°), soluble in sodium hydroxide solution and giving a red coloration with ferric chloride.

The *p*-toluidino-compound, prepared from 79 mg. according to Briggs, Hassall, and Short (*loc. cit.*), formed pale yellow needles, m. p. 100°, undepressed by pure *p*-toluidinoleptospermone.

The anilino-compound prepared in the same way from 63 mg. crystallised from 60% alcohol in long colourless needles, m. p. 92°, undepressed by anilinoleptospermone.

The *benzylamino*-compound prepared by heating this fraction (78 mg.) with benzylamine (93 mg.) for a few minutes was worked up as for the above compounds. After crystallisation from light petroleum (b. p. 40—50°) and 60% alcohol it formed long rods, m. p. 99°, undepressed by a similar derivative of the same m. p. from natural leptospermone (Found: C, 74·7; H, 8·3. $C_{22}H_{29}O_3N$ requires C, 74·4; H, 8·2%). This derivative exists in polymorphic forms (cf. Chattaway and Lambert, *J.*, 1915, 1766), that from natural leptospermone crystallising in plates from the same solvent as for the synthetic sample, but crystallising in rods of the same m. p. on seeding with this form. However, on seeding a solution of the synthetic material with the plate form only a partial conversion into the plate form could be achieved.

The remainder of the fraction was converted into the benzylamino-compound. This (230 mg.) was

hydrolysed with oxalic acid (200 mg.) in aqueous alcohol for two days at 100°. The regenerated leptospermone separating after removal of the alcohol was purified by distillation in a micro-column [Craig, *Ind. Eng. Chem.* (*Anal.*), 1936, **8**, 219], and then had $n_D^{25°}$ 1·4975, $n_D^{19·5°}$ 1·5007 (Briggs, Penfold, and Short, *loc. cit.*, record $n_D^{19·5°}$ 1·5000 for the natural compound) (Found: C, 67·8; H, 8·5. Calc. for $C_{15}H_{22}O_4$: C, 67·6; H, 8·3%).

We are grateful to the Chemical Society and the Royal Society of New Zealand for grants, and to Mr. R. N. Seelye for the combustion data. One of us (W. I. T.) is indebted for a Duffus Lubecki Scholarship.—AUCKLAND UNIVERSITY COLLEGE, NEW ZEALAND. OTAGO UNIVERSITY, DUNEDIN, NEW ZEALAND. [*Received, April 15th*, 1947.]

The Preparation of o-*Nitroacetophenone.* By K. SCHOFIELD and T. SWAIN.

ALTHOUGH the nitration of acetophenone is a source of pure *m*-nitroacetophenone, the *o*-isomer formed at the same time cannot be freed completely from the *m*-compound (Simpson *et al.*, *J.*, 1945, 646; Leonard and Boyd, *J. Org. Chem.*, 1946, **11**, 465). The classical acetoacetic ester condensation with *o*-nitrobenzoyl chloride has been effected in two ways: by using sodium ethoxide in absolute alcohol (Needham and Perkin, *J.*, 1904, **85**, 148; McCluskey, *J. Amer. Chem. Soc.*, 1922, **44**, 1573), and by using a suspension of sodioacetoacetic ester in ether (Gevekoht, *Annalen*, 1883, **221**, 323; Ruggli and Reichwein, *Helv. Chim. Acta*, 1937, **20**, 913). Whilst the hydrolysis of the intermediate ethyl *o*-nitrobenzoylacetoacetate, according to Kermack and Smith (*J.*, 1929, 814) gave excellent results, in our hands the first method of effecting the condensation has not proved uniformly satisfactory, since it appears to depend very critically on the quality of the ethanol used. The separation of sodium *o*-nitrobenzoylacetoacetic ester was usually very slow and in several experiments incomplete, and the modification suggested by McCluskey (*loc. cit.*) was unsuitable. Yields of *o*-nitroacetophenone were never higher than 65%, and often much lower. The method is evidently unsatisfactory for large scale work (cf. Ford-Moore and Rydon, *J.*, 1946, 679). In contrast, by using a suspension of the sodio-compound in ether, decomposing the reaction product with dilute acid, and extracting with ether (cf. Ruggli and Reichwein, *loc. cit.*) steady yields of ca. 65% of *o*-nitroacetophenone were obtained, which, though not so high as those claimed by the Swiss authors, were completely reliable. The yield was the same whether the mixture was kept overnight, or refluxed and stirred for 3 hours.

We then decided to investigate the use of malonic ester in this synthesis, but since our work was done two other preparations of *o*-nitroacetophenone have been described. Ford-Moore and Rydon (*loc. cit.*) obtained it from both phenylmethylcarbinol and ethylbenzene, whilst Walker and Hauser (*J. Amer. Chem. Soc.*, 1946, **68**, 1386) utilised the reaction between *o*-nitrobenzoyl chloride and the ethoxymagnesium-derivative of ethyl malonate. Our experiments are complementary to the work of the American authors, and illustrate a possible shortcoming to the use of malonic ester in such reactions, and we describe them briefly. Bischoff and Rach (*Ber.*, 1884, **17**, 2781, 2788) showed that reaction between *o*-nitrobenzoyl chloride (1 mole) and ethyl sodiomalonate (1 mole) yielded ethyl di-(*o*-nitrobenzoyl)-malonate, m. p. 93°, whilst reaction of the acid chloride (1 mole) with ethyl disodiomalonate (1 mole) gave ethyl *o*-nitrobenzoylmalonate, m. p. 54°. We have checked the first statement, and also find that using two equivalents of ethyl sodiomalonate to one of acid chloride gives ethyl *o*-nitrobenzoylmalonate, as proved by hydrolysis to *o*-nitroacetophenone. This is illustrated by the selection of experiments tabulated below, in each of which 0·12 mole of acid chloride was used :

Ethyl sodiomalonate (moles).	Medium.	Conditions.	Yield of *o*-nitroacetophenone (%).
0·26	Benzene	1*a*	73
,,	Ether	,,	70
,,	,,	1*b*	57
,,	,,	1*c*	71
,,	,,	2*b*	79
0·14 *	,,	1*a*	20

(1) At room temperature for 24 hours. (2) Refluxed and stirred for 2 hours, then kept for 12 hours more. (*a*) Hydrolysis by refluxing for 4 hours with 250 c.c. of 35% sulphuric acid. (*b*) Hydrolysis according to Walker and Hauser (*loc. cit.*). (*c*) As (*b*) but prolonged by 5 hours.

* Here the total product of the condensation, a mixture of oil and crystals of the di(nitrobenzoyl) compound, was submitted to hydrolysis. Besides the *o*-nitroacetophenone, 10·7 g. of ethyl di-(*o*-nitrobenzoyl)malonate, m. p. 93°, and 1·5 g. of *o*-nitrobenzoic acid were recovered, suggesting that partial fission of the diacyl compound had occurred.

Clearly, the use of two moles of the monosodium compound, with refluxing and stirring, provides yields of the order claimed by Walker and Hauser (*loc. cit.*); also, the heterogeneous hydrolysis (*a*) would appear to be equally efficient with that in homogeneous solution (*b*). Whether this limitation, necessitating the use of two moles of sodiomalonic ester in such condensations is general has not been investigated, but in the few examples of similar reactions noted in the literature (cf. Wilds and Beck, *J. Amer. Chem. Soc.*, 1944, **66**, 1688; Atkinson and Simpson, *J.*, 1947, 232; Gabriel and Lowenberg, *Ber.*, 1918, **51**, 1493) authors appear to have employed at least a molar excess of the ester. In our opinion, for both convenience and economy, the method of Walker and Hauser (*loc. cit.*) is the best yet described for the preparation of *o*-nitroacetophenone.—UNIVERSITY COLLEGE, EXETER. [*Received, April 21st*, 1947.]

The Interaction of Tetra-arylglycols and Pyridinium Salts. By ALEXANDER SCHÖNBERG and AHMED MUSTAFA.

THE discovery (Schönberg and Michaelis, *J.*, 1936, 1571) that tetraphenylglycol reacts in benzene with pyridine in presence of ethereal hydrogen chloride, forming a crystalline addition product $CPh_2(OH)\cdot CPh_2\cdot OH,C_5H_5N,HCl$, has now been investigated more fully and the reaction found to be of wide application; hydrogen chloride may be replaced by hydrogen bromide; pyridine may be replaced by α-picoline, 2 : 3-lutidine, quinoline, or quinaldine; tetraphenylglycol may be replaced by 9 : 10-dihydroxy-9 : 10-diphenyldihydrophenanthrene or ωωω'ω'-tetraphenyl-*p*-xylylene glycol, $C_6H_4(CPh_2\cdot OH)_2$. Nine new compounds of the above type have been obtained in crystalline form. They are all colourless and can be kept in a closed vessel for months without decomposition; they are destroyed by the action of aqueous alkali, with regeneration of the glycol.

Experimental.—(1) *Complexes from Tetraphenylglycol.* (a) Tetraphenylglycol (0·5 g.) was dissolved in hot benzene (5 c.c.; dried over sodium; thiophen-free), followed by addition of α-picoline (0·3 g.). The mixture was cooled to room temperature, a saturated dry ethereal solution of hydrogen chloride (10 c.c.) added, and the vessel immediately closed and cooled. The ether–benzene layer was then decanted, and the remaining crystals were boiled with absolute ethyl alcohol (6 c.c.) and collected; this residue (0·6 g.) was immediately recrystallised from absolute ethyl alcohol, forming crystals, m. p. *ca.* 190° (decomp., efferv., red melt) (Found : C, 77·4; H, 6·2; N, 2·8; Cl, 7·5. $C_{32}H_{30}O_2NCl$ requires C, 77·5; H, 6·1; N, 2·8; Cl, 7·2%). The addition *product* is very difficultly soluble in cold water.

(b) 2 : 3-Lutidine similarly gave crystals from absolute ethyl alcohol, m. p. *ca.* 190° (decomp., red-brown melt) (Found : C, 77·4; H, 6·3; N, 2·9; Cl, 7·3. $C_{33}H_{32}O_2NCl$ requires C, 77·7; H, 6·3; N, 2·7; Cl, 7·0%).

(c) The *product* from quinoline, crystallised from benzene–absolute ethyl alcohol, had m. p. *ca.* 198° (decomp., red-brown melt); it was difficultly soluble in hot absolute ethyl alcohol (Found : C, 78·6; H, 5·8; N, 2·5; Cl, 7·0. $C_{35}H_{30}O_2NCl$ requires C, 79·0; H, 5·7; N, 2·6; Cl, 6·7%).

(d) An additive *compound* from pyridine was obtained as in (a), but with use of dry, ethereal hydrogen bromide; it crystallised from absolute ethyl alcohol; m. p. *ca.* 195° (decomp.) (Found : N, 2·4; Br, 15·3. $C_{31}H_{28}O_2NBr$ requires N, 2·7; Br, 15·2%).

(2) *Complexes from* 9 : 10-*dihydroxy*-9 : 10-*diphenyldihydrophenanthrene.* (a) This glycol (1 mol.) (Werner and Grob, *Ber.*, 1904, **37**, 2902) and pyridine (2½ mols.) were allowed to react in the presence of dry ethereal hydrogen chloride, as described above. The *complex* formed crystals from hot absolute ethyl alcohol, m. p. *ca.* 238—239° (decomp.) (Found : C, 77·3; H, 6·0; N, 2·8; Cl, 6·8. $C_{31}H_{26}O_2NCl$ requires C, 77·6; H, 5·5; N, 2·9; Cl, 7·4%). When treated with aqueous alkali on the boiling water-bath, they evolved pyridine and regenerated 9 : 10-dihydroxy-9 : 10-diphenyldihydrophenanthrene (m. p. and mixed m. p.).

(b) From α-picoline similarly were obtained crystals, m. p. *ca.* 200° (decomp.), from absolute ethyl alcohol (Found : C, 77·1; H, 6·3; N, 2·5; Cl, 7·5. $C_{32}H_{28}O_2NCl$ requires C, 77·8; H, 5·7; N, 2·9; Cl, 7·2%).

(3) *Complexes from* ωωω'ω'-*tetraphenyl*-p-*xylylene glycol.* The glycol (1 mol.) (Ullmann and Schlaepfer, *Ber.*, 1904, **37**, 2003) and pyridine were treated as described above. An additive *product* was obtained from absolute ethyl alcohol, m. p. *ca.* 215° (decomp., red-brown melt) (Found : C, 79·8; H, 6·2; N, 2·1; Cl, 6·1. $C_{37}H_{32}O_2NCl$ requires C, 79·6; H, 5·8; N, 2·5; Cl, 6·4%). The *product* from quinoline, crystallised from absolute ethyl alcohol, had m. p. *ca.* 240° (with decomposition and red brown melt) (Found : C, 80·8; H, 5·3; N, 2·7; Cl, 5·8. $C_{41}H_{34}O_2NCl$ requires C, 81·0; H, 5·6; N, 2·3; Cl, 5·8%); and that from quinaldine, similarly crystallised, had m. p. *ca.* 235° (decomp., brown melt) (Found : C, 80·8; H, 5·8; N, 2·6; Cl, 5·8. $C_{42}H_{36}O_2NCl$ requires C, 81·1; H, 5·8; N, 2·3; Cl, 5·7%).—FOUAD I UNIVERSITY, FACULTY OF SCIENCE, ABBASSIA-CAIRO, EGYPT. [*Received, May 1st*, 1947.]