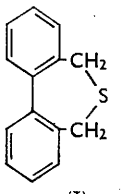
625. *Synthetical Applications of Activated Metal Catalysts. Part XIV.* The Desulphurisation of 2,7-Dihydrodibenzo*[c, e]*thiepin.*

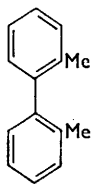
By G. M. Badger, P. Cheuychit, and W. H. F. Sasse.

The formation of free radicals as intermediates in the desulphurisation of organosulphur compounds over Raney nickel has been postulated on many occasions.[1] Experimental support has been provided by the work of Hauptmann and his co-workers using hydrogen-free nickel,[2] by the formation of " dimeric " products during the desulphurisation of some thiophen derivatives,[3] by the formation of some bicycloheptane in addition to the expected 1,3-dimethylcyclopentane following desulphurisation of 6-thiabicyclo-octane,[4] and by the observation that desulphurisation of optically active α-phenyl-α-phenylthiopropionamide is accompanied by complete racemisation.[5] As a further contribution to this study the desulphurisation of 2,7-dihydrodibenzo[*c*, *e*]thiepin (I) has been examined, with a hydrogen-rich catalyst (W-7 Raney nickel), a hydrogen-deficient catalyst (W-7J Raney nickel), and a catalyst of medium activity (W-2 Raney nickel).

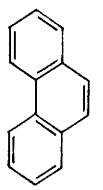
Use of W-7 Raney nickel gave the expected 2,2′-dimethylbiphenyl (II) in excellent yield. Use of neutral W-2 Raney nickel also gave this product, together with a trace of a compound believed to be a paraffin. Use of a Raney nickel which had been heated in a vacuum to reduce the hydrogen content (W-7J Raney nickel), however, gave a much smaller yield of the expected 2,2′-dimethylbiphenyl together with phenanthrene (III) and a dihydrophenanthrene (?) (not obtained pure; all purification processes seemed to result in some dehydrogenation to phenanthrene).



(I)



(II)


(III)

The isolation of phenanthrene is consistent with the view that the removal of the sulphur atom gives first a diradical. In the presence of an excess of hydrogen this is reduced to 2,2′-dimethylbiphenyl; but in its absence this diradical is largely converted into dihydrophenanthrene and thence phenanthrene. The steric arrangement of the diradical facilitates this cyclisation.

Experimental.—*2,7-Dihydrodibenzo*[c, e]*thiepin.* 2,2′-Dimethylbiphenyl [6] was prepared by the Ullmann reaction from *o*-iodotoluene, and brominated to give 2,2′-bisbromomethylbiphenyl.[7] Treatment with sodium sulphide, by the method of Truce and Emrick,[8] gave 2,7-dihydrodibenzo[*c*, *e*]thiepin as prisms (from absolute ethanol), m. p. 89—90° (lit.,[8] 89—90°).

Raney nickel. W-7 Raney nickel was prepared by the method of Billica and Adkins,[9] except that the catalyst was washed with methanol instead of ethanol. W-2 Raney nickel was

* Part XIII, preceding paper.

[1] Badger, *Austral. J. Sci.*, 1958, **21**, 45.
[2] Hauptmann, Wladislaw, and Camargo, *Experientia*, 1948, **4**, 385; Hauptmann and Wladislaw, *J. Amer. Chem. Soc.*, 1950, **72**, 707, 710.
[3] Badger and Sasse, *J.*, 1957, 3862.
[4] Birch and Dean, *Annalen*, 1954, **585**, 234.
[5] Bonner, *J. Amer. Chem. Soc.*, 1952, **74**, 1034.
[6] Wynberg, Logothetis, and VerPloeg, *J. Amer. Chem. Soc.*, 1957, **79**, 1972; Hall, Lesslie, and Turner, *J.*, 1950, 712; Ullmann and Meyer, *Annalen*, 1904, **332**, 49.
[7] Hall, Lesslie, and Turner, *J.*, 1950, 712.
[8] Truce and Emrick, *J. Amer. Chem. Soc.*, 1956, **78**, 6133.
[9] Billica and Adkins, *Org. Synth.*, 1949, **29**, 24.

prepared as described by Ralph and Mozingo [10] and washed with a continuous stream of distilled water until neutral to litmus, then with methanol by decantation. W-7J Raney nickel was prepared by the method of Badger and Sasse.[11]

Desulphurisation with W-7 Raney nickel. The dihydrodibenzothiepin (3 g.) was added to a suspension of W-7 Raney nickel (from 30 g. of alloy) in methanol (200 ml.), and the mixture refluxed for ½ hr. The catalyst was collected with Celite, washed with hot methanol (3 × 100 ml.), and extracted with methanol (Soxhlet) overnight. The combined filtrates and extracts were evaporated. Distillation of the dried residue gave 2,2′-dimethylbiphenyl (2·35 g., 91%) and a yellow wax (0·063 g.). No impurity could be detected in the dimethylbiphenyl by gas–liquid chromatography (Griffin and George VPC mark II), and the retention time was identical with that of an authentic specimen. Recrystallisation of the product from absolute ethanol (freezing mixture) gave the dimethylbiphenyl as prisms, m. p. and mixed m. p. 18°.

Desulphurisation with W-2 Raney nickel.—The dihydrodibenzothiepin (10 g.) was added to a suspension of W-2 Raney nickel (from 150 g. of alloy) in methanol (600 ml.), and the mixture refluxed for 2 hr. After working up as before, the product was distilled, to give 2,2′-dimethylbiphenyl (7·08 g.) and a residue (0·72 g.). The latter was chromatographed on alumina in light petroleum (b. p. 40—70°) and gave a further quantity of 2,2′-dimethylbiphenyl (0·42 g., total yield, 87·4%) and a colourless solid (0·008 g.), $\nu_{max.}$ (in CCl_4) 2867 (CH_2), 2860 and 1450 cm.$^{-1}$ (C-CH_3).

Desulphurisation with W-7J Raney nickel. Xylene (sulphur-free; 200 ml.) was cautiously added from a separating funnel to the dry W-7J Raney nickel (from 125 g. of alloy) in a vacuum. The dihydrodibenzothiepin (10 g.) in sulphur-free xylene (300 ml.) was then run in slowly, followed by more xylene (100 ml.). The mixture was refluxed for 15 hr., and the catalyst was collected over Celite, washed with boiling xylene (2 × 50 ml.), and then extracted with xylene (Soxhlet) for 36 hr. Evaporation of the combined xylene filtrates and extracts, and distillation, gave 2,2′-dimethylbiphenyl (2·56 g., 29·8%) and a brown residue (6·9 g.). Chromatography of the residue in hexane on alumina gave (*a*) a pale yellow wax (2·4 g.), (*b*) plates, m. p. 92—94° (2·18 g.), (*c*) prisms (1·37 g.), and (*d*) prisms (0·91 g.).

Fraction (*a*) was chromatographed on partially acetylated paper (prepared by the method of Spotswood [12]), with ethanol–toluene–water (17 : 4 : 1 v/v). Under ultraviolet light two spots were seen: one showed blue fluorescence, the other violet. The spots were cut out and separately extracted into 95% ethanol. The extract from the violet-fluorescing area gave an absorption maximum at 252 mμ, identical with that given by phenanthrene [13] (which also had the same R_F value). The extract from the blue-fluorescing area gave absorption maxima at 252 (phenanthrene) and 265 mμ (dihydrophenanthrene ?).[14] Attempts to separate the phenanthrene and dihydrophenanthrene by column chromatography on acetylated cellulose were unsuccessful, as was attempted separation by picrate formation. Recrystallisation of fraction (*b*) gave phenanthrene, m. p. and mixed m. p. 101°. Its picrate had m. p. 144° (lit., 144°), and its R_F value was identical with that of an authentic specimen.

Fraction (*c*) was chromatographed on partially acetylated paper. Two spots were obtained. The first (violet-fluorescing) was identified as phenanthrene (ultraviolet spectrum); the second (brown in ultraviolet light) had the same R_F value as the dihydrodibenzothiepin and the general appearance of the ultraviolet spectra was the same. Sodium-fusion of the crude fraction gave a positive test for sulphur.

Recrystallisation of fraction (*d*) gave dihydrodibenzothiepin, m. p. and mixed m. p. 89—90°.

This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. We are also grateful to the Commonwealth Government for a maintenance grant (to P. C.) under the Colombo Plan.

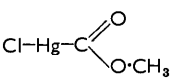
UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, March 13th,* 1962.]

[10] Ralph and Mozingo, *Org. Synth.*, 1955, **29**, 181.
[11] Badger and Sasse, *J.*, 1956, 616.
[12] Spotswood, *J. Chromatog.*, 1959, **2**, 90.
[13] Clar, " Aromatische Kohlenwasserstoffe," 2nd edn., Springer, Berlin, 1952, p. 142.
[14] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.

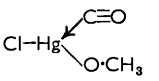
626. *The Crystal and Molecular Structure of Methoxycarbonylmercuric Chloride.*

By T. C. W. Mak and J. Trotter.

Methoxycarbonylmercuric chloride is a member of a series of carbon monoxide adducts of mercury salts, whose structure has been in doubt for many years;[1] structure (II) seems to have gained general acceptance,[2] but recent evidence[3] is more in line with structure (I). The present *X*-ray analysis indicates that (I) is the correct structure.



(I)



(II)

Experimental.—The compound forms needles elongated along the *c*-axis with (100) developed. The crystal data, determined from various oscillation, Weissenberg, and precession films, are: *M*, 295·1; m. p. 107°. Orthorhombic, $a = 8{\cdot}30$, $b = 17{\cdot}20$, $c = 7{\cdot}52$ Å. $U = 1074$ Å^3. $D_{calc.}$(with $Z = 8$) = 3·64, $D_{meas.}$ (displacement of CCl_4) = 3·58 g. cm.$^{-3}$. Absorption coefficients, $\lambda = 1{\cdot}542$ Å, $\mu = 610$ cm.$^{-1}$; $\lambda = 0{\cdot}7107$ Å, $\mu = 336$ cm.$^{-1}$. $F(000) = 1024$. Absent spectra: $0kl$ when l is odd; $h0l$ when l is odd, $hk0$ when $(h + k)$ is odd. Space group is *Pccn*.

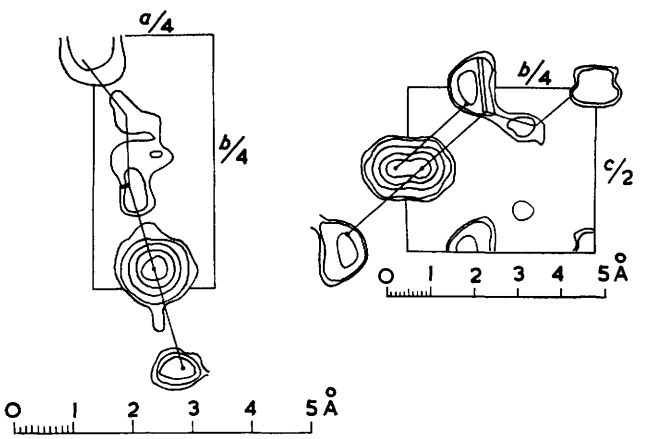


Fig. 1. Electron-density projections along the *c*- and *a*-axes.

$hk0$ (Weissenberg films, Cu-K_α) and $0kl$ (precession films, Mo-K_α) intensity data were recorded, estimated visually, corrected for absorption (cylindrical crystal, diameter = 0·09 mm.), and the structure amplitudes derived. The positions of the mercury and chlorine atoms were derived from Patterson projections, and location of carbon and oxygen atoms and refinement of the structure proceeded by Fourier methods. The final electron-density projections along the *a*- and *c*-axes are shown in Fig. 1, and the values of measured and calculated structure factors (Sagel's scattering factor tables[4] were used) are listed in Table 1; the *R* values for the $hk0$ and $0kl$ reflexions are 0·20 and 0·22, respectively, for mercury and chlorine only, falling to 0·15 and 0·17 when the light atoms are included. The final positional parameters are listed in Table 2 (as fractions of the unit-cell edges), the standard deviations[5] being 0·007 Å for Hg, 0·044 Å for Cl, and 0·054 Å for carbon and oxygen.

[1] Schoeller, Schrauth, and Essens, *Ber.*, 1913, **46**, 2864; Schoeller, *Ber.*, 1920, **53**, 2144; Whitmore, "Organic Compounds of Mercury," The Chemical Catalogue Company Inc., New York, 1921; Manchot, *Ber.*, 1920, **53**, 984; 1921, **54**, 571.
[2] Sidgwick, "Chemical Elements and their Compounds," Oxford Univ. Press, 1950, Vol. I, p. 306.
[3] Halpern and Kettle, *Chem. and Ind.*, 1961, 668.
[4] Sagel, "Tabellen zur Röntgenstrukturanalyse," Springer-Verlag, Berlin, 1958.
[5] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

TABLE 1.

Comparison of the observed and calculated structure factors for methoxycarbonylmercuric chloride.

h k	F_o	F_c	*h k*	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
0 0 0		+1024	3 3 0	188	−194	6,10,0	<5	−4	0 6 2	486	−390	0 6 8	60	+69
0 2 0	352	+625	3 5 0	149	−162	6,12,0	<5	+6	0 8 2	198	−209	0 8 8	27	+36
0 4 0	361	+397	3 7 0	155	−163	6,14,0	<4	+12	0,10,2	61	−54	0,10,8	<9	+9
0 6 0	244	+227	3 9 0	161	−144	6,16,0	<3	+4	0,12,2	<8	+20	0,12,8	<7	0
0 8 0	186	+163	3,11,0	142	−146	6,18,0	<3	−9	0,14,2	31	+53	0,14,8	<5	−11
0,10,0	135	+128	3,13,0	127	−151				0,16,2	36	+49	0,16,8	24	−11
0,12,0	89	+72	3,15,0	108	−96	7 1 0	25	+25	0,18,2	40	+53			
0,14,0	<5	−34	3,17,0	68	−50	7 3 0	58	+69	0,20,2	42	+47	0,0,10	33	−42
0,16,0	66	−80	3,19,0	52	−31	7 5 0	63	+71	0,22,2	38	+42	0,2,10	33	−36
0,18,0	84	−71	3,21,0	<2	−13	7 7 0	42	+71	0,24,2	17	+29	0,4,10	31	−29
0,20,0	80	−63				7 9 0	40	+56				0,6,10	20	−18
0,22,0	35	−42	4 0 0	468	−383	7,11,0	41	+56	0 0 4	383	+333	0,8,10	10	−11
0,24,0	38	−24	4 2 0	463	−379	7,13,0	55	+54	0 2 4	377	+345			
			4 4 0	301	−281	7,15,0	45	+47	0 4 4	384	+289	0 3 2	15	+18
1 1 0	59	−44	4 6 0	255	−127				0 6 4	133	+170	0 5 2	16	−8
1 3 0	88	−90	4 8 0	123	−127	8 0 0	107	+106	0 8 4	116	+117	0 9 2	23	−13
1 5 0	114	−146	4,10,0	79	−69	8 2 0	108	+106	0,10,4	46	+59	0,11,2	32	−23
1 7 0	243	−255	4,12,0	30	−7	8 4 0	96	+119	0,12,4	<9	+7			
1 9 0	312	−261	4,14,0	<5	+29	8 6 0	79	+92	0,14,4	<9	−13	0 3 4	20	+24
1,11,0	290	−218	4,16,0	40	+47	8 8 0	59	+59	0,16,4	23	−37	0 5 4	46	+30
1,13,0	211	−156	4,18,0	55	+45	8,10,0	18	+13	0,18,4	51	−52	0 7 4	15	−11
1,15,0	103	−85	4,20,0	46	+43	8,12,0	<3	−10	0,20,4	51	−43	0 9 4	27	−21
1,17,0	68	−50				8,14,0	<3	−14	0,22,4	33	−30	0,11,4	22	−12
1,19,0	56	−40	5 1 0	<5	−14							0,13,4	23	−5
1,21,0	37	−26	5 3 0	24	+41	9 1 0	<4	−10	0 0 6	169	−211	0,15,4	28	+13
			5 5 0	86	+109	9 3 0	<4	−29	0 2 6	151	−183	0,17,4	16	+6
2 0 0	70	+44	5 7 0	110	+148	9 5 0	22	−45	0 4 6	132	−145			
2 2 0	74	−70	5 9 0	128	+148	9 7 0	26	−36	0 6 6	133	−100	0 7 6	39	−13
2 4 0	<4	+4	5,11,0	111	+119	9 9 0	25	−36	0 8 6	77	−75	0 9 6	49	−18
2 6 0	<4	+16	5,13,0	85	+73	9,11,0	<2	−32	0,10,6	39	−65	0,11,6	39	−6
2 8 0	<5	+33	5,15,0	67	+58				0,12,6	<9	−5	0,13,6	28	−5
2,10,0	<5	−4	5,17,0	48	+44	10,0,0	<3	+5	0,14,6	<9	+18			
2,12,0	<5	−5	5,19,0	25	+27	10,2,0	<3	0	0,16,6	22	+30	0 3 8	16	+11
2,14,0	<5	−25				10,4,0	<3	−3	0,18,6	23	+26	0 5 8	16	+7
2,16,0	<5	−2	6 0 0	<5	+5	10,6,0	<2	−7	0,20,6	14	+22	0 7 8	22	−2
2,18,0	<4	+12	6 2 0	<5	+11							0 9 8	16	−9
2,20,0	<3	+8	6 4 0	<5	+20	0 0 2	359	−375	0 0 8	70	+79	0,11,8	15	−6
			6 6 0	<5	−27	0 2 2	452	−460	0 2 8	70	+81	0,13,8	19	+1
3 1 0	112	−136	6 8 0	<5	−2	0 4 2	467	−458	0 4 8	69	+75	0,15,8	17	+5

TABLE 2.

Final positional parameters.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hg ...	0·1256	0·0203	0·2500	C_1	0·075	0·101	0·426	O_2	0·069	0·169	0·373
Cl	0·1820	−0·0785	0·0425	O_1	0·076	0·095	0·588	C_2	−0·013	0·237	0·442

DISCUSSION

The resolution of the lighter atoms is not very good, partly because of overlap in the projections, but chiefly owing to the dominating effect on the scattering of the heavy mercury atom. Both projections, however, indicate unambiguously that the true structure is (I). The co-ordination around the mercury atom is exactly linear, and the molecule is

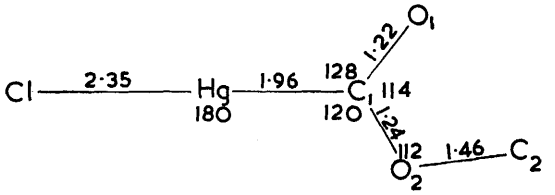


Fig. 2. Dimensions of the molecule.

planar, except for the methyl group, whose carbon is displaced 0·4 Å from the plane of the other atoms. The Hg–Cl (2·35 Å, $\sigma = 0{\cdot}04$ Å) and Hg–C (1·96 Å, $\sigma = 0{\cdot}05$ Å) distances are normal;[6] the other molecular dimensions (Fig. 2) have been determined only rather imprecisely, but do not differ significantly from normal values.

There are two short intermolecular distances, a Hg···Cl separation of 3·21 Å and a Hg···O (carbonyl) contact of 3·01 Å, which are very similar to corresponding approaches

[6] Sutton *et al.*, " Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.

in crystalline mercuric chloride.[7] All the other contacts are considerably longer, the shortest Hg · · · Hg distance being 4·29 Å.

We are indebted to the National Research Council of Canada for financial support and for the award of a research bursary (to T. C. W. M.), and to Dr. J. Halpern and Mr. A. L. W. Kemp for suggesting the problem and for the crystal sample.

UNIVERSITY OF BRITISH COLUMBIA, DEPT. OF CHEMISTRY,
VANCOUVER, 8, CANADA. [*Received, October 16th*, 1961.]

[7] Braekken and Scholten, *Z. Krist.*, 1934, **89**, 448; Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, 1950, pp. 119, 632.

---

627. *Pleiocarpa Alkaloids. Part I. Pleiocarpine, the Major Alkaloid of* Pleiocarpa mutica *Benth.*

By A. R. BATTERSBY and D. J. LE COUNT.

THE genus *Pleiocarpa* (Apocynaceae) comprises some twenty species which grow mainly in tropical Africa.[1] At the outset of the present work published chemical information on this group of plants was limited to the report by Raymond-Hamet that the roots of *Pleiocarpa tubicina* Stapf. are rich in alkaloids and that the total aqueous extract from such roots shows a long-lasting hypotensive activity in the dog.[2]

Pleiocarpa mutica Benth. is a shrub or small tree [1] the bark of which has yielded 1·4—1·5% of total alkaloids by the process described below. So far only the ether-extractable bases have been examined further, and by a combination of chromatography, countercurrent distribution, and crystallisation they have yielded crystalline pleiocarpine, $C_{23}H_{28}N_2O_4$, m. p. 142·5°, which readily affords crystalline salts. The application of countercurrent distribution to the crude bases obtained by direct crystallisation from the total alkaloids allows the ready isolation of large quantities of pleiocarpine. This alkaloid has also been isolated independently by Drs. Seebeck and Stauffacher (Sandoz, Basel) from *Pleiocarpa tubicina* [3] and more recently by Kump and Schmid,[4] together with several related alkaloids, from *P. mutica*. As a result of our common interest in *Pleiocarpa* alkaloids, it has been arranged that the chemistry of pleiocarpine should be studied jointly by the Zürich and the Bristol group. The present Note will therefore describe the isolation work and preliminary investigations.

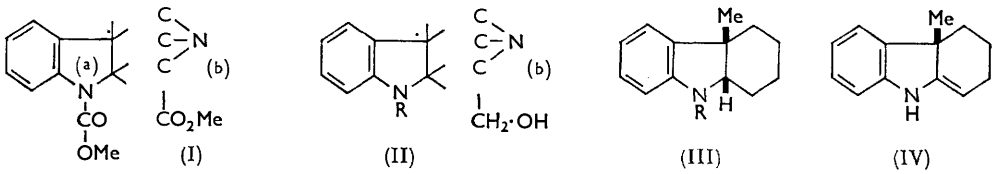
Our early attempts to isolate pleiocarpine by fractional crystallisation alone gave an apparently constant mixture of this base with a minor alkaloid; the presence of the latter was shown by thin-layer chromatography on silica gel.[5] Separation of the two alkaloids was readily effected by countercurrent distribution. Pure pleiocarpine gives a deep violet colour with the ceric sulphate reagent (for spot-plate tests [6]) and no colour reaction with ceric sulphate spray reagent.[6]

We find, in agreement with Kump and Schmid,[4] that pleiocarpine is a hexacyclic base with the partial formula (I). Some of the experiments on which this conclusion is based do not differ greatly from those reported [4] during the preparation of this manuscript, so these will only be outlined in the sequel; for the rest, full experimental details will be given.

Pleiocarpine contains two methoxyl groups but neither *N*-methyl not *C*-methyl groups. It is a mono-acid base (pK_a' 6·26 for $N_{(b)}$ in 80% methylcellosolve–20% water) and $N_{(a)}$.

[1] Hutchinson and Danziel, "Flora of West Tropical Africa," The Crown Agents for the Colonies, 1931, Vol. II, p. 37.
[2] Raymond-Hamet, *Compt. rend.*, 1957, **244**, 2991.
[3] Personal communication from Professor H. Schmid, Zürich.
[4] Kump and Schmid, *Helv. Chim. Acta*, 1961, **44**, 1503.
[5] Stahl, *Chem.-Ztg.*, 1958, **82**, 232.
[6] Schmid, Kebrle, and Karrer, *Helv. Chim. Acta*, 1952, **35**, 1864.

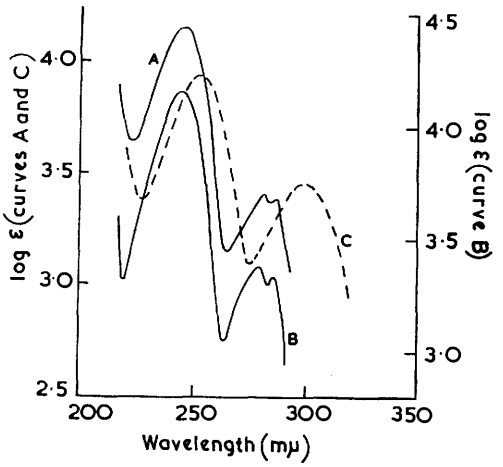
is present in the neutral acylindoline chromophore (see Figure). The only characteristic bands in the infrared spectrum were at 1710 cm.$^{-1}$ (>N–CO–) and 1720 cm.$^{-1}$ (–CO_2R) and those corresponding to an *o*-disubstituted benzene ring. Pleiocarpine was unaffected by methanolic borohydride, by acetic anhydride at 80° for 15 hr. ($N_{(b)}$ is therefore



(I) (II) (III) (IV)

tertiary), and by being shaken in glacial acetic acid with hydrogen and Adams platinum catalyst. This is strong evidence for the absence of olefinic residues in the alkaloid.

Several features of the partial structure (I) were established by reducing pleiocarpine with lithium aluminium hydride. It is confirmed [4] that reduction by this reagent in ether yields *N*(a)-methylkopsinyl alcohol (II; R = Me), $C_{21}H_{28}N_2O$, (*N*-alkylindoline chromophore, see Figure) with a small amount of kopsinyl alcohol (II; R = H), $C_{20}H_{26}N_2O$. The



Ultraviolet absorption spectra determined in 1 : 1 aqueous ethanol of (A) pleiocarpine, (B) the urethane (III; R = CO_2Me), and (C) *N*(a)-methylkopsinyl alcohol (II; R = Me).

yield of the latter is increased when the reduction is carried out in boiling tetrahydrofuran. The presence of free imino and hydroxyl groups in the base (II; R = H) was established by acetylation to give a derivative with infrared bands at 1666 cm.$^{-1}$ (>N–COMe) and 1743 cm.$^{-1}$ (O·COMe). Both reduction products (II; R = Me and H), which have been further characterised here as the *N*(b)-methiodide and dipicrate respectively, were correlated [4] with the alkaloid kopsinine first isolated by Crow and Michael [9] from *Kopsia longiflora*. The reduction of urethanes to yield *N*-methyl groups [7] and the cleavage of *N*-acyl groups by lithium aluminium hydride [8] both have precedent.

Many different acyl groups are known in *N*-acylindoline alkaloids,[10] but pleiocarpine seems to be the first example to possess a urethane system at N(a).

Methyl chloroformate reacted with the indoline (III; R = H) to yield the urethane (III; R = CO_2Me). This shows ultraviolet absorption almost identical with that of pleiocarpine (see Figure) and the >N–CO– infrared absorption lies at 1702 cm.$^{-1}$ (cf. pleiocarpine above). The indoline (III; R = H) is readily available by borohydride reduction

[7] *E.g.*, Dannley, Lukin, and Shapiro, *J. Org. Chem.*, 1955, **20**, 92.
[8] *E.g.*, Micovic and Mihailovic, *J. Org. Chem.*, 1953, **18**, 1190; Battersby and Edwards, *J.*, 1960, 1214.
[9] Crow and Michael, *Austral. J. Chem.*, 1955, **8**, 129.
[10] *E.g.*, Taylor, Raab, Lehner, and Schmutz, *Helv. Chim. Acta*, 1959, **42**, 2750; Djerassi, Archer, George, Gilbert, Shoolery, and Johnson, *Experientia*, 1960, **16**, 532.

of the methyleneindoline (IV),[11] and its *N*-acetyl derivative (III; R = Ac) agrees in m. p. with an earlier preparation [12] which involved a different reduction method.

Experimental

Evaporations were carried out at <40° under a reduced pressure of nitrogen (unless otherwise stated). Melting points were determined on a Kofler hot-stage. Column chromatography was controlled by thin-layer chromatography.[5] Samples for analysis were dried at 100° over phosphoric oxide *in vacuo* unless otherwise stated.

Isolation of Pleiocarpine.—A column of finely-ground *P. mutica* bark (1·1 kg.) was slowly percolated with methanol (10 l.), and the extract was concentrated to 500 ml. This was mixed with aqueous acetic acid (275 ml. of acetic acid diluted to 1·5 l. with water) and the solution was kept at 0° overnight. After the solution had been filtered (" Filtercel "), it was extracted with ether (3 × 1·5 l.), then adjusted to pH 9 with sodium carbonate and extracted again with ether (3 × 1 l.). The aqueous alkaline layer was further extracted with 3 : 1 (by vol.) ether–chloroform (3 × 1 l.) and finally with chloroform (3 × 1 l.). Each set of extracts was washed with water, dried, and concentrated to yield three separate resins: from ether (11·5 g.), from ether–chloroform (1·0 g.), and from chloroform (3·4 g.).

Part of the ether extract (0·5 g.) was fractionated on alumina (40 g.; Woelm neutral, activity III) in benzene to give crude crystals (0·3 g.), m. p. 128—136°. This product was used to seed a solution of the remaining ether extract (11 g.) in ethanol (25 ml.); the solid obtained was crystallised once from ethanol to give slightly impure pleiocarpine (2·5 g.), m. p. 142°. The total mother liquors from this crop were concentrated to dryness and a solution of the residue in benzene was run on to alumina (400 g., as above). Elution with benzene and crystallisation of the early fractions from ethanol gave more slightly impure pleiocarpine (1·9 g.), m. p. 141—142°.

Part of the combined crystalline material (1 g.) was partitioned between ethyl acetate and 0·5M-potassium dihydrogen phosphate for 100 transfers (scattered in first two tubes). Analysis showed a well-separated peak between tubes 40 and 72. The contents of these tubes were combined and the ethyl acetate layer was separated. After the aqueous layer had been adjusted to pH 9 with sodium carbonate, it was extracted thrice with ethyl acetate, and the four organic extracts were combined, washed with water, dried, and evaporated to yield a gum. This crystallised from ethanol to give pure pleiocarpine (825 mg.), m. p. 142·5° (Found: C, 69·7, 69·8, 70·0, 69·7; H, 7·1, 6·8, 7·0, 7·2; N, 7·05, 7·0; OMe, 15·3, 15·25, 15·5; *N*-Me, 0·0; *C*-Me, 0·0. Calc. for $C_{23}H_{28}N_2O_4$: C, 69·7; H, 7·1; N, 7·1; 2OMe, 15·7%), $[\alpha]_D^{24} = -151°$ (*c* 1·39 in $CHCl_3$).

The picrate was prepared in ethanol as usual; it recrystallised from the same solvent to give needles, m. p. 199—200° (decomp.) (Found: C, 55·9; H, 5·2; N, 11·1. Calc. for $C_{23}H_{28}N_2O_4,C_6H_3N_3O_7$: C, 55·7; H, 5·0; N, 11·2%). The m. p. 157—159° reported [4] for this salt was shown to be due to a less stable dimorphic form by comparison with the above preparation.[3]

Pleiocarpine hydrochloride was prepared by addition of ethereal hydrochloric acid to a solution of the base in ether and recrystallisation of the precipitate from ethanol; it had m. p. 234—235° (decomp.), lit.,[4] m. p. 229—230° (decomp.) (Found: C, 63·6; H, 6·4; N, 6·4; Cl, 7·7. Calc. for $C_{23}H_{28}N_2O_4$,HCl: C, 63·8; H, 6·75; N, 6·5; Cl, 8·2%).

Pleiocarpine perchlorate was precipitated from a solution of the base in ethanol by the addition of perchloric acid. The solid was washed with ethanol and recrystallised, without being dried, from ethanol; it had m. p. 264—265° (decomp.).

Reduction of Pleiocarpine by Lithium Aluminium Hydride.—Our method differed little from that reported [4] and the major product was the alcohol (II; R = Me), m. p. 134—135° (Found: C, 77·6, 77·7; H, 8·5, 8·4; N, 8·6; OMe, 0·0; *N*-Me, 6·7. Calc. for $C_{21}H_{28}N_2O$: C, 77·7; H, 8·7; N, 8·6; *N*-Me, 4·6%). High *N*-Me values have been observed before for some alkaloids.[13]

[11] Pausacker, *J.*, 1950, 621; Schuster, Diplomarb., Univ. Frankfurt, 1953.
[12] Booth, King, and Parrick, *J.*, 1958, 2302.
[13] Conroy, Brook, Rout, and Silverman, *J. Amer. Chem. Soc.*, 1958, **80**, 5178; Orazi, Corral, Holker, and Djerassi, *J. Org. Chem.*, 1956, **21**, 979; McLean, Palmer, and Marion, *Canad. J. Chem.*, 1960, **38**, 1547.

This base (0·1 g.) was kept in ether (15 ml.) with methyl iodide (1 ml.) for 18 hr., and the product was recrystallised from ethanol to yield N(*a*)-*methylkopsinyl alcohol methiodide* (128 mg.), m. p. 179—181° (Found: C, 56·4; H, 6·9. $C_{22}H_{31}IN_2O$ requires C, 56·6; H, 6·7%).

A minor product from the reduction in tetrahydrofuran was kopsinyl alcohol (II; R = H), m. p. 162° (Found: C, 75·8, 75·6; H, 8·8, 8·5; N, 8·75. Calc. for $C_{20}H_{26}N_2O,\frac{1}{2}EtOH$: C, 75·6; H, 8·8; N, 8·4%).

The *dipicrate* of the base (II; R = H) was prepared in ethanol and recrystallised from the same solvent; it had m. p. 215° (decomp.) (Found: C, 50·5; H, 4·3; picric acid,[14] 59·0. $C_{32}H_{32}N_8O_{15}$ requires C, 50·0; H, 4·2; picric acid, 59·6%).

cis-1,2,3,4,10,11-*Hexahydro*-9-*methoxycarbonyl*-11-*methylcarbazole* (III; R = CO_2Me).—Sodium borohydride (0·93 g.) was added portionwise during 15 min. to a solution of 2,3,4,9-tetrahydro-11-methylcarbazole [11] (3·26 g.) in methanol (25 ml.). After the solution had been kept at 20° for 1 hr., it was acidified (N-hydrochloric acid; 50 ml.) and then freed from methanol by evaporation. The solution was basified (Na_2CO_3) and extracted with ether to yield the hexahydrocarbazole (III; R = H) as an oil (3·2 g.). The *N*-acetyl derivative, prepared in the usual way, crystallised from aqueous ethanol and had m. p. 90—91° (lit.,[12] m. p. 87—88°).

Methyl chloroformate (10 ml.) was added in portions during 5 min. to a solution of the above hexahydrocarbazole (1·13 g.) in dioxan (30 ml.) and triethylamine (0·97 ml.) at room temperature. Water (30 ml.) was then added, the volatile organic materials were evaporated and the solution, after acidification, was extracted with ether (3 × 25 ml.). Evaporation of the dried extracts yielded the *urethane* (III; R = CO_2Me) as a gum which was distilled at 130° (bath)/0·3 mm. for analysis and physical measurements (Found: C, 73·3; H, 7·7. $C_{15}H_{19}NO_2$ requires C, 73·4; H, 7·8%); $\lambda_{max.}$ 245, 280, 287, $\lambda_{min.}$ 220, 265, 284·5 mμ (log ε 4·17, 3·39, 3·34, 3·31, 3·05, 3·32 respectively) in 1 : 1 aqueous ethanol. The urethane subsequently crystallised and, recrystallised from aqueous ethanol, had m. p. 45—46°.

Grateful acknowledgement is made to Drs. H. T. Openshaw and T. Dewing (Burroughs Wellcome and Company) for arranging the large-scale extraction of bark, to Dr. W. Simon (Zürich) for a microtitration, and to the Department of Scientific and Industrial Research for awarding a Research Studentship to D. J. Le C.

THE UNIVERSITY, BRISTOL. [*Received, November 6th*, 1961.]

[14] Cunningham, Dawson, and Spring, *J.*, 1951, 2305.

---

628. *Nitro-complexes of Osmium.*

By W. P. GRIFFITH.

THREE nitro-complexes of osmium have been reported. These are $K_2[Os(NO_2)_5]$,[1] recently re-formulated as $K_2[Os(NO)(OH)(NO_2)_4]$; [2] and the two complexes with which this Note is concerned, $K_2[OsO_2(OH)_2(NO_2)_2]$ and $K_2[OsO_2(NO_3)(NO_2)_3]$.

Potassium Dioxydihydroxydinitro-osmate(VI), $K_2[OsO_2(OH)_2(NO_2)_2]$.—The reaction between solid osmium tetroxide and an excess of a saturated solution of potassium nitrite yields dark brown crystals which were formulated by Wintrebert [3] as $K_2[OsO_2{\cdot}O{\cdot}(NO_2)_2]3H_2O$. The compound is diamagnetic, and its infrared spectrum has been reported,[4] but its structure has not been established.

Analytical data for potassium, osmium, and nitrogen indicate that a more reasonable formula would be $K_2[OsO_2(OH)_2(NO_2)_2]$. The infrared spectrum (see Table 1) indicates the presence of co-ordinated hydroxyl groups, and the bands near 1300 and 820 cm.$^{-1}$ are typical of those expected for terminal nitro-groups; [5] there are none arising from bridging $-NO_2$ or terminal $-NO_3$ groups. The peak at 883 cm.$^{-1}$ is not shifted or split when the complex is deuterated and is assigned to the Os=O stretching vibration: this appears at

[1] Wintrebert, *Ann. Chim. Phys.*, 1903, **28**, 134.
[2] Irving, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.
[3] Wintrebert, *Ann. Chim. Phys.*, 1903, **28**, 102.
[4] Lewis and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **6**, 12.
[5] Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.

TABLE 1.

Infrared spectra of osmium complexes (Nujol mulls; cm.$^{-1}$).

Complex	OH	NO_3	NO_2	Os=O	Others
$K_2[OsO_2(OH)_4]$	3270s, b			790vs *	1575w *; 1090w
OsO_4 g				953	
K[OsO_3N] ‡				890; 858	
$K_2[OsO_2(OH)_2(NO_2)_2]$	3300s, b		1340s, b *; 1320s, b *; 840vs *; 831vs *; 825vs *	883vs *	1640m *
$K_2[OsO_2(NO_3)(NO_2)_3]$		1540m, sh; 1490m, sh; 990m; 955s	1340s, b; 840vs; 820vs	871vs	
$Cs_2[OsO_2(CN)_4]$				830vs	2152vs

* These bands do not shift or split on deuteration of the complex.
† Ref. 6. ‡ Ref. 4.

953 cm.$^{-1}$ in OsO_4,[6] at 890 and 858 cm.$^{-1}$ in K(OsO_3N),[3] at 830 cm.$^{-1}$ in $Cs_2[OsO_2(CN)_4]$, and at 790 cm.$^{-1}$ in $K_2[OsO_2(OH)_4]$. For complexes of the type $(OsO_2X_4)^{2-}$ or $(OsO_2X_2X'_2)^{2-}$, the Os–O bond distance will decrease (and the Os–O stretching frequency increase) the greater the electron-attracting power of the osmium atom, and the latter effect will in its turn be enhanced when the ligands X and X′ are themselves highly electronegative. In the series of complexes studied here, where X is NO_2^-, CN^-, and OH^-, the electronegativities of the ligands fall in the sequence $NO_2^- > CN^- > OH^-$, so that the Os–O stretching frequency should decrease in that order, as observed. (This neglects the effect of metal–ligand back-bonding which, since the osmium has such a high oxidation state, is probably not an important factor.)

The diamagnetism of the complex suggests that it may contain osmium(VI). Octahedral osmium(VI) complexes such as $[OsO_2Cl_4]^{2-}$ and $[OsO_2(OH)_4]^{2-}$ are diamagnetic [7,8] owing to a splitting of the t_{2g} metal orbitals to a lower singlet (d_{xy}) and an upper doublet (d_{xz} and d_{yz}), the separation between the two levels being sufficient for the two d-electrons of osmium(VI) to pair in the singlet.[7] Further, the nitro-complex reacts quantitatively with CN^- to give $[OsO_2(CN)_4]^{2-}$ and with OH^- to give $[OsO_2(OH)_4]^{2-}$ (in the absence or presence of oxygen) which indicates that it contains osmium(VI). (Wintrebert [3] also reports conversion of the complex into $[OsO_2Cl_4]^{2-}$ by reaction with hydrochloric acid.) Cathodic reduction of the complex in nitrite solutions at the dropping-mercury electrode indicates the osmium as sexivalent.

It thus appears that the correct formulation is $K_2[OsO_2(OH)_2(NO_2)_2]$, though $K_2[Os^{VI}O_3(H_2O)(NO_2)_2]$ is also a possibility consistent with all the above results and would explain the appearance of a sharp band at 1640 cm.$^{-1}$ in the infrared spectrum as arising from a water molecule.* Since this nitro-complex is a member of the " oxy-osmyl " series, $[OsO_2{\cdot}O{\cdot}X_2]^{2-}$ (X = Cl^-, NO_2^-, or $\frac{1}{2}Ox^{2-}$), it is possible that all the complexes in this series may be $[OsO_2(OH)_2X_2]^{2-}$.

Potassium Dioxynitratotrinitro-osmate(VI), $K_2[OsO_2(NO_3)(NO_2)_3]$.—This was prepared by Wintrebert,[9] who considered it to have formula $K_2[OsO_2(NO_2)_4]$, by the reaction of osmium tetroxide with nitric oxide in saturated potassium nitrite solution at 40°. The bright orange crystals are diamagnetic. The infrared spectrum contained no peaks which could be attributed to nitrosyl (NO) stretching frequencies, but the bands at 1540, 1490, 990, and 953 cm.$^{-1}$ are typical of those produced by co-ordinated monodentate nitrato-groups,[10] and those at 1320, 840, and 820 cm.$^{-1}$ probably arise from both the nitrato- and the nitro(terminal)-groups. The band at 871 cm.$^{-1}$ is tentatively assigned

* However, deuteration does not cause a shift of the band which thus may be an overtone of the 825 cm.$^{-1}$ peak.

[6] Woodward and Roberts, *Trans. Faraday Soc.*, 1956, **52**, 615.
[7] Lott and Symons, *J.*, 1960, 973.
[8] Hepworth and Robinson, *J. Inorg. Nuclear Chem.*, 1957, **4**, 24.
[9] Wintrebert, *Ann. Chim. Phys.*, 1903, **28**, 54.

to an Os=O stretching mode. There were no bands in the 3500 cm.$^{-1}$ region, indicating the absence of hydroxyl groups.

The diamagnetism of the complex again suggests the presence of osmium(VI). Reaction with hydrochloric acid gives $[OsO_2Cl_4]^{2-}$ and prolonged treatment with hydroxyl ion yields $[OsO_2(OH)_4]^{2-}$.[9] There does not appear to be any reaction with cyanide ion. The cathodic wave has the same characteristics as that of $[OsO_2(OH)_2(NO_2)_2]^{2-}$ and so it appears likely that the correct formulation for the complex is $K_2[Os^{VI}O_2(NO_3)(NO_2)_3]$, and the analytical data for potassium, osmium, and nitrogen fit this rather better than they do the original formula $K_2[OsO_2(NO_2)_4]$. The total reaction equation for the formation of the compound from osmium tetroxide, potassium nitrite, and nitric oxide may be written:

$$6NO_2^- + 2OsO_4 + 4NO + H_2O = 2[OsO_2(NO_3)(NO_2)_3]^{2-} + 2OH^- + N_2O$$

The presence of nitrous oxide in the product was confirmed by infrared spectroscopy.

The visible and ultraviolet absorption spectra of a number of osmium(VI) dioxy-complexes has been measured for aqueous solutions (Table 2). It will be seen that they are qualitatively similar.

TABLE 2.

Visible and ultraviolet spectra of osmium(VI) dioxy-complexes in water (λ in mμ).

Complex	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
$K_2[OsO_2(OH)_4]$ *	529	32			320	370	309	630	231	5210
$K_2[OsO_2(CN)_4]$					349	273	312	723	254	3810
$K_2[OsO_2(OH)_2(NO_2)_2]$ †					367	256			256	2560
$K_2[OsO_2(NO_3)(NO_2)_3]$			385	349	367	440	295	1423	249	4270

* Spectrum taken in 0·1M-potassium hydroxide. † Spectrum taken in 0·1M-potassium nitrite.

Experimental.—Potassium dioxydihydroxydinitro-osmate(VI). The *salt* $K_2[OsO_2(OH)_2(NO_2)_2]$ was prepared by the method of Wintrebert [3] (Found: K, 18·5; Os, 44·6; N, 6·3. $H_2K_2N_2O_8Os$ requires K, 18·3; Os, 44·6; N, 6·6. Calc. for the old formulation $H_6K_2N_2O_{16}Os$: K, 16·9; Os, 41·1; N, 6·05%).

Potassium dioxynitratotrinitro-osmate(VI), $K_2[OsO_2(NO_3)(NO_2)_3]$. This *salt* was prepared by Wintrebert's method [9] (Found: K, 15·7; Os, 39·5; N, 10·8. $K_2N_4O_{11}Os$ requires K, 15·6; Os, 38·0; N, 11·2. Calc. for the old formulation as $K_2N_4O_{10}Os$: K, 16·1; Os, 39·1; N, 11·6%).

Cæsium dioxytetracyano-osmate(VI), $Cs_2[OsO_2(CN)_4]$. This *salt* was prepared by the method of Krauss and Schrader [11] (Found: Cs, 45·5; N, 9·5. $C_4Cs_2N_4O_2Os$ requires Cs, 44·9; N, 95%).

Microanalyses were performed by the Microanalytical Laboratory, Imperial College, London. Osmium was analysed spectrophotometrically as $[OsCl_6]^{2-}$, and potassium as the tetraphenylboronate. The gaseous products from the reaction of osmium tetroxide in nitrite solution with nitric oxide were pumped into a 10-cm. infrared gas cell with sodium chloride windows. Four peaks were observed at 2235, 2212, 1307, and 1275 cm.$^{-1}$, in good agreement with the four frequencies observed for nitrous oxide by Saier and Pozefsky.[12]

Deuterated samples of $K_2[OsO_2(OH)_4]$ and $K_2[OsO_2(OH)_2(NO_2)_2]$ were made by using deuterium oxide as the solvent during the preparation.

Physical measurements. Infrared spectra were measured on a Perkin–Elmer model 21 recording spectrophotometer with sodium chloride optics; visible and ultraviolet spectra on a Cary recording spectrophotometer with 1-cm. silica cells; and polarographic curves on a Tinsley model 19 recording intrument. Magnetic measurements were made at room temperatures in a field of 7000 gauss by the Gouy method.

The author acknowledges the help of Dr. L. Pratt, who carried out the magnetic measurements, and research funds from the Louis Block Fund and a Fulbright travel grant are also gratefully acknowledged.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO,
CHICAGO 37, ILL., U.S.A.
[Present address: DEPARTMENT OF CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.]

[*Received, January 18th*, 1962.]

[11] Krauss and Schrader, *J. prakt. Chem.*, 1928, **120**, 36.
[12] Saier and Pozefsky, *Analyt. Chem.*, 1954, **26**, 1079.

629. *Separation of Inositols and their Monomethyl Ethers by Gas Chromatography.*

By Z. S. Krzeminski and S. J. Angyal.

Gas–liquid partition chromatography has been used in the separation of aliphatic polyols and sugars.[1] We now report a successful separation of inositols and their monomethyl ethers as hexa-*O*-acetyl and penta-*O*-acetyl derivatives, respectively. The eight known isomers of inositol have been separated previously by paper chromatography,[2] but gas chromatography offers the advantage of comparative speed and ease of quantitative evaluation.

The separations described below were carried out on materials containing a comparatively low proportion of the stationary phase, a polyester resin. The retention times, corrected for the dead volume of the column, of the hexa-*O*-acetyl inositols and some penta-*O*-acetyl inositol monomethyl ethers are given in the Table.

Retention times (min.) of fully acetylated cyclitols.

Hexa-acetates		*Penta-acetates*	
Neoinositol	9·17	2-*O*-Methyl-(−)-inositol	6·90
(±)-Inositol	9·62	3-*O*-Methyl-(+)-inositol	7·07
Alloinositol	12·30	1-*O*-Methylmyoinositol	8·27
Myoinositol	13·42	5-*O*-Methylmyoinositol	9·76
Mucoinositol	13·64		
Scylloinositol	22·25		
Epi-inositol	23·75		
Cis-inositol	42·30		

The column used in the measurement of the retention times was 115 cm. in length and had 2500 theoretical plates; [3] it separated the eight inositol isomers into six peaks, two of which represented the pairs, neo–(±)- and myo–muco-inositol. The peak of the former showed partial separation.

In an attempt to separate these multiple peaks a 350-cm. column was constructed. It had an efficiency of 5500 theoretical plates and almost completely separated neoinositol from (±)-inositol. However, a mixture of myo- and muco-inositol still gave only a single peak. It is possible that myoinositol could be separated from mucoinositol on long capillary columns.

The correlation between the retention times and the conformation [4] of the isomeric inositols is obscure. The isomers possess a surprisingly wide spread of retention times. It is notable that the all-*cis*-isomer is widely separated from the others.

Experimental.—The gas chromatographic apparatus employed an electrically heated tubular oven whose temperature was maintained constant to ±0·1° by means of a thermocouple-actuated controller. The hydrogen-flame ionisation detector, the column, and the heated sample-injection tube were made of borosilicate glass, connected by spherical joints, and fitted into the oven. The signal from the detector was recorded on a 100 mv full-scale strip-chart recorder. The impedance of the detector was matched to that of the recorder by means of a vibrating-reed electrometer. A polarising e.m.f. of 215 v d.c. was applied to the detector. Nitrogen (30 ml./min.) was used as carrier gas and was mixed with hydrogen before entering the detector, where the gas mixture was burnt in an air stream.

Solutions (0·2—1·0 μl.; 0·5—1·0%) of the samples in chloroform (hot acetic acid in the case of hexa-*O*-acetylscylloinositol) were introduced by means of a Hamilton microlitre syringe into

[1] Gunner, Jones, and Perry, *Chem. and Ind.*, 1961, 255; VandenHeuvel and Horning, *Biochem. Biophys. Res. Comm.*, 1961, **4**, 399; Ferrier, *Chem. and Ind.*, 1961, 831.
[2] Angyal, McHugh, and Gilham, *J.*, 1957, 1432.
[3] Desty, "Vapour Phase Chromatography," Butterworths, London, 1956.
[4] Angyal, *Quart. Rev.*, 1957, **11**, 212.

a heated (350°) injection tube where they were vaporised. Two different glass columns were used in the separation of fully acetylated inositols and their monomethyl ethers.

(*a*) A single column, 115 cm. long and 4·5 mm. internal diameter, packed with 60—100 mesh kieselguhr (Embacel; May and Baker, Ltd.) coated with 1·5% w/w of a polyester resin (LAC 1-R-296; Cambridge Industries Co., Cambridge, Mass.), and operated at 215°. The retention times reported in the Table were recorded on this column.

(*b*) A folded column, 350 cm. long and 4·5 mm. internal diameter, packed with 1·0% w/w LAC 1-R-296 on Embacel (60—100 mesh), and operated at 220°. This column was used to separate neoinositol from (±)-inositol.

The column packings were prepared by dissolving the polyester resin in a volatile solvent such as ethyl acetate, acetone, or methylene chloride, mixing the solution with a calculated quantity of kieselguhr, and evaporating the solvent by the simultaneous application of heat and agitation. The correct ratio of solvent to kieselguhr, so as to obtain a slurry of just-liquid appearance, was first determined by trial and error. The column packings were heat-treated for 24 hr. at 215° in a stream of nitrogen before the columns were filled.

The authors thank the Directors of the Company for making available the gas chromatographic equipment developed in the Company's laboratories.

C.S.R. Chemicals Pty. Ltd., Rhodes, N.S.W., Australia.
School of Chemistry, University of New South Wales, Sydney, Australia.

[*Received, January 26th*, 1962.]

---

630. *The Isomerization of Propyl Radicals.*

By B. H. M. Billinge and B. G. Gowenlock.

In the equilibrium, $Pr^n \underset{(2)}{\overset{(1)}{\rightleftharpoons}} Pr^i$, the reaction (1) is exothermic by about 5 kcal./mole.[1] However evidence for the occurrence of either this or the reverse reaction is ambiguous. Glazebrook and Pearson [2] obtained n-propylmercuric iodide on treatment of the products of photolysis of di-isopropyl ketone in the presence of metallic mercury with mercuric iodide. This suggests that reaction (2) may occur, or alternatively that isomerization occurs in the presence of the metal. Masson [3] has shown that 98% of the hexanes formed on photolysis of di-n-propyl ketone in the temperature range 55—357° are n-hexane: this suggests slight occurrence of reaction (1). Some years ago the boiling points of the hexanes produced on pyrolysis of both dipropyl compounds of mercury were measured and it was claimed [4] that these supported the absence of isomerization.

Experimental.—Di-n-propylmercury was pyrolysed in a flow system,[4] conditions being: reaction time about 0·5 sec., temperature range 380—460°, carrier-gas pressures about 4 mm., di-n-propylmercury pressures about 0·1 mm. In some cases the surface : volume ratio of the reaction vessel was altered by a factor of eleven, in other cases about 0·5 mm. of perfluorocyclohexane was present [5] in the gases flowing through the reaction vessel. The hexane product was analysed mass-spectrometrically and was found to be pure n-hexane.

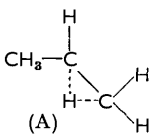
Di-isopropylmercury was pyrolysed similarly, in the temperature range 150—300°. In this case the hydrocarbon products were analysed by gas–liquid chromatography on a squalane–firebrick column which was capable of separating completely a test mixture of the five isomeric hexanes. The only hexane produced was 2,3-dimethylbutane. Similarly the only C_4 hydrocarbon was isobutane.

[1] Szwarc, *Discuss. Faraday Soc.*, 1951, **10**, 336.
[2] Glazebrook and Pearson, *J.*, 1936, 1777.
[3] Masson, *J. Amer. Chem. Soc.*, 1952, **74**, 4731.
[4] Chilton and Gowenlock, *Trans. Faraday Soc.*, 1953, **49**, 1451; 1954, **50**, 824.
[5] Batt and Gowenlock, *Trans. Faraday Soc.*, 1960, **56**. 682.

Discussion.—The above evidence shows that reactions (1) and (2) can take place only under more extreme conditions than we have employed. It is known [6] that decomposition of isopropyl radicals occurs readily at 300° the reaction being

$$(CH_3)_2CH\cdot \longrightarrow CH_3\cdot + C_2H_4 \qquad (3)$$

It seems likely that this reaction proceeds through an intermediate complex of structure (A) and that this transition-state complex would be the same as that necessary for the isomerization (2), and therefore also for reaction (1). The absence of n-hexane and 2-methylpentane in the decomposition products of di-isopropylmercury suggests that the relative rates of the decomposition reaction (3) and the isomerization reaction (2) are very different and are in favour of reaction (3). The presence of isobutane in our products supports this view. Our results are thus concordant with those of Heller and Gordon,[7] who found that the C_6 hydrocarbon produced on photolysis of di-isopropyl ketone contained at least 95% of 2,3-dimethylbutane, as well as with those of McNesby and Jackson,[8] who demonstrated that the reaction, $CD_3\cdot CH(CH_3)\cdot \longrightarrow \cdot CD_2\cdot CHD\cdot CH_3$, does not occur at temperatures up to 550°. We therefore conclude that there is no evidence for the homogeneous intramolecular isomerization reactions (1) and (2), and that these reactions are not promoted by a glass surface. The possibility of isomerization at other surfaces remains to be explored. The presence of isobutane and of ethylene in the products is evidence that reaction (3), *i.e.*, isomerization with decomposition, does occur. In addition our results provide no support for the suggestion [9] that isomerization is due to the reaction with propane, $Pr^i + C_3H_8 \rightleftharpoons C_3H_8 + Pr^n$.


(A)

We thank Dr. J. R. Majer for mass-spectrometric analyses and Dr. J. R. McNesby for discussion.

UNIVERSITY OF BIRMINGHAM. [*Received, February 1st*, 1962.]

[6] Kerr and Trotman-Dickenson, *Trans. Faraday Soc.*, 1959, **55**, 921.
[7] Heller and Gordon, *J. Phys. Chem.*, 1956, **60**, 1315.
[8] McNesby and Jackson, 18th Internat. Congr. Pure Appl. Chem., Montreal, Abs. A 1-50, p. 37.
[9] Stepukhovich, Kosyreva, and Petrosyan, *Zhur. fiz. Khim.*, 1961, **35**, 600.

631. *Aromatic Polyfluoro-compounds. Part XII.*[1] *Orientation Reactions of Pentafluorobenzene.*

By G. M. BROOKE, J. BURDON, and J. C. TATLOW.

IN previous papers,[2,3] we have described the reactions of fluoroaromatic compounds C_6F_5X (X = H, NH_2, NHMe, or NO_2) with various nucleophiles such as hydrazine, ammonia, and methylamine. We now report the nucleophilic replacement of fluorine in an aromatic polyfluoro-compound by hydrogen, effected by using lithium aluminium hydride. This reagent reacts with fluorinated olefins in ether solution,[4] the overall effect being the replacement of vinylic fluorine by hydrogen.

Pentafluorobenzene was refluxed with an excess of lithium aluminium hydride in diethyl ether for 53 hours. The product was isolated by preparative-scale vapour-phase chromatography in high yield (90%) and was shown by infrared spectroscopy and analytical vapour-phase chromatography, to consist of 1,2,3,4-,[4-6] 1,2,3,5-,[4,7] and 1,2,4,5-tetrafluorobenzene [4,8] in the ratio 7 : 1 : 92.

[1] Part XI, Coe, Stephens, and Tatlow, *J.*, 1962, 3227.
[2] Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.
[3] Brooke, Burdon, and Tatlow, *J.*, 1961, 802.
[4] Evans and Tatlow, unpublished work; Nield, Stephens, and Tatlow, *J.*, 1960, 3800.
[5] Florin, Pummer, and Wall, *J. Res. Nat. Bur. Stand.*, 1959, **62**, 113.
[6] Coe, Patrick, and Tatlow, *Tetrahedron*, 1960, **9**, 240.
[7] Finger, Reed, and Oesterling, *J. Amer. Chem. Soc.*, 1951, **73**, 152.
[8] Finger, Reed, Burness, Fort, and Blough, *J. Amer. Chem. Soc.*, 1951, **73**, 145.

The replacement of fluorine in hexafluorobenzene by hydrogen over palladium and platinum catalysts at 300° has been described.[5] Pentafluorobenzene was one of the major products, but tetrafluorobenzene, probably a mixture of isomers, was also formed.

In view of the production of three isomeric compounds from pentafluorobenzene, its reaction with aqueous ethanolic hydrazine, described in a previous paper,[2] was reinvestigated. 2,3,5,6-Tetrafluorophenylhydrazine was isolated in 65% yield. The crude residues were then treated with Fehling's solution [2] and gave a mixture of the three isomeric tetrafluorobenzenes. This showed that all three tetrafluorophenylhydrazines must have been formed in the original reaction, the ratio of the isomers being estimated as 2,3,4,5- : 2,3,4,6- : 2,3,5,6- = 3 : 0·5 : 96·5. These two experiments show that, as would be expected, all three isomers are formed in a nucleophilic replacement of fluorine in pentafluorobenzene, but that very little attack occurs on the atoms *ortho* or *meta* to the hydrogen.

In a previous paper [2] we described the preparation of 2,3,5,6-tetrafluoroaniline from pentafluorobenzene and ammonia. The structure of this compound was assigned from its nuclear magnetic resonance spectrum and by analogy with 2,3,5,6-tetrafluorophenylhydrazine, prepared similarly. We have now confirmed this orientation. The benzaldehyde derivative of 2,3,5,6-tetrafluorophenylhydrazine was refluxed with zinc dust in glacial acetic acid to give 2,3,5,6-tetrafluoroaniline, identical with that made previously. The cleavage of benzaldehyde phenylhydrazone to aniline by this method has been described.[9] In the fluoro-aromatic series this conversion of readily orientated phenylhydrazines into amines should be useful for characterisation since diazonium reactions of the latter have not yet been worked out.

Experimental.—Reaction of pentafluorobenzene with lithium aluminium hydride. Pentafluorobenzene (5·03 g.) in dry diethyl ether (10 ml.) was added to lithium aluminium hydride (1·56 g.) in dry diethyl ether, in an apparatus fitted with a water condenser and a second condenser cooled in solid carbon dioxide. After being refluxed for 53 hr., the mixture was cooled and 4N-sulphuric acid (70 ml.) was added very slowly. The volatile components (isomeric tetrafluorobenzenes and ether) were distilled on a vacuum-line into a separate receiver, dried with phosphoric oxide, and redistilled. The bulk of the ether was removed by fractional distillation through a 6″ column packed with glass helices. The isomeric tetrafluorobenzenes (4·0 g.) were isolated by preparative-scale vapour-phase chromatography.

The analytical vapour-phase chromatogram on dinonyl phthalate–kieselguhr of the isomeric tetrafluorobenzenes had three peaks, the retention times of which corresponded to those of (i) 1,2,3,5-tetrafluorobenzene + pentafluorobenzene, (ii) 1,2,4,5-tetrafluorobenzene, and (iii) 1,2,3,4-tetrafluorobenzene. The ratio of the areas under the peaks (i) : (ii) : (iii) was 3 : 90 : 7. The infrared spectrum of the product confirmed the presence of all three isomeric tetrafluorobenzenes, together with a small amount (*ca.* 2%) of pentafluorobenzene. The identity of each peak of the analytical vapour-phase chromatogram was confirmed in a separate experiment by isolating the component by preparative vapour-phase chromatography and identifying it by infrared spectroscopy.

Reaction of pentafluorobenzene with hydrazine. Pentafluorobenzene (4·63 g.), 100% hydrazine hydrate (14·4 g.), water (10·5 ml.), and ethanol (25 ml.) were refluxed together for 7 hr., then poured into ice–water. The product (3·41 g.), m. p. 89—90·5°, was filtered off and recrystallised from light petroleum (b. p. 80—100°), to give pure 2,3,5,6-tetrafluorophenylhydrazine (3·24 g., 65%), m. p. 90—91·5°.

A further quantity of crude product (0·83 g.), m. p. 75—120°, was obtained by extraction of the filtrate with methylene chloride. This was combined with the residue (0·05 g.) from the recrystallisation mother-liquors and refluxed with Fehling's solution [mixture of solution " A " (50 ml.) and solution " B " (50 ml.)] for 1 hr. The organic phase (0·37 g., 50%) was steam-distilled from the reaction mixture. Analytical vapour-phase chromatography showed the presence of three components, the retention times of which corresponded with those of (i) 1,2,3,5-, (ii) 1,2,4,5-, and (iii) 1,2,3,4-tetrafluorobenzene. The relative areas under these

[9] Clark, " Hydrazine," Mathieson Chemical Corporation, Baltimore, 1953, p. 40.

three peaks were 3 : 83 : 14. Infrared spectroscopy confirmed the presence of all the isomeric tetrafluorobenzenes.

2,3,5,6-*Tetrafluoroaniline from benzaldehyde* 2,3,5,6-*tetrafluorophenylhydrazone*. The phenylhydrazone [2] (1·65 g.), powdered zinc (3·45 g.), and glacial acetic acid (10 ml.) were refluxed together for 3 hr. 4N-Sulphuric acid (25 ml.) was added and the mixture was steam-distilled. The distillate was extracted with ether, and the extracts were neutralised with sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated, to leave 2,3,5,6-tetrafluoroaniline (0·80 g., 79%), m. p. 29—31·5°. The infrared spectrum showed that it was a purer sample than that prepared previously.[2] The latter material (m. p. 23·5—26·5°) might have contained small amounts of isomeric tetrafluoroanilines.

We thank the Wellcome Trust for a grant (to G. M. B.).

CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15. [*Received, February 1st*, 1962.]

---

632. *The Preparation of Active Solids by Thermal Decomposition. Part XIV.* Calcination of Lead Dioxide* in vacuo.

By S. J. GREGG and R. F. S. TYSON.

LEAD DIOXIDE appeared to be an interesting substance for a study of the production of an active solid by thermal decomposition, for it is known to decompose, on being heated, to give lead monoxide, with trilead tetroxide (Pb_3O_4) as an intermediate product; the formation of two further intermediate products, *viz.*, α-PbO_x and β-PbO_x, with x lying between 1·67 and 1·50 in the first case and between 1·51 and 1·47 in the second, has also been claimed.[1,2] According to Katz,[3] however, a series of solid solutions is formed from the oxides Pb_7O_{11} and Pb_3O_4.

By analogy with other cases [4] the decomposition of lead dioxide might be expected to produce an increase in surface area, *i.e.*, a more " active " solid. In the event, however, the area diminished when decomposition occurred, probably because of the rapid sintering of the product.

Materials.—" AnalaR " lead dioxide was stated to contain >95% of PbO_2, with a chloride content below 0·35%; *X*-ray examination failed to reveal any impurity. The loss in weight on calcination at 700° corresponded to the formula $PbO_{1\cdot98}$ for the material dried at 100°, on the assumption that the fully calcined product is accurately $PbO_{1\cdot00}$; this result agrees with that of Butler and Copp [1] who found a similar " AnalaR " material to have the composition $PbO_{1\cdot98},0\cdot04H_2O$.

Procedure.—It had been intended to heat separate portions of the starting material on an electrical sorption balance [5] for 3 hr., each at a different fixed temperature T. Because of the tendency to spurt, however, it was necessary to modify the procedure for heating: the temperature of the sample, on the balance, was raised at the rate of 3° per minute from 125° to T°, and then maintained (by a Sunvic controller of type RT2) at a temperature of $T° \pm 2°$ for such a period as to make the total time of heating 3 hr. The resultant weight-loss was measured by the sorption balance.

Since the surface areas of the samples were small they were measured by the adsorption of krypton at −195° with a volumetric apparatus [6,7] and the assumption that the cross-sectional area of krypton was 19·5 Å^2 per molecule.

* Part XIII, Gregg and Pope, *J.*, 1961, 1252.

[1] Butler and Copp, *J.*, 1956, 725.
[2] Bystrom, *Arkiv Kemi, Min., Geol.*, 1945, **20***A*, No. 11, 1.
[3] Katz, Thesis, Paris, 1949.
[4] See, *e.g.*, Gregg and Packer, *J.*, 1955, 51.
[5] Gregg, *J.*, 1955, 1438.
[6] Smith, Thesis, Exeter, 1958.
[7] Rosenberg, *J. Amer. Chem. Soc.*, 1956, **78**, 2929.

The samples were also examined by *X*-ray diffraction, with a Debye–Scherrer type of camera, for their chemical identification.

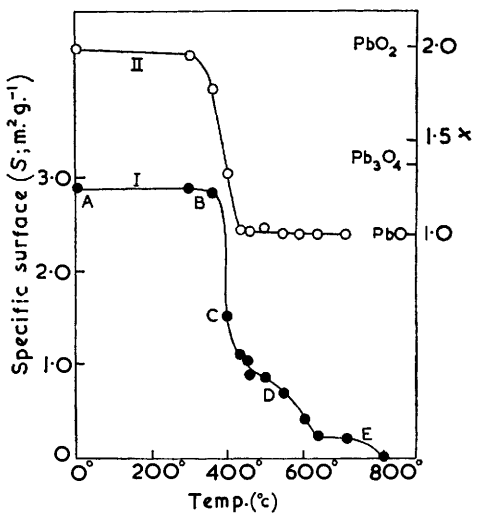
Results and Discussion.—The curve of specific surface (S) against temperature of calcination (T) is shown in the Figure, whence it is seen that S decreases monotonously as T increases from *ca.* 350° onwards. Reference to the data for chemical composition shown in the graph and in the Table shows that this loss of area accompanies the chemical decomposition of the PbO_2 first to Pb_3O_4 and then to PbO.

The composition of the solid produced by heating lead dioxide for a total of 3 hr.

Final temp. of sample	x *	Compounds present as shown by *X*-rays	Final temp. of sample	x *	Compounds present as shown by *X*-rays
Room temp.	1·98	PbO_2	500°	1·03	Red PbO
300°	1·95	,,	550	1·00	—
360	1·77	Little PbO_2; Pb_3O_4	592	1·00	Yellow PbO, some red
400	1·32	Pb_3O_4	644	1·00	Yellow PbO, no red
433	1·02	—	715	1·00	,, ,,
448	1·01	—			

* The value of x in the formula PbO_x, calc. from the weight loss during preparation.

When a solid decomposes to give a second solid having a different lattice, the specific surface usually increases [8] (because the new solid has more crystallites per gram than the old); if the product is heated further it begins to sinter and its area correspondingly



Variation of (I) specific surface and (II) composition with temperature of calcination (x = value in PbO_x).

diminishes, the rate of sintering rapidly increasing as the temperature increases above the Tammann temperature.[9,10] [T_t has been defined [11] by $T_t = \alpha T_m$ where T_m (°K) is the melting point of the substance and the value of α depends on the nature of the substance but lies within the range 0·37—0·53; it often lies close to 0·5.]

Now the melting point of yellow lead monoxide [12] is 890°, corresponding to a Tammann temperature of about 310°; the melting point of the red form is unknown because of its conversion into the yellow form but, in view of the similarity [13] between the lattice types of the two forms, the Tammann temperature of the red form is not likely to

[8] Gregg, *J.*, 1953, 3940.
[9] Tammann, *Z. anorg. Chem.*, 1925, **149**, 67; 1928, **176**, 46.
[10] Finch and Sinha, *Proc. Roy. Soc.*, 1957, *A*, **239**, 145.
[11] Hüttig, *Kolloid Z.*, 1942, **99**, 262.
[12] Brewer, *Chem. Rev.*, 1953, **52**, 1.
[13] Wyckoff, " Crystal Structures," Vol. I, Section III, Tables 17, 17a, Fig. III 21, Interscience Publ. Inc., New York.

differ greatly from that of the yellow. If this is so, the rapid decrease in specific surface along CDE is readily understood: the product being formed along this branch, *viz.*, lead monoxide (in the red form at the lower temperatures and in the yellow at the higher temperatures) finds itself above its Tammann temperature; consequently it sinters rapidly, so rapidly in fact that the " activation," or increase in area, which would normally be expected is completely masked.

The reason for the rapid diminution in area between B and C is more speculative, inasmuch as the melting point, and consequently the Tammann temperature, of the substance being produced, *viz.*, trilead tetroxide, is unknown. The very rapidity of the diminution strongly suggests, however, that the temperature range in question, 350—400°, is indeed above the Tammann temperature of the tetroxide.

Conclusion.—On calcination of lead dioxide *in vacuo* at temperatures in the range 350—800° the specific surface of the product is always less than that of the starting material. This is probably because the temperature at which the product is formed, *viz.*, ~350—400° for Pb_3O_4, 400—500° for red lead monoxide, and 500° upwards for yellow lead monoxide, is in each case above the Tammann temperature for the substance.

It is therefore impossible to prepare lead monoxide or a red lead having a high specific surface (many square metres per gram.) by thermal decomposition of lead dioxide *in vacuo*.

WASHINGTON SINGER LABORATORIES,
PRINCE OF WALES ROAD, EXETER.

[*Received, February 6th*, 1962.]

633. *Infrared Spectra of Steroid Esters of Fatty Acids.*

By W. CARRUTHERS and J. R. PLIMMER.

THE infrared spectra, measured in the solid state, of long-chain fatty acids [1,2] and esters,[1,3] of glycerides,[4] and of polymethylene αω-dicarboxylates,[5] exhibit a series of bands between 1350 and 1180 cm.$^{-1}$ like those found in the spectra of n-alkanes.[6] These bands have been assigned to CH_2 wagging vibrations.[1,4,7] Similar series of regularly spaced bands have been observed also in the spectra of crystalline films of the steroid esters listed in the Table. Nujol mulls were not examined, for it has been shown in the fatty acid series that spectra determined in Nujol may be affected by polymorphism of the specimen and are less useful for analytical purposes.

Infrared maxima (cm.$^{-1}$) of steroid esters in the region 1350—1180 cm.$^{-1}$.

Stigmasteryl				β-Sitosteryl			
Laurate	Myristate	Palmitate	Stearate	Laurate	Myristate	Palmitate	Stearate
1329	1327	1328	1330	1326	1329	1328	1332
1299	1300	1306	1308	1298	1301	1306	1310
1268	1279	1282	1293	1267	1279	1282	1294
1241	1251	1265	1270			1264	1272
1206	1228	1240	1255	1239	1252		1256
		1220	1233		1228	1240	1234
			1214	1205		1220	1215
1196	1199	1196	1195		1200	1196	1195
1183	1177	1176	1180	1178	1179	1178	1180

[1] Sinclair, McKay, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2570; Jones, McKay, and Sinclair, *ibid.*, p. 2575.
[2] Meiklejohn, Meyer, Aronovic, Schuette, and Meloch, *Analyt. Chem.*, 1957, **29**, 329.
[3] Labarrère, Chipault, and Landberg, *Analyt. Chem.*, 1958, **30**, 1466.
[4] Chapman, *J.*, 1956, 55, 2522.
[5] Gunthard, Heinemann, and Prelog, *Helv. Chim. Acta*, 1953, **36**, 1147.
[6] Brown, Sheppard, and Simpson, *Discuss. Faraday Soc.*, 1950, **9**, 261.
[7] Brown and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 535; Brown, Sheppard, and Simpson, *Phil. Trans.*, 1954, *A*, **247**, 35.

In general the spectra resemble each other and those of the corresponding cholesteryl esters [3] closely, with strong bands at 1730 cm.$^{-1}$ and in the region of 1460 and 1380 cm.$^{-1}$; stigmasteryl derivatives are distinguished by a prominent band at 970 cm.$^{-1}$. In the 1350—1180 cm.$^{-1}$ region the bands are well marked and appear at closely similar frequencies, in corresponding esters in the two series. In line with the earlier work mentioned the number of bands in this region increases with the chain length of the acid moiety. The lower end of the series is obscured by absorption associated with the ester grouping at about 1170 cm.$^{-1}$ so that there is some difficulty in determining where the progression starts (cf. ref. 1), but, if the band at about 1180 cm.$^{-1}$ is considered as the first in the series, there is one band for every two carbon atoms in the chain, with the exception of stigmasteryl laurate which has an " extra " band at 1196 cm.$^{-1}$. A similar relation was noted for a number of fatty-acid soaps [2] and cholesteryl esters.[3] These bands appear to be of some value for identifying fatty-acid esters of stigmasterol and β-sitosterol, and probably of other sterols as well (cf. ref. 3), particularly since melting points and optical rotations are unreliable for this purpose.[8]

In addition to the frequencies listed a number of minor bands appear as inflections, at 1316, 1285, and 1258 cm.$^{-1}$ in the spectra of stigmasteryl and β-sitosteryl laurate Both the stigmasteryl and the sitosteryl derivatives show maxima in the region of 1012 and 1029 cm.$^{-1}$. It has been pointed out [9] that bands in this region do not occur in the spectra of glycerides, but they are evidently not specific for cholesteryl esters as suggested by Labarrère *et al.*[3]

Experimental.—Spectra were determined with a Hilger H-800 spectrophotometer on solid films of the esters prepared by melting them between rock-salt plates, and allowing the melt to cool slowly to room temperature.

Stigmasteryl acetate, purified by the method of Windaus and Hauth,[10] had m. p. 143—144°, $[\alpha]_D^{28}$ −56°; the free sterol had m. p. 168°. β-Sitosterol had m. p. 139°, $[\alpha]_D^{28}$ −36°, after fractional crystallisation of the acetate and the benzoate followed by chromatography on alumina. Steroid esters were prepared [11] from the sterol and the acid chloride in boiling benzene in presence of pyridine, purified by chromatography on silica gel and crystallised from ethanol or acetone. M. p.s and specific rotations were essentially similar to those reported by Kuksis and Beveridge.[8]

We thank Dr. J. W. Cook, F.R.S., for his interest.

MEDICAL RESEARCH COUNCIL, CARCINOGENIC SUBSTANCES RESEARCH UNIT,
UNIVERSITY OF EXETER.
UNIVERSITY COLLEGE OF THE WEST INDIES,
KINGSTON, JAMAICA.

[*Received, February 8th*, 1962.]

[8] Kuksis and Beveridge, *J. Org. Chem.*, 1960, **25**, 1209.
[9] Freeman, Lindgren, Yook C. Ng, and Nichols, *J. Biol. Chem.*, 1953, **203**, 293.
[10] Windaus and Hauth, *Ber.*, 1907, **40**, 368.
[11] Cf. King and Jurd, *J.*, 1953, 1192.

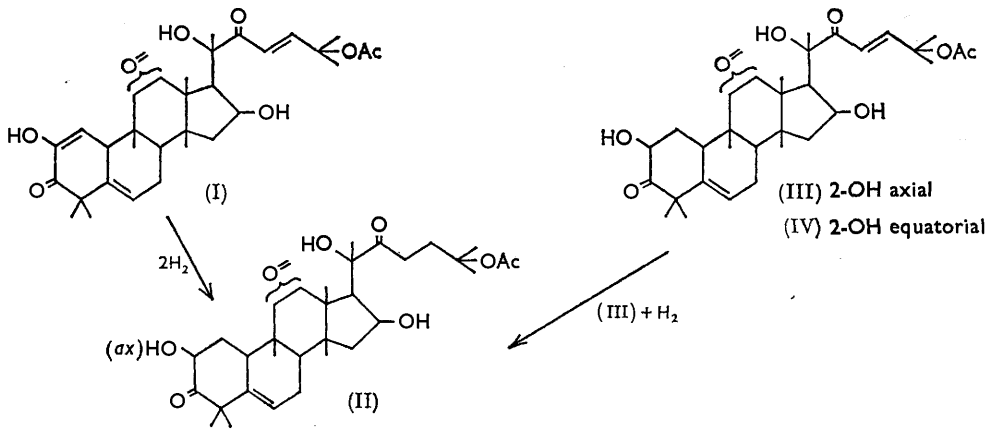
634. *The Occurrence of 2-Epicucurbitacin B in* Luffa echinata.

By D. Lavie, Y. Shvo, O. R. Gottlieb, R. B. Desai, and M. L. Khorana.

Luffa echinata Roxb. (family Cucurbitaceae) is a plant commonly used in India as a medicine.[1] Recent studies [2-4] of the cucurbitacins prompted us to investigate its constituents, as other *Luffa* species contain members of this group.[5]

The complete structure of the cucurbitacins is still uncertain [4,6] but the conformational observations regarding the 2-hydroxyl group are still valid.[3]

Two crystalline constituents isolated from an ether extract of the fruit of *L. echinata* were separated by fractional crystallisation into elaterin (cucurbitacin E) [7] (I), and a less soluble substance. The latter gave with triphenyltetrazolium chloride a red precipitate of formazan, which indicates a secondary α-hydroxy-ketone.[3] The ultraviolet spectrum has a maximum at 230 mμ which was related, as in the other cucurbitacins, to the αβ-unsaturated ketone of the side chain.[8] The formula is $C_{32}H_{46}O_8$, so the substance is



isomeric with cucurbitacin B.[9] Their infrared spectra differed in that the new compound has a band at 1100 cm.$^{-1}$; this frequency has been ascribed [3] to the C–OH stretching of a secondary axial 2-hydroxyl group in the cucurbitacins. It is noteworthy that this conformation has been found in substances in which the double bond of the diosphenol system in ring A had been reduced by hydrogenation, as, for example, in tetrahydroelaterin [3] (II). This product (II) should differ therefore from the new substance only by the absence of the double bond in the side chain. Indeed, the new compound absorbed one mol. of hydrogen in presence of palladium giving tetrahydroelaterin (II). It is therefore 2-epicucurbitacin B (III).

All the naturally occurring cucurbitacins previously described, in which ring A is saturated, have equatorial 2-hydroxyl groups (IV). Axial 2-alcohols of type (III) have been obtained only by hydrogenation of the diosphenol system of (I). However, the double bond in the side chain is preferentially reduced during this reaction, leading to

[1] Bhatt and Khorana, *Indian J. Pharm.*, 1957, **19**, 208; Nadkarni, "Indian Materia Medica," Bhatkal, Bombay, 1954, 3rd edn., Vol. I, p. 753.
[2] Lavie and Shvo, *Chem. and Ind.*, 1960, 403.
[3] Lavie and Gottlieb, *Chem. and Ind.*, 1960, 929.
[4] Lavie, Shvo, Gottlieb, and Glotter, *Tetrahedron Letters*, 1961, No. 18, 615.
[5] Enslin, Rehm, and Rivett, *J. Sci. Food Agric.*, 1957, **8**, 673.
[6] Noller, Melera, and Gut; Shoolery and Johnson, *Tetrahedron Letters*, 1960, No. 15, 15.
[7] Lavie and Szinai, *J. Amer. Chem. Soc.*, 1958, **80**, 707.
[8] Lavie, Shvo, and Willner, *J. Amer. Chem. Soc.*, 1959, **81**, 3062.
[9] Eisenhut and Noller, *J. Org. Chem.*, 1958, **23**, 1984; Melera, Schlegel, and Noller, *ibid.*, 1959, **24**, 291.

compound (II).[3] A 2-*ax*-hydroxy-Δ^{23}-cucurbitacin, as the 2-epicucurbitacin B (III), described in the present paper, was therefore neither previously known to occur in Nature nor available from other naturally occurring cucurbitacins.

Experimental.—M. p.s were taken on a Kofler hot-stage microscope. Ultraviolet absorption spectra were measured with a Unicam model S.P. 500 spectrophotometer for methanol solutions. Infrared spectra were recorded on a Perkin–Elmer Infracord model 137 spectrometer in pellets of potassium bromide. Optical rotation measurements were for chloroform solutions.

Extraction. Fruits (2·3 kg.) of *L. echinata* [1] were powdered, treated exhaustively with light petroleum (b. p. 40—60°), and then extracted by percolation with ether. The solvent was evaporated, leaving a green, viscous residue (8 g.). The colouring and oily materials were eliminated by trituration with light petroleum. The crude solid obtained (7·7 g.), m. p. 170—192°, was resolved by fractional crystallisations from methanol into the more soluble elaterin (I) (*ca.* 3 g.) and the less soluble 2-epicucurbitacin B (III) (*ca.* 0·2 g.).

Elaterin formed hexagonal plates (from methanol), m. p. 232—233° (decomp.), $[\alpha]_D$ −58° (*c* 1·0), gave a strong colour with ferric chloride, and had the same m. p. on admixture with elaterin (I) obtained from *Ecballium elaterium* L.[7] The ultraviolet and infrared spectra of the two samples were superimposable.

2-Epicucurbitacin B formed elongated plates (from methanol), m. p. 229—231° (decomp.), $[\alpha]_D$ +41° (*c* 1·1), $\lambda_{max.}$ 230 mμ (ε 11,000), $\nu_{max.}$ 3550 (OH), 1730 (overlapping of ester and 3-C=O), 1695 (overlapping of 12- and 22-C=O), 1630 (Δ^{23}), 1260 (OAc), and 1102 (2-OH) cm.$^{-1}$ (Found: C, 68·4; H, 8·4. $C_{32}H_{46}O_8$ requires C, 68·8; H, 8·3%). No colour was observed with ferric chloride. A red precipitate of formazan was obtained with triphenyltetrazolium chloride.

Tetrahydroelaterin. 2-Epicucurbitacin B (12·5 mg.) (III) in ethanol solution (20 ml.) containing 10% palladium–carbon (5 mg.) absorbed 1 mol. of hydrogen very rapidly at room temperature and pressure. When the filtered solution had been evaporated under reduced pressure, the residue crystallised from ether as rods (6 mg.), m. p. 231—233° alone or mixed with tetrahydroelaterin (II). The infrared and ultraviolet spectra of the two samples were superimposable.

We (D. L., Y. S., and O. R. G.) thank the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service, for a grant, and (R. B. D. and M. L. K.) are grateful to Messrs. May and Baker Ltd. for sponsoring this scheme. One of the authors (O. R. G., on leave of absence from the Instituto de Química Agrícola, Rio de Janeiro) acknowledges support from the Conselho Nacional de Pesquisas, Brasil.

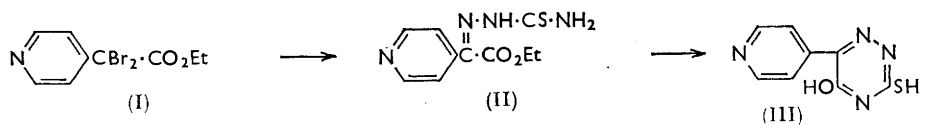
THE DANIEL SIEFF RESEARCH INSTITUTE,
WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL.
DEPARTMENT OF CHEMICAL TECHNOLOGY,
UNIVERSITY OF BOMBAY, BOMBAY, INDIA. [*Received, February 15th,* 1962.]

---

635. 5-*Hydroxy*-3-*mercapto*-6-4′-*pyridyl*-1,2,4-*triazine*.

By A. HOLLAND.

HAGENBACH *et al.* [1] claimed first that 5-hydroxy-3-mercapto-6-4′-pyridyl-1,2,4-triazine (III) had been prepared from ethyl α-hydroxyiminopyridylacetate, but found later [2] that it was acccompanied by 4-formylpyridine thiosemicarbazone. The triazine has now been obtained by the following route from ethyl 4-pyridylacetate; it was not necessary to purify the intermediates (I) and (II).



(I) (II) (III)

[1] Hagenbach, Hodel, and Gysin, *Angew. Chem.*, 1954, **66**, 359.
[2] Hagenbach and Gysin, *Experientia*, 1955, **11**, 314.

Cyclisation of the thiosemicarbazone (II) by Hagenbach's method gave a product which was deficient in sulphur but cyclisation in dilute alkali at room temperature gave the pure triazine, albeit in rather low yield. The triazine was readily converted into the dimercapto-compound by treatment with phosphorus pentasulphide in pyridine.

Experimental.—*5-Hydroxy-3-mercapto-6-4′-pyridyl-1,2,4-triazine.* Ethyl 4-pyridylacetate (1·65 g.), glacial acetic acid (12·5 c.c.), and anhydrous sodium acetate (7 g.) were treated on the steam-bath, by dropwise addition and shaking, with bromine (1 c.c.) and acetic acid (6 c.c.). The mixture was then heated for 1 hr., cooled, and poured into ice–water, and the oil which separated was extracted with ether. The extract was washed with water and sodium hydrogen carbonate solution, dried (Na_2SO_4), and concentrated. The residue was treated with dilute sulphuric acid [concentrated acid (0·6 g.) and water (30 c.c.)] with ice-cooling, and thiosemicarbazide (0·91 g.) immediately added with continuous stirring. When precipitation was complete, the mixture was neutralised by the addition of ammonia solution, and the yellow solid (1·4 g.) was collected and dried *in vacuo*. The crude derivative (2·24 g.) was shaken with N-sodium hydroxide (30 c.c.) for 7 days. The resulting solution was filtered (charcoal) and acidified with acetic acid (ice-cooling). The crude material (0·5 g., 30%), m. p. 290°, was crystallised from aqueous dioxan giving the triazine, m. p. 304° (lit.,[2] m. p. 308°) (Found: C, 46·95; H, 3·3; S, 15·6. Calc. for $C_5H_6N_4OS$: C, 46·6; H, 2·9; S, 15·5%).

3,5-Dimercapto-6-4′-pyridyl-1,2,4-triazine. 5-Hydroxy-3-mercapto-6-4′-pyridyl-1,2,4-triazine (2·08 g.) and phosphorus pentasulphide (2·75 g.) were heated under reflux with dry pyridine (14 c.c.) for 1 hr. The cooled mixture was poured into water (140 c.c.), and the precipitate was washed with water, dissolved in 2N-ammonia solution (100 c.c.), and acidified with hydrochloric acid. The crude dithiol (1·4 g.; 63%) formed yellow crystals, m. p. 275°, and was characterised by conversion into the disodium *salt* (Found: S, 15·7; Na, 11·5; loss in weight at 110°, 33·2. $C_5H_4N_4Na_2S_2,7{\cdot}5H_2O$ requires S, 16·0; Na, 11·5; loss in weight, 33·6%).

RESEARCH LABORATORIES, MAY & BAKER LTD.,
DAGENHAM, ESSEX.

[*Received, February 6th*, 1962.]

---

636. *A Stereospecific Synthesis of 3α-Cyanocholestane.*

By LEO A. POHORYLES, IZHAR GAT, and SHALOM SAREL.

THE introduction of a cyano-group at position-3 in cholestane could not be effected in reasonable yields by replacement of either the chloro- or the toluene-*p*-sulphonyloxy-group with cyanide,[1] though alternative methods have been recorded.[2] This Note reports the preparation of 3α-cyano-5α-cholestane in 60% yield by treating 3β-chlorocholestane with sodium cyanide at 180—190° in dimethyl sulphoxide,[3] with only small amounts of cholest-2-ene (<15%) and 3β-cyano-5α-cholestane (5%). Unlike the concurrent elimination, the extent of which does not seem to be materially affected by change of conditions, the ratio of the amounts of the two cyanides largely depended on the temperature and duration of reaction. At 180—190° extending the time of reaction from 2 to 5—6 hours resulted in a change in the α : β ratio from 12 : 1 to 1 : 3. Lowering the reaction temperature to 140—150°, although favouring the formation of the predominant α-cyanide, decreased its overall yield. Thus the formation of the α-cyanide is kinetically controlled and occurs with inversion, whereas that of the β-cyanide requires double inversion and seems to be thermodynamically controlled.

Experimental.—*3α-Cyano-5α-cholestane.* To sodium cyanide (750 mg.) and dimethyl sulphoxide (10 ml.), heated at 180—190°, was added portionwise, with stirring, 3β-chlorocholestane [4] {m. p. 114—115°, $[\alpha]_D^{20}$ +26·5° (1% in $CHCl_3$)} (4 g.) during 3 hr. Heating and

[1] Roberts, Shoppee, and Stephenson, *J.*, 1954, 2705.
[2] Labler, Cerny, and Sorm, *Coll. Czech. Chem. Comm.*, 1954, **19**, 1249.
[3] Smiley and Arnold, *J. Org. Chem.*, 1960, **25**, 275.
[4] Marker, Whitmore, and Kamm, *J. Amer. Chem. Soc.*, 1935, **57**, 2358.

stirring were continued for an additional 2 hr. The mixture was then cooled and poured into water. The product (4 g.) obtained by ether-extraction, drying, and removal of solvent was chromatographed on alumina. Elution by light petroleum provided (1) cholest-3-ene (460 mg., 12·5%), m. p. 64—70°, (2) 3α-cyano-5α-cholestane (2·15 g., 58%), m. p. 168° (from ethanol), $[\alpha]_D^{20}$ +21° (1% in $CHCl_3$), $\nu_{max.}$ (in KBr) 2260 cm.$^{-1}$ (C≡N) (lit.,[1] m. p. 168°, $[\alpha]_D^{20}$ +21°) (Found: C, 84·4; H, 11·2. Calc. for $C_{28}H_{47}N$: C, 84·6; H, 12·1%), and (3) colourless crystals (150 mg.), m. p. 120—157°, of impure 3β-cyano-5α-cholestane which were not further investigated.

[*Added in proof:* After this Note was submitted for publication, Henbest and Jackson (*J.*, 1962, 954) reported an 81% yield in a similar preparation of 3α-cyano-5α-cholestane, using *N*-methylpyrrolidone as an aprotic solvent.]

Department of Pharmaceutical Chemistry, The Hebrew University, Jerusalem, Israel. [*Received, February 19th*, 1962.]

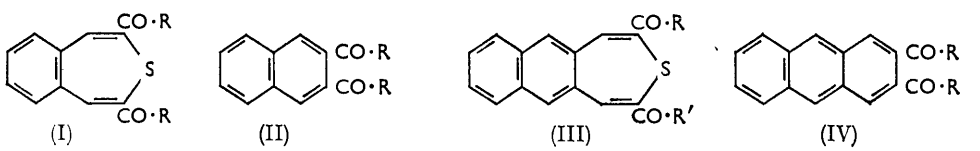
---

637. *Extrusion of Sulphur. Part V.*[1]

By J. D. Loudon and A. D. B. Sloan.

An arresting example of sulphur extrusion is the formation[2] of naphthalene-2,3-dicarboxylic acid (II; R = OH) on attempted crystallisation of the benzothiepindicarboxylic acid (I; R = OH) from ethanol. The latter acid is obtained by condensing *o*-phthalaldehyde with diethyl thiodiacetate, $S(CH_2{\cdot}CO_2Et)_2$, in an alkaline medium. It affords a dimethyl ester[3] which is appreciably more stable.

By condensing phthalaldehyde with diphenacyl sulphide we obtained 2,3-dibenzoylnaphthalene (II; R = Ph) without detecting the intermediate thiepin. Substituted diphenacyl sulphides likewise gave appropriately substituted dibenzoylnaphthalenes. On the other hand, naphthalene-2,3-dialdehyde reacted with diphenacyl sulphide affording the naphthothiepin (III; R = R′ = Ph), and with diethyl thiodiacetate forming a mixture of the diethyl (III; R = R′ = OEt) and monoethyl (III; R = OH, R′ = OEt) esters and dicarboxylic acid (III; R = R′ = OH). These naphthothiepins showed a marked tendency to crystallise from hydrocarbons with solvent of crystallisation. On pyrolysis they yielded 2,3-disubstituted anthracenes (IV) with extrusion of sulphur.



(I) (II) (III) (IV)

Experimental.—Petroleum refers to light petroleum, b. p. 60—80°.

2,3-*Dibenzoylnaphthalene* (II; R = Ph). (*a*) Sodium hydroxide (0·065 g.) was added to a solution of *o*-phthalaldehyde (0·25 g.) and diphenacyl sulphide (0·5 g.) in dioxan (1 ml.) and methanol (1·5 ml.) at 18°, and the whole was shaken for 1 hr. The resultant coloured solution was added to acidified ice–water, and the precipitated solid was collected and chromatographed in benzene on alumina. 2,3-*Dibenzoylnaphthalene* (0·35 g.) had m. p. 145° (from acetic acid) (Found: C, 85·85; H, 4·8. $C_{24}H_{16}O_2$ requires C, 85·7; H, 4·8%).

(*b*) The same compound (33% yield) was formed when the reactants were heated for 30 min. in a solution of ethanol–water containing potassium carbonate. With hydrazine hydrate in warm acetic acid it formed 1,4-*diphenylbenzo*[g]*phthalazine*, m. p. 228° (from acetic acid) (Found: C, 86·7; H, 5·0; N, 8·5. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·85; N, 8·4%).

2,3-*Di*-p-*bromobenzoylnaphthalene*, m. p. 158° (from petroleum) was obtained from di-*p*-bromophenacyl sulphide as in method (*a*) (above) (Found: C, 58·1; H, 3·0. $C_{24}H_{14}Br_2O_2$

[1] Part IV, Galt and Loudon, *J.*, 1959, 885.
[2] Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 6332.
[3] Dimroth and Lenke, *Chem. Ber.*, 1956, **89**, 2608.

requires C, 58·3; H, 2·8%). With hydrazine hydrate in acetic acid it formed 1,4-*di*-p-*bromophenylbenzo*[g]*phthalazine*, m. p. 309° (from acetic acid) (Found: C, 58·8; H, 3·1; N, 5·7. $C_{24}H_{14}Br_2N_2$ requires C, 58·8; H, 2·85; N, 5·7%).

Di-p-*phenylphenacyl sulphide*, m. p. 147° (from ethanol) was prepared from *p*-phenylphenacyl bromide and sodium sulphide in ethanol (Found: C, 79·3; H, 5·5. $C_{28}H_{22}O_2S$ requires C, 79·6; H, 5·25%).

2,3-*Di*-(p-*phenylbenzoyl*)*naphthalene*, m. p. 275° (from acetic acid), was obtained from *o*-phthalaldehyde in reaction with the preceding sulphide (Found: C, 88·4; H, 5·2. $C_{36}H_{24}O_2$ requires C, 88·5; H, 4·95%).

2,4-*Dibenzoylnaphtho*[2,3-d]*thiepin* (III; R = R′ = Ph) was obtained as solvated orange crystals (0·68 g.), m. p. 172° (decomp.) (from benzene), by interaction of naphthalene-2,3-dialdehyde [4] (0·34 g.) and diphenacyl sulphide (0·5 g.) essentially as described for 2,3-dibenzoylnaphthalene in (*a*). Heated for 2 hr. at 75° *in vacuo*, the crystals lost benzene (2 mol.), disintegrating to a yellow powder (0·496 g.), m. p. 174° (decomp.; sample inserted in hot block at 160°) (Found: C, 80·5; H, 4·3. $C_{28}H_{18}O_2S$ requires C, 80·4; H, 4·35%).

2,3-*Dibenzoylanthracene* (IV; R = Ph). The foregoing thiepin (0·1 g.) was slowly heated from 180° to 250° at 0·5 mm. in a horizontal subliming tube, the higher temperature being maintained for 40 hr. (to facilitate separation of products). Rhombic sulphur, m. p. 112°, and the dibenzoylanthracene (0·068 g.) were collected at 7·5 and 1·5 cm., respectively, from the source of heat. The bright-yellow *dibenzoylanthracene*, m. p. 180° (from acetonitrile) was purified in benzene on alumina (Found: C, 87·0; H, 5·1. $C_{28}H_{18}O_2$ requires C, 87·0; H, 4·7%). It reacted with hydrazine hydrate in acetic acid affording 1,4-*diphenyl*-2,3-*diazatetracene*, m. p. 256° (Found: C, 87·85; H, 4·8; N, 7·2. $C_{28}H_{18}N_2$ requires C, 87·9; H, 4·7; N, 7·3%).

Esters of naphtho[2,3-d]*thiepin*-2,4-*dicarboxylic acid* (III; R = R′ = OH). A solution (1 ml.) of sodium ethoxide (0·15 g.) in dry ethanol was added to a warm solution of naphthalene-2,3-dialdehyde [4] (0·37 g.) and diethyl thiodiacetate (0·41 g.) also in ethanol (3 ml.). An orange precipitate was formed and, after addition of acidified ice–water, the whole was extracted with ether. The ethereal extract was washed with aqueous sodium carbonate (cf. below), dried, and evaporated, and the residue was chromatographed in benzene on alumina. The eluted yellow band afforded the *diethyl ester* as scarlet needles, (micro) m. p. 101—103° (0·012 g.) (from petroleum), $\lambda_{max.}$ (in EtOH) 228 (log ε 4·56), 277 (log ε 4·63), and 323 mμ (log ε 4·72). When left in contact with the mother-liquor the needles gradually changed to a yellow variety but without change in the m. p. or spectral character (Found, in specimen dried *in vacuo*: C, 67·6; H, 5·0. $C_{20}H_{18}O_4S$ requires C, 67·8; H, 5·1%). Acidification of the sodium carbonate washings gave the *half-ester* as orange crystals, m. p. 167—170° (from methanol) (Found: C, 65·95; H, 4·55%; equiv., 327. $C_{18}H_{14}O_4S$ requires C, 66·25; H, 4·3%; equiv., 326).

When the experiment was repeated with the reaction time extended to 17 hr. at 0°, acidification of the water-soluble product gave naphthothiepin-2,4-dicarboxylic acid as a buff-coloured solid (0·37 g.) which was converted by ethereal diazomethane into the *dimethyl ester*, orange-yellow crystals of m. p. 178° (decomp.) (from benzene) (Found: C, 66·5; H, 4·3. $C_{18}H_{14}O_4S$ requires C, 66·25; H, 4·3%).

Derivatives of Anthracene-2,3-*dicarboxylic acid*. (*a*) The monoethyl ester (III; R = OEt, R′ = OH) was heated at 180—250°/0·5 mm., anthracene-2,3-dicarboxylic acid anhydride being obtained as sublimate and crystallised from acetonitrile, ν (in KCl) 1820, 1770, and 1222 cm.$^{-1}$ (Found: C, 77·4; H, 3·6. Calc. for $C_{16}H_8O_3$: C, 77·4; H, 3·25%). Fairbourne [5] has described the anhydride which sublimes without melting.

(*b*) The dimethyl ester (III; R = R′ = OMe), heated at 180—210°/0·5 mm., gave as sublimates sulphur and *dimethyl anthracene*-2,3-*dicarboxylate*, m. p. 151° (from methyl acetate–methanol) (Found: C, 73·7; H, 5·0. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8%).

The authors thank Mr. G. Milmine for help with preparative work.

THE UNIVERSITY, GLASGOW, W.2. [*Received, February 26th*, 1962.]

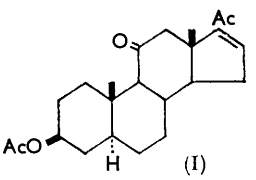
[4] Ried and Bodem, *Chem. Ber.*, 1956, **89**, 708.
[5] Fairbourne, *J.*, 1921, **119**, 1573.

638. *The Michael Reaction of 3β-Acetoxy-5α-pregn-16-ene-11,20-dione and Malonic Ester Derivatives.*

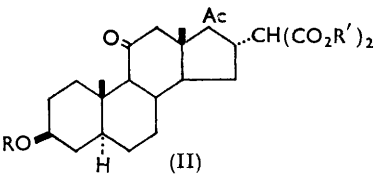
By Peter Bladon and Thomas Sleigh.

This Note describes extensions of previous work [1] on the reaction between steroid Δ^{16}-20-ketones and sodiomalonic esters (cf. Mazur and Cella [2]).

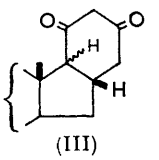
The reaction between 3β-acetoxy-5α-pregn-16-ene-11,20-dione (I) and sodiomalonic ester in the presence of an excess of ethyl malonate gave, after brief alkaline hydrolysis and acidification, the desired 3β-hydroxy-11,20-dioxo-5α-pregnan-16α-ylmalonic acid (IIa). Reaction with approximately equal molecular quantities of sodium and diethyl malonate followed by brief alkaline hydrolysis gave an amorphous product from which a small amount of poorly crystalline material of indefinite melting point was obtained. This has been formulated as (III) because the ultraviolet spectra in neutral and alkaline solution resemble the corresponding spectra of 5,5-dimethylcyclohexane-1,3-dione (dimedone). Further, as in the case of the corresponding compound obtained by the Michael reaction of 3β-acetoxypregna-5,16-dien-20-one and malonic ester,[1] the infrared spectrum had a strong band at 1590 cm.$^{-1}$, characteristic of the enol form of a β-diketone. If the hydrolysis step was omitted, the product was the ethyl ester (IIb) which was, however, not obtained crystalline.



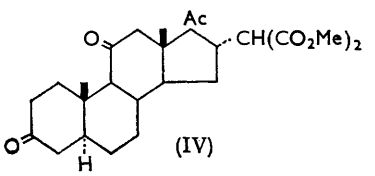
(I)



(II)

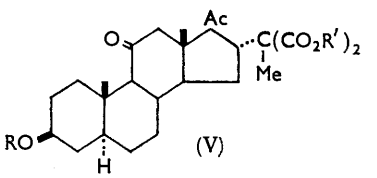


(III)



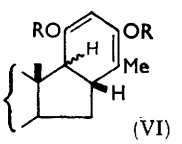
(IV)

(IIa: R = R′ = H)
(IIb: R = Ac or H, R′ = Et)
(IIc: R = H, R′ = Me)
(IId: R = Ac, R′ = Me)
(IIe: R = Bz, R′ = Me)



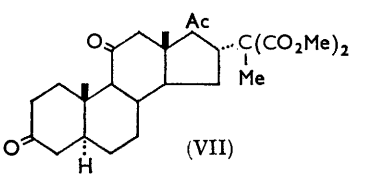
(V)

(Va: R = R′ = H)
(Vb: R = Ac or H; R′ = Et)
(Vc: R = H; R′ = Me)
(Vd: R = Ac; R′ = Me)
(Ve: R = Bz; R′ = Me)



(VI)

(VIa: R = H)
(VIb: R = Me)



(VII)

The methyl ester (IIc) was obtained by esterification of the acid (IIa) with diazomethane and chromatography of the product on deactivated alumina. If the Michael reaction was carried out with dimethyl sodiomalonate, thus avoiding the hydrolysis and

[1] Bladon, *J.*, 1958, 3723.
[2] Mazur and Cella, *Tetrahedron*, 1959, **7**, 130.

methylation steps, the product was pure methyl ester (IIc). Oxidation of the methyl ester with an excess of chromic acid–sulphuric acid in acetone gave dimethyl 3,11,20-trioxo-5α-pregnan-16α-ylmalonate (IV).

The reaction between 3β-acetoxy-5α-pregn-16-ene-11,20-dione and diethyl sodiomethylmalonate gave an impure acidic product after hydrolysis even when an excess of the malonic ester was present. The ultraviolet spectra in neutral and alkaline solution showed that this was probably a mixture of the desired acid (Va) and a cyclonorcholanetrione (VIa). Methylation and chromatography gave only a small quantity of a crystalline compound, melting over a wide range, which has been assigned the structure (VIb). The ultraviolet spectrum in neutral solution again resembles that of dimedone, but in this case there is very little bathochromic shift on the addition of alkali. Cyclisation to the cyclonorcholanetrione presumably takes place during the hydrolysis of the intermediate ester (Vb) since, if the hydrolysis step was omitted, the product was the oily ethyl ester (Vb). Furthermore, carrying out the reaction with dimethyl sodiomethylmalonate and chromatography of the product gave a crystalline ester (Vc). Oxidation of this with chromic acid–sulphuric acid in acetone gave dimethyl methyl-(3,11,20-trioxo-5α-pregnan-16α-yl)malonate (VII).

Experimental.—M. p.s were determined on a Kofler hot stage. Unless otherwise stated, optical rotations were determined for chloroform solutions at room temperature, ultraviolet spectra for ethanol solutions, and infrared spectra for potassium chloride discs.

3β-*Hydroxy*-11,20-*dioxo*-5α-*pregnan*-16α-*ylmalonic acid* (IIa). Sodium (200 mg., 8 mmoles) was dissolved in ethanol (25 ml.) and diethyl malonate (3·2 g., 20 mmoles) added, followed by 3β-acetoxy-5α-pregn-16-en-11,20-dione (744 mg., 2 mmoles). The mixture was refluxed for 3 hr. under anhydrous conditions; then a solution of potassium hydroxide (4 g.) in 50% v/v aqueous ethanol (20 ml.) was added and refluxing continued for 5 min. Water was added and the solution extracted with ether, to give a small neutral fraction (20 mg.). Acidification of the aqueous layer gave a white solid (660 mg.). Two recrystallisations of a sample (100 mg.) of the dried material from ethanol–water gave 3β-*hydroxy*-11,20-*dioxo*-5α-*pregnan*-16α-*ylmalonic acid* (IIa) as plates, m. p. 245—255° (decomp. begins at 220°), $[\alpha]_D$ +94·6° (*c* 0·24 in methanol) (Found: C, 66·0; H, 8·2. $C_{24}H_{34}O_7$ requires C, 66·3; H, 7·9%), $\nu_{max.}$ 1740, 1690, and 2900 (broad) cm.$^{-1}$.

If the reaction mixture was extracted with ether after the initial refluxing, there was isolated the corresponding ethyl ester (IIb) which was an oil (838 mg.) even after chromatography on deactivated alumina.

In another experiment on the same scale, but with only 1·6 g. (10 mmoles) of diethyl malonate, 640 mg. of crude acidic product were obtained. Two recrystallisations from ethanol–water gave a small, poorly crystalline sample of 3β-*hydroxy*-16α,24-*cyclo*-21-*norcholan*-11,20,23-*trione* (III), m. p. 210—320° (decomp.), $[\alpha]_D$ +76·1° (*c* 0·57 in pyridine) (Found: C, 74·2; H, 8·5. $C_{23}H_{32}O_4$ requires C, 74·2; H, 8·7%), $\lambda_{max.}$ 259 mμ (ε 15,000), $\lambda_{max.}$ (in NaOH) 284 mμ (ε 24,900), $\nu_{max.}$ 1695, 1590, 1030, and 2900 (broad) cm.$^{-1}$. Dimedone under similar conditions had $\lambda_{max.}$ 257 mμ (ε 16,600) and $\lambda_{max.}$ (in NaOH) 282 (ε 25,700).

Dimethyl 3β-*hydroxy*-11,20-*dioxo*-5α-*pregnan*-16α-*ylmalonate* (IIc). (*a*) 3β-Hydroxy-11,20-dioxo-5α-pregnan-15α-ylmalonic acid (2·66 g.) was suspended in a little methanol and treated with excess of ethereal diazomethane for 30 min. A few drops of acetic acid were then added. Removal of the solvents under reduced pressure gave a yellow oil (2·56 g.), which was chromatographed on deactivated alumina (100 g.). Benzene–ether (1 : 1 eluted a yellow oil, which crystallised from ether to give impure *dimethyl*-3β-*hydroxy*-11,20-*dioxo*-5α-*pregnan*-16α-*ylmalonate* (IIc) (1·39 g.), m. p. 150—160°. Two recrystallisations from methanol–isopropyl ether gave rosettes (624 mg.), m. p. 161—164°, $[\alpha]_D$ +90·2° (*c* 0·88) (Found: C, 67·6; H, 8·3. $C_{26}H_{38}O_7$ requires C, 67·5; H, 8·3%), $\nu_{max.}$ 3445, 1749, and 1695 cm.$^{-1}$.

(*b*) Sodium (100 mg., 4 mmoles) was dissolved in methanol (15 ml.), and dimethyl malonate (1·32 g., 10 mmoles) was added, followed by 3β-acetoxy-11,20-dioxo-5α-pregn-16-ene (372 mg., 1 mmole). The solution was refluxed for 3 hr. under anhydrous conditions, then cooled, water was added, and the product extracted twice with chloroform. The chloroform extracts were washed with water, dried (Na_2SO_4), and evaporated, to give colourless material (409 mg.)

which was recrystallised from methanol–isopropyl ether, affording dimethyl 3β-hydroxy-11,20-dioxo-5α-pregnan-16α-ylmalonate as rosettes (265 mg.), m. p. 157—162°, $[\alpha]_D$ +87·4° (*c* 0·78), $\nu_{max.}$ 3520, 1750, and 1698 cm.$^{-1}$, identical with material prepared by method (*a*).

Acetylation of this ester with acetic anhydride and pyridine at room temperature gave the 3β-*acetate* (IId), m. p. 133—136·5° (from methanol), $[\alpha]_D$ +70·9° (*c* 0·80) (Found: C, 67·0; H, 8·1. $C_{28}H_{40}O_8$ requires C, 66·6; H, 8·0%), $\nu_{max.}$ 1762, 1740, and 1710 cm.$^{-1}$.

The 3β-*benzoate* (IIe), prepared with benzoyl chloride and pyridine, formed feathery needles, m. p. 187—189°, $[\alpha]_D$ +71·8° (*c* 0·65), from methanol (Found: C, 69·9; H, 7·45. $C_{33}H_{42}O_8$ requires C, 69·9; H, 7·5%), and had $\nu_{max.}$ 1755, 1740, 1710, and 709 cm.$^{-1}$.

Dimethyl 3,11,20-*trioxo*-5α-*pregnan*-16α-*ylmalonate* (IV). Dimethyl 3β-hydroxy-11,20-dioxo-5α-pregnan-16α-ylmalonate (207 mg.) in acetone (10 ml.) was stirred at room temperature and chromic acid solution added (1 ml. of a solution of 26·7 g. of chromium trioxide and 23 ml. of concentrated sulphuric acid made up to 100 ml. with water). The excess of oxidant was destroyed after 5 min. by the addition of dilute hydrochloric acid and sodium sulphite. The product was extracted twice with ether, and the combined extracts were washed with sodium hydrogen carbonate solution and water, dried (Na_2SO_4), and evaporated to dryness to give the trioxo-*ester* (IV) as platelets or needles (180 mg.), m. p. 190—193°, $[\alpha]_D$ +103° (*c* 0·78) (Found: C, 68·1; H, 8·0. $C_{26}H_{36}O_7$ requires C, 67·8; H, 7·9%), $\nu_{max.}$ 1723 and 1702 cm.$^{-1}$.

Reaction of diethyl methylmalonate and 3β-*acetoxy*-5α-*pregn*-16-*ene*-11,20-*dione*. Sodium (100 mg., 4 mmoles) was dissolved in ethanol (15 ml.), and diethyl methylmalonate (1·74 g., 10 mmoles) added, followed by 3β-acetoxy-5α-pregn-16-ene-11,20-dione (372 mg., 1 mmole). The mixture was refluxed for 4 hr., with the exclusion of moisture; then potassium hydroxide (2 g.) in 50% v/v aqueous ethanol (10 ml.) was added and refluxing continued for 5 min., water was added, and the solution extracted with ether to give a small neutral fraction (18 mg.). Acidification of the aqueous layer gave a slightly yellow solid (318 mg.), m. p. 175—240° (decomp.), $\lambda_{max.}$ 258 mμ (ε 8800), $\lambda_{max.}$ (in NaOH) 288 mμ (ε 13,800), $\nu_{max.}$ 1710, 1651, 1592, and 2900 (broad) cm.$^{-1}$. Recrystallisation from methanol–isopropyl ether gave crystals (152 mg.), m. p. 182—264° (decomp.).

All the material (recrystallised and from the mother-liquor) was esterified with diazomethane, and the product passed through deactivated alumina (10 g.) to give a gum (191 mg.) which, on crystallisation from ethyl acetate, gave 3β-*hydroxy*-20,23-*dimethoxy*-24-*methyl*-16α,24-*cyclo*-21-*norcholan*-20,23-*dien*-11-*one* (VIb) as needles (19 mg.), m. p. 265—293° (decomp.), $\lambda_{max.}$ 248 mμ (ε 13,400), $\lambda_{max.}$ (in NaOH) 254 mμ (ε 14,600), $\nu_{max.}$ 1720, 1658, and 1605 cm.$^{-1}$. Recrystallisation from chloroform–ethyl acetate gave needles (4 mg.), m. p. 278—294° (decomp.), $[\alpha]_D$ +53·4° (*c* 0·15) (Found: C, 73·4; H, 9·4. $C_{28}H_{38}O_4$ requires C, 73·5; H, 9·2%). Mother-liquors yielded a second crop of crystals (6 mg.).

Ether-extraction of the reaction mixture after the initial refluxing gave the ethyl ester (Vb) that was as an oil (218 mg.) even after chromatography on deactivated alumina (8 g.).

Dimethyl (3β-*hydroxy*-11,20-*dioxo*-5α-*pregnan*-16α-*yl*) (*methyl*)*malonate* (Vc). The reaction was carried out as above but with dimethyl methylmalonate (1·46 g., 10 mmoles). Ether-extraction after the initial refluxing gave yellow crystals (267 mg.), which, recrystallised twice from methanol–isopropyl ether, gave an impure product as rosettes (82 mg.), m. p. 173—175°, recrystallising and melting at 186—204°; they had $[\alpha]_D$ +88·7° (*c* 0·76).

Impure methyl ester (500 mg.) was chromatographed in benzene and on deactivated alumina (20 g.). 4 : 1 Benzene–ether eluted colourless crystals which after two recrystallisations from methanol–isopropyl ether gave the pure *ester* (Vc) as prisms (110 mg.), m. p. 224—227° (decomp.), $[\alpha]_D$ +82·3° (*c* 0·8) (Found: C, 67·8; H, 8·3. $C_{27}H_{40}O_7$ requires C, 68·0; H, 8·5%), $\nu_{max.}$ 3581, 1736, and 1700 cm.$^{-1}$.

This ester with acetic anhydride and pyridine at room temperature gave its *acetate* (Vd), m. p. 180—188° (decomp.) (from hexane). Recrystallisation from dichloromethane–hexane gave plates, m. p. 187—189° (decomp.), $[\alpha]_D$ +69·0° (*c* 1·1) (Found: C, 67·2; H, 8·2. $C_{29}H_{42}O_8$ requires C, 67·2; H, 8·2%), $\nu_{max.}$ 1735, 1710, and 1241 (broad) cm.$^{-1}$. The *benzoate* (Ve), prepared with benzoyl chloride and pyridine, formed needles (from dichloromethane–methanol), m. p. 236—238° (decomp.), $[\alpha]_D$ +64·8° (*c* 0·8) (Found: C, 70·3; H, 7·5. $C_{34}H_{44}O_8$ requires C, 70·3;H, 7·6%), $\nu_{max.}$ 1725, 1269 (broad), and 710 cm.$^{-1}$.

Dimethyl methyl-(3,11,20-*trioxo*-5α-*pregnan*-16α-*yl*)*malonate* (VII). The ester (Vc) (100 mg.) was oxidised with chromic acid–sulphuric acid in acetone, as described above. Working up as before gave colourless crystals (85 mg.), m. p. 229—240°. Two recrystallisations from ether–

methanol gave the *keto-ester* (VII) as plates (30 mg.), m. p. 238—241° (decomp.), $[\alpha]_D$ +100·5° (*c* 0·9) (Found: C, 67·3; H, 8·25. $C_{27}H_{38}O_7$,0·5CH_3·OH requires C, 67·3; H, 8·2%), $\nu_{max.}$ 1729 and 1695 cm.$^{-1}$.

The authors thank Dr. C. L. Hewett of Organon Laboratories Ltd. for a generous gift of 3β-acetoxy-5α-pregn-16-ene-11,20-dione, and Mr. Wm. McCorkindale for microanalyses. One of the authors (T. S.) thanks the Cross Trust for a maintenance grant.

THE ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW, C.1. [*Received, February 26th*, 1962.]

---

639. 1,3,5-*Triazines. Part II.*[1] *The Reaction of Acid Chlorides with Triphenyl Phosphite.*

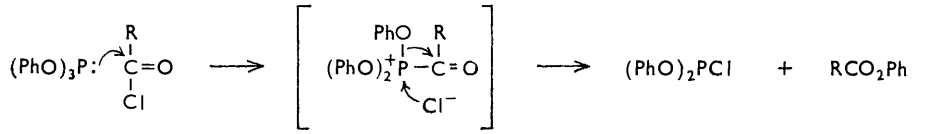
By W. HEWERTSON, R. A. SHAW, and B. C. SMITH.

CYANURIC CHLORIDE reacts with trialkyl phosphites, between room temperature and 80°, to form alkyl chlorides and dialkylphosphonato-derivatives of 1,3,5-triazine.[2,3] Reaction does not occur between cyanuric chloride and triphenyl phosphite in boiling benzene, but reaction in boiling decalin to give diphenyl phosphorochloridite and triphenyl cyanurate is reported here.

$$N_3C_3Cl_3 + 3(PhO)_3P \longrightarrow 3(PhO)_2PCl + N_3C_3(OPh)_3$$

This is in contrast to the reported [2] Arbuzov-type reaction. Although cyanuric chloride behaves as an acid chloride [4] and acyl chlorides undergo a normal Arbuzov reaction with trialkyl phosphites,[5] reaction with triphenyl phosphite is now shown to give diphenyl phosphorochloridite and the corresponding phenyl esters. Yields of diphenyl phosphorochloridite, which disproportionates,[6,7] are lower than yields of esters, but reaction of propionyl chloride provides a convenient method of preparation of the chloridite.

Quasi-phosphonium intermediates have not been observed, but it is supposed that the first stage of the reaction involves nucleophilic attack by phosphorus to form the expected Arbuzov intermediate.



Intermediates in Arbuzov reactions of alkyl halides with trialkyl phosphites [8] have not been characterised, whereas alkyl halides react with triphenyl phosphite to give stable quasi-phosphonium compounds [9] which are decomposed by water [9] or alcohols [10] to give diphenyl alkylphosphonates, phenol, and hydrogen halides or alkyl halides.

Triphenyl phosphite undergoes exchange reactions with phosphorus trichloride,[6] boron halides,[11] and halogens,[12] to give diphenyl phosphorohalidites; whilst oxidation to

[1] Part I, Golesworthy, Shaw, and Smith, *J.*, 1962, 1507.
[2] Coover, U.S.P. 2,685,581 (1954).
[3] Morrison, *J. Org. Chem.*, 1957, **22**, 444.
[4] Thurston, Schaefer, Dudley, and Holm-Hansen, *J. Amer. Chem. Soc.*, 1951, **73**, 2992.
[5] Kabachnik and Rossiskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1945, 364 (*Chem. Abs.*, 1946, **40**, 4688); Ackerman, Jordan, Eddy, and Swern, *J. Amer. Chem. Soc.*, 1956, **78**, 4444.
[6] Conant, Wallingford, and Gandheker, *J. Amer. Chem. Soc.*, 1923, **45**, 726.
[7] Forsman and Lipkin, *J. Amer. Chem. Soc.*, 1953, **75**, 3145.
[8] B. A. Arbuzov and Fuzhenkova, *Proc. Acad. Sci.* (*U.S.S.R.*), 1957, **113**, 381.
[9] Michaelis and Kaehne, *Ber.*, 1898, **31**, 1048.
[10] Landauer and Rydon, *J.*, 1953, 2224; A. E. Arbuzov and Nesterov, *Bull. Acad. Sci.* (*U.S.S.R.*), 1954, 361.
[11] Frazer, Gerrard, and Patel, *Chem. and Ind.*, 1959, 90, 728.
[12] Rydon and Tonge, *J.*, 1956, 3043; Rydon, *Chem. Soc. Special Publ.* No. 8, 1957, p. 61.

quinquevalent phosphorus occurs with *N*-chlorodiethylamine,[13] ethyl hypochlorite,[14] and with acid chlorides of sulphur [15] including benzenesulphonyl chloride.

Experimental.—Cyanuric chloride was recrystallised from carbon tetrachloride and dried *in vacuo* (4 hr.). Other acid chlorides and triphenyl phosphite were distilled before use. Reactions were carried out in an atmosphere of dry nitrogen. Reaction conditions and yields are recorded in the Table.

	Acid halide		$P(OPh)_3$		Bath	Time	$(PhO)_2PCl$			Ester	
	(g.)	(mole)	(g.)	(mole)	temp.	(hr.)	(g.)	(%)		(g.)	(%)
$N_3C_3Cl_3$	2·3	0·0125	11·7	0·0375	260° [a]	20	5·7	60	$N_3C_3(OPh)_3$	4·0	90
	4·6	0·025	23·3	0·075	100 [b]	20	nil			nil	
MeCO·Cl	9·8	0·125	31·0	0·10	160—170° [c]	48	15·7	62	$MeCO_2Ph$	9·8	72
	9·8	0·125	31·0	0·10	80	48	nil			nil	
EtCO·Cl	92·5	1·00	310·0	1·00	100—195	8	157	62	$EtCO_2Ph$	127·3	85
Pr^nCO·Cl	10·7	0·10	31·0	0·10	100—210	20	12·1	48	Pr^nCO_2Ph	12·5	76
	10·7	0·10	31·0	0·10	180° [c]	5	13·1	52		13·0	79
PhCO·Cl	15·0	0·10	31·0	0·10	200—255	40	10·2	40	$PhCO_2Ph$	17·6	89
PCl_3	13·7	0·10	62·0	0·20	110° [c]	18	32·6	44			
PCl_3 [d]	13·7	0·10	76·0	0·25	150° [c]	8	38	50 [e]			

[a] Boiling decalin (5 ml.). [b] Boiling benzene (20 ml.). [c] Sealed tube. [d] Ref. 6. [e] Calc. from wt. of phosphorus trichloride.

Cyanuric chloride. No reaction was observed in boiling benzene: cyanuric chloride (4·4 g., 95%) and triphenyl phosphite (21·2 g., 91%) were recovered. Cyanuric chloride reacts with triphenyl phosphite in boiling decalin. The long white needles formed on cooling were washed with ether, and two recrystallisations from benzene gave triphenyl cyanurate, m. p. and mixed m. p. 235—237° (Found: C, 70·7; H, 4·5; N, 11·7. Calc. for $C_{21}H_{15}N_3O_3$: C, 70·6; H, 4·2; N, 11·8%). Fractional distillation of the ether extract gave diphenyl phosphorochloridite, b. p. 158—168°/2 mm., n_D^{25} 1·5776 (Found: Cl, 13·8. Calc. for $C_{12}H_{10}ClO_2P$: Cl, 14·0%). This was characterised further as diphenyl phosphorochloridothionate,[16] m. p. and mixed m. p. 64—66°, b. p. 124—127°/0·01 mm.

Acyl chlorides. Butyryl chloride and triphenyl phosphite were heated in an oil-bath at 120°, and boiling under reflux was maintained by raising the temperature gradually to 210°. Distillation gave: (*a*) phenyl butyrate containing phenyl phosphorodichloridite (17·6 g.), b. p. 52—57°/0·7 mm.; (*b*) diphenyl phosphorochloridite, b. p. 110—120°/0·6—0·5 mm.; and (*c*) crude triphenyl phosphite (5·1 g.). Fraction (*a*) in ether was washed with saturated sodium hydrogen carbonate solution and water, and dried ($CaCl_2$). Distillation gave phenyl butyrate, b. p. 115—117°/17 mm., 226—228°/760 mm., n_D^{20} 1·4924 (lit.,[17] b. p. 227·5°/763 mm., $n_D^{20\cdot5}$ 1·4918).

Similar reactions of propionyl chloride and benzoyl chloride gave diphenyl phosphorochloridite and, respectively, phenyl propionate, b. p. 209—211°, n_D^{20} 1·4986 (lit.,[17] b. p. 211·7°/769 mm., $n_D^{20\cdot5}$ 1·4977), and phenyl benzoate, m. p. and mixed m. p. 70—71°.

Acetyl chloride and triphenyl phosphite were recovered almost quantitatively after attempted reaction at atmospheric pressure. Reaction in a sealed tube gave diphenyl phosphorochloridite and phenyl acetate, b. p. 194—196°, n_D^{20} 1·5028 (lit.,[17] b. p. 195·6°/769 mm., n_D^{20} 1·5029).

Phosphorus trichloride. Reaction of phosphorus trichloride with triphenyl phosphite in a sealed tube gave diphenyl phosphorochloridite and phenyl phosphorodichloridite (11·74 g.), b. p. 60—61°/1·5 mm., n_D^{25} 1·5608.

The authors thank Cyanamid of Great Britain Limited for a gift of cyanuric chloride. This research was supported by the Wright Air Development Centre of the Research and Development Command, United States Air Force, through its European Office.

Department of Chemistry, Birkbeck College (University of London),
Malet Street, London, W.C.1. [*Received, February 26th*, 1962.]

[13] Petrov and Sokolsky, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 3761.
[14] Petrov and Sokolsky, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 3759.
[15] Poshkus, Herweh, and Hass, *J. Amer. Chem. Soc.*, 1957, **79**, 4245; 1958, **80**, 5022.
[16] Gottleib, *J. Amer. Chem. Soc.*, 1932, **54**, 748.
[17] Angus, Llewelyn, and Stott, *Trans. Faraday Soc.*, 1954, **50**, 1311.

640. *Olefin Complexes of the Type* [Pt(olefin)(PPh_3)$_2$].

By J. Chatt, B. L. Shaw, and A. A. Williams.

In 1957 the discovery of a stable series of acetylene complexes [Pt(acetylene)(PPh_3)$_2$] and a corresponding series of unstable olefin complexes was reported from these laboratories.[1] We now believe that the unsaturated hydrocarbon in these complexes takes the place of two anionic ligands such as chloride ion, and that the derivatives are planar platinous complexes.[2] Here we record the preparation and properties of the olefin complexes.

The olefin complexes are formed from *cis*-dichlorobistriphenylphosphineplatinum in ethyl alcohol containing hydrazine hydrate and the olefin at 60°; nitrogen is evolved and the complex crystallises. In this way complexes were prepared from *trans*-stilbene, *trans*-4,4-dinitrostilbene, and acenaphthylene. The complexes were usually obtained pure from the preparation and deteriorated on attempted recrystallisation. All other olefins which were tried failed to yield stable complexes. These were ethylene, butadiene, hex-1-ene, cyclohexene, allyl alcohol, styrene, and tetraphenylethylene.

In the acetylenic series of complexes we showed that the acetylenic substances displaced one another from their complexes, indicating ready equilibration of the type:

$$[Pt(\text{acetylene-A})(PPh_3)_2] + \text{Acetylene-B} \rightleftharpoons [Pt(\text{acetylene-B})(PPh_3)_2] + \text{acetylene-A}$$

This displacement series showed that the stabilities of the complexes increased in the order of acetylene: C_2H_2 < alkylacetylenes < arylacetylenes < nitroarylacetylenes. The stabilities of the very incomplete series of olefin complexes which we are now describing appear to fit this pattern, but all are less stable than the acetylene complex. Even dinitrostilbene was displaced from its complex by gaseous acetylene.

A number of displacements are described in the Experimental section.

Experimental.—Preparation of olefinbis(triphenylphosphine)platinum complexes (general method). *cis*-Dichlorobis(triphenylphosphine)platinum (0·5 g.) was suspended in ethyl alcohol (10 ml.) and treated with hydrazine hydrate (0·5 ml.). A colourless solution was formed which was filtered, treated with the olefin, and warmed to 60°; nitrogen was evolved and the complex crystallised. After cooling, the complex was collected, washed with ethyl alcohol and then water (to remove any hydrazine hydrochloride), and dried. Attempted recrystallisation of the complexes usually resulted in some decomposition, probably *via* dissociation of the complex. This decomposition precluded the determination of molecular weights and the complexes are assumed to be monomeric by analogy with the corresponding and much more stable acetylene complexes obtained in the same way. The analyses show that the preparations of the three compounds listed below are remarkably clean, only the 4,4′-dinitrostilbene complex showing slight possibility of impurity.

In this way were prepared the trans-*stilbene complex* (0·39 g.) from the olefin (0·15 g.) as colourless needles, m. p. 131—141° (decomp.) (Found: C, 66·65; H, 4·75. $C_{50}H_{42}P_2Pt$ requires C, 66·75; H, 4·75%); the trans-4,4′-*dinitrostilbene complex* (0·42 g.) from *trans*-4,4′-dinitrostilbene (0·14 g.), as red plates, m. p. 205—210° (decomp.) (Found: C, 60·2, 61·15; H, 3·95, 4·05; N, 3·2. $C_{50}H_{40}N_2O_4P_2Pt$ requires C, 60·65; H, 4·05; N, 2·85%; and the *acenaphthylene complex* (0·51 g.), from acenaphthylene (0·5 g.), as yellow plates (0·51 g.), m. p. 160—164° (decomp.) (Found: C, 66·0; H, 4·5. $C_{48}H_{38}P_2Pt$ requires C, 66·1; H, 4·4%).

Replacement of acenaphthylene by phenylacetylene. The acenaphthylene complex (0·15 g.) in benzene (2 ml.) and ethyl alcohol (10 ml.) was warmed with an excess of phenylacetylene (0·4 ml.). The colourless phenylacetylene complex [1] separated and was identified by its infrared absorption spectrum. The filtrate was evaporated to dryness, and the residue dissolved in light petroleum (b. p. 40—60°) and chromatographed on alumina (Spence's grade H). Elution

[1] Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, 208, and forthcoming publication.
[2] Chatt, "Chimica Inorganica, IV° Corso, Estivo di Chimica," Varenna 1959, Publ. Accad. Naz. Lincei, Rome, 1961, p. 155.

with light petroleum (b. p. 40—60°) gave acenaphthylene which sublimed at 60°/0·01 mm. as plates (18 mg.), m. p. 93—94°.

Replacement of acenaphthylene by tolan. The acenaphthylene complex (0·144 g.) in benzene (5 ml.) was treated with tolan (diphenylacetylene) (17·8 mg.). The solution was boiled for 2 min., cooled, and evaporated to dryness, and the residue was extracted with hot alcohol. The alcohol-insoluble portion was substantially pure tolanbis(triphenylphosphine)platinum. The alcohol extract was evaporated to dryness and the residue extracted with light petroleum (b. p. 40—60°). This extract on evaporation gave somewhat impure acenaphthylene, m. p. 82—88°.

Replacement of 4,4′-dinitrostilbene by acetylene. The 4,4′-dinitrostilbene complex (150 mg.) in ethyl alcohol (10 ml.) and benzene (10 ml.) was shaken in an atmosphere of acetylene at 25°. The red solution lightened rapidly and orange needles of 4,4′-dinitrostilbene (35 mg.), m. p. 297—298°, separated. The filtrate, on evaporation, yielded the acetylene complex [1] as a cream-coloured powder (identified by its infrared spectrum).

Replacement of trans-*stilbene by 4,4′-dinitrostilbene.* The stilbene complex (145 mg.) in benzene (1 ml.) and ethyl alcohol (10 ml.) was treated with 4,4′-dinitrostilbene (50 mg.). On warming, the red dinitrostilbene complex (72 mg.) separated. The mother-liquors were evaporated to dryness and dissolved in hot light petroleum (b. p. 80—100°). On cooling, crystals separated. These were collected and sublimed, giving *trans*-stilbene, m. p. 128°.

Replacement of 4,4′-dinitrostilbene by phenylacetylene. The dinitrostilbene complex (150 mg.) in benzene (5 ml.) and ethyl alcohol (5 ml.) was treated with phenylacetylene (0·4 ml.). The red colour of the solution changed to yellow, and a yellow solid separated. This was warmed with benzene, leaving a residue of 4,4′-dinitrostilbene (42 mg.; m. p. 292—294°). The benzene solution was evaporated to dryness and treated with ethyl alcohol, giving the phenylacetylene complex (50 mg.) (identified by its infrared spectrum).

Replacement of 4,4′-dinitrostilbene by tolan. The 4,4′-dinitrostilbene complex (0·20 g.) in benzene (10 ml.) was treated with tolan (0·050 g.). The solution lightened in colour and 4,4′-dinitrostilbene (0·04 g.) separated as pale yellow rhombs, m. p. 306—307°.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, HEAVY ORGANIC CHEMICALS DIVISION,
AKERS RESEARCH LABORATORIES, THE FRYTHE,
WELWYN, HERTS.

[*Received, February 27th,* 1962.]

---

641. *The Mass Spectra of the Methylphosphines.*

By M. HALMANN.

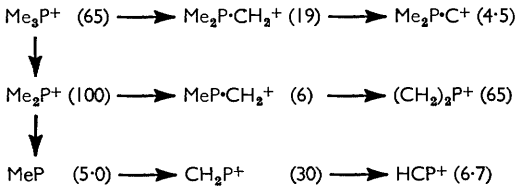
MASS spectra of triaryl and alkyl phosphates,[1] trialkyl phosphites, and dialkyl phosphonates [2] have been recorded and related to the radiolytic decomposition in the liquid phase.[3] No mass-spectrometric measurements of alkylphosphines have been reported. The annexed Table gives results obtained by us at an ionising potential of 62 ev. Those for phosphine are similar to those reported at an ionising potential of 100 ev,[4] but differ from those observed at 70 ev.[5a]

Considerable breakdown of the parent ion occurs with all these phosphines. However, the abundance of the parent ion (relative to the most abundant peak in each spectrum) is quite large for all the phosphines except methylphosphine.

Compound bombarded	Me_3P	Me_2PH	$MePH_2$	PH_3
Relative abundance of parent ion	65	61	0·1	89
Most abundant peak (100% intensity)	Me_2P^+	MeP^+	CH_2P^+	PH^+

[1] Quayle, "The Mass Spectra of Some Organic Phosphates," in "Advances in Mass Spectrometry," ed. Waldron, Pergamon Press, London, 1959, p. 365.
[2] Harless, *Analyt. Chem.*, 1961, **33**, 1387.
[3] Wilkinson and Williams, *J.*, 1961, 4098.
[4] Neuert and Clasen, *Z. Naturforsch.*, 1952, **7a**, 410; cf. Stevenson, *Radiation Res.*, 1959, **10**, 610.
[5] Mass Spectral Data, American Petroleum Institute, Res. Proj. 44, (*a*) No. 1219, (*b*) No. 1127 (1955).

The breakdown of the parent ion of trimethylphosphine may be described by the following tentative scheme, in which the relative abundances of the peaks are written alongside the formulæ (only one of the possible isomeric structures is written):



Several other schemes are possible, and the time interval available for the complete decomposition must be of the order of several bond vibrations. All reactions occur within the ion source, because no diffuse peaks (due to metastable states decomposing in the analyser tube) were observed. The remarkably intense peak written as $(CH_2)_2P^+$ (m/e = 59) may have the cyclic structure $H_2C\overset{P^+}{\diagup\!\!\diagdown}CH_2$; it may have the linear structure $CH_2{=}\overset{+}{P}{=}CH_2$, or a non-symmetric structure $CH_3{-}\overset{+}{P}{\equiv}CH$. In the analogous mass spectrum of trimethylamine, the peak at $m/e = 42$ is one of the most abundant;[5b] it is probably due to $(CH_2)_2N^+$ and may be ethyleneimine (less one hydrogen atom) or a linear isomer.

The ion HCP^+($m/e = 44$) has been described[6] in the mass spectrum of methinophosphide, H–C≡P. It was observed in fairly high abundance in the mass spectra of di- and tri-methylphosphine, but only in very low abundance in the mass spectrum of methylphosphine.

In addition to the mass spectra listed, which were made at an ionising potential of 62 ev, some measurements were made also at 45 and 25 ev. The only effect observed was on the mass spectrum of phosphine, in which the doubly charged ions disappeared, as

TABLE 1.

Relative intensities in the mass spectra of phosphine and the methylphosphines (at 62 ev).

m/e	Me_3P	Me_2PH	$MePH_2$	PH_3	Tentative assignment	m/e	Me_3P	Me_2PH	$MePH_2$	Tentative assignment
2		1·65	0·6	1·77	H_2^+	43	0·44	2·18	1·37	CP^+
14			2·25			44	6·74	14·05	0·63	HCP^+
15		1·76	27·5			45	29·6	43·8	*100*	H_2CP^+
15·5				0·32	P^{++}	46	5·65	*100*	48·4	H_3CP^+
16	0·66		1·25	0·22	PH^{++}	47	10·3	17·25	1·32	H_3CPH^+
16·5				0·127	PH_2^{++}	48			(p) 0·10	$H_3CPH_2^+$
17			3·20	0·27	PH_3^{++}	55		1·50		
18	0·67	2·29	12·7			56		4·25		
27	4·5	2·95			$C_2H_3^+$	57	4·59	14·62		$(HCPCH)^+$
28	3·50	3·20	0·87		$C_2H_4^+$	58	7·35	5·50		$(HCPCH_2)^+$
29	3·53	1·43	35·9		$C_2H_5^+$	59	65·3	22·9		$(H_2C)_2P^+$
30			1·17		$C_2H_6^+$	60	6·35	1·33		
31	0·73	1·82	3·02	18·7	P^+	61	*100*	14·05		$(CH_3)_2P^+$
32	0·76	3·88		*100*	PH^+	62	3·53	(p) 60·6		$(CH_3)_2PH^+$
33	1·1	3·64		26·2	PH_2^+	73	4·5			$(CH_3)_2PC^+$
34		8·13		(p) 89·4	PH_3^+	74				
35	0·6					75	19·1			$(CH_3)_2PCH_2^+$
41	7·86	1·38			$C_3H_5^+$	76	(p) 65·3			$(CH_3)_3P^+$

shown in Table 2. The singly charged ions such as PH^+ decreased in absolute abundance only by about 26% during the change from 62 to 25 ev. The doubly charged bare phosphorus atom P^{++} (m/e = 15·5) disappeared between 62 and 45 ev; the ions PH^{++}, PH_2^{++}, and PH_3^{++} disappeared between 45 and 25 ev.

[6] Gier, *J. Amer. Chem. Soc.*, 1961, **83**, 1769.

TABLE 2.

Relative abundance of doubly charged ions from phosphine at several ionising potentials.

m/e	62 ev	45 ev	25 ev	Assignments
15·5	0·32	0·013	0·01	P^{++}
16	0·22	0·10	0·015	PH^{++}
16·5	0·125	0·089	0·01	PH_2^{++}
17	0·27	0·23	0·01	PH_3^{++}
32	100·00	100·00	100·00	PH^{+}

The mass spectra of the methylphosphines should be useful for their identification, in addition to infrared absorption spectroscopy and gas–liquid chromatography.[7] Thus tri- and di-methylphosphine may be recognised by the large parent peaks (*m/e* = 76 and 62), which are about 63% in abundance of the base peaks. Methylphosphine has only a very small parent peak (*m/e* = 48) but very highly abundant peaks at masses of two and three hydrogen atoms less than the parent peak. Phosphine is recognised by a large parent peak at mass 34, which is 88% in abundance of the base peak at mass 32.

The appreciable decomposition of trimethylphosphine under electron bombardment in the ion source of a mass spectrometer is in contrast to its relative stability to radiolysis at higher gas pressure. Thus irradiation of trimethylphosphine at 85 mm. with 5×10^6 rad from a ^{60}Co-γ-source did not produce detectable amounts of decomposition products.[7b] While the yields in the two experiments cannot be compared directly, the results resemble those found in the radiolysis of trialkyl phosphates.[3] At the long mean free path in the mass spectrometer ion-source, the primary ions formed undergo considerable decomposition before deactivation. During radiolysis at higher pressures energy transfer by collision is predominant, and no extensive bond-breakage is observed.

Experimental.—Phosphine and the methylphosphines were prepared and purified, as described,[7] by distillation in a vacuum-system. Samples of a few mm. pressure were stored in sealed tubes with break-seals, and were opened at 10^{-4} mm. in the gas-inlet system of the Consolidated Engineering Corp. model 21-401 mass-spectrometer.

The temperature of the ion-source was 250°. The accelerating potential in the analyser was 210 v. The magnet positions were calibrated for *m/e* values by the mass spectra of samples of oxygen and krypton. Mass spectra presented in Table 1 have been corrected for background; reproducibility of ion currents was ±3%.

The author is indebted to Dr. F. S. Klein for helpful criticism, to Miss L. Kugel for the samples of methyl- and dimethyl-phosphine, and to Mrs. V. Fischhof for the mass-spectrometric measurements.

THE ISOTOPE DEPARTMENT, THE WEIZMANN INSTITUTE OF SCIENCE,
REHOVOTH, ISRAEL. [*Received, January 24th*, 1962.]

[7] (*a*) Halmann, *Spectrochim. Acta*, 1960, **16**, 407; (*b*) Proc. Sympos. on the Chem. Effects of Nuclear Transformations, Prague, Oct. 1961, p. 200.

---

642. *The Reaction of Nitric Oxide with the Methylphosphines.*

By M. HALMANN and L. KUGEL.

THE liquid-phase reaction of nitric oxide with triethyl phosphite has been stated[1] to yield triethyl phosphate and nitrous oxide. An analogous reaction has now been found to occur with trimethylphosphine, which is very rapidly oxidised by nitric oxide to yield trimethylphosphine oxide and nitrous oxide: $2NO + Me_3P \longrightarrow N_2O + Me_3PO$. The reaction can be carried out either (*a*) by mixing the vapours, a particulate cloud being formed instantaneously, or (*b*) by allowing a mixture at −180° to warm to room

[1] Kuhn, Doali, and Wellman, *J. Amer. Chem. Soc.*, 1960, **82**, 4792.

temperature. Method (*b*) is a convenient rapid procedure for preparing anhydrous trimethylphosphine oxide, which is usually made by prolonged drying of the hydrate.[2] It is unknown whether the reaction (*a*) occurs in the gas phase or on the walls of the container. The electron-pair acceptor properties of nitric oxide have been suggested as responsible for its reaction with alkylamines;[3] in that case stable addition compounds were obtained and formation of nitrous oxide was not reported.

Nitric oxide also oxidised dimethylphosphine: $4NO + Me_2PH \longrightarrow 2N_2O + Me_2PO_2H$. This reaction was slower than that with trimethylphosphine. Only after about 30 min. did a gaseous mixture of nitric oxide (8·4 cm. Hg) and dimethylphosphine (17·2 cm. Hg) deposit crystals (identified as dimethylphosphinic acid).

Nitric oxide did not react with methylphosphine or phosphine in the gas phase, as shown by the invariance of pressure and by gas chromatography. However, when a mixture of nitric oxide and phosphine was introduced into a mass-spectrometer, a large proportion of the nitric oxide was reduced to nitrous oxide; apparently reaction occurred under the electron bombardment in the ion source, but no appreciable peak at mass 50 due to the hypothetical[4] " phosphine oxide " OPH_3 was observed and the relative intensities of ions PH^+, PH_2^+, PH_3^+, were as found in the mass spectrum of pure phosphine.[5]

Experimental.—Phosphine, methyl-, dimethyl-, and trimethyl-phosphine were prepared and purified as described.[6]

Trimethylphosphine (0·0083 mmole) was condensed at −180° into a tube connected to a vacuum system at 10^{-4} mm. Nitric oxide (0·0166 mmole) was added to it. The tube was brought to room temperature while connected to a mercury manometer. The pressure developed was half that of the initial nitric oxide. In the tube, a white solid remained, of m. p. 140—141° (in a sealed tube) (as recorded for trimethylphosphine oxide [2]).

Dimethylphosphine similarly reacted with nitric oxide. The crystals were identified as dimethylphosphinic acid by paper chromatography[7] (R_F 0·57) and by proton magnetic resonance.[8]

Phosphine and nitric oxide (1 : 2 by vol.) were introduced into a Consolidated Engineering Corp. model 21—401 mass spectrometer (ionising potential of 62 ev). The largest peaks were (relative intensities in parentheses) at the *m/e* values: 30, mainly NO (100); 32 (780); 33 (201); 44, mainly N_2O (784). In the mass-spectrum of NO alone, the major peaks were at 30 (100), 43 (4·3), 44 (0·2). Thus, in the presence of phosphine, most of the nitric oxide was converted into nitrous oxide.

Gas chromatography was carried out at 50° through a column (2·4 m. long; 4 mm. internal diameter) of silicone oil (Dow Corning 702; 25% by wt. on 35—50 mesh fire-brick), and with a helium flow of 30 ml. $min.^{-1}$. Peak maxima were: NO 0·98; N_2O 1·13; PH_3 1·30; $MePH_2$ 2·58; Me_2PH 6·66; Me_3P 10·5 min.

The authors are indebted to Professor R. Schaeffer for discussions. This investigation was supported in part by a grant by Indian Head Mills, Inc., New York, N.Y.

Isotope Department, The Weizmann Institute of Science,
Rehovoth, Israel. [*Received, March 5th*, 1962.]

[2] Goubeau and Berger, *Z. anorg. Chem.*, 1960, **304**, 152.
[3] Drago, Ragsdale, and Eyman, *J. Amer. Chem. Soc.*, 1961, **83**, 4337, giving previous references.
[4] Wiberg and Müller-Schiedmayer, *Z. anorg. Chem.*, 1961, **308**, 352.
[5] Neuert and Clasen, *Z. Naturforsch.*, 1952, **7a**, 410.
[6] Halmann, *Spectrochim. Acta*, 1960, **16**, 407; Proceedings of symposium on " Chemical Effects of Nuclear Transformations," Prague, October 1960; IAEA, Vienna, 1961, p. 200.
[7] Halmann and Kugel, *Bull. Res. Council Israel*, 1961, **10A**, 124.
[8] Fiat, Halmann, Kugel, and Reuben, unpublished work.

643. *Oxidation of Tyrosine with Hydrogen Peroxide.*

By G. W. Kirby.

Davies and Harris [1] recently described the oxidation of tyrosine by hydrogen peroxide in hydrochloric acid and assigned structure (I) to one of the products, compound X_1, $C_{18}H_{22}Cl_2N_2O_6,4H_2O$, m. p. 143° (decomp.). This material was formed in good yield at room temperature and was only stable as the hydrochloride. Attempts to isolate the corresponding amino-acid led to the formation of 3-chlorotyrosine. Compound X_1 was rapidly reduced by iodide in acidic solution to tyrosine.

The diaryl peroxide structure (I) is without adequate precedent and seemed to deserve

$$[Cl^- \; HO_2C{\cdot}CH(NH_3^+){\cdot}CH_2{\cdot}C_6H_4{\cdot}O^-]_2 \quad (I)$$
$$p\text{-}$$

further investigation, the previous diaryl peroxides [2] cited by Davies and Harris being in fact diaroyl rather than diaryl compounds.[3] In the conditions described by these authors tyrosine was converted into a mixture which proved difficult to separate by crystallisation. Paper chromatography showed two amino-acid components present in roughly equal amounts, one running alongside tyrosine and the other alongside 3-chlorotyrosine. The infrared spectrum of the product was almost indistinguishable from that of a 1 : 1 mixture of tyrosine and 3-chlorotyrosine hydrochlorides. The product showed only feeble oxidising power towards iodide and this property was destroyed completely by catalase at pH 7. In a parallel experiment t-butyl hydroperoxide was stable towards the crude catalase preparation in these conditions. In another experiment the tyrosine oxidation mixture was evaporated to dryness at room temperature and the total crude product examined. Addition of potassium iodide and hydrochloric acid liberated iodine equivalent to 2·82% of active oxygen, but 97% of the oxidising power disappeared after treatment with catalase and must have been due to the presence of hydrogen peroxide.

When tyrosine was oxidised with hydrogen peroxide for much longer periods a single crystalline product was isolated in good yield. This had a melting point close to that of compound X_1 and gave similar analytical values. However, it did not oxidise iodide and its nuclear magnetic resonance spectrum suggested that it might be an ethanol solvate of 3-chlorotyrosine hydrochloride. This was confirmed by comparison with a sample made by chlorination of tyrosine with sulphuryl chloride.[4] It appears therefore that tyrosine is smoothly chlorinated by hydrogen peroxide in hydrochloric acid and it has not been possible to detect intermediate organic peroxides at any stage during the reaction.

Dr. G. Harris has kindly repeated the experiments described here with substantially the same results.[5] The infrared spectrum of the original specimen [1] of compound X_1 closely resembles that of 3-chlorotyrosine but unfortunately supplies of the original substance are no longer available for further investigation.

Experimental.—Oxidation of tyrosine with hydrogen peroxide. (1) A solution of L-tyrosine (1·0 g.) in 2N-hydrochloric acid (6 ml.) and 30% hydrogen peroxide (4 ml.) was kept at room temperature for 16 hr. The resulting yellow solution was evaporated at room temperature *in vacuo* and the solid residue extracted with cold ethanol (20 ml.). The extract was filtered and evaporated at room temperature and the residue triturated with ether (20 ml.) to give a crystalline product, A (0·85 g.). Paper chromatography in the butan-1-ol–acetic acid–water (4 : 1 : 1) system described by Davies and Harris showed two ninhydrin-positive components running alongside tyrosine and 3-chlorotyrosine. Comparison of the product's infrared

[1] Davies and Harris, *J.*, 1961, 3193.
[2] Wieland and Meyer, *Annalen*, 1942, **551**, 249; Breitenbach and Derkosch, *Monatsh.*, 1950, **81**, 530.
[3] Cf. Müller, Schurr, and Scheffler, *Annalen*, 1959, **627**, 132, and preceding papers.
[4] Zeynek, *Z. physiol. Chem.*, 1925, **144**, 246.
[5] Dr. G. Harris, personal communication.

spectrum (in Nujol) with those of known mixtures of tyrosine hydrochloride and 3-chlorotyrosine hydrochloride hemiethanolate indicated that these amino-acids were present in product A in approximately equal amounts. When product A was treated with an excess of potassium iodide and hydrochloric acid iodine was liberated (thiosulphate titration) corresponding to 0·44% of active oxygen.

This experiment was repeated and the solid product, B (1·3 g.), obtained by evaporation of the reaction mixture to dryness *in vacuo* was examined without further manipulation. Its chromatographic properties were similar to those of A and addition of acidified potassium iodide gave iodine corresponding to 2·82% of active oxygen.

Experiments with catalase. A solution of oxidation product A (50 mg.) in water (10 ml.) was adjusted to pH 7 with sodium hydrogen carbonate, and catalase (10 mg.; crude preparation from beef liver) was added. After 5 min. addition of acidified potassium iodide gave no iodine. Repetition without addition of catalse gave iodine corresponding to 0·43% of active oxygen. The oxygen evolved from a neutralised solution of product A (250 mg.) by decomposition with catalase (10 mg.) was measured in a microhydrogenator (Found: 0·91 ml.; calc. from iodine titration, 0·83 ml.). A neutralised solution of product B (100 mg.) in water (10 ml.) was treated with an excess of potassium iodide and hydrochloric acid and, after 10 min., the liberated iodine was titrated with 0·1N-sodium thiosulphate, 3·50 ml. being required. Repetition with corresponding neutral solutions of product B which had been incubated with 10 mg. and with 20 mg. of catalase for 10 min. at room temperature gave thiosulphate titres of 0·10 ml. in both cases.

An aqueous solution of t-butyl hydroperoxide (5 ml., *ca.* 0·3%) was adjusted to pH 7, and potassium iodide (5 ml., 10%) and 6N-hydrochloric acid (5 ml.) were added. After 3 hr. the liberated iodine required 3·35 ml. of 0·1N-thiosulphate. Corresponding solutions of hydrogen peroxide which had been kept at room temperature for 10 min. in the presence of 10 mg. and of 20 mg. of catalase gave thiosulphate titres of 3·28 and 3·25 ml., respectively.

Oxidation of tyrosine with hydrogen peroxide. (2) A solution of L-tyrosine (1·0 g.) in 2N-hydrochloric acid (6 ml.) and 30% hydrogen peroxide (8 ml.) was kept at room temperature for 14 days. The deep yellow solution was evaporated *in vacuo* and the residue extracted with ethanol (50 ml.). The extract was filtered and evaporated and the residue redissolved in ethanol (15 ml.) and again filtered. Addition of ether to the filtrate gave crystals (0·62 g.) which slowly separated during 2 hr. Recrystallisation from ethanol–ether gave needles, m. p. 140°, recrystallising at *ca.* 160° and remelting by *ca.* 210°, $[\alpha]_D$ +13° (*c* 1·0 in EtOH) (Found: C, 43·3; H, 5·2; N, 5·3; ionic Cl, 12·5; total Cl, 25·3. $C_9H_{11}Cl_2NO_3$,0·5EtOH requires C, 43·6; H, 5·1; N, 5·1; ionic Cl, 12·9; total Cl, 25·8%). The nuclear magnetic resonance spectrum was measured in deuterium oxide with t-butyl alcohol (τ 8·69) as an internal standard. τ values for proton peaks are given with multiplicities and relative areas in parentheses: CH_3, 8·75 (triplet, 3); CH_2, 6·77 (doublet, 4); CH_2, 6·27 (quartet, 2); CH, 5·63 (triplet, 2); aryl CH, 2·83 (envelope, 6). The infrared spectrum (in Nujol) was identical with that of 3-chlorotyrosine hydrochloride [4] (recrystallised from ethanol–ether). The latter material crystallised from glacial acetic acid as needles, m. p. 140°, recrystallising, and remelting at 240° (decomp.) (Found: C, 42·7; H, 4·5; N, 5·3. $C_9H_{11}Cl_2NO_3$,0·5CH_3·CO_2H requires C, 42·6; H, 4·6; N, 5·0%); its nuclear magnetic resonance spectrum (as above) showed a sharp singlet, τ 7·85, of expected intensity.

The author thanks Professor D. H. R. Barton, F.R.S., for helpful advice, Mr. R. G. Foster for measuring the nuclear magnetic resonance spectra, and Dr. G. Harris for cordial discussions.

CHEMISTRY DEPARTMENT, IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, March 6th*, 1962.]

644. *Isolation of Lupeol from the Common Spangle Gall of Oak.*

By G. Shaw and A. Yeadon.

An alcoholic extract of oak spangle galls, which are produced by the gall wasp *Neuroterus baccarum* forma *lenticularis* on the underside of leaves of a common oak (*Quercus robur*),[1] readily gave crystals (~1·5% of the dry weight) and an amorphous wax. The crystals have been separated from the wax without chromatography, and shown to be lupeol by mixed m. p. determinations and by comparison of infrared spectra (potassium bromide disc).

A similar extract of dead gall-free leaves gave a Liebermann–Burchardt colour reaction similar to that given by lupeol, and an infrared spectrum of the extract on a potassium bromide disc showed a band at 885 cm.$^{-1}$ characteristic of the methylidene group present in lupeol. The amount of triterpene in the leaves, however, was less than 1% of that in the galls.

Experimental.—Dead or dying oak leaves infected with spangle galls were collected in Northcliffe Woods, Shipley, Yorkshire, during October and November, both from the ground and from the trees. The galls were readily removed from the leaves by scraping, several hundred grams of material being obtained in this way with little difficulty. The galls (400 g.) were extracted with boiling 95% ethanol (2 × 750 ml.). The cooled solution gave an amorphous white precipitate of a wax which was centrifuged off. The supernatant liquid with 6N-hydrochloric acid (325 ml.) then gave a red solution which was set aside. Crystals separated contaminated with a little wax. The substance, after three crystallisations from ethanol (charcoal), gave lupeol as needles, m. p. 213—214° not depressed when mixed with an authentic specimen (Found: C, 84·25; H, 11·85. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%); the yield of lupeol was about 0·9% of the wet or 1·5% of the dry weight of the galls. The substance also gave a monoacetate, needles (from methanol–chloroform), m. p. 217—218° (Found: C, 81·6; H, 11·15. Calc. for $C_{32}H_{52}O_2$: C, 81·9; H, 11·2%), and a monobenzoate, plates (from chloroform–methanol), m. p. 274—275°, both m. p.s being in good agreement with those quoted for corresponding derivatives of lupeol.[2]

We thank Professor E. R. H. Jones (Oxford) for a specimen of lupeol.

Institute of Technology, Bradford, 7. [*Received, March 6th,* 1962.]

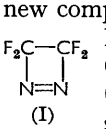
[1] Richards and Davies, "A General Textbook of Entomology," Methuen, London, 1960, p. 706; Step, "Bees, Wasps, Ants, and Allied Insects of the British Isles," Warne, London, 1946, p. 214.
[2] "Elsevier's Encyclopedia of Organic Chemistry," ed. Josephy and Radt, Elsevier, New York, Series III, 1940, **14**, 575, and supplement 1952, p. 1115s.

---

645. *The Fluorination of Cyanogen.*

By H. J. Emeléus and G. L. Hurst.

A recent publication by Robson, McLoughlin, Hynes, and Bigelow [1] describes the fluorination of cyanogen by a fluorine–nitrogen mixture at 250°. One of the major products was the compound $F_2N{\cdot}CF_2{\cdot}CF_2{\cdot}NF_2$, but a number of minor products were also identified. All of these were accounted for by postulating an initial cleavage of the cyanogen molecule and the formation of cyanogen fluoride, which underwent a series of further reactions. We have done parallel studies of the fluorination of cyanogen by argentic fluoride at 105—115° and, under these comparatively mild conditions, the main product (*ca.* 90%) is the new compound $C_2F_4N_2$, the reactions of which show that it is probably tetrafluoro-3,4-dihydro-1,2-diazete (I). The yield decreases with increase in reaction temperature. Other products have not yet been fully characterised, but they probably include $CF_3{\cdot}N{=}N{\cdot}CF_3$, which was also found by Bigelow and his co-workers. Complete separation of the main product from the small amounts of impurities of similar



(I)

[1] Robson, McLoughlin, Hynes, and Bigelow, *J. Amer. Chem. Soc.*, 1961, **83**, 5010

volatility was achieved by repeated vacuum-fractionation, and examination of the purified material by vapour-phase chromatography showed no trace of contamination. This material gave a linear log p–$1/T$ plot and the derived b. p. was −36°. The compound was colourless in both the gaseous and the liquid state.

The compound (I) has an ultraviolet absorption spectrum showing vibrational fine structure centred around 3300 Å, with twenty-two clearly discernible peaks between 3000 and 3500 Å at a pressure of 1·5 cm. in a 10-cm. cell. Maximum absorption at 3332 Å was several hundred times stronger than that of $CF_3{\cdot}N{=}N{\cdot}CF_3$ or $CH_3{\cdot}N{=}N{\cdot}CH_3$. The chief infrared frequencies between 670 and 4000 cm.$^{-1}$ were 773s, 781s, 788s, 1144vs, 1236vs, 1242vs, 1374s, and 1485s cm.$^{-1}$. The fluorine nuclear magnetic resonance spectrum showed a single peak with a chemical shift of +102·5 p.p.m. relative to CCl_3F. This spectroscopic evidence, which will be reported in detail later, is consistent with the formulation (I) rather than $F_2C{=}N{-}N{=}CF_2$. The nuclear magnetic resonance spectrum shows that the molecule does not contain both N–F and C–F bonds, and the infrared spectrum shows no absorption attributable to the former.

The compound decomposes thermally above about 150°. Decomposition was rapid at 240° and gave an almost quantitative yield of nitrogen, together with tetrafluoroethylene, a small amount of the cyclic dimer C_4F_8, which was identified by its infrared spectrum, and a very small amount of polytetrafluoroethylene. Reaction with chlorine at 200° gave nitrogen and 1,2-dichlorotetrafluoroethane. Preliminary observations on the photolysis show that nitrogen and tetrafluoroethylene are again formed, but that other liquid products also occur (these are being studied). This chemical evidence is again consistent with formulation (I). The compound did not react with water in a sealed tube at −120° or with hydrogen chloride at 120°. Other reactions are being examined. The compound detonated on two occasions at room temperature, but the exact conditions leading to this have not been established.

Experimental.—In a typical preparation, cyanogen (10·8 g.) was carried in a stream of nitrogen through a copper tube (60 × 3·1 cm.) containing 350 g. of argentic fluoride supported on copper gauze and heated to 105—115°. The reaction time was 3 hr. The product (25·3 g.) was separated by fractional condensation in the vacuum-apparatus. Over 90% of the product (M = 132·5) passed a trap cooled at −120° but was retained at −131°. Repeated fractionation gave *tetrafluoro-3,4-dihydro-1,2-diazete* (Found: C, 18·3, 19·0; N, 22·1; F, 60·0%; M, 128·8. $C_2F_4N_2$ requires C, 18·8; N, 21·9; F, 59·4%; M, 128·0). Fluorine was determined as lead chloride fluoride after decomposition of the compound with sodium in liquid ammonia.

The product (0·148 g., 25·5 ml.; M, 130) was heated in a sealed tube (100 ml.) at 240° for 2 hr. Nitrogen (0·0318 g., 25·4 ml.) was pumped off. The condensable products gave, on fractionation, tetrafluoroethylene (0·0919 g., 20·4 ml.; M, 100) and perfluorocyclobutane (1·5 ml.), identified by their infrared spectra. A very small amount of involatile white solid was formed. In a further experiment the compound (0·505 g., 87·1 ml.) was heated in a sealed tube at 200° for 4 hr. with an excess of chlorine. Nitrogen (0·103 g., 82·6 ml.) was recovered, together with 1,2-dichlorotetrafluoroethane (0·669 g., 89·3 ml.) (Found: M, 168. Calc. for $C_2Cl_2F_4$: M, 171). The identity of the latter was confirmed by its infrared spectrum which, however, showed two unidentified extraneous peaks of low intensity. These may be due to an impurity in the starting material or to a secondary reaction product. The pyrolysis and the reaction with chlorine were examined with material containing a small amount of impurity (M = 130).

One of the authors (G. L. H.) thanks the National Science Foundation (U.S.A.) for a Fellowship.

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD, CAMBRIDGE.

[*Received, March 7th*, 1962.]

646. *The Mercuration of Phenanthrene.*

By JOHN G. CAREY and IAN T. MILLAR.

THE direct mercuration of aromatic hydrocarbons is of interest, in that the mercuri-group is introducible under mild conditions and is replaceable by other substituents.[1] Although this route to substituted polycyclic aromatic compounds which are not readily available by direct substitution has been used for biphenylene,[2] it has been little employed with other tricyclic aromatic hydrocarbons. Orientation in aromatic mercuration is markedly dependent on reaction conditions;[3] the rate and selectivity of the reaction are increased by ionizing catalysts such as perchloric acid and the mechanism may then be different. Aromatic mercuration is reversible.[4]

Goswami and Das-Gupta[5] studied the mercuration of anthracene, phenanthrene, acenaphthene, and fluorene with mercuric acetate in acetic acid without an added catalyst and claimed to secure a monomercurated product, of sharp melting point but unspecified orientation, in fair to good yield in each case. However, other workers have obtained different products from the mercuration of fluorene.[6] We have studied the mercuration of acenaphthene and phenanthrene under the conditions used by Goswami and Das-Gupta, and the mercuration of phenanthrene in several other conditions. The products of mercuration were identified by converting the crude mixtures of acetoxymercuri-compounds into mercurichlorides which were progressively extracted with organic solvents. The isolated mercurichlorides were orientated by examination of the adjacent hydrogen frequencies in their infrared absorption spectra, and by conversion into aryl halides of known orientation.

The product from the uncatalyzed mercuration of acenaphthene has the 5-orientation also observed in most electrophilic substitutions. From phenanthrene in similar conditions 9-, 3-, and 1-chloromercuriphenanthrene were obtained (total yield, ~25%); 9,10- and 3,9-bischloromercuriphenanthrene were also formed (yield, ~25%) and were characterized by conversion into the dibromides. Both hydrocarbons doubtless also undergo some polymercuration and unchanged hydrocarbons were recovered.

9,10-Dibromophenanthrene has been obtained by heating 9-bromo-10-nitrophenanthrene with ammonium bromide in a sealed tube;[7] but we find it is more conveniently obtained from the bromonitro-compound through reduction with " neutral iron " and diazotization; 9-bromo-10-iodophenanthrene can be obtained similarly.

Experimental.—M. p.s were determined on a Kofler hot stage. Assigned orientations are in accord with infrared absorption spectra. Compounds are colourless unless otherwise stated.

Mercuration of acenaphthene. Acenaphthene (10 g.) was heated in a pressure bottle with mercuric acetate (24 g.) in acetic acid (70 ml.) at 115—120° for 15 hr. The resulting red solution was filtered, concentrated, and mixed with an excess of ethanolic calcium chloride; the precipitate was washed with water, ethanol, and ether and dried *in vacuo* [28 g.; m. p. 170—300° (lit.,[5] m. p. 148°)]. The solid was extracted in a Soxhlet apparatus with ether which removed acenaphthene (3·5 g., m. p. and mixed m. p. 94°). 5-*Chloromercuriacenaphthene* was then extracted by chloroform; it recrystallized from chloroform or benzene as needles, m. p. 208°·(7 g., 28%) (Found: C, 37·1; H, 2·4. $C_{12}H_9ClHg$ requires C, 37·0; H, 2·3%). With bromine in chloroform it gave 5-bromoacenaphthene, m. p. 52—53° (from ethanol) (lit.,[8] m. p. 52—53°).

[1] Kobe *et al.*, *Ind. Eng. Chem.*, 1941, **33**, 170; 1946, **38**, 247; Whitmore, " Organic Compounds of Mercury," Chemical Catalog Co., Inc., New York, 1921.
[2] Baker, Barton, and McOmie, *J.*, 1958, 2666.
[3] Klapproth and Westheimer, *J. Amer. Chem. Soc.*, 1950, **72**, 4461; Brown and Dubeck, *ibid.*, 1959, **81**, 5608.
[4] Malaiyandi, Sawatzky, and Wright, *Canad. J. Chem.*, 1961, **39**, 1827.
[5] Goswami and Das-Gupta, *J. Indian Chem. Soc.*, 1931, **8**, 475.
[6] Miller and Bachmann, *J. Amer. Chem. Soc.*, 1935, **57**, 2447; Campbell and Stafford, *J.*, 1952, 299.
[7] Schmidt and Ladner, *Ber.*, 1904, **37**, 4402.
[8] Paillard and Favarger, *Helv. Chim. Acta*, 1933, **16**, 614.

Mercuration of phenanthrene. Phenanthrene (5 g.) was heated in a pressure bottle with mercuric acetate (10 g.) in acetic acid (40 ml.) at 125° for 4 hr. Conversion of the product into crude mercurichlorides and extraction as above gave phenanthrene (2·0 g., extracted by ether); a mixture of chloromercuriphenanthrenes was then extracted successively by chloroform and by toluene, leaving a residue. The chloroform extract deposited 3-*chloromercuriphenanthrene*, needles (from benzene), m. p. 332° (Found: C, 40·6; H, 2·4. $C_{14}H_9ClHg$ requires C, 40·7; H, 2·2%). With bromine in chloroform it gave 3-bromophenanthrene, m. p. 82—83° (lit.,[9] 83—84°). The chloroform mother-liquors deposited 1-*chloromercuriphenanthrene*, plates (from ethyl acetate or benzene), m. p. 272° (Found: C, 40·6; H, 2·2%), similarly giving 1-bromophenanthrene, m. p. 108—109° (lit.,[9] m. p. 109—110°). 9-*Chloromercuriphenanthrene* was precipitated from the toluene extract by ethanol, and was purified by reprecipitation; it formed needles, m. p. 240° (Found: C, 39·8; H, 2·3%), and gave 9-bromophenanthrene, m. p. and mixed m. p. 63—65°. The residue after extraction was shaken with bromine in chloroform for 48 hr. at room temperature, the solvent removed, and the residue distilled. A crude crystalline distillate, b. p. *ca.* 190°/5 × 10^{-3} mm., was purified by chromatography in benzene on alumina, giving 9,10-dibromophenanthrene, m. p. and mixed m. p. 179—182°, and 3,9-dibromophenanthrene, m. p. 142—143° (lit.,[10] m. p. 143—143·5°), both recrystallized from ethanol.

Mercuration of phenanthrene in acetic acid with a solution of mercuric oxide in perchloric acid at 60° for 6 hr., or at 30° for 4 hr., and working-up as above, gave phenanthrene and mixtures of its mono- and di-mercurated derivatives in comparable amounts; after a similar reaction mixture without acetic acid had been shaken at the ordinary temperature for 150 hr., phenanthrene (98%) was recovered.

Other similar reaction mixtures to which methanol or ethanol was added, and the whole boiled under reflux, gave 1-chloromercuriphenanthrene, and a mixture of 1- and 3-chloromercuriphenanthrene, respectively, in very small yield. Mercuration of phenanthrene with mercuric acetate in nitrobenzene, with perchloric acid as catalyst, at 40° for 3 hr., gave the products obtained by uncatalyzed mercuration in acetic acid, and much residue of presumed polymercurated compounds.

9,10-*Dibromophenanthrene.* 10-Bromo-9-phenanthrylamine[11] (10 g.) in 48% hydrobromic acid (32·5 g.) was diazotized at 0° with sodium nitrite (2·7 g.) in water (10 ml.). After 15 minutes' stirring the pale yellow suspension was poured with stirring into a solution of freshly prepared cuprous bromide (40 g.) in hydrobromic acid (400 ml.). After being kept for 10 min. and boiled for 10 min. the mixture was cooled and extracted with benzene. The dried extract was chromatographed on alumina and eluted with 1 : 1 benzene–light petroleum, giving 9,10-dibromophenanthrene, m. p. 185° (from ethanol) (lit.,[7] m. p. 181—182°) (5·6 g., 45%) (Found: C, 49·85; H, 2·35. Calc. for $C_{14}H_8Br_2$: C, 50·05; H, 2·4%).

9-*Bromo*-10-*iodophenanthrene.* The preceding amine (10 g.) in sulphuric acid (15 ml.) and water (45 ml.) was diazotized as above. Potassium iodide (9 g.) in water (10 ml.) was then added, and the mixture set aside for 1 hr. before being heated on a steam-bath for 1 hr. After cooling, the solid was collected, washed with water, dried, and chromatographed on alumina in benzene, giving 9-*bromo*-10-*iodophenanthrene* as nearly colourless needles (from ethanol), m. p. 174—175° (8·5 g., 60%) (Found: C, 44·25; H, 2·15. $C_{14}H_8BrI$ requires C, 43·9; H, 2·1%).

We are indebted to the Department of Scientific and Industrial Research and the Harrison Memorial Fund for grants (to J. G. C.).

Department of Chemistry, The University,
Keele, Staffordshire. [*Received, March 15th,* 1962.]

[9] Bachmann and Boatner, *J. Amer. Chem. Soc.*, 1936, **58**, 2194.
[10] Sandqvist, *Ber.*, 1920, **53**, 168.
[11] Mosby, *J. Org. Chem.*, 1959, **24**, 421.

647. *Complex Formation during the Preparation of Benzyloxycarbonylserine.*

By Stanley S. Brown and Roy Wade.

In the course of a recent investigation we prepared several batches of benzyloxycarbonyl-DL-serine by the usual bicarbonate procedure.[1] It was noticed that the product of the reaction varied with the method of acidification. If the reaction mixture was acidified by dropwise addition of concentrated hydrochloric acid at 10—15°, a quantity of material, m. p. *ca.* 190°, insoluble in ethyl acetate was formed, and the yield of benzyloxycarbonyl-DL-serine, m. p. 125°, was reduced; if the acidification was carried out rapidly, the solution being made strongly acid and the temperature not controlled, no by-product was formed and the required derivative was obtained in about 80% yield. The material insoluble in ethyl acetate contained sodium, even after repeated washing with dilute acid, and was slightly soluble in cold water and much more so on warming. It dissolved with effervescence in aqueous sodium hydrogen carbonate and the solution, when acidified rapidly, deposited benzyloxycarbonyl-DL-serine.

The substance of m. p. 190° appears to be a complex of the benzyloxycarbonylamino-acid with its salt, and some analogues have been described.[2,3] Titration gave an equivalent weight of 499, indicating a 1 : 1 complex (theor. equiv., 500). Recrystallisation from methanol or from aqueous ethanol did not affect this ratio (Grommers and Arens [3] obtained different proportions depending on the solvent used for recrystallisation).

The complex was also prepared by addition to benzyloxycarbonylserine of half an equivalent of N-sodium hydroxide, or even one equivalent of sodium hydrogen carbonate solution, evaporation, and recrystallisation of the residue.

It was considered that the 1 : 1 relationship of acid and salt might be of significance in this case, as complexes previously described [2,3] have often been of variable composition or comprised acid and salt in a complex ratio. Possibly the sodium ion is situated midway between an L- and a D-molecule, maintaining the overall symmetry. Thus it might be expected that the L-isomer would not form a complex of this type. However, during a preparation of benzyloxycarbonyl-L-serine, a complex was precipitated in an analogous manner, showing that the above line of reasoning is probably not valid. As a measure of lattice stability, the melting points of the complexes lay much closer to those of the corresponding sodium salts than to those of the acids.

Infrared spectra of the acids, sodium salts, and complexes in Nujol mulls have peaks in the range 2000—1500 cm.$^{-1}$ (see Table). Whereas the carboxylic acid absorption

Benzyloxycarbonylserine	ν(CO) acid	ν(CO) urethane		ν(CO) $\cdot CO_2^-$	δ(NH)
L-Acid	1750s	1690s	1660sh	—	1540s
L-Complex	1750sh	1695s	1655sh	—	1540s
L-Salt	—	1690s	—	1590s	1545s
DL-Acid	1760s	1695s	—	—	1520s
DL-Complex	1750sh	1695s	—	—	1540s
DL-Salt	—	1695s	—	1580s	1530s

(near 1750 cm.$^{-1}$) weakens and finally disappears in going from acid to complex to salt, the corresponding absorption due to the carboxylate ion (near 1580 cm.$^{-1}$) is apparent only in the completely neutral salt. A shoulder in the spectrum of the benzyloxycarbonyl-L-serine complex at 1655 cm.$^{-1}$ is not thought to be due to this grouping as the same shoulder occurs in the spectrum of the free acid.

[1] Greenstein and Winitz, "Chemistry of The Amino Acids," Wiley, New York, 1961, Vol. II, p. 891; Riley, Turnbull, and Wilson, *J.*, 1957, 1373.

[2] Grassmann and Wünsch, *Chem. Ber.*, 1958, **91**, 462; Goodman and Stueben, *J. Org. Chem.*, 1959, **24**, 112.

[3] Grommers and Arens, *Rec. Trav. chim.*, 1959, **78**, 558.

*Experimental.—Benzyloxycarbonyl-*DL*-serine–sodium salt complex.* DL-Serine (60 g.) was dissolved in water (1·1 l.) containing sodium hydrogen carbonate (120 g.), and benzyl chloroformate (115 ml.) was added. The mixture was stirred for 2·5 hr., then extracted with ether (2 × 500 ml.). The aqueous layer was covered with ethyl acetate (500 ml.), cooled (ice-bath), and acidified by dropwise addition of concentrated hydrochloric acid to pH 2. The insoluble material was filtered off and dried (yield, 24 g., 17%; m. p. 186—188°). Recrystallisation from methanol (poor recovery) or aqueous ethanol afforded the pure *complex* as needles, m. p. 189—190° (Found: C, 52·9; H, 5·0; N, 5·8%; equiv., 499. $C_{22}H_{25}N_2NaO_{10}$ requires C, 52·9; H, 5·0; N, 5·6%; equiv., 500).

The ethyl acetate layer was separated and the acid solution extracted twice more with ethyl acetate. After drying (Na_2SO_4) and concentration, addition of light petroleum (b. p. 60—80°) gave needles of benzyloxycarbonyl-DL-serine, m. p. 125—127° (65 g., 48%).

*Benzyloxycarbonyl-*L*-serine–sodium salt complex.* By the method described above, L-serine (6 g.) gave benzyloxycarbonyl-L-serine (7·75 g., 58%) and *complex* (2·1 g., 15%), m. p. 188—190°, $[\alpha]_D^{22}$ 5·2° (*c* 3·1 in AcOH) (Found: C, 53·1; H, 5·0; N, 5·8%; equiv., 500). Sodium analyses were not consistent.

The complexes were insoluble in the usual organic solvents, except methanol.

This work has been supported by grants to this Institute from the Medical Research Council, the British Empire Cancer Campaign, the Anna Fuller Fund, and the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service.

CHESTER BEATTY RESEARCH INSTITUTE,
INSTITUTE OF CANCER RESEARCH: ROYAL CANCER HOSPITAL,
FULHAM ROAD, LONDON, S.W.3. [*Received, March 16th,* 1962.]

---

648. *The Structure of Cæsium Tungstoaluminate.*

By D. H. BROWN.

IN a previous paper,[1] on the basis of analytical evidence, tungstoaluminic acid was described as a 1 : 11 acid. However, the properties described for the acid resembled rather those of a 1 : 12 acid: in particular, the ability of the acid to form an ether addition compound, the stability of the anion, the high solubility of the free acid, and the method of preparation, all suggest a 12-acid. *X*-Ray powder photography has now shown that tungstoaluminic acid is a 1 : 12 acid. Photographs were taken with the specimens mounted in fine Lindemann glass tubes and Cu-K_α radiation. The structure was found to be cubic with a unit cell length of 11·80 Å, very close to those of cæsium 12-tungstosilicate [2] (11·80 Å), 12-tungstophosphate (11·83 Å), 12-tungstozincate [3] (11·86 Å) and 12-tungstoferrate [4] (11·88 Å). The intensities agreed with those calculated for a structure similar to that proposed for cæsium 12-tungstophosphate but with aluminium as the central ion. The lines and intensities, measured visually, are given in the Table along with those of cæsium 12-tungstosilicate for comparison.

These results suggest that tungstoaluminic acid is a 1 : 12 acid with a central aluminium(III) ion. The acid when heated on a thermogravimetric balance decomposed around 260° (cf. 12-tungstosilicic and 12-tungstoboric acid, 270°). The acid is fairly stable in aqueous solution, but heating causes some hydrolysis and gives traces of the relatively insoluble aluminium paratungstate; this could account for the low tungsten analysis previously reported. The reported basicity [1] of 5 agrees with the $(8 - n)$ rule for the basicity of 12-heteropolytungstic acids (where n is the valency of the central ion). Thus the formula for 12-tungstoaluminic acid should be $2{\cdot}5H_2O,\frac{1}{2}Al_2O_3,12WO_3,xH_2O$ ($H_5AlW_{12}O_{40},xH_2O$). Various samples of 12-tungstoaluminic acid were prepared and

[1] Mair and Waugh, *J.*, 1950, 2372.
[2] Santos, *Proc. Roy. Soc.*, 1935, *A*, **150**, 309.
[3] Brown and Mair, *J.*, 1958, 2597.
[4] Brown and Mair, *J.*, 1962, 1512.

X-Ray lines and intensities for cæsium 12-tungstoaluminate and 12-tungstosilicate.

	Aluminate		Silicate		Aluminate		Silicate
$h^2 + k^2 + l^2$	Calc.	Obs.	Obs.	$h^2 + k^2 + l^2$	Calc.	Obs.	Obs.
6	13·7	15	15	32	86·8	90	80
8	5·8	5	5	33	10·2	10	10
10	25·7	25	25	34	9·1	10	10
12	150	150	150	36	15·1	15	15
14	0·9	Absent	Absent	38	92·2	100	100
16	80·0	70	80	40	2·1	Absent	Absent
18	17·6	20	15	41	28·9	30	25
20	0·2	Absent	Absent	42	47·5	50	50
22	94·5	100	90	44	80·1	80	75
24	11·8	10	15	46	2·7	Absent	Absent
26	79·9	80	70	48	29·5	30	25
27	8·8	10	10	50	207	200	200
30	46·7	50	50				

analysed. The following values were obtained for the ratio $\frac{1}{2}Al_2O_3 : WO_3$—1 : 12·1, 1 : 12·0, 1 : 12·0, 1 : 11·8, and 1 : 11·7.

ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW, C.1.

[*Received, March 26th*, 1962.]

---

649. *Some Equilibrium States Arising in Aqueous Systems Involving Silver and Glycine.*

By D. J. ALNER.

THE complex ion AgG_2^-, where HG = glycine, has been shown to exist and its stability constant found by solubility and e.m.f. measurements to be $10^{7·26}$ at 20°. From e.m.f. measurements the step formation constants for AgG^0 and AgG_2^- have been assessed as $10^{4·00}$ and $10^{3·29}$.

Experimental.—Solubility of silver hydroxide in aqueous solutions of the sodium salt of glycine at 20°. Silver hydroxide was precipitated from dilute silver nitrate solution with the stoicheiometric amount of carbonate-free sodium hydroxide solution. The precipitated hydroxide was washed with warm water until free from extraneous ions and finally filtered off. An excess of the still moist silver hydroxide was added to standard solutions of the sodium salt of glycine (prepared from weighed amounts of glycine and carbonate-free sodium hydroxide) and equilibrated at 20° in black bottles (these solutions were found to be sensitive to light). The solutions were filtered from the excess of silver hydroxide and analysed for their total silver contents by Volhard's thiocyanate method.

TABLE 1.

Solubility of silver hydroxide in sodium glycinate at 20°.

NaG (10^{-1}M)	0·5	1·0	1·5	2·0	2·5
AgOH (10^{-2}M)	1·27	2·54	3·80	5·05	6·26
log β_2	7·27	7·27	7·27	7·26	7·25

pH *and potentiometric titrations of aqueous silver nitrate with the sodium salt of glycine at* 20°. 50 ml. of 0·01M-silver nitrate were titrated with 0·25M-sodium glycine. A sufficient known excess of the solution of glycine sodium salt was first added to the silver nitrate to ensure complete redissolution of the silver hydroxide initially precipitated and to stabilise the silver complex in its limiting form as AgG_2^-. After each subsequent addition of glycine sodium salt the pH value was measured with a glass electrode and the activity of the free silver ion calculated from the e.m.f. values of the cell

$$Ag|AgNO_3 + NaG \text{ (excess)}|\text{Satd. } KNO_3 \text{ bridge}|\text{Satd. calomel}$$

where G = $NH_2{\cdot}CH_2{\cdot}CO_2$.

Similar silver-electrode and pH titrations of 50 ml. of a solution 0·01M in silver nitrate and 0·003M in glycine were made with 0·25M-glycine sodium salt. These covered the range where glycine sodium salt was not present in excess, the purpose of the glycine being to prevent precipitation of silver hydroxide.

Discussion.—The high pH values (pH 12—13) found to occur in solutions of glycine salt saturated with silver hydroxide showed that silver was present in solution in a relatively stable complex ion. The complex-forming mechanism probably occurs in step-wise manner:[1]

$$AgOH(s) + G^- \rightleftharpoons AgG^0 + OH^-$$
$$AgG^0 + G^- \rightleftharpoons AgG_2^-$$

where $HG = NH_2{\cdot}CH_2{\cdot}CO_2H$.

The limiting complex must necessarily be in equilibrium with silver ions, *viz.*, $AgG_2^- \rightleftharpoons Ag^+ + 2G^-$, this equilibrium condition being defined by the stability constant

$$\beta_2 = \{AgG_2^-\}/\{Ag^+\}\{G\}^2,$$

where braces denote activities.

The solution conditions must also necessarily [1a] satisfy the solubility relation $k_s = \{Ag^+\}\{OH^-\} = 1{\cdot}143 \times 10^{-8}$, since the solutions were saturated with silver hydroxide.

The glycine anion is able to function as a base, $G^- + H_2O \rightleftharpoons HG + OH^-$, but owing to the high pH values known to prevail in the experimental solutions, it can be assumed that ionisation of the glycine anion is suppressed.

If S represents the concentration (mole/l.) of silver hydroxide dissolved, then $S = [Ag^+] + [AgG^0] + [AgG_2^-]$. However glycine silver salt, AgG^0, has only a limited solubility in water and in solution probably gives rise to the equilibrium $2AgG^0 \rightleftharpoons Ag^+ + AgG_2^-$, and this system undergoes extensive hydrolysis accompanied by precipitation of silver hydroxide, the resulting solution having pH ~8·3. At pH 12—13, the silver salt AgG^0 would be virtually completely decomposed, silver hydroxide being precipitated; and in view of this and the fact that relatively large excesses of glycine anions exist in the experimental solutions, it may be assumed that the silver was present in solution almost completely in the limiting complex form AgG_2^-; hence we may write $[AgG_2^-] \gg [AgG^0] > [Ag^+]$. Then, by stoicheiometry, $[AgG_2^-] \equiv [OH^-]$. If f represents the mean activity coefficient of univalent ions it follows that $Sf = \{AgG_2^-\} = \{OH^-\}$. If C represents the initial concentration (mole/l.) of glycine sodium salt, the activity of the excess of glycine anion is $(C - 2S)f$. Hence the expression for the stability constant becomes $\beta_2 = S^2/[k_s(C - 2S)^2]$, being independent of f. If the assumptions are correct, a plot of S against $(C - 2S)$ should give a straight line passing through the origin and having a slope $(\beta_2 k_s)^{0.5}$. This was verified graphically. Substitution of the experimental results in this expression enabled β_2 to be evaluated and the constancy of the value obtained affords evidence of the correctness of writing the complex ion as AgG_2^-. The calculated values of β_2 are recorded in Table 1, the mean value for log β_2 being 7·26.

In the potentiometric titrations of silver the saturated potassium nitrate bridge was assumed to eliminate diffusion potential, and the silver potentials derived from the e.m.f. values were used to compute the activities of the silver ions present. In the titration where relatively large excesses of glycine sodium salt were maintained, it was assumed that the concentration of the AgG_2^- ion could be equated to the total silver content of the solution, and the activity of the excess of glycine anion was computed from the known excess of glycine sodium salt corrected for the amounts ionised by use of the measured pH data. Substitution of these values into the expression defining β_2 enabled values for

[1] (*a*) Alner and Smeeth, *J.*, 1958, 852, 4207; (*b*) Alner and Lansbury, *J.*, 1961, 619, 3169; Monk, *Trans. Faraday Soc.*, 1951, **47**, 292, 297; Dubois, *Compt. rend.*, 1947, **224**, 113; Flood and Loras, *Tidsskr. Kjemi Bergvesen Met.*, 1945, **5**, 83; Keefer and Reiber, *J. Amer. Chem. Soc.*, 1941, **63**, 689; Datta and Grzybowski, *J.*, 1959, 222, 1091.

the stability constant of the AgG_2^- ion to be calculated, these being recorded in Table 2. The mean value found for log β_2 was 7·19.

TABLE 2.

Titration of 0·01M-$AgNO_3$ (50 ml.) with 0·25M-NaG at 20°.

NaG (ml.)	pH (obs.)	pAg (obs.)	G^- (10^{-2}M)	AgG_2^- (10^{-3}M)	log β_2	NaG (ml.)	pH (obs.)	pAg (obs.)	G^- (10^{-3}M)	AgG_2^- (10^{-3}M)	log β_2
6	10·60	5·084	0·7152	7·423	7·24	15	11·04	6·434	3·263	6·067	7·19
8	10·82	5·582	1·367	7·057	7·16	20	11·10	6·719	4·337	5·539	7·19
10	10·92	5·926	1·962	6·726	7·17						
12·8	10·99	6·169	2·503	6·427	7·19					Mean	7·19

The pH and potentiometric silver titrations of the solution containing both silver nitrate and glycine, with glycine sodium salt, enabled the formation constants for AgG^0 (k_1) and AgG_2^- (k_2) to be evaluated, these being defined by:

$$k_1 = \{AgG^0\}/\{Ag^+\}\{G^-\} = [Agb^0]/\{Ag^+\}\{G^-\},$$

where the activity coefficient of the uncharged complex AgG^0 is taken as unity; and

$$k_2 = \{AgG_2^-\}/[AgG^0]\{G^-\}.$$

The total concentration of glycine anion, free and combined, was given by $[G^-] + [AgG^0] + 2[AgG_2^-]$, and the total silver content by $[Ag^+] + [AgG^0] + [AgG_2^-]$. The values for $\{Ag^+\}$ were known from the e.m.f. data and for $\{G^-\}$ were calculated from the measured pH values by application of the Henderson equation [pK for glycine being taken as 9·78 (see Monk [1])]. Use of the approximations $\{Ag^+\} \simeq [Ag^+]$ and $\{G^-\} = [G^-]$ enabled initial values for $[AgG^0]$ and $[AgG_2^-]$ to be computed. From these data the approximate ionic strengths were calculated and hence the corresponding values for the mean activity coefficients of the univalent ionic species. By the process of successive approximations more accurate values for $[AgG^0]$ and $[AgG_2^-]$ were derived. Hence for each solution corresponding values for $\{Ag^+\}$, $[AgG^0]$, $\{AgG_2^-\}$, and $\{G^-\}$ were known, and substitution into the relations defining these constants enabled values for k_1 and k_2 to be calculated (see Table 3). The mean values found were log $k_1 = 4·00$ and log $k_2 = 3·29$.

TABLE 3.

Titration of a solution (50 ml.) 0·01M in $AgNO_3$ and 0·003M in HG with 0·25M-NaG at 20°.

NaG (ml.)	pH (obs.)	pAg (obs.)	I (10^{-2}M)	$[AgG^0]$ (10^{-3}M)	$\{AgG_2^-\}$ (10^{-3}M)	$\{G^-\}$ (10^{-4}M)	log k_1	log k_2
1·6	8·40	2·499	2·184	4·411	1·600	1·212	4·06	3·41
2·0	8·71	2·707	2·315	5·324	2·002	2·456	4·04	3·12
2·4	8·84	2·863	2·564	4·802	3·131	3·287	4·03	3·23
3·0	9·07	3·095	2·991	3·465	5·015	5·518	3·89	3·42
3·4	9·31	3·476	3·251	3·149	5·817	9·519	3·99	3·29
						Mean	4·00	3·29

The values found in the present work agree reasonably with those reported by other workers,[1] *e.g.*: Monk, log $k_1 = 3·51$, log $k_2 = 3·38$ at 25°; Flood and Loras, log $k_1 = 3·70$, log $k_2 = 3·30$ at 20°; Keefer and Reiber, log $k_1 = 4·28$ at 20°.

NORTHAMPTON COLLEGE, ST. JOHN STREET,
LONDON, E.C.1.

[*Received, December 12th*, 1961.]