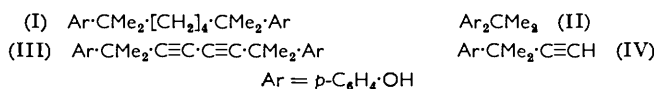


NOTES.

616. *Synthesis of 2,7-Bis-p-hydroxyphenyl-2,7-dimethyloctane.*

By A. C. DAVIS and R. F. HUNTER.

2,7-BIS-*p*-HYDROXYPHENYL-2,7-DIMETHYLOCTANE (I) was required to ascertain the effect of lengthening the hydrocarbon bridge on the physical properties of cured resins obtained from its diglycidyl ether, in comparison with the dihydroxydiphenylpropane (II). The diacetylene (III) was prepared by condensing 2,7-dimethylocta-3,5-diyne-2,7-diol with phenol in the presence of phosphoric acid and also from *p*-1,1-dimethylprop-2-ynylphenol (IV) [obtained in very poor yield by condensation of 2-ethynylpropan-2-ol with phenol (cf. Nazarov and Kuynetsova ¹)] by oxidation with oxygen in the presence of cuprous and ammonium chloride.



Reduction of the diacetylene with hydrogen in the presence of palladium-charcoal yielded the required compound (I). Its constitution was confirmed by synthesis from 2,7-dimethylocta-2,7-diol and phenol. On condensation with epichlorohydrin in ethanol, with gradual addition of aqueous sodium hydroxide, it yielded the diglycidyl ether, which had the expected properties.

Experimental.—2,7-Bis-*p*-hydroxyphenyl-2,7-dimethylocta-3,5-diyne (III). (i) A mixture of 2,7-dimethyl-3,5-octadiyne-2,7-diol (200 g.), phenol (1 kg.), and phosphoric acid (*d* 1.71, 200 c.c.) was stirred at 60° for 3 hr., then diluted with water, and the organic layer was washed with water. The solvent and unchanged phenol were removed in steam, the residue cooled, and the aqueous layer was decanted and discarded. The crude resinous bisphenol was dissolved in a solution of potassium hydroxide (140 g.) in water (400 c.c.), added to 10% aqueous sodium hydroxide (2.5 l.), and kept for 3 hr. at room temperature. The precipitate sodium salt was collected, washed with a small amount of water, and treated with an excess of cold dilute hydrochloric acid under a layer of ether. The ethereal solution was washed with water, dried (K₂CO₃),

¹ Nazarov and Kuynetsova, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. chim.*, 1942, 392; *Chem. Abs.*, 1945, **39**, 1620.

and concentrated under reduced pressure to a partially crystalline residue, which on recrystallisation from toluene (1 l.) gave the bisphenol (90 g., 23% crude yield) in two crops, m. p. 134—137° and 131—133°. For analysis a sample was recrystallised from ethylene dichloride and thereafter several times from 50% acetic acid to give the pure *bisphenol* in needles, m. p. 150—152° (Found: C, 83.25; H, 7.2. $C_{22}H_{22}O_2$ requires C, 83.0; H, 7.0%).

Treatment of the sodium salt of the bisphenol in water with benzoyl chloride gave the *dibenzoate*, which crystallised from ethyl acetate in leaflets, m. p. 200—201° (Found: C, 82.3; H, 5.6. $C_{36}H_{30}O_4$ requires C, 82.1; H, 5.7%).

(ii) Considerable difficulty was experienced in preparing *p*-1,1-dimethylprop-2-ynylphenol by condensation of 2-ethynylpropan-2-ol with phenol.¹ The acetylenic phenol was finally obtained in 3% yield only, as an oil of 30% concentration (estimated by hydrogenation) which did not give correct analytical figures. The presence of an ethynyl group was verified by the formation of a silver derivative. The alternative method of alkylation of phenol with isopropenylacetylene in presence of phosphoric acid surprisingly yielded *p*-*t*-pentylphenol (6%) as the only non-resinous phenolic product, m. p. 90° (Found: C, 80.4; H, 9.8. Calc. for $C_{12}H_{16}O$: C, 80.4; H, 9.8%). The benzoyl derivative had m. p. 58—59°. Huston and Hsieh² reported m. p.s 94—95° and 60—61° respectively.

The crude dimethylpropynylphenol (3.2 g.) was shaken under oxygen with a solution of cuprous chloride (5 g.) and ammonium chloride (8 g.) in water (20 c.c.) and ethanol (10 c.c.) until an excess of oxygen had been absorbed. The ethanol was distilled in a vacuum, and ether and dilute sulphuric acid were added. The product, isolated by washing and concentration of the ethereal solution, was a viscous brown oil (3.0 g.) giving no precipitate with silver nitrate solution. This was purified through the sodium salt to give an oil (1.2 g.) which after a single crystallisation from 60% acetic acid yielded 2,7-bis-*p*-hydroxyphenyl-2,7-dimethylocta-3,5-diyne (0.32 g.), m. p. 145—152°, undepressed on admixture with the specimen obtained in (i).

2,7-Bis-*p*-hydroxyphenyl-2,7-dimethyloctane.—(i) 2,7-Bis-*p*-hydroxyphenyl-2,7-dimethylocta-3,5-diyne (71 g.) in ethanol (250 c.c.) was shaken under hydrogen with 5% palladium charcoal (5 g.) until 22.1 l. had been absorbed. Evaporation of the filtered solution and crystallisation from 50% acetic acid (850 c.c.) gave pale brown leaflets (58.3 g.) which were dried to constant weight at 100°/0.5 mm. (m. p. 125—128°). An analytical sample of the *bisphenol* obtained after several recrystallisations from toluene and drying at 90°/10⁻⁵ mm. had m. p. 137—138° (Found: C, 81.8; H, 9.4. Calc. for $C_{22}H_{30}O_2$: C, 80.9; H, 9.3. $C_{22}H_{30}O_2, \frac{1}{2}C_7H_8$ requires C, 82.2; H, 9.2%). Analytical samples prepared by crystallisation from aqueous acetic acid gave consistently low microanalytical figures for carbon even after drying in a high vacuum near the m. p. (cf. Davis, Hayes, and Hunter³). The *dibenzoate*, prepared by a Schotten-Baumann reaction, crystallised from ethyl acetate in prisms, m. p. 191—192° (Found: C, 80.85; H, 6.9. $C_{36}H_{38}O_4$ requires C, 80.9; H, 7.2%). The diglycidyl ether was prepared by addition in small portions during 3½ hr. of sodium hydroxide (16.8 g.) in water (17 c.c.) to a stirred solution of the bisphenol (58.3 g.) in 95% ethanol (27 c.c.) and epichlorohydrin (99 g.) in a constant-temperature bath at 60°. Stirring was continued for a further ½ hr., the solvents were evaporated under reduced pressure at 60°, and water (75 c.c.) and toluene (60 c.c.) were added. After being washed with water, the organic layer was concentrated under reduced pressure, finally at 100°/0.5 mm.; the diglycidyl ether formed a viscous clear brown liquid which was not further purified and gradually crystallised (n_D^{17} 1.5492) (Found: epoxide equiv., 254. Calc., 219). (ii) 2,7-Dimethyloctane-2,7-diol (3.5 g., 0.02 mole) was boiled in phenol (37.6 g., 0.4 mole) with zinc chloride (5.5 g.) for 8 hr. and unchanged phenol removed in steam. The ethereal solution obtained on treatment of the residue with ether and dilute hydrochloric acid was washed with water and extracted with 10% aqueous potassium hydroxide. Saturation of the alkaline extract with carbon dioxide gave a brown gum (0.3 g.) which on purification through a solid sodium salt, neutralisation with carbon dioxide, and crystallisation from 40% acetic acid gave the bisphenol in plates, m. p. 130° after sintering and 132—134° when mixed with the specimen described in (i). The oily residue (3.6 g.) recovered from the ethereal solution, on distillation at 130°/10⁻⁵ mm., gave a *product* as a viscous yellow oil, n_D^{15} 1.5338 (Found: C, 83.3; H, 10.7. $C_{16}H_{24}O$ requires C, 82.7; H, 10.4%).

RESEARCH AND DEVELOPMENT DEPARTMENT, BAKELITE LIMITED,
TYSELEY, BIRMINGHAM, 11.

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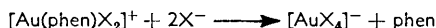
² Huston and Hsieh, *J. Amer. Chem. Soc.*, 1936, **58**, 439.

³ Davis, Hayes, and Hunter, *J. Appl. Chem.*, 1953, **3**, 312; 1957, **7**, 521.

617. *Nitrogenous Chelate Complexes of Transition Metals.*
*Part II.*¹ *The Tervalent Gold Complexes of 2,2'-Bipyridyl.*

By C. M. HARRIS and T. N. LOCKYER.

TERVALENT gold complexes of 1,10-phenanthroline (phen) have been recently examined in nitrobenzene and acetone solutions by means of conductometric and spectrophotometric measurements.¹ The rapid reaction of halide ions (*i.e.*, Cl⁻ and Br⁻) with the dihalogeno-(1,10-phenanthroline)gold(III) ion proceeds virtually to completion in these solvents, thus:



An explanation of this phenomenon, as well as the marked difference in colour between the simple halides, $[\text{Au}(\text{phen})\text{X}_2]\text{X}$, and the corresponding perchlorates, $[\text{Au}(\text{phen})\text{X}_2]\text{ClO}_4$, has been given in terms of the ability of trivalent gold, under suitable conditions, to utilise two additional *6p6d* bonds perpendicular to its normal *5d6s6p*² square planar arrangement. The reactions of the 2,2'-bipyridyl complexes of gold(III) have since been shown to be similar to those of 1,10-phenanthroline, and the preparations and properties of these compounds are briefly reported here.

Block and Bailar² have previously reported the isolation of the dihalogeno-(2,2'-bipyridyl)gold(III) ions as their tetrahalogenoaurate(III) derivatives, $[\text{Au}(\text{bipy})\text{X}_2][\text{AuX}_4]$ (bipy = 2,2'-bipyridyl; X = Cl, Br), as well as an impure specimen of $\text{Au}(\text{bipy})\text{Cl}_3$. The pure chloride $\text{Au}(\text{bipy})\text{Cl}_3$ has now been isolated from aqueous solution, as well as the compounds $[\text{Au}(\text{bipy})\text{X}_2]\text{ClO}_4$ (where X = Cl, Br) and $[\text{bipy H}][\text{AuX}_4]$ (X = Cl, Br). Attempts to isolate the simple bromide $\text{Au}(\text{bipy})\text{Br}_3$ were unsuccessful. The dichloro-(2,2'-bipyridyl)gold(III) ion is hydrolysed in aqueous solution, and the hydroxy-chloro-(2,2'-bipyridyl)gold(III) ion was isolated as the perchlorate $[\text{Au}(\text{bipy})\text{Cl}(\text{OH})]\text{ClO}_4$. It is noteworthy that Bjerrum³ has reported that the $[\text{AuCl}_4]^-$ ion undergoes a slow hydrolysis, forming the $[\text{AuCl}_3\text{OH}]^-$ species. Attempts to prepare analogous iodo-complexes were unsuccessful. The black insoluble tetraiodoaurate(III) complex $[\text{N}(\text{Et})_4][\text{AuI}_4]$ was obtained but it decomposed in solution and was not further investigated.

The molecular conductivities of these compounds both in nitrobenzene and in nitromethane solution are listed in the Table. The chloro-complex $\text{Au}(\text{bipy})\text{Cl}_3$ exhibits conductivities in these solvents of the order expected for rearrangement to $[\text{Au}(\text{bipy})\text{Cl}_2][\text{AuCl}_4]$, as has been previously observed for the analogous 1,10-phenanthroline complex in nitrobenzene or acetone. This was confirmed by conductometrically titrating the perchlorate $[\text{Au}(\text{bipy})\text{Cl}_2]\text{ClO}_4$ ($5 \times 10^{-4}\text{M}$) with methyltriphenylarsonium chloride (10^{-2}M) in nitrobenzene, a sharp end-point corresponding to the addition of two chloride ions being observed. A similar result was obtained for the titration of $[\text{Au}(\text{bipy})\text{Br}_2]\text{ClO}_4$ with $[\text{N}(\text{Et})_4]\text{Br}$ in nitromethane.

Spectrophotometric measurements were made on the chloro-complexes in nitromethane solution (see Fig. 1) in the range 5500—3750 Å. Although these compounds exhibit no definite absorption maxima in this region, it can be seen that the curve for 10^{-3}M - $[\text{Au}(\text{bipy})\text{Cl}_2][\text{AuCl}_4]$ is practically identical with the composite curve constructed from those for 10^{-3}M - $[\text{Au}(\text{bipy})\text{Cl}_2]\text{ClO}_4$ and 10^{-3}M - $\text{Na}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$. The curve for $2 \times 10^{-3}\text{M}$ - $[\text{Au}(\text{bipy})\text{Cl}_2]\text{Cl}$ is the same as that for 10^{-2}M - $[\text{Au}(\text{bipy})\text{Cl}_2][\text{AuCl}_4]$, as expected for the postulated equilibrium. The bromo-complexes were also examined in this solvent (see Fig. 2), and it can be seen that the curve for $5 \times 10^{-4}\text{M}$ - $[\text{Au}(\text{bipy})\text{Br}_2][\text{AuBr}_4]$ is practically identical with the composite curve constructed from $5 \times 10^{-4}\text{M}$ - $[\text{Au}(\text{bipy})\text{Br}_2]\text{ClO}_4$ and $[\text{N}(\text{Et})_4][\text{AuBr}_4]$.

¹ Part I, Harris, *J.*, 1959, 682.

² Block and Bailar, *J. Amer. Chem. Soc.*, 1951, **73**, 4722.

³ Bjerrum, *Bull. Soc. chim. Belg.*, 1948, **57**, 432.

Molecular conductivities (mho) of gold(III)-2,2'-bipyridyl complexes in 10^{-3}M -nitrobenzene and -nitromethane at 25° .

Compound	In PhNO_2	In MeNO_2	Compound	In PhNO_2	In MeNO_2
$[\text{Au}(\text{bipy})\text{Cl}_2]\text{Cl}$	14.4	43.7	$[\text{Au}(\text{bipy})\text{Br}_2]\text{ClO}_4$	—	94.0
$[\text{Au}(\text{bipy})\text{Cl}_2]\text{ClO}_4$	29.0	88.6	$[\text{Au}(\text{bipy})\text{Br}_2][\text{AuBr}_4]$...	—	86.5
$[\text{Au}(\text{bipy})\text{Cl}(\text{OH})]\text{ClO}_4$...	29.5	92.0	$[\text{N}(\text{Et})_3][\text{AuBr}_4]$	32.8	96.0
$[\text{Au}(\text{bipy})\text{Cl}_2][\text{AuCl}_4]$	28.8	87.3	$[\text{bipy H}][\text{AuBr}_4]$	30.8	89.7
$[\text{bipy H}][\text{AuCl}_4]$	31.1	87.5			

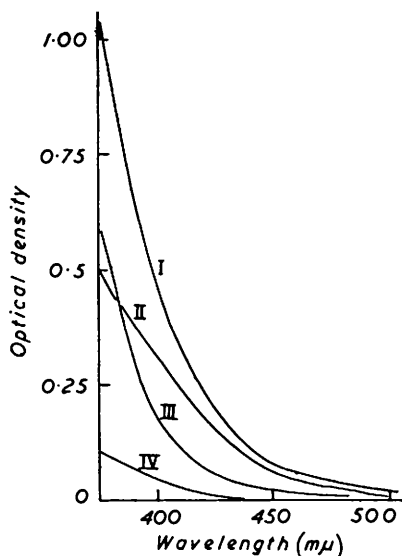


FIG. 1. Absorption spectra of the chloro-complexes in nitromethane (1 cm. cell).

- I Observed curve for 10^{-3}M - $[\text{Au}(\text{bipy})\text{Cl}_2][\text{AuCl}_4]$, also for $2 \times 10^{-3}\text{M}$ - $[\text{Au}(\text{bipy})\text{Cl}_2]\text{Cl}$, also composite curve from addition of II and III.
 II 10^{-3}M - $\text{Na}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$.
 III 10^{-3}M - $[\text{Au}(\text{bipy})\text{Cl}_2]\text{ClO}_4$.
 IV 10^{-3}M - $[\text{Au}(\text{bipy})\text{Cl}(\text{OH})]\text{ClO}_4$.

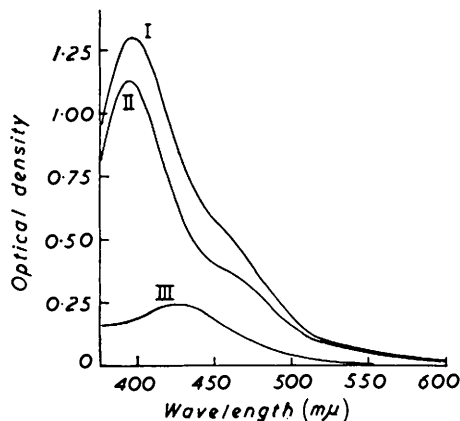


FIG. 2. Absorption spectra of the bromo-complexes in nitromethane (1 cm. cell).

- I $5 \times 10^{-4}\text{M}$ - $[\text{Au}(\text{bipy})\text{Br}_2][\text{AuBr}_4]$, also composite curve from addition of II and III.
 II $5 \times 10^{-4}\text{M}$ - $[\text{NET}_3][\text{AuBr}_4]$.
 III $5 \times 10^{-4}\text{M}$ - $[\text{Au}(\text{bipy})\text{Br}_2]\text{ClO}_4$.

Experimental.—*Dichloro-(2,2'-bipyridyl)gold(III) chloride.* To a boiling solution of 2,2'-bipyridyl (0.65 g.) in water (10 ml.) was added $\text{Na}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$ (0.80 g.) in water (10 ml.) with stirring. The yellow precipitate of $[\text{Au}(\text{bipy})\text{Cl}_2][\text{AuCl}_4]$, which was first deposited, dissolved on boiling for a few minutes. Lithium chloride (5 g.) was stirred in and the clear solution was left overnight in the refrigerator. The orange needles were washed with a large excess of anhydrous acetone followed by anhydrous ether (yield of vacuum-dried salt, 0.35 g.) (Found: C, 25.8; H, 1.6; N, 5.8; Au, 42.4. $\text{C}_{10}\text{H}_8\text{N}_2\text{Cl}_3\text{Au}$ requires C, 26.1; H, 1.75; N, 6.1; Au, 42.8%).

Dichloro-(2,2'-bipyridyl)gold(III) perchlorate. To a boiling aqueous solution of $[\text{Au}(\text{bipy})\text{Cl}_2]\text{Cl}$, prepared as above, excess of 75% perchloric acid was added dropwise, with stirring. The solution was cooled, and the pale yellow crystals were filtered off and washed in turn with water, ethanol, and ether (Found: C, 23.2; H, 1.7; N, 5.3; Au, 37.7%. $\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2\text{Cl}_3\text{Au}$ requires C, 22.9; H, 1.5; N, 5.4; Au, 37.6%).

Hydroxy-chloro-(2,2'-bipyridyl)gold(III) perchlorate. To a boiling solution of $\text{Na}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$ (0.20 g.) and 2,2'-bipyridyl (0.26 g.) in water (20 ml.) was added dropwise a hot solution of sodium perchlorate (2.0 g.) in water (10 ml.). The pale cream compound was washed with water, ethanol, and ether (yield, 0.24 g.) (Found: C, 23.7; H, 1.8; N, 5.5; Au, 39.0; Cl, 7.3. $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_2\text{Cl}_2\text{Au}$ requires C, 23.9; H, 1.8; N, 5.6; Au, 39.0; Cl, 7.0%).

Dichloro-(2,2'-bipyridyl)gold(III) tetrachloroaurate(III). This compound was prepared by treating 2,2'-bipyridyl dropwise with a hot aqueous solution of $\text{Na}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$. The yellow compound was washed with water, ethanol, and ether (Found: C, 16.2; H, 1.05; N, 3.8; Au, 51.6. Calc. for $\text{C}_{10}\text{H}_8\text{N}_2\text{Cl}_6\text{Au}_2$: C, 15.7; H, 1.1; N, 3.7; Au, 51.6%).

2,2'-Bipyridylum tetrachloroaurate(III). Sodium tetrachloroaurate(III) dihydrate (0.40 g.) in *m*-hydrochloric acid (20 ml.) was added to 2,2'-bipyridyl (0.16 g.) in *m*-hydrochloric acid (20 ml.). The yellow salt was precipitated immediately; it was washed with water, ethanol, and ether (yield, 0.35 g.) (Found: C, 24.5; H, 1.8; N, 5.7; Au, 39.5. $\text{C}_{10}\text{H}_8\text{N}_2\text{Cl}_4\text{Au}$ requires C, 24.2; H, 1.8; N, 5.7; Au, 39.8%).

Dibromo-(2,2'-bipyridyl)gold(III) tetrabromoaurate(III). This compound was prepared in an analogous manner to the corresponding chloro-complex from a solution of $\text{Na}[\text{AuBr}_4]$ (Found: C, 11.9; H, 1.0; N, 2.7; Au, 38.3. Calc. for $\text{C}_{10}\text{H}_8\text{N}_2\text{Br}_8\text{Au}_2$: C, 11.7; H, 0.8; N, 2.7; Au, 38.3%).

Dibromo-(2,2'-bipyridyl)gold(III) perchlorate. $[\text{Au}(\text{bipy})\text{Br}_2][\text{AuBr}_4]$ (0.5 g.) was dissolved in boiling water (600 ml.) in the presence of 2,2'-bipyridyl (0.15 g.). The solution was filtered hot to remove some undissolved starting material and 75% perchloric acid (10 ml.) was added to the hot solution. Crystallisation began almost immediately, and after cooling, the golden crystals were washed in turn with cold water, ethanol, and anhydrous ether (yield of vacuum-dried perchlorate, 0.44 g.) (Found: C, 19.6; H, 1.45; N, 4.6; Au, 32.1. $\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2\text{ClBr}_2\text{Au}$ requires C, 19.6; H, 1.3; N, 4.6; Au, 32.2%).

Tetraethylammonium tetrabromoaurate(III). This compound was prepared by Harris's method¹ (Found: Au, 30.2. Calc. for $\text{C}_8\text{H}_{20}\text{NBr}_4\text{Au}$: Au, 30.4%).

2,2'-Bipyridylum tetrabromoaurate(III). This compound was prepared in an analogous manner to the tetrachloro-derivative (Found: C, 17.5; H, 1.4; N, 4.1; Au, 29.1. $\text{C}_{10}\text{H}_8\text{N}_2\text{Br}_4\text{Au}$ requires C, 17.8; H, 1.35; N, 4.2; Au, 29.2%).

Tetraethylammonium tetraiodoaurate(III). $\text{Na}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$ (0.5 g.) in water (20 ml.) was added slowly to a large excess of potassium iodide (4.0 g.) in water (20 ml.). The dark solution was filtered, and to it was added a solution of tetraethylammonium iodide (0.4 g.) in water (25 ml.), slowly with stirring. The black salt was precipitated immediately; it was washed with water and dried over P_2O_5 *in vacuo* at 80° (yield, 1.00 g.) (Found: C, 11.8; H, 2.2; N, 1.7; Au, 23.6. $\text{C}_8\text{H}_{20}\text{NI}_4\text{Au}$ requires C, 11.5; H, 2.4; N, 1.7; Au, 23.6%).

Physical measurements. The spectra were recorded on a Cary 11-MS-50 Spectrophotometer. The nitromethane and nitrobenzene were purified as described elsewhere.⁴

We thank Dr. E. Challen for micro-analyses (C,H,N) and Mr. I. Reece for spectrophotometric measurements. One of us (T. N. L.) thanks I.C.I.A.N.Z. for a research fellowship.

DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF NEW SOUTH WALES,
BROADWAY, SYDNEY, AUSTRALIA.

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⁴ Harris, Livingstone, and Reece, *J.*, 1959, 1505.

618. Interaction of Tetranitromethane with Aromatic Hydrocarbons.

By (MISS) JAYANTI NAG CHAUDHURI and SADHAN BASU.

MACBETH¹ has shown that the red colour produced by ethylenic compounds with tetranitromethane is much less intense with conjugated compounds, especially with aromatic hydrocarbons. Nitro-compounds in general are good electron-acceptors and form molecular complexes of charge-transfer type with electron donors.² As aromatic compounds are good electron donors they should form molecular complexes with tetranitromethane. With this in view the present investigation was undertaken.

Experimental.—Tetranitromethane, 99% pure, supplied by L. Light & Co., in water, chloroform, and carbon tetrachloride, showed a characteristic absorption band in the range 270—280 $\mu\mu$, which corresponds well with the 275 $\mu\mu$ band observed for the vapour.³ In normal

¹ Macbeth, *J.*, 1915, **107**, 1826; Harper and Macbeth, *J.*, 1915, **107**, 87.

² Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

³ Nicholson, *J.*, 1949, 1555.

heptane, however, it showed a general absorption with no characteristic maximum in the region of 200—400 $m\mu$. Evans ⁴ observed a similar spectrum in cyclohexane and attributed it to contact charge-transfer interaction.

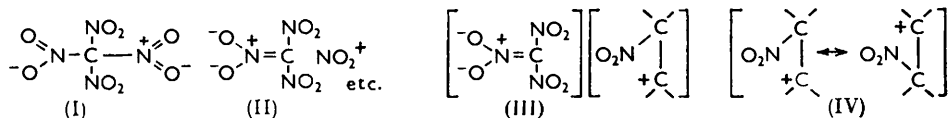
The solvents used were E. Merck's spectroscopically pure samples and were used without further purification. Polynuclear hydrocarbons, supplied by B.D.H. and L. Light & Co., were purified by chromatography on alumina from neutral solvents and subsequent recrystallisation. The purified samples were >99% pure, as shown by their extinctions at the characteristic absorption maxima in ethanol.

Spectral measurements were made in a Beckman Spectrophotometer Model DU with 5 cm. silica cells. Above 320 $m\mu$ tetranitromethane in the concentration range used in the present series of measurements gave 100% transmission. The measurements with mixtures of hydrocarbons and tetranitromethane were made with a balancing solution containing the hydrocarbon in the same concentration as in the mixture.

The Table shows the characteristic absorption maximum (in $m\mu$) of systems containing tetranitromethane ($10^{-4}M$) and nine polynuclear aromatic hydrocarbons ($0.01M$) in chloroform. The value of $h\nu$ (in eV) corresponding to these wavelengths, and ionisation potentials I.P. (in volts) of these hydrocarbons were calculated by the molecular orbital method.⁵

Compound	λ	$h\nu$	I.P.	Compound	λ	$h\nu$	I.P.
Naphthalene	359	3.46	8.30	Triphenylene	397	3.28	8.48
Anthracene	407	3.05	7.74	Biphenyl	330	3.76	8.53
Phenanthrene	390	3.18	8.27	Stilbene	405	3.07	7.99
Chrysene	397	3.13	8.04	Fluoranthene	416	2.98	8.30
Pyrene	388	3.20	7.82				

Discussion.—The peaks of the absorption band of tetranitromethane—olefinic systems usually appear in the range of 450—500 $m\mu$. It is evident from the Table that the band for tetranitromethane—aromatic hydrocarbons lies at much shorter wavelengths, although from the consideration of ionisation potentials of ethylene (10 v) and the aromatic hydrocarbons the band for the latter should appear at much longer wavelengths. This suggests that the tetranitromethane undergoes interaction with olefinic compounds which is not of charge-transfer type. Patterson ⁶ represented tetranitromethane by means of a resonance hybrid of the covalent (I) and ionic structures (II). He represented the tetranitromethane



complex of ethylenic compounds by structures of the type (III) and attributed the visible colour to charge resonance in the ion (IV). We suggest that for ethylenic compounds the colour is due to charge-resonance absorption, while for aromatic hydrocarbons the absorption is of charge-transfer type. But this does not mean that the interaction of the type (III) and (IV) cannot take place with aromatic hydrocarbons. In fact Maatman and Rogers ⁷ noted absorption in the region 400—500 $m\mu$ with polynuclear aromatic hydrocarbons, using somewhat higher tetranitromethane concentrations; this is probably the charge-resonance band. That tetranitromethane undergoes heteropolar dissociation in systems containing polynuclear aromatic hydrocarbons is shown by the following observations.

The complex-forming reaction of tetranitromethane with aromatic hydrocarbons was found to be time-dependent. This did not interfere with the location of the characteristic charge-transfer band but accurate measurement of optical density was not possible. For tetranitromethane—anthracene the 407 $m\mu$ band increased in intensity at first rapidly, then more slowly. After about a week the peak at 407 $m\mu$ had been completely replaced by a more

⁴ Evans, *J.*, 1957, 4232.

⁵ Bhattacharya and Basu, *Trans. Faraday Soc.*, 1958, 54, 1286.

⁶ Patterson, *J. Org. Chem.*, 1955, 20, 1277.

⁷ Maatman and Rogers, Amer. Chem. Soc. Div. Petroleum Chem., Gen. Papers, 1955, No. 33, pp. 5—11.

intense band at 365 μ . The absorption spectrum of the system at this stage resembled that of 9-nitroanthracene fairly closely,⁸ indicating nitration of the anthracene nucleus. Similarly, the absorption spectrum of tetranitromethane-naphthalene resembled that of α -nitronaphthalene after about a week. Nitration of hydrocarbons by tetranitromethane⁶ has also been observed by previous workers, but the present investigation shows that it is preceded by charge-transfer interaction. Since nitration involves the NO_2^+ radical, it is evident that the ionic structure (II) of the tetranitromethane must also participate in the interaction of tetranitromethane with aromatic hydrocarbons. Charge resonance of the type (IV) has not been observed by us, probably because of the low concentration of the constituents.

We thank Professor R. S. Mulliken and one of the referees for helpful criticism, and the Council of Scientific & Industrial Research, India, for a Junior Research Fellowship (to J. N. C.).

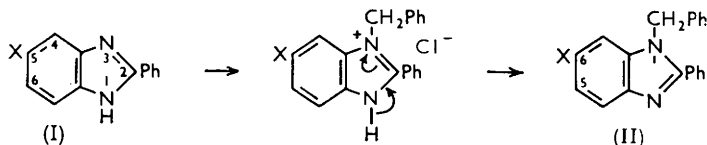
DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE OF SCIENCE & TECHNOLOGY,
CALCUTTA-9, INDIA. [Received, February 16th, 1959.]

* Jones, *Chem. Rev.*, 1947, **41**, 353.

619. Benzylation of 2-Phenylbenzimidazoles.

By N. V. SUBBA RAO and C. V. RATNAM.

HINSBERG,¹ heating 5-methyl-2-phenylbenzimidazole (I; X = Me) at 160° with benzyl chloride and benzene, obtained the *N*-benzyl derivative, but did not determine whether the methyl group was in the 5- or the 6-position. We have benzylated 5-methyl-, 5-chloro-, and 5-nitro-2-phenylbenzimidazole, obtaining better yields by refluxing the benzimidazoles with benzyl chloride in the presence of fused sodium acetate and a trace of iodine. The products were characterised by comparison with synthetic samples.^{2, 3, 4} 5-Methyl-2-phenylbenzimidazole gave 1-benzyl-6-methyl- whereas 5-chloro-2-phenylbenzimidazole yielded 1-benzyl-5-chloro-2-phenylbenzimidazole. The 5-nitrobenzimidazole, on the other hand, gave a 2 : 1 mixture of 5- and 6-nitro-compounds.



Phillips,⁵ methylating 5-bromo-2-methyl-, 2-methyl-5-nitro-, and 5-methyl-benzimidazole, found the Bz-substituent to be mainly in the 5- or the 6-position in the product according to the reagent used; 2:5-dimethylbenzimidazole, however, gave only the 1 : 2 : 5-compound.

Our results may be explained as follows: A benzimidazole having an electron-releasing group (*e.g.*, methyl) at position 5 will exist mainly in form (I) since the "*para*-"nitrogen atom will have a greater electron density for holding the proton; if the 5-substituent is an electron-withdrawing group (*e.g.*, chloro or nitro), the tautomer of structure (I) will be the major component. Benzylation in the absence of aqueous alkali may be expected to take place by the addition of a benzyl cation to the more basic, tertiary nitrogen atom, leading to the 6-substituted compound (II) from compound (I), and the 5-substituted isomer from its tautomer, as found for the methyl and chloro-derivatives. In the case of the nitrobenzimidazole the 5-nitro-compound is the major product, as expected; however,

¹ Hinsberg, *Ber.*, 1886, **19**, 2025.

² Rao and Ratnam, *Proc. Indian Acad. Sci.*, 1956, **44**, 331.

³ *Idem*, *ibid.*, 1958, **47**, 77.

⁴ *Idem*, *ibid.*, p. 81.

⁵ Phillips, *J.*, 1931 1143.

owing to the deactivating influence of the nitro-group, the reaction is slowed down and form (I; X = NO₂), though the minor entity, is the more reactive and so some of the 6-nitro-isomer is also obtained.

Experimental.—*Benylation of 5-methyl-2-phenylbenzimidazole.* The benzimidazole (1 g.), freshly fused sodium acetate (0.5 g.), redistilled benzyl chloride (2 ml.) and a speck of iodine were refluxed for 9 hr., then added to an excess of water with stirring. The resulting mass on trituration with ethanol gave a solid (0.8 g.) which, recrystallised from alcohol and then benzene, yielded prismatic rods of 1-benzyl-6-methyl-2-phenylbenzimidazole,² m. p. and mixed m. p. 195°. The alcoholic filtrate from the crude solid, on evaporation and repeated washing with light petroleum, gave a further 0.1 g. of the same compound.

Benylation of 5-chloro-2-phenylbenzimidazole. The chlorobenzimidazole (0.5 g.) yielded the 1:2-disubstituted benzimidazole 1-benzyl-5-chloro-2-phenylbenzimidazole³ (0.45 g.), prismatic rods (from alcohol), m. p. and mixed m. p. 170°.

Benylation of 5-nitro-2-phenylbenzimidazole. The nitrobenzimidazole (0.5 g.) was benyated as above. The crude product (0.45 g.) which was insoluble in aqueous potassium hydroxide had m. p. 140°. Chromatography over alumina with benzene as eluant gave a fraction, m. p. 185°, and benzene-alcohol gave a fraction, m. p. 159°. The higher- and the lower-melting compound were identical with the 6- and the 5-nitro-isomer,⁴ respectively. By repeated chromatography, the 5- and the 6-nitro-isomer were obtained in the ratio of 2:1.

We thank Professor T. R. Seshadri of Delhi University for discussions of the mechanism.

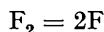
OSMANIA UNIVERSITY, HYDERABAD-7, DECCAN, INDIA.

[Received, February 23rd, 1959.]

620. The Dissociation Constant of Fluorine.

By A. F. TROTMAN-DICKENSON.

DOESCHER¹ measured the dissociation of fluorine in a static system and expressed his observations of the equilibrium



by the equation

$$\ln K \text{ (in atmospheres)} = 14.5 - 19000/T,$$

where T is the absolute temperature. Stamper and Barrow² analysed Doescher's results by a third-law treatment and found that $\Delta H_0^\circ = 36.71 \pm 0.13$ kcal. mole⁻¹. Although Doescher's equation satisfactorily represents his observations, it is not suitable for lengthy extrapolations. The Table below lists equilibrium constants that have been calculated

Temp. (° K)	log $K_{\text{obs.}}$	log K_d	log K_c	log (K_d/K_c)	Temp. (° K)	log $K_{\text{obs.}}$	log K_d	log K_c	log (K_d/K_c)
100	—	77.777	76.231	-0.454	600	—	8.545	8.364	0.181
200	—	55.037	53.831	0.206	760	5.34	5.440	5.342	0.098
300	—	22.791	22.501	0.290	1112	2.90	2.877	2.912	-0.035
400	—	15.668	15.399	0.269	1500	—	0.796	0.902	-0.106
500	—	11.794	11.570	0.224	2000	—	2.172	2.364	-0.192

by the standard methods of statistical mechanics,³ the new value of ΔH_0° being used. The following physical constants of the fluorine molecule were used: $\omega_0 = 891.8$ cm.⁻¹,⁴ $x_c \omega_c = 15.6$ cm.⁻¹,⁵ $r_0 = 1.418$ Å⁴ (Stamper and Barrow incorrectly list r_0 as 1.442 Å). The deviations of the true values of the equilibrium constants from those of Doescher's

¹ Doescher, *J. Chem. Phys.*, 1952, **20**, 330.

² Stamper and Barrow, *Trans. Faraday Soc.*, 1958, **54**, 1592.

³ Guggenheim and Prue, "Physicochemical Calculations," North Holland Publ. Co., Amsterdam, 1955.

⁴ Andrychuk, *Canad. J. Phys.*, 1951, **29**, 151.

⁵ Rees, *J. Chem. Phys.*, 1957, **26**, 1567.

equation are considerable. Intermediate values of the equilibrium constant between 100 and 2000° K can most simply be found from Doescher's equation by the application of a correction obtained by interpolation.

All equilibrium constants are in atmospheres. K_{obs} are the observed values, K_d those from Doescher's equation, and K_c those calculated by statistical mechanics.

DEPARTMENT OF CHEMISTRY, EDINBURGH UNIVERSITY.

[Received, March 4th, 1959.]

621. *The Infrared Spectrum of a Platinous Complex having a Bridging Ethylenediamine Group with the trans-Configuration: [Bisethylene-tetrachloro- μ -ethylenediaminediplatinum(II)].*

By D. B. POWELL and N. SHEPPARD.

In a recent study of the infrared spectra of chelated metal complexes of ethylenediamine, it has been shown that two types of infrared spectrum occur and it was suggested¹ that they may correspond to *gauche*- and *cis*-configurations of the ligand. It is therefore of interest to examine the spectrum of complexes where the ethylenediamine has the *trans*-configuration. A compound where this structure seems probable is the complex $(\text{C}_2\text{H}_4)_2\text{PtCl}_2\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2\text{PtCl}_2(\text{C}_2\text{H}_4)$ (I*), obtained by the addition of aqueous ethylenediamine to an aqueous solution of Zeise's salt, $\text{KPt}(\text{C}_2\text{H}_4)\text{Cl}_3\cdot\text{H}_2\text{O}$.²

The absorption bands due to the ethylene group can be identified by comparison with the spectrum of *trans*- $\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2$.³ The remaining bands due to the ethylenediamine group (Figure, *b*) show an extremely simple spectrum,† which is in marked contrast to that of the chelated ethylenediamine complex, $\text{Pt}(\text{en})\text{Cl}_2$ (Figure, *a*). In these spectra absorption peaks due to the ethylene group are marked "e". The simple spectrum obtained for the bridged complex (I) can be readily explained if the ethylenediamine group has the symmetrical *trans*-configuration.

The absorption bands which are not found in the simple ethylene complex, and which are therefore assigned to the ethylenediamine group, can be further differentiated by comparison with the spectrum of compound (II), in which the NH_2 groups of (I) are replaced by ND_2 (Figure, *c*). By using this method it is relatively easy to identify the vibrations associated primarily with $-\text{NH}_2$ vibrations and to arrive at a reasonable assignment of many of the absorption bands to fundamental vibrations in the molecule. The results obtained and the suggested assignments are listed in the Table, together with the absorption frequencies observed in the spectrum of *trans*- $\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2$. The spectrum of the latter has been recorded previously.³

The frequency shifts due to deuteration of the NH_2 groups are mostly fairly obvious from the spectra in the Figure, *b* and *c*. However, the band centred at 1000 cm^{-1} in the deuterio-compound (II) causes some confusion, as the absorption is made up of the band shifted from 1336 cm^{-1} in (I), superimposed on the doublet at 1023—1016 cm^{-1} due to the ethylene group. The absorption band at 653 cm^{-1} is undoubtedly due to an N-H deformation as shown by the marked frequency shift on deuteration, but the latter appears to be accompanied by a surprising reduction in intensity. It is possible that the assignments of the NH_2 twisting and NH_2 wagging modes should be interchanged. This would be preferable on intensity grounds, but less likely on the basis of the frequencies.

* This compound will be referred to subsequently as I, whereas the compound where the NH_2 groups have been replaced by ND_2 , will be shown as II.

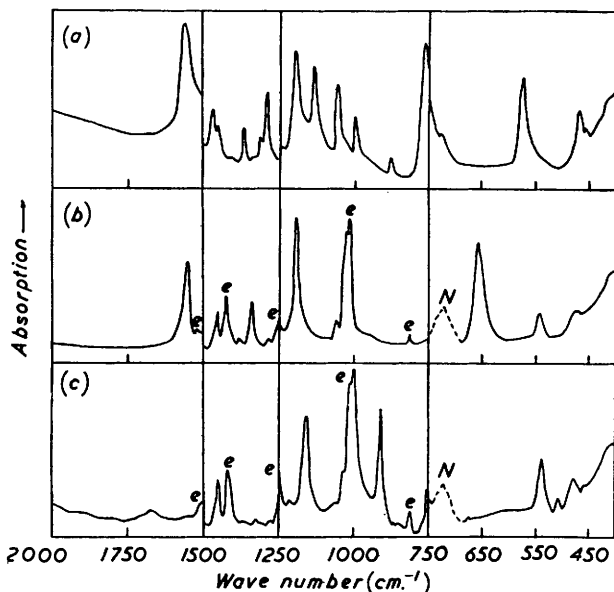
† It is suggested that this pattern of spectrum be provisionally described as type C to distinguish it from the more complex type A and type B spectra found previously for chelated ethylenediamine complexes.¹

¹ Powell and Sheppard, *J.*, 1959, 791.

² Helman, *Compt. rend. Acad. Sci., U.R.S.S.*, 1943, 38, 243.

³ Powell, *J.*, 1956, 4459.

Infrared absorption spectra of (a) $\text{Pt}(\text{en})\text{Cl}_2$, (b) (I), (c) the deuterio-compound (II). 2000—1500 and 1250—400 cm^{-1} , Nujol mull; 1500—1250 cm^{-1} , hexachlorobutadiene; N = Nujol band.



A difficulty in the assignment of the CH_2 vibrations is caused by the weakness of the absorption bands compared with those from the NH_2 groups and the co-ordinated ethylene molecule. It is therefore difficult to distinguish absorption due to these vibrations from the stronger overtone and combination frequencies; there is also a considerable danger of these weak bands' being obscured by other strong absorptions. The CH_2 bending

Infrared absorption frequencies (cm^{-1}) of compounds (I) and (II) compared with those of $\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2$.

$\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2$	(I)	(II)	$\nu\text{N-H}/\nu\text{N-D}$	Assignment *
Not investigated	3265 s	2412 s	1.35	$\nu\text{N-H}$
2045 w	2034 w	2032 w		<i>e</i>
1520 vw	1520 vw	1520 vw	1.34	NH_2 bend
1432 } _s	1452 m	1450 m		<i>e</i>
1422 } _s	1421 m	1417 m		CH_2 bend
	1375 w	?		<i>e</i>
	1336 m	1000 m	1.34	CH_2 wag?
	1280 w	1324 w		NH_2 wag
? (1250 in Zeise's salt)	1250 m	1277 w		CH_2 twist
	1190 s	1251 m		<i>e</i>
	1118 vw	912	1.31	NH_2 twist
	1052 w	—		ν skeletal
1023 } _s	1023 } _s	1026 } _s		<i>e</i>
1010 } _s	1016 } _s	1013 } _s		
980 vw	895 vw	880 } _{vw}		
		841 } _{vw}		
816 w	818 w	810 m		<i>e</i>
	?	752 w		CH_2 rock
691 m	712 vw	716 vw		<i>e</i>
Absorption peaks due to NH_3 group omitted	653 s	506 w	1.29	NH_2 rock
	540 w	537 m		$\nu\text{Pt-N}$ and skeletal bending
	475 w	475 w		

* "*e*" indicates that the peak is assigned to the ethylene group. Detailed assignments of the spectra of ethylene-platinum complexes have been discussed elsewhere.⁴

mode is fairly strong and easily distinguished, and the remaining CH_2 deformations may be expected to follow the usual order of frequencies for CH_2 angle deformation modes, as observed for n-butane⁵ and for ethylenediamine itself,⁶ namely, bend > wag > twist > rock; a skeletal vibration probably occurs near 1000 cm.^{-1} , by analogy with n-butane.⁵ The band at 750 cm.^{-1} in (II) appears to have no counterpart in (I). It seems probable that it is a CH_2 rocking frequency, the intensity of which is increased on deuteration of the NH_2 group.

The absorptions found from 600 to 450 cm.^{-1} may arise either from skeletal bending modes of the ethylenediamine group, or from platinum–nitrogen stretching vibrations; there are two bands in this region, at 540 and 475 cm.^{-1} . In *trans*- $\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_2)\text{Cl}_2$,³ the $\nu(\text{Pt-N})$ vibration has been identified at 480 cm.^{-1} .

The characteristic spectrum associated with an ethylenediamine group having the *trans*-configuration should enable this structure to be identified in other ethylenediamine complexes. Evidence of the *trans*-configuration has been found for crystalline ethylenediamine dihydrochloride, but this somewhat different spectrum will be discussed elsewhere.

Experimental.—All spectra were obtained with a Hilger H 800 spectrometer, with rock-salt and potassium bromide prisms. The samples were examined as dispersions in liquid paraffin and hexachlorobutadiene.

Zeise's salt, $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$, was prepared as described by Chatt and Duncanson.⁷ The ethylenediamine complex (I) was precipitated by the addition of aqueous ethylenediamine to the salt. The precipitate was centrifuged, washed, and dried *in vacuo* over phosphoric oxide.

The deuterio-compound (II) was prepared by repeatedly evaporating a D_2O solution of ethylenediamine hydrochloride in a vacuum desiccator over phosphoric oxide, until spectroscopic examination showed that replacement of NH_2 by ND_2 was essentially complete. This deuterio-derivative was then dissolved in 99.98% D_2O and added to a D_2O solution of Zeise's salt. On neutralisation of the solution with potassium carbonate, also in D_2O , the complex was precipitated; it was then washed with D_2O and dried overnight *in vacuo*.

Thanks are due to Imperial Chemical Industries Limited for financial assistance and particularly for the gift of the deuterium oxide.

SIR JOHN CASS COLLEGE, JEWRY STREET, LONDON, E.C.3 (D. B. P.).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE (N. S.).

[Received, March 11th, 1959.]

⁴ Powell and Sheppard, *Spectrochim. Acta*, 1958, **13**, 69.

⁵ Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261.

⁶ Bellanato, *Anales. Fis. Quim.*, 1956, **52**, B, 363.

⁷ Chatt and Duncanson, *J.*, 1953, 2939.

622. *Lycopodium Alkaloids. Part I. Extraction of Alkaloids from Lycopodium fawcettii, Lloyd and Underwood.*¹

By R. H. BURNELL.

PLANT material collected near Cinchona, in the Blue Mountain Range of Jamaica (*ca.* 5500 ft. elevation), was extracted by a procedure similar to that of Manske and Marion.² The crude ether-soluble base was separated into strong and weak bases by countercurrent distribution and the strong bases were distributed again. Although no separation of the stronger bases could be detected from the weight curve, the following compounds were isolated from fractions:

Base A, obtained as the perchlorate, $\text{C}_{16}\text{H}_{27}\text{O}_2\text{N}\cdot\text{HClO}_4$, showed an infrared carbonyl peak at 1695 cm.^{-1} as well as a bonded hydroxyl absorption at 3340 cm.^{-1} .

Base B, which melted at 178 – 179° , gave a perchlorate, m. p. 314 – 315° , identical (mixed m. p. and infrared comparison) with the *Lycopodium* alkaloid L.30³ described by

¹ Lloyd and Underwood, *Bull. Torrey Bot. Club.*, 1900, **27**, 167.

² Manske and Marion, *Canad. J. Res.*, 1946, **24**, B, 57.

³ Perry and MacLean, *Canad. J. Chem.*, 1956, **34**, 1189.

Manske and Marion.⁴ The base contained no *N*-methyl group and gave infrared maxima at 1703 and 3195 cm^{-1} . Active-hydrogen determinations agree with an earlier suggestion that the nitrogen atom is tertiary.

Base C, the major component, was named fawcettiine and was characterised as its perchlorate, $\text{C}_{18}\text{H}_{29}\text{O}_3\text{N}\cdot\text{HClO}_4\cdot\text{H}_2\text{O}$ (m. p. 272—273°), which showed, besides hydroxyl peaks at 3463 (H_2O) and 3229 cm^{-1} , infrared absorption characteristic of an *O*-acetyl group (1732, 1250, and 1238 cm^{-1}). Methoxyl and *N*-methyl groups are absent and the nitrogen is tertiary. The presence of the acetyl group has been confirmed by both analysis and hydrolysis of fawcettiine to deacetylfawcettiine, $\text{C}_{16}\text{H}_{27}\text{O}_2\text{N}$, which no longer absorbed in the carbonyl region. Active-hydrogen determinations indicate two hydroxyl groups to be present in deacetylfawcettiine and this confirms the molecular formula for fawcettiine which can therefore contain only one. Kuhn–Roth figures are inconclusive. Dehydration of deacetylfawcettiine with thionyl chloride afforded a new unsaturated compound, deacetyldehydrofawcettiine, characterised as the hygroscopic hydrochloride $\text{C}_{16}\text{H}_{25}\text{ON}\cdot\text{HCl}$.

One further base (D) (10 mg.) was obtained from the distribution but this was identical with deacetylfawcettiine.

From the mixture of weak bases a small quantity of a crystalline perchlorate was obtained directly. The base, E, is $\text{C}_{17}\text{H}_{25}\text{O}_2\text{N}$ and shows a broad infrared carbonyl band (1697 cm^{-1}); hydroxyl absorption is absent. A distinguishing feature of the infrared spectrum of Base E perchlorate is an ammonium band of medium intensity at 2020 cm^{-1} which is absent from the spectra of the salts of the other bases isolated.

From the remaining weak bases a volatile alkaloid was distilled. This is the second most abundant, and has been named fawcettidine (Base F). Analyses suggest $\text{C}_{16}\text{H}_{23}\text{ON}$ as the molecular formula and while the picrate is normal, the hydrochloride apparently decomposes during recrystallisation. The infrared carbonyl absorption of 1740 cm^{-1} must be due to a five-membered ring ketone. The base gives a dark orange colour with diazotised sulphanilic acid.

The residue from the distillation of fawcettidine afforded a perchlorate, m. p. 198°, $\text{C}_{18}\text{H}_{27}\text{O}_3\text{N}\cdot\text{HClO}_4$ (Base G) which showed two infrared carbonyl peaks and a hydroxyl stretching band at 3450 cm^{-1} .

To check the analyses of the alkaloids perchlorate determinations were carried out with essentially the method described by Bodenheimer and Weiler.⁵ Results of reasonable accuracy could be obtained on samples containing as little as 1 mg. of perchlorate ion, but with smaller quantities discrepancies arose owing to discoloration of the reagent by the alkaloids.

Experimental.—Infrared spectra are for KBr pellets unless stated to the contrary.

Extraction. The dried ground plant material (16 kg.) was extracted continuously with methanol for 48 hr. and the solution concentrated to a thick black residue *in vacuo*. The residue was digested for 24 hr. with dilute hydrochloric acid. The solution was then filtered and neutral components were removed by ether-extraction. After basification with ammonia the crude ether-soluble base (19.0 g.) was obtained by continuous ether-extraction. Chloroform extraction of the aqueous layer afforded a further 9.5 g. of crude base, which is being studied.

Ether-soluble bases. The brown oil from the extraction (19.0 g.) was distributed between aqueous phosphate buffer (pH 5.28) and chloroform (stationary phase) in a 20-tube multiple extractor, a single-withdrawal technique being used until 34 transfers were complete. To the individual tubes was added concentrated aqueous ammonia (*ca.* 15 ml.), and the aqueous layer chloroform extracted three times. The extracts from each tube were combined and evaporated and then grouped as follows: Fraction A (weak bases), tubes 1—10 (8.7 g.); Fraction B (weak bases), tubes 11—18 (1.3 g.); Fraction C (strong bases), tubes 19—35 (6.6 g.).

Strong bases. Fraction C (6.5 g.) from the first distribution was shaken between chloroform (stationary phase) and acetate buffer (pH 5.23) for 20 transfers. The weight curve for the aqueous and organic phases showed no definite separation of the bases but the following products were obtained :

⁴ Manske and Marion, *J. Amer. Chem. Soc.*, 1947, **69**, 2126.

⁵ Bodenheimer and Weiler, *Analyt. Chem.*, 1955, **27**, 1293.

Base A. Fractions 3—7 (570 mg.) gave a crystalline *perchlorate* (270 mg.) which recrystallised from acetone and then water as colourless prisms, m. p. 221—222° (Found: C, 52.2; H, 7.3; N, 3.8. $C_{16}H_{27}O_2N, HClO_4$ requires C, 52.5; H, 7.7; N, 3.8%), infrared peaks at 1695 and 3340 cm^{-1} .

Base B. Fractions 9—10 (860 mg.) gave a crystalline *base* (540 mg.) which recrystallised from acetone as plates, m. p. 178—179° (Found: C, 72.8; H, 9.3; O, 11.8; N, 5.1. $C_{16}H_{25}O_2N$ requires C, 73.0; H, 9.6; O, 12.2; N, 5.3%). Analyses for OCH_3 and $N-CH_3$ were nil. Active-hydrogen determination gave 0.27% at 21°; $C_{16}H_{24}ON(OH)$ requires 0.36%. Mixed m. p. with L.30 showed no depression. The base gave a crystalline *perchlorate*, rhombic plates, m. p. 314—315° (Found: N, 3.9; ClO_4^- , 27.6. $C_{16}H_{25}O_2N, HClO_4$ requires N, 3.9; ClO_4^- , 27.4%). The infrared spectrum (Nujol), which showed peaks at 1703 and 3195 cm^{-1} , was identical to that of L.30 perchlorate.

Base C (Fawcettiine). Fractions 13—17 (2.52 g.) gave a crystalline *perchlorate* (1.7 g.), from acetone or water as prisms, m. p. 272—275° (decomp.) (Found: C, 50.7; H, 7.5; N, 3.3; ClO_4^- , 22.7; Cl, 8.5. $C_{18}H_{29}O_3N, HClO_4, H_2O$ requires C, 50.8; H, 7.6; N, 3.3; ClO_4^- , 23.3; Cl, 8.3%). Methoxyl groups were absent and analysis for *O*-Ac residues gave 9.2% (one acetyl group requires 10.1%).

The base regenerated from the perchlorate was a glass which sublimed with slight decomp. (100°/1 mm.) and readily decolorised a solution of potassium permanganate in acetone but did not react with bromine water, tetranitromethane, or potassium metaperiodate. The alkaloid is readily destroyed by nitric acid giving a highly insoluble brick-red amorphous substance, and the hydrobromide and hydrochloride decompose on recrystallisation.

The base was refluxed for 3 min. with excess of methyl iodide and then concentrated *in vacuo*, affording *fawcettiine methiodide* as a white solid, m. p. 279—280°, which was recrystallised from acetone (Found: C, 48.5; H, 7.1; N, 3.2; I, 28.2. $C_{19}H_{32}O_3NI, H_2O$ requires C, 48.8; H, 7.3; N, 3.0; I, 27.2%).

To fawcettiine (140 mg.) in methanol (10 ml.) was added 5*N*-sodium hydroxide in 50% methanol (7 ml.), and the solution kept at room temperature for 15 hr. Dilution with water and chloroform extraction gave white *deacetylfawcettiine* (110 mg.), m. p. 203—204° (needles from acetone) (Found: C, 72.1; H, 10.1; O, 12.2; N, 5.5. $C_{16}H_{27}O_2N$ requires C, 72.4; H, 10.3; O, 12.1; N, 5.3%). Active-hydrogen determination gave 0.413% at 21° and 0.303% at 90° (0.38% required for one mol.). The base showed no infrared carbonyl absorption. Acidification of an acetone solution of the base with perchloric acid diluted with acetone gave the *perchlorate*, m. p. 224—227° (Found: N, 3.9. $C_{16}H_{27}O_2N, HClO_4$ requires N, 3.8%).

Deacetylfawcettiine was dissolved in benzene and treated with excess of thionyl chloride at room temperature for 90 min. The residue after evaporation *in vacuo* was taken up in methanol containing a trace of hydrochloric acid and then evaporated to dryness. The white *deacetyl-dehydrofawcettiine hydrochloride* was recrystallised from methanol-acetone (Found: C, 67.2; H, 9.5; N, 4.9; Cl, 12.4. $C_{16}H_{25}ON, HCl$ requires C, 67.7; H, 9.3; N, 4.9; Cl, 12.5%).

Weak bases. Base E. Fraction A from the first distribution was taken up in acetone and made slightly acidic with perchloric acid. After several days a crystalline *perchlorate* (80 mg.), m. p. 267—269° (decomp.), was collected (Found: C, 55.0; H, 7.4; N, 3.8; Cl, 9.3. $C_{17}H_{25}O_2N, HClO_4$ requires C, 54.3; H, 7.0; N, 3.7; Cl, 9.4), infrared peak at 1697 cm^{-1} .

Base F. The base regenerated from the mother liquors of Base E was distilled at 0.1 mm. giving a volatile colourless *oil* (780 mg.) at 125° (Found: C, 78.5; H, 9.4. $C_{16}H_{23}ON$ requires C, 78.3; H, 9.5%). Treatment with an ethereal solution of picric acid afforded the *picrate*, m. p. 222—223° (Found: C, 56.1; H, 5.5; N, 12.0; O, 26.5. $C_{16}H_{23}ON, C_6H_3O_7N_3$ requires C, 55.7; H, 5.5; N, 11.8; O, 26.2%). Both the base (liquid film) and the picrate (Nujol) showed an infrared carbonyl peak at 1740 cm^{-1} .

Base G. The residue from the distillation was dissolved in dilute hydrochloric acid, filtered, and extracted with ether to remove neutral impurities. After basification with ammonia the crude base was extracted with ether and converted into the *perchlorate* (112 mg.), m. p. 198—200° (Found: C, 53.6; H, 7.3; N, 3.4; ClO_4^- , 25.2. $C_{18}H_{27}O_3N, HClO_4$ requires C, 53.3; H, 7.0; N, 3.4; ClO_4^- , 24.5%), infrared peaks at 3450, 1740, and 1694 cm^{-1} .

The author thanks Dr. A. W. Sangster (U.C.W.I.) for the infrared spectra, Dr. A. R. Loveless (Dept. of Botany, U.C.W.I.) for identifying the *Lycopodium* and for his assistance in collecting the material, and Dr. L. Marion (N.R.C., Ottawa) for a sample of L.30.

623. Syntheses of the Four Dimethoxy-*N*-methylphthalimides.

By H. R. ARTHUR and (Miss) Y. L. NG.

In our work on the benzophenanthridine alkaloids, nitidine and oxynitidine,¹ we had occasion to prepare 4:5-dimethoxy-*N*-methylphthalimide which was shown to be a degradation product of oxynitidine. We also synthesised 3:4-dimethoxy-*N*-methylphthalimide which is a degradation product obtainable from chelerythrine.² Our syntheses of these two known compounds include variations in the methods previously used.

The two remaining previously unknown dimethoxy-*N*-methylphthalimides have also been synthesised. Ultraviolet spectra are recorded.

Experimental.—Except where otherwise stated m. p.s (which are uncorrected) were taken with a gas-heated copper block.

3:4-Dimethoxy-*N*-methylphthalimide. *o*-Vanillin (30.0 g.) was melted and potassium hydroxide (16 g.) in water (24 ml.) was added, with stirring, at a rate of 2 drops per second. Purified methyl sulphate (24 ml.) was then added at the same rate. After 2 hr. ice was added. The precipitate of crude *o*-veratraldehyde (30.0 g.) was collected, washed with ice-water, and dried. This product (10.0 g.) was oxidised by the method of Edwards, Perkin, and Stoyle³ to *o*-veratric acid (10.0 g.), m. p. 120°, which was converted into crude meconine (5.0 g.), m. p. 100°. This product (3.0 g.), with manganese dioxide, yielded opianic acid (3.0 g.), m. p. 145°, which with lead dioxide gave hemipinic acid³ (1.0 g.), m. p. 173—175° (after drying at 120°). Anhydrous hemipinic acid (0.5 g.) was heated with acetyl chloride (10 ml.) for 1 hr. Distillation of the halide left a residue which was dissolved in glacial acetic acid. Sodium acetate (1.0 g.) and methylamine hydrochloride (0.8 g.) were added and the mixture was heated under reflux for 20 min., after which removal of inorganic salts and concentration of the filtrate gave a product which was dissolved in benzene. The benzene solution was filtered through alumina and then concentrated. Colourless needles of 3:4-dimethoxy-*N*-methylphthalimide (0.08 g.), m. p. 166—167°, were obtained (Found: C, 60.2; H, 5.1; N, 6.6; OMe, 27.8%; *M*, 215. Calc. for C₁₁H₁₁O₄N: C, 59.7; H, 5.0; N, 6.3; 2OMe, 28.0%; *M*, 221), λ_{max.} (log ε), 337 (3.71), 234 mμ (2.53).

3:5-Dimethoxy-*N*-methylphthalimide. Benzoic acid (10 g.) was heated under reflux with fuming sulphuric acid (65% SO₃; 24 ml.) for 10 hr. at 160—175°, then for 5 hr. at 180—190°. The cooled mixture was added slowly to a suspension of barium carbonate (300 g.) in water (1 l.). The mixture was boiled, then filtered hot; the residue was washed with hot water. The combined filtrates were treated with a concentrated solution of potassium carbonate until precipitation of barium carbonate was just complete. The precipitate was removed, and the filtrate, after concentration under reduced pressure, deposited the potassium salt of 3:5-disulphobenzoic acid (35.0 g.). Fusion of this salt (30.0 g.) with potassium hydroxide (70 g.), suspended in water (15 ml.), by Birkinshaw and Bracken's method⁴ yielded 3:5-dihydroxybenzoic acid (5.0 g.), m. p. 234°, which gave a port-wine colour with ferric chloride solution. This product (10.0 g.) was converted into 3:5-dimethoxybenzoic acid (9.8 g.), m. p. 182—184°, by methyl sulphate. To 3:5-dimethoxybenzoic acid (10.0 g.) in absolute ethanol (30 ml.) was added concentrated sulphuric acid (2.5 ml.) with shaking. The mixture was boiled under reflux for 6 hr., and the product, isolated in the usual manner, was treated with a mixture of concentrated sulphuric acid (35 ml.), water (7 ml.), and chloral hydrate (12.0 g.) as stated by Graves and Adams.⁵ 4:6-Dimethoxy-3-(trichloromethyl)phthalide (18.0 g.), m. p. 245—248° (lit., m. p. 125°), was obtained. This was converted into 4:6-dimethoxyphthalide-3-carboxylic acid (7.7 g.), which (2.0 g.) was decarboxylated and then oxidised⁶ with potassium permanganate to give 3:5-dimethoxyphthalic acid (1.0 g.), m. p. 155—158° (decomp.). This acid (1.0 g.) was boiled under reflux with acetic anhydride (20 ml.) for 2 hr. The solvent was distilled, then glacial acetic acid, fused sodium acetate (3.0 g.), and methylamine hydrochloride (2.0 g.) were added and the mixture was treated as stated for the preparation above. 3:5-Dimethoxy-*N*-methylphthalimide (0.15 g.) was obtained as colourless prisms, m. p. 185° (m. p. 195°; Kofler) (Found: C, 59.9; H, 5.2; N, 6.5; OMe, 27.9%; *M*, 234), λ_{max.} (log ε) 342 (3.63), 239 mμ (4.50).

¹ Arthur, Hui, and Ng, *J.*, 1959, 1840.

² Späth and Kuffner, *Ber.*, 1931, **64**, 1123.

³ Edwards, Perkin, and Stoyle, *J.*, 1925, 195.

⁴ Birkinshaw and Bracken, *J.*, 1942, 369.

⁵ Graves and Adams, *J. Amer. Chem. Soc.*, 1923, **45**, 2439.

3 : 6-Dimethoxy-*N*-methylphthalimide. *p*-Benzoquinone (purification was essential; 1.0 g.) was converted by Helferich's method⁶ into 2 : 3-dicyanoquinol, obtained as brown hydrated crystals (0.5 g.) which blackened at 230°. This product (0.5 g.) was converted by Thiele and Meisenheimer's method⁷ into 3 : 6-dihydroxyphthalimide (0.55 g.), which separated from water as greenish-yellow needles. 3 : 6-Dihydroxyphthalimide (0.25 g.) was ground with potassium carbonate (1.0 g.). The bright red potassium salt obtained was heated in a sealed tube with methyl iodide (4 ml.) on a steam-bath. After 4 hr. the mixture changed from red to brown. After 8 hr. the methyl iodide was evaporated and the residue was washed with water, then recrystallised from alcohol. Buff-coloured needles (0.1 g.) of 3 : 6-dimethoxy-*N*-methylphthalimide, m. p. 202—204° (m. p. 206—208°; Kofler), separated (Found; C, 60.2; H, 5.2; N, 7.0; OMe, 27.7%; *M*, 235), λ_{\max} . (in ethanol) 221 m μ (log ϵ 4.27) [between 285 and 310 m μ the extinction coefficient remained approximately constant (log ϵ 2.6)].

4 : 5-Dimethoxy-*N*-methylphthalimide. By the method of Edwards, Perkin, and Stoyle,³ veratraldehyde was converted into veratric acid, m. p. 175°. The acid (10.0 g.) was converted into *m*-meconine, colourless needles (3.2 g.), m. p. 153—156°. This (1.0 g.) with potassium permanganate gave yellow *m*-hemipinic acid (0.5 g.), m. p. 193—199° (decomp.), which (0.5 g.) was converted into the anhydride and into 4 : 5-dimethoxy-*N*-methylphthalimide (0.1 g.), as stated in an earlier communication.¹ The product crystallised from alcohol as colourless prisms, m. p. 256—258° (214—225° decomp.; Kofler), λ_{\max} . (log ϵ), (in ethanol), 295 (3.24), 247 m μ (4.69). Deulofeu *et al.*⁸ give λ_{\max} . (log ϵ) 295 (3.22), 261 m μ (3.73).

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UNIVERSITY OF HONG KONG, HONG KONG.

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⁶ Helferich, *Ber.*, 1921, **54**, 157; Helferich and Bodenbender, 1923, **56**, 1113.

⁷ Thiele and Meisenheimer, *Ber.*, 1900, **33**, 676.

⁸ Vernengo, Cerezo, Iacobucci, and Deulofeu, *Annalen*, 1957, **610**, 173.

624. Carcinogenic Nitrogen Compounds. Part XXVII.¹ Benzacridines and Related Compounds Derived from *o*-Ethylaniline.

By NG. PH. BUU-HOÏ and P. JACQUIGNON.

IN a broad investigation on the relation between structure and carcinogenic activity of angular benzacridines,² it was of interest to determine the influence of a 9-ethyl group in the 1,2- and 3,4-benzacridine series; in the corresponding homocyclic group, 5-ethyl-1,2-benzanthracene has considerable activity.³

In the 1,2-benzacridine series, condensation of *o*-ethylaniline with α -naphthol in the presence of iodine⁴ furnished *N*-*o*-ethylphenyl-1-naphthylamine, and Bernthsen reactions of this secondary amine with acetic anhydride and higher homologues afforded the 5-alkyl-9-ethyl-1,2-benzacridines listed in Table 1; 9-ethyl-1,2-benzacridine was prepared directly from *o*-ethylaniline with α -naphthol and paraformaldehyde.⁵ A similar reaction with β -naphthol yielded 9-ethyl-3,4-benzacridine, and several of its 5-alkyl derivatives, obtained by Bernthsen reactions with *N*-*o*-ethylphenyl-2-naphthylamine, are listed in Table 2.

TABLE 1. 9-Ethyl-1,2-benzacridines (I).

Substituent	M. p.	Formula	Found (%)			Reqd. (%)		
			C	H	N	C	H	N
H	127°	C ₁₉ H ₁₆ N	88.4	6.1	5.1	88.7	5.9	5.4
Me	115	C ₂₀ H ₁₇ N	88.2	6.0	—	88.5	6.3	—
picrate	157	C ₂₆ H ₂₀ O ₇ N ₄	—	—	10.8	—	—	11.2
Et	94	C ₂₁ H ₁₉ N	88.3	6.6	4.7	88.4	6.7	4.9
picrate	135	C ₂₇ H ₂₂ O ₇ N ₄	—	—	10.6	—	—	10.9
Pr	77	C ₂₂ H ₂₁ N	88.1	6.9	—	88.3	7.1	—

¹ Part XXVI, Buu-Hoï, Saint-Ruf, Jacquignon, and Barrett, *J.*, 1958, 4308.

² Cf. Lacassagne, Buu-Hoï, Daudel, and Zajdela, *Adv. Cancer Res.*, 1956, **4**, 315.

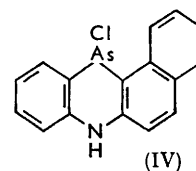
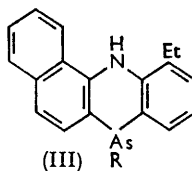
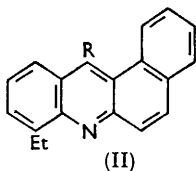
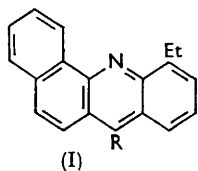
³ Cook, Robinson, and Goulden, *J.*, 1936, 393.

⁴ Knoevenagel, *J. prakt. Chem.*, 1914, **89**, 1; Buu-Hoï, *J.*, 1952, 4346.

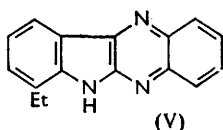
⁵ Ullmann and Fetvadjan, *Ber.*, 1903, **36**, 1027; Buu-Hoï, *J.*, 1949, 670.

TABLE 2. 9-Ethyl-3,4-benzacridines (II).

Substituent	M. p.	Formula	Found (%)			Reqd. (%)		
			C	H	N	C	H	N
H	106°	C ₁₉ H ₁₅ N	88.4	6.0	5.3	88.7	5.9	5.4
picrate	275	C ₂₅ H ₁₈ O ₇ N ₄	—	—	11.4	—	—	11.5
Me	72	C ₂₀ H ₁₇ N	88.2	6.3	—	88.5	6.3	—
picrate	238	C ₂₆ H ₂₀ O ₇ N ₄	—	—	10.9	—	—	11.2
Et	110	C ₂₁ H ₁₉ N	88.7	6.8	4.6	88.4	6.7	4.9
picrate	220	C ₂₇ H ₂₂ O ₇ N ₄	—	—	10.7	—	—	10.9
Pr	76	C ₂₂ H ₂₁ N	88.0	6.8	—	88.3	7.1	—



Condensation of *N*-*o*-ethylphenyl-1- and -2-naphthylamine with arsenic trichloride⁶ readily afforded 10-chloro-6-ethyl-5,10-dihydro-3,4-(III; R = Cl) and -1,2-benzophenarsazine (IV); Grignard reaction of the former with methylmagnesium iodide gave 6-ethyl-5,10-dihydro-10-methyl-3,4-benzophenarsazine (III; R = Me).



Other nitrogen-heterocyclic compounds prepared from *o*-ethylaniline include 8-ethyl-2,4-dimethylquinoline, obtained by a Combes reaction with acetylacetone,⁷ and 7-ethylisatin, which was readily prepared by the Sandmeyer reaction⁸ although other *o*-substituted anilines resist conversion into isatins by this method.⁹ Condensation of 7-ethylisatin with *o*-phenylenediamine yielded the indophenazine (V).

The biological properties of these compounds are being investigated; preliminary results show 9-ethyl-5-methyl-1,2-benzacridine to be carcinogenic.

Experimental (with R. Roy).—*o*-Ethylaniline was prepared by reduction of *o*-ethylnitrobenzene; its *toluene-p-sulphonyl* derivative crystallised as prisms, m. p. 135°, from ethanol (Found: C, 65.2; H, 6.4. C₁₅H₁₇O₂NS requires C, 65.4; H, 6.1%).

1-*o*-Ethylphenyl-2,5-dimethylpyrrole. A mixture of hexane-2,5-dione (5 g.) and *o*-ethylaniline (6.5 g.) was refluxed with acetic acid (1 drop) until water ceased to be evolved, and the product was fractionated *in vacuo*, giving the *pyrrole* (5 g.), b. p. 138°/15 mm. (Found: C, 84.1; H, 8.5; N, 6.7. C₁₄H₁₇N requires C, 84.4; H, 8.6; N, 7.0%).

N-*o*-Ethylphenyl-1-naphthylamine. *o*-Ethylaniline (150 g.), α -naphthol (190 g.), and iodine (0.5 g.) were refluxed for 24 hr., and the product fractionated *in vacuo*, giving the *amine* (62 g.), b. p. 233°/11 mm. (Found: C, 87.3; H, 6.9. C₁₈H₁₇N requires C, 87.4; H, 6.9%). The isomeric *N*-*o*-ethylphenyl-2-naphthylamine, similarly prepared from β -naphthol, had b. p. 240°/14 mm. (Found: C, 87.2; H, 7.0%).

Preparation of the benzacridines (see Tables). Those not substituted in the 5-position were prepared by addition of paraformaldehyde (5 g.) in small portions to a boiling mixture of *o*-ethylaniline (10 g.) and α - or β -naphthol (15 g.), and fractionation of the product *in vacuo*. The portion of b. p. 265—275°/15 mm. was dissolved in ethanol and treated with picric acid; the picrate was precipitated on cooling and recrystallised from ethanol; the free benzacridine obtained on basification with aqueous ammonia was recrystallised from ethanol (yield, 15—35%). The 5-alkylated benzacridines were prepared by refluxing for 24 hr. a mixture of the secondary arylamine with an excess of the appropriate acid anhydride and fused zinc chloride; after cooling, the dark mass was treated with aqueous sodium hydroxide and the product was taken up in benzene and fractionated *in vacuo*, purification being *via* the picrate as above (yield, 30—45%).

10-Chloro-6-ethyl-5,10-dihydro-3,4-benzophenarsazine (III; R = Cl). A solution of *N*-*o*-ethylphenyl-1-naphthylamine (3 g.) and arsenic trichloride (2.2 g.) in *o*-dichlorobenzene (5 c.c.)

⁶ Cf. Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2219; Burton and Gibson, *J.*, 1926, 2243; Buu-Hoï and Royer, *J.*, 1951, 795.

⁷ Combes, *Compt. rend.*, 1888, **106**, 1536; Buu-Hoï and Guettier, *Rec. Trav. chim.*, 1946, **65**, 502.

⁸ Sandmeyer, *Helv. Chim. Acta*, 1919, **2**, 234.

⁹ Cf. Yen, Buu-Hoï, and Xuong, *J. Org. Chem.*, 1958, **23**, 1858.

was gently refluxed for 1 hr.; the *phenarsazine* (4 g.) formed on cooling and addition of cyclohexane was recrystallised from toluene as golden-yellow needles, m. p. 211°, giving a blood red halochromy in sulphuric acid (Found: C, 61.0; H, 4.2. $C_{18}H_{15}NAsCl$ requires C, 60.8; H, 4.2%).

6-*Ethyl-5,10-dihydro-10-methyl-3,4-benzophenarsazine* (III; R = Me) was prepared by refluxing the foregoing phenarsazine (0.2 g.) with ethereal Grignard reagent from methyl iodide (0.5 g.) and magnesium for 20 min. on a water-bath; after decomposition with aqueous ammonium chloride and evaporation of the solvent, the precipitate obtained (0.15 g.) was recrystallised from methanol as needles, m. p. 96°, giving an orange-yellow halochromy in sulphuric acid (Found: C, 67.7; H, 5.1. $C_{18}H_{16}NAs$ requires C, 68.0; H, 5.4%).

10-*Chloro-6-ethyl-5,10-dihydro-1,2-benzophenarsazine* (IV). Prepared from *N-o*-ethylphenyl-2-naphthylamine (3 g.) and arsenic trichloride (22 g.) in the usual way, this compound crystallised as golden-yellow needles, m. p. 225°, from toluene, giving an orange-red halochromy in sulphuric acid (Found: C, 60.5; H, 4.3%).

8-*Ethyl-2,4-dimethylquinoline*. A mixture of acetylacetone (10 g.) and *o*-ethylaniline (12 g.) was refluxed for 1 hr., and, after cooling, treated with warm sulphuric acid (80 c.c.); the product obtained on basification with cold aqueous ammonia was taken up in benzene, the benzene solution washed with water and dried (Na_2SO_4), the solvent distilled off, and the residue fractionated *in vacuo*. The *quinoline* (8 g.) had b. p. 148°/13 mm., n_D^{22} 1.5988, and crystallised in the refrigerator (Found: C, 84.2; H, 8.3. $C_{13}H_{15}N$ requires C, 84.3; H, 8.2%). The *picrate* formed yellow leaflets, m. p. 168–169°, from ethanol (Found: N, 13.5. $C_{18}H_{18}O_7N_4$ requires N, 13.5%).

7-*Ethylisatin*. A solution of *o*-ethylaniline hydrochloride (7 g.), chloral hydrate (9 g.), hydroxylamine hydrochloride (11 g.), and sodium sulphate (130 g.) was heated to the b. p. during 45 min. and kept at that temperature for 2 min.; the aqueous phase was then decanted and the solid residue washed with water and heated with sulphuric acid (50 c.c.) for 10 min. at 70–80°. The *product* was then poured on ice, and the solid precipitate washed with water and recrystallised from ethanol, giving orange needles, m. p. 193° (Found: C, 68.3; H, 5.1; N, 8.3. $C_{10}H_9O_2N$ requires C, 68.6; H, 5.1; N, 8.0%).

7-*Ethylindophenazine* (V). A solution of 7-ethylisatin (1 g.) and *o*-phenylenediamine (0.7 g.) in acetic acid (10 c.c.) was refluxed for 20 min., and the precipitate (1.2 g.) obtained on dilution with water formed yellow leaflets, m. p. 268°, from ethanol, giving a brown halochromy in sulphuric acid (Found: N, 16.8. $C_{16}H_{13}N_3$ requires N, 17.0%). 7-*Ethyl-2-* or *-3-nitroindophenazine*, similarly prepared with 4-nitro-1,2-phenylenediamine, crystallised as orange, sublimable needles, m. p. 263°, from acetic acid (Found: N, 18.9. $C_{16}H_{12}O_2N_4$ requires N, 19.2%).

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625. Molybdenum(II) Benzoate.

By E. W. ABEL, APAR SINGH, and G. WILKINSON.

RECENTLY a number of workers have reported¹⁻⁴ the reaction between substituted aromatic compounds and chromium hexacarbonyl to produce tricarbonyl aromatic chromium compounds. It has been noted,¹ however, that certain substituents (CO_2H , CN, CHO, NO_2) on the aromatic nucleus cause decomposition, with no formation of a metal-tricarbonyl compound.

In the process of treating molybdenum hexacarbonyl with a variety of compounds, we have obtained molybdenum dibenzoate, $(C_6H_5 \cdot CO_2)_2Mo$, by the direct interaction of benzoic acid and the hexacarbonyl in dimethylcarbitol (diethylene glycol dimethyl ether). This compound we believe is a novel type of oxygen chelate complex, (I) and (II), where,

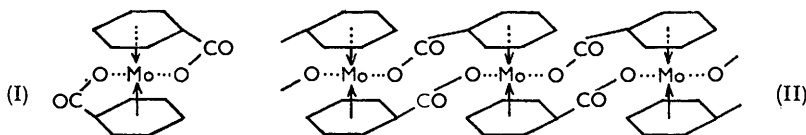
¹ Nicholls and Whiting, *J.*, 1959, 551.

² Natta, Ercoli, and Calderazzo, *Chim. e Ind.*, 1958, 40, 287.

³ Fischer, Öfele, Essler, Fröhlich, Mortensen, and Semmlinger, *Z. Naturforsch.*, 1958, 13b, 458.

⁴ Fischer and Öfele, *Chem. Ber.*, 1957, 90, 2532.

in addition, the arene nucleus is bound to the metal atom by a sandwich-type bond, as in the arene-metal carbonyls.



The absence of the CO_2H group is confirmed by the insolubility of the substance in alkali, and the failure to liberate any hydrogen chloride on warming with either phosphorus pentachloride or thionyl chloride. Further, there are no hydroxyl frequencies observable in the infrared spectrum, either in the free OH or hydrogen-bonded OH regions.

There is also a complete absence of absorption in the metal carbonyl and carboxylic acid regions, but the presence of the $-\text{C}(\text{O})\text{O}^-$ group is confirmed by very strong absorption at 1404 and 1494 cm^{-1} , these two regions being very characteristic⁵ of the symmetrical and asymmetrical vibrations of the COO^- structure.

From the structures proposed it can be seen that it is possible for the aromatic ring to co-ordinate to the same (I) or different (II) metal atoms from its carboxylate group, the latter giving chain formation. This polymerisation is confirmed by the solubility properties of the compound. A very small portion of the initial product is soluble in chloroform to give a bright yellow solution which undergoes rapid decomposition; the residual yellow crystals, however, are completely insoluble in any solvent. These possess remarkable thermal stability and have been recovered unchanged after 24 hours' heating at 350° in the absence of air.

The polymeric structure does break down at a higher temperature, however, and it is possible to sublime molybdenum dibenzoate at 420°/0.01 mm. The crystalline yellow condensate has identical analysis and infrared spectrum with those of an unsublimed sample. Again, the condensed compound appears to be mainly polymeric and has the same solubility properties as it had before sublimation.

Similar compounds with the same properties have also been obtained from *o*-toluic and anisic acids. These also have very strong infrared absorptions in the COO^- regions, *viz.*: molybdenum *o*-toluate (1384 and 1500 cm^{-1}), and molybdenum anisate (1390 and 1504 cm^{-1}). All three compounds were diamagnetic. The reaction of nitrobenzene with molybdenum hexacarbonyl gives a blue, insoluble, presumably polymeric material, perhaps of a rather similar nature to the benzoate; we have been unable to purify the material or to obtain reliable analyses.

Experimental.—Microanalyses were by the Microanalytical Laboratory, Imperial College. Infrared spectra, in Nujol and hexachlorobutadiene mulls and potassium bromide discs, were recorded on a Perkin-Elmer Model 21 double-beam spectrometer with sodium chloride optics.

Interaction of molybdenum hexacarbonyl and benzoic acid. The carbonyl (5.0 g., 1 mol.) and acid (4.7 g., 2 mol.) in freshly distilled diethylene glycol dimethyl ether were heated at 160° until there was no further evolution of carbon monoxide (about 9 hr.). Crystals separated during the reaction, and after cooling, volatile matter was removed (60°/10⁻³ mm.). Washing with warm alcohol (4 × 20 c.c.) and subsequent vacuum drying left a mass of lemon-yellow needle crystals of molybdenum(II) dibenzoate (2.72 g., 38%) (Found: C, 49.7; H, 3.1; Mo, 28.0; O, 19.2. $\text{C}_{14}\text{H}_{10}\text{O}_4\text{Mo}$ requires C, 49.7; H, 3.0; Mo, 28.4; O, 18.9%).

In a similar manner molybdenum di-*o*-toluate (41%) (Found: C, 52.7; H, 4.5; Mo, 26.2; O, 17.4. $\text{C}_{16}\text{H}_{14}\text{O}_4\text{Mo}$ requires C, 52.5; H, 3.8; Mo, 26.2; O, 17.5%) and molybdenum dianisate (38%) (Found: C, 48.1; H, 4.3; Mo, 24.3; O, 23.7. $\text{C}_{16}\text{H}_{14}\text{O}_8\text{Mo}$ requires C, 48.2; H, 3.5; Mo, 24.1; O, 24.1%) were prepared as yellow crystalline solids.

Sublimation of molybdenum benzoate. The salt was placed under a thick pad of glass-wool in a small sublimator with an air-cooled probe. After evacuation (0.01 mm.), the sublimer was slowly heated in a Woods-metal bath. At *ca.* 350° the pale yellow crystals became orange (but returned to yellow on cooling), and then at *ca.* 420° yellow crystals started to condense on the

⁵ Duval, Gerding, and Lecomte, *Rec. Trav. chim.*, 1950, **69**, 391 (and references listed therein).

probe. The temperature was kept at this value until most of the benzoate had sublimed. On cooling, the probe was removed and the condensate (78%) was unchanged molybdenum (II) benzoate (Found: C, 49.6; H, 3.05; Mo, 28.2; O, 19.0%) (strong infrared absorptions at 1404 and 1494 cm^{-1}).

Infrared spectrum of molybdenum(II) dibenzoate. 677(s), 707(s), 717(s), 842(m), 930(w), 1028(m), 1067(w), 1137(m), 1172(w), 1404(vs), 1442(m), 1494(vs), 1583(m), 3020(w).

We thank the Climax Molybdenum Company for a gift of molybdenum hexacarbonyl and the Ethyl Corporation for financial support (E. W. A.).

INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.

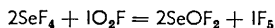
[Received, March 26th, 1959.]

626. Iodyl Fluoride.

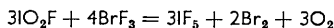
By E. E. AYNLEY and S. SAMPATH.

CHLORYL FLUORIDE, ClO_2F , has been shown by Woolf¹ and by Schmeisser and Ebonhöch² to form complex compounds with a number of inorganic fluorides including BF_3 , SiF_4 , AsF_5 , SbF_5 , and PF_5 . The isolation by Schmeisser and Lang³ of a white crystalline compound, $\text{IO}_2\text{F}\cdot\text{AsF}_5$, from IO_2F and AsF_5 with use of anhydrous hydrogen fluoride suggested that other complexes of iodyl fluoride might be prepared. The similarity in the modes of decomposition of KIF_6 and IOF_3 led Aynley, Nichols, and Robinson⁴ to believe that IOF_3 might have the structure, $\text{IO}_2^+\text{IF}_6^-$ which suggests that $\text{IO}_2\text{F}\cdot\text{AsF}_5$ should be written $\text{IO}_2^+\text{AsF}_6^-$. The reactions of iodyl fluoride have therefore been studied and attempts made to prepare complexes containing the IO_2^+ ion. The absence of results suggest that the arsenic complex may rather be formulated as $\text{AsF}_4^+\text{IO}_2\text{F}_2^-$, in view of the isolation of $\text{K}^+\text{IO}_2\text{F}_2^-$ by Helmholtz and Rogers.⁵

Iodyl fluoride dissolved readily in warm selenium tetrafluoride to form a clear liquid. The products were selenium oxyfluoride and iodine pentafluoride in amounts indicating that the reaction may be represented:



Similarly, bromine trifluoride reacted vigorously with iodyl fluoride, producing iodine pentafluoride, oxygen, and bromine. One mole of oxygen was evolved for every mole of iodyl fluoride, probably in accordance with the equation:



Antimony pentafluoride when heated with iodyl fluoride forms a blue solid having the composition $\text{IO}_2\text{F}\cdot 0.8\text{SbF}_5$.

On the other hand, boron trifluoride, silicon tetrachloride, arsenic pentafluoride, and sulphur trioxide when separately passed over iodyl fluoride at various temperatures did not react with it. Moreover, when boron trifluoride was passed into (a) a suspension of iodyl fluoride in "Arcton 9," (b) a solution of iodyl fluoride in iodine pentafluoride (cf. the reaction $\text{KF} + \text{BF}_3 = \text{KBF}_4$), and (c) iodyl fluoride dissolved in anhydrous hydrogen fluoride, no reaction occurred. Nor was there any reaction with nitryl fluoride, though a compound of the type $\text{NO}_2^+\text{IO}_2\text{F}_2^-$ might have been expected.

Thus iodyl fluoride is much less prone to form complex compounds than chloryl fluoride; some fluorinating agents, however, e.g., SeF_4 , BrF_3 , convert iodyl fluoride into iodine pentafluoride.

The authors thank Imperial Chemical Industries Limited for the loan of a fluorine generator, and one of them (S. S.) is indebted to the U.K. Government for a maintenance grant under the Colombo Plan.

KING'S COLLEGE, NEWCASTLE UPON TYNE, 1.

[Received, March 30th, 1959.]

¹ Woolf, *J.*, 1954, 4113.

² Schmeisser and Ebonhöch, *Angew Chem.*, 1954, **66**, 230.

³ Schmeisser and Lang, *ibid.*, 1955, **67**, 156.

⁴ Aynley, Nichols, and Robinson, *J.*, 1953, 623.

⁵ Helmholtz and Rogers, *J. Amer. Chem. Soc.*, 1940, **62**, 1537.

627. *Some Fatty Acid Esters of α -Tocopherol.*

By P. F. G. PRAILL.

IN view of the importance of some of the unsaturated fatty acids in the diet and the prevention of their autoxidation by the tocopherols it seemed that the biological study of the esters of α -tocopherol might be of interest. However, the fact that in autoxidative control the essential agent is free tocopherol was borne in mind. Several esters of α -tocopherol are well known but those of the fatty acids are restricted to the D- and the DL-forms of the acetate¹ and palmitate.² The present communication is to record the general characteristics of some other fatty acid esters.

Experimental.—Materials. Fatty acids were purified by standard procedures, and had m. p., n_D , and iodine value in good agreement with those reported in the literature. Acid chlorides were prepared by treatment with oxalyl chloride.

D- α -Tocopherol was a 70% concentrate or was prepared by hydrolysis of the pure acetate. DL- α -Tocopherol was a commercial sample (>99.5% pure).

Preparation of the esters of tocopherol. α -Tocopherol (0.02 mole) was dissolved in 1,2-dichloroethane (22.5 ml.) and pyridine (12.2 ml.). The acid chloride (0.022 mole) in 1,2-dichloroethane (17 ml.) was then added during 15 min., there being a transient pink coloration and pyridine hydrochloride separating. After 20 hr. at room temperature the mixture was poured into water and extracted with ether. The ethereal solution was washed with 2N-hydrochloric acid, then with 2% potassium hydroxide solution, and finally with water. The dried (Na₂SO₄) ethereal solution was evaporated, and the residue dissolved in the minimum amount of hot propan-2-ol. The oil, or solid, which separated from the propanol on cooling, was taken up in hot acetone. The treatment with alcohol and acetone was repeated until no further improvement in the spectrum of a sample was obtained.

The method for removing traces of acid from the esters used by Robeson *et al.*² was to adsorb the crude material from a light petroleum solution on "Doucil" and to re-extract the ester with large volumes of light petroleum. We tried this process using "Doucil" and also "Decalco F;" although some improvement of the crude materials was effected, generally the purification was not so good as by successive acetone extractions.

For the unsaturated esters the entire process was carried out in an inert atmosphere so far as possible.

TABLE I. D- α -Tocopheryl esters.

Ester	M. p.	n_D^{20}	n_D^{50}	$E_{1\text{cm.}}^{1\%}$ *	$\log \epsilon_{\text{max.}}$ †	$E_{1\text{cm.}}^{1\%}$ ‡	$\log \epsilon_{\text{max.}}$ ¶	$[\alpha]_{5461}^{\text{¶}}$	Yield (%)
Acetate ¹	26.5—27.5°	—	—	41.2	3.29	—	—	—	—
Acetate	—	1.4970	1.4860	—	—	46.5	3.34	+2.56°	—
Palmitate ²	42—43	—	—	26.8	3.25	—	—	—	33
Palmitate ^{a,e} ...	42—43	—	—	—	—	27.9	3.27	—	50
Palmitate ^{b,d} ...	42	—	1.4792	31.0	3.32	31.7	3.33	+2.47	67
Stearate ^e	48.5	—	1.4782	—	—	30.5	3.33	+2.87	90
Oleate ^{a,f}	—	1.4960	1.4875	—	—	25.4	3.25	+2.44	32
Elaidate ^g	27.5	—	1.4814	—	—	32.0	3.35	+2.71	71
Petroselinat ^h	—	1.4928	1.4830	—	—	31.3	3.34	+2.86	42
Erucate ^{a,i}	—6 to —4	1.4946	1.4848	—	—	26.6	3.30	—	46
Brassidate ^{a,j} ...	35.2	—	1.4802	22.5	3.23	—	—	—	61
Linoleate ^k	—	1.4962	1.4888	—	—	33.1	3.36	+2.61	33
Linolenate ^l ...	—	1.5007	—	—	—	34.1	3.37	—	45

^a From 70% tocopherol. ^b From pure tocopherol. ^c Found: C, 81.4; H, 11.6. C₄₅H₈₀O₃ requires C, 80.8; H, 12.0%. ^d Found: C, 80.6; H, 11.8%. ^e Found: C, 81.0; H, 11.9. C₄₇H₈₄O₃ requires C, 81.0; H, 12.1%. ^f Found: C, 81.3; H, 11.9%. C₄₇H₈₂O₃ requires C, 81.3; H, 11.7%. ^g Found: C, 81.4; H, 12.1%. ^h Found: C, 81.5; H, 11.7%. ⁱ Found: C, 81.3; H, 11.7%. ^j Found: C, 81.6; H, 11.8. C₄₇H₈₀O₃ requires C, 81.5; H, 11.6%. ^k Found: C, 82.5; H, 11.2. C₄₇H₇₈O₃ requires C, 81.7; H, 11.3%. ^l Found: C, 81.4; H, 11.6%. ^{*} At 286 μ in EtOH. [†] In EtOH. [‡] At 285 μ in cyclohexane. [¶] In cyclohexane.

Table I gives the main characteristics of the D- α -tocopheryl esters, and Table 2 those for the DL-esters. Some values from the literature are included.

In cyclohexane, maximum absorption occurred at 285 μ ; there was a peak with an intensity approaching that of the maximum at 288 μ , and a less intense peak at 279 μ . Pure esters had little or no absorption at 300 μ but partly isomerised materials had a low, but

¹ Robeson, *J. Amer. Chem. Soc.*, 1942, **64**, 1487.

² Baxter, Robeson, Taylor, and Lehman, *ibid.*, 1943, **65**, 918.

TABLE 2. DL- α -Tocopheryl esters.

Ester	M. p.	n_D^{20}	n_D^{50}	$E_{1\text{cm.}}^{1\%}$ *	$\log \epsilon_{\text{max.}}$ *	$E_{1\text{cm.}}^{1\%}$ †	$\log \epsilon_{\text{max.}}$ †	Yield (%)
Acetate ^a	—	1.4964	1.4860	44.4	3.32	45.4	3.33	—
Palmitate ^b	36—38°	—	—	30.9	3.31	—	—	—
Stearate ^c	40.5	—	1.4760	—	—	30.7	3.33	71
Oleate ^d	—	1.4918	—	—	—	32.0	3.35	48
Erucate ^e	—	1.4898	1.4800	27.3	3.31	—	—	42
Brassidate ^f	26.5	—	1.4800	28.7	3.33	—	—	82
Linoleate ^g	—	1.4960	—	—	—	35.4	3.39	48

^a Material from Roche Products Ltd. ^b Ref. 2. ^c Found: C, 81.3; H, 12.2. $C_{47}H_{84}O_2$ requires C, 81.0; H, 12.1%. ^d Found: C, 81.3; H, 11.9. $C_{47}H_{82}O_2$ requires C, 81.3; H, 11.7%. ^e Found: C, 81.3; H, 11.7. $C_{51}H_{90}O_2$ requires C, 81.6; H, 12.0%. ^f Found: C, 81.9; H, 11.6. ^g From α -linoleic acid. Found: C, 81.2; H, 11.5. $C_{47}H_{80}O_2$ requires C, 81.5; H, 11.6%. *†‡¶ See Table 1.

measurable, absorption in this region. In cyclohexane α -tocopherol had a maximum absorption at 298 m μ ($E_{1\text{cm.}}^{1\%}$, 85).

Analytical values for carbon and hydrogen are given but are of little value for distinguishing between the individual esters. Some experiments with Wijs solution indicated that determinations of the iodine values for the esters by this method were not reproducible.

The author thanks Messrs. Vitamins Ltd. for financial assistance, and Professor H. Burton for his interest in this work. Dr. D. A. F. Munday kindly prepared the pure oleic acid and Mrs. M. Phillips gave some technical assistance. The work was carried out under the tenure of a grant from the Central Research Fund of the University of London.

QUEEN ELIZABETH COLLEGE, UNIVERSITY OF LONDON,
LONDON, W.8.

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628. The Synthesis of 9-Alkyl- or 9-Aryl-9-arsafluorenes or 9-stibiafluorenes.

By DENYS M. HEINEKEY and IAN T. MILLAR.

9-ARSA- and 9-STIBIA-FLUORENES having an alkyl or aryl substituent in the 9-position have normally been prepared by the cyclisation of arsonic, arsenic, stibonic or stibinic acids, or chloro-arsines or -stibines, followed by introduction of the alkyl or aryl substituent by reaction of the appropriate Grignard reagent with the 9-halogeno-compound.¹

9-Methyl-9-arsafluorene has also been prepared by the thermal decomposition of certain cyclic quaternary diarsonium salts.² We now record the synthesis of 9-methyl-9-arsafluorene and 9-phenyl-9-stibiafluorene by the interaction of 2,2'-dilithiodiphenyl and the appropriate dihalogeno-arsine or -stibine. We find that 2,2'-dilithiodiphenyl is conveniently prepared by the action of lithium on 2,2'-dibromo- or 2,2'-di-iodo-diphenyl, but the dibromo-compound is more readily available.

By the action of other alkyl- or aryl-dihalogeno-arsines or -stibines on the dilithio-compound, a variety of 9-alkyl- and 9-aryl-9-arsafluorenes and -stibiafluorenes should be obtainable in good yield.

Experimental.—9-Methyl-9-arsafluorene. 2,2'-Dibromodiphenyl (5.5 g.) in ether (100 ml.) was added slowly to lithium foil (1 g.) under nitrogen during 1 hr., so that the mixture boiled gently. After being stirred for 2.5 hr., the solution of 2,2'-dilithiodiphenyl was separated from insoluble material by decantation under nitrogen. Di-iodomethylarsine (5.5 g.) in benzene (50 ml.) was added during 20 min., and the mixture was then boiled for 30 min., cooled in ice, and hydrolysed with cold air-free water. The separated organic layer was dried (Na_2SO_4), evaporated, and distilled under nitrogen, giving diphenyl (b. p. 75°/0.01 mm., 0.1 g.) followed by the arsafluorene, b. p. 102—104°/0.01 mm. (2.25 g., 60%), which, crystallised from methanol, had m. p. 40—41° (lit.² m. p. 41—41.5°). It gave a methiodide monohydrate, m. p. and mixed m. p. 206—207° (lit.² m. p. 206—207°), and methopicate, m. p. and mixed m. p. 215° (lit.² m. p. 214.5—215.5°).

9-Phenyl-9-stibiafluorene. Phenyl-di-iodostibine, prepared as described by Schmidt³ and

¹ See, e.g., Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth and Silicon," Interscience Publ. Inc., New York, 1950; Campbell and Morrill, *J.*, 1955, 1662; Campbell and Peller, *J.*, 1956, 1195.

² Heaney, Heinekey, Mann, and Millar, *J.*, 1958, 3838.

³ Schmidt, *Annalen*, 1920, 421, 219.

recrystallised from light petroleum (b. p. 60—80°), had m. p. 62° (lit.,³ 69°) (Found: C, 16.2; H, 1.4. Calc. for C₆H₅I₂Sb: C, 16.0; H, 1.1%). Phenyldi-iodostibine (8 g.) in benzene (50 ml.) was added during 20 min. to a solution of 2,2'-dilithiodiphenyl, prepared as described above, under nitrogen. The mixture was boiled under reflux for 1 hr., then cooled and hydrolysed as before: the solvents were removed under nitrogen from the dried organic layer. The residue was dissolved in benzene and percolated through a short column of alumina; removal of solvent from the filtrate and recrystallisation of the residue from ethanol gave the colourless *stibiafluorene* m. p. 101° (3.0 g., 50%) (Found: C, 61.0; H, 3.9. C₁₈H₁₃Sb requires C, 61.6; H, 3.75%). The ultraviolet absorption spectrum of this compound in the region 230—300 m μ shows a close similarity to that of 9-*p*-tolyl-9-stibiafluorene, recorded by Campbell and Poller.⁴ The 9-phenyl compound shows λ_{\max} 287 m μ (ϵ 13,700) and λ_{\min} 276 m μ (ϵ 11,800), whereas the 9-*p*-tolyl compound⁴ shows λ_{\max} 286 m μ (ϵ 12,100) and λ_{\min} 275 m μ (ϵ 10,900), both in ethanol.

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UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE,
KEELE, STAFFORDSHIRE.

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⁴ Campbell and Poller, *Chem. and Ind.*, 1953, 1126; Campbell, *J.*, 1955, 3116.

629. *Thioxan and 2,2'-Dihydroxydiethyl disulphide.*

By K. J. M. ANDREWS and F. N. WOODWARD.

HITHERTO thioxan $\text{O} \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right\rangle \text{S}$ has been prepared by two methods, neither of which gave high yields. Clarke prepared it by the interaction of 2,2'-di-iododiethyl ether and alcoholic potassium sulphide,¹ and it was later obtained as a by-product when 2,2'-dichlorodiethyl ether was treated with sodium hydrogen sulphide.² It has also been produced by heating thiodiglycol with an equal weight of potassium hydrogen sulphate for several hours at 210°, after which a mixture of water, thioxan, and dithian was obtained by distillation.³ An improved dehydration method has now been devised by using sulphuric acid as dehydrating agent which gives a pure product in 60% yield.

2,2'-Dihydroxydiethyl disulphide is normally obtained by oxidising 2-hydroxyethane-1-thiol with hydrogen peroxide, ferric chloride, or hypobromous acid.^{4,5} A method using air as oxidant has now been devised.

Experimental.—*Thioxan.* A mixture of thiodiglycol (100 g.) and concentrated sulphuric acid (5 g.) was heated at 160° and the distillate was collected. After 5 hr. a vacuum of 300—400 mm. was applied and the distillation was continued until dithian began to block the condenser. The oily layer in the distillate was separated and fractionally distilled, to give thioxan (51 g.), b. p. 148—149°/760 mm. (lit.,⁶ b. p. 147°) (Found: S, 30.2. Calc. for C₄H₈OS: S, 30.8%).

2,2'-Dihydroxydiethyl disulphide. Distilled 2-hydroxyethane-1-thiol to which was added 1% w/w of manganous sulphate and an equivalent quantity of 50% sodium hydroxide solution was stirred and heated at 55—60° under reflux. Air, washed with sodium hydroxide solution and dried (CO₂-EtOH cold trap), was drawn through at a rate of 2 l./hr. The contents of thiol found⁷ after 0, 3, and 6 hr. were 95.4, 44.1, and 35.4% respectively. After removal of the unchanged thiol by distillation at 110 mm., a yield of 54% of almost pure disulphide remained. This almost all distilled at 92°/0.002 mm. (lit.,⁵ b. p. 158—163°/3.5 mm.) and was characterised by preparation of the bis- α -naphthylurethane, m. p. 152° (undepressed on admixture with an authentic specimen⁵). An air input of 10 l./hr. did not increase the rate of oxidation.

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ROCHE PRODUCTS, LTD., BROADWATER ROAD, WELWYN GARDEN CITY, HERTS.
ARTHUR D. LITTLE RESEARCH INSTITUTE,
INVERESK, MIDLOTHIAN.

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¹ Clarke, *J.*, 1912, 1806.

² Meadow and Reid, *J. Amer. Chem. Soc.*, 1934, **56**, 2177.

³ Fromm and Ungar, *Ber.*, 1923, **56**, 2288.

⁴ Bennett, *J.*, 1921, 418.

⁵ Williams and Woodward, *J.*, 1948, 38.

⁶ Johnson, *J.*, 1933, 1530.

⁷ Woodward, *Analyst*, 1949, **74**, 179.