

NOTES.

826. *Constituents of the Leaves of Thujopsis dolabrata.*

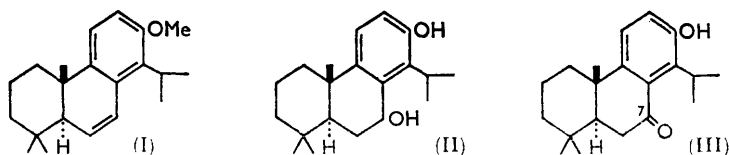
By R. HODGES.

THE heartwood and the leaf oil of *Thujopsis dolabrata* have been the subjects of many investigations.¹ It was thought that extraction of the leaves might yield different products and, indeed, none of the substances isolated from them has been previously reported as occurring in this tree.

A light petroleum extract of the dried leaves was separated by repeated chromatography on alumina. The hydrocarbon fraction consisted of saturated straight-chain hydrocarbons (0.05%) and a mixture of sesqui- and di-terpenes (0.18%) which have not been further investigated.

Hydrolysis of the ester fraction yielded β -sitosterol (0.06%) together with nonacosan-10-ol (ginnol) (0.05%), a substance previously reported¹ in at least five varieties of gymnosperms. In addition, the corresponding ketone, ginnone (0.01%), was obtained.

From the more polar fractions the following substances were isolated: ginnol (0.04%), totarol (0.3%), and an inseparable mixture (*A*) (0.06%), m. p. 180–209°. This mixture gave analytical results agreeing with $C_{20}H_{30}O_2$ and formed a diacetate, $C_{24}H_{34}O_4$. It was



stable to hot 5% alcoholic sodium hydroxide, but when treated with acid it yielded an oil, having ultraviolet absorption at 267 $m\mu$, $\epsilon = 9800$ (in methanol). Methylation of this oil gave the methyl ether (I) as a crystalline solid (λ_{max} 266 $m\mu$; ϵ 9900 in hexane). Hydrogenation of the ether (I) produced totarol methyl ether. Thus material *A* appears

¹ See Karrer, "Konstitution und Vorkommen der organischen Pflanzenstoffe," Birkhäuser, A.-G., Basle, 1958, and references therein.

to be a 7-hydroxy-derivative (II) of totarol * and, in view of the high overall yield during its conversion into totarol methyl ether, is most probably a mixture of the 7 α - and 7 β -epimeric alcohols. This was confirmed by its oxidation to the corresponding ketone (III) as the sole product, identical with a specimen prepared by oxidation of totarol acetate followed by subsequent hydrolysis. The low extinction coefficient (λ_{\max} , 260 m μ , ϵ 6400 in methanol) of this ketone is consistent with the placing of the isopropyl group in totarol at C₍₁₄₎,* and its infrared absorption spectrum which shows no intramolecular hydrogen bonding in dilute solution confirms that the phenolic hydroxyl group is not at this position.

It has been stated² that di- and tri-terpenes do not appear to have been found together in Nature. This may generally be true, but the co-occurrence in *T. dolabrata* of totarol and β -sitosterol, which must be biogenetically derived from a triterpene precursor, would indicate that true triterpenes and diterpenes may well be found together.

Experimental.—Rotations were measured in chloroform at room temperature. M. p.s were determined on a Kofler block and are corrected. Light petroleum refers to the fraction with b. p. 60—80°. The alumina used for chromatography had activity II.

Extraction of Thujopsis dolabrata. The leaves and terminal branches of *T. dolabrata* (collected in Scotland in the autumn) were dried for 12 hr. at 40°, ground, and extracted with light petroleum in a Soxhlet apparatus. The extracts (from 6 kg. of dry material) were washed with sodium hydroxide, adsorbed from light petroleum on alumina, and eluted in the following sequence.

(a) Light petroleum gave a fraction which yielded a mixture of straight-chain hydrocarbons (2.4 g.), m. p. 55—70°, from chloroform. The liquid mother liquors (10.9 g.) appeared to be a mixture of unsaturated sesqui- and di-terpene hydrocarbons.

(b) The fraction obtained with benzene, after hydrolysis with methanolic sodium hydroxide and further chromatography, yielded ginnone (520 mg.), ginnol (2.3 g.), and β -sitosterol (2.6 g.), all identified by comparison with authentic specimens.

(c) Benzene-ether (19:1) eluted material which, on repeated crystallisation from light petroleum, gave ginnol (2.1 g.).

(d) Elution with benzene-ether (4:1) and crystallisation of the eluate from light petroleum gave totarol (18.4 g.), m. p. 131—132°, $[\alpha]_D^{25} + 42^\circ$ (*c* 0.8).

(e) Crystallisation of the ether-eluate from light petroleum-chloroform gave material *A* as prisms (3.4 g.), m. p. 180—209°, $[\alpha]_D^{25} + 10^\circ$ (*c* 1.0), unaltered by further chromatography on alumina or silica gel or by recrystallisation (Found: C, 79.25; H, 9.95. Calc. for C₂₀H₃₀O₂: C, 79.4; H, 10.0%). Material *A* (68 mg.) gave a diacetate when warmed with pyridine (1 ml.) and acetic anhydride (0.2 ml.) for 30 min. This crystallised from methanol as needles (49 mg.), m. p. 162—171° (Found: C, 74.3; H, 8.75. Calc. for C₂₄H₃₄O₄: C, 74.55; H, 8.9%).

Dehydration of material A. Material *A* (430 mg.) in benzene (10 ml.) was heated under reflux with naphthalene-2-sulphonic acid (200 mg.) in water (5 ml.) for 2 hr. The product was adsorbed from benzene on alumina and eluted with benzene-ether (4:1). The oily eluate (400 mg.) in *t*-butyl alcohol (2 ml.) was heated under reflux with sodium hydroxide (1 g.), dimethyl sulphate (1 g.), and water (10 ml.) for 2 hr. The product in light petroleum was filtered through alumina and crystallised from methanol-chloroform, forming prisms of 14-isopropyl-13-methoxypodocarp-6-ene (I) * (355 mg.), m. p. 74—76°, $[\alpha]_D^{25} - 133^\circ$ (*c* 0.9) (Found: C, 84.55; H, 10.2. C₂₁H₃₀O requires C, 84.5; H, 10.15%).

Totarol methyl ether. The isopropylmethoxypodocarpene (95 mg.) in ethyl acetate (10 ml.) was hydrogenated with use of 10% palladium on charcoal catalyst. Crystallisation from ethanol gave totarol methyl ether (81 mg.), m. p. 92.5—93°, $[\alpha]_D^{25} + 42^\circ$ (*c* 0.8).

*14-Isopropyl-13-hydroxypodocarp-7-one (III).** Material *A* (108 mg.) in acetone (5 ml.) was oxidised with chromic acid-sulphuric acid. The product was adsorbed from benzene on alumina, eluted with benzene-ether (2:3) and crystallised from light petroleum, forming prisms of "7-oxototarol" (III) (78 mg.), m. p. 240—241°, $[\alpha]_D^{25} + 16^\circ$ (*c* 0.9) (Found: C, 79.9; H, 9.2. C₂₀H₂₈O₂ requires C, 79.95; H, 9.4%).

Oxidation of totarol acetate. Totarol acetate (1.0 g.), chromium trioxide (450 mg.), and

* Steroid numbering.

² Cocker, Halsall, and Bowers, *J.*, 1956, 4259.

acetic acid (15 ml.) were heated at 70—80° for 10 min. The product was hydrolysed with methanolic sodium hydroxide and separated by chromatography on alumina, giving totarol (460 mg.) and its 7-oxo-derivative (370 mg.), identical with the sample prepared above.

The author thanks Professor R. A. Raphael for his interest, Mr. J. M. Cameron for micro-analyses, and the Forestry Commission (Scotland) for assistance with the collection of leaves.

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827. *The 2 : 1 Addition Compound of Pyridine with Silicon Tetranitrate, and Related Compounds.*

By I. R. BEATTIE and G. J. LEIGH.

EABORN¹ has suggested that there is no evidence that co-ordination to silicon occurs in silane derivatives other than halides. If it is assumed that it is the electronegativity of the halogens which favours complex formation, either by decreasing the electron density at the silicon atom or by rendering the 3*d*-orbitals less diffuse, then it is not obvious why other highly electronegative groups,² such as nitrate or perchlorate, should not similarly promote complex formation.

A reasonably stable addition compound of silicon tetraperchlorate with acetonitrile has been prepared by Schmeisser,³ who found that the free tetraperchlorate was unstable; and the corresponding tetrafluorosulphate complex is also known.⁴ Reactions of triethylsilyl halides with silver nitrate and silver nitrite at 60° produced hexaethyldisiloxane together with oxides of nitrogen,⁵ but recently the preparation of unstable liquids claimed to be trimethylsilyl nitrate and dimethylsilyl dinitrate has been described,⁶ though the results were not supported by analytical evidence. Further, reaction of alcoholic silver nitrate with tris(trimethylsilylmethyl)silyl chloride yielded an immediate quantitative precipitate of silver chloride⁷ but no further product was mentioned; and treatment of silicon tetrachloride with silver nitrite, sodium nitrite, pentyl nitrite, or dinitrogen tetroxide did not yield a tetranitrite.⁸

Reaction of silver nitrite and silver nitrate with trimethylsilyl chloride and triphenylsilyl chloride under a variety of experimental conditions has now been examined. The only clearly identifiable products were the disiloxane, together with nitrosyl chloride and oxides of nitrogen in variable amounts, even from reactions carried out at —80°. Although it is probable that the initial reaction produces a nitrite or nitrate, these compounds are so unstable that decomposition yielding oxides of nitrogen readily occurs. It seemed that this approach was unlikely to be productive.

Addition compounds of silicon tetrahalides and tertiary amines are usually insoluble in organic solvents.⁹ It seemed reasonable to assume that an addition compound of silicon tetranitrate, tetranitrite, or tetraperchlorate with pyridine would be also insoluble. Complex formation thus represented a useful way of isolating these compounds from a reaction mixture with the additional possibility of increased stability. At —40°, the reaction of silver nitrate in acetonitrile with silicon tetrachloride in ether yielded a precipitate of silver chloride. The supernatant liquid slowly evolved oxides of nitrogen, but if treated rapidly with cold pyridine gave a white precipitate which had an analysis

¹ Eaborn, *J.*, 1955, 2047.

² Clifford, *J. Chem. Phys.*, 1959, **63**, 1227.

³ Schmeisser, *Angew. Chem.*, 1955, **67**, 493.

⁴ Hayek, Czaloun, and Kriemer, *Monatsh.*, 1956, **87**, 741.

⁵ Eaborn, *J.*, 1950, 3077.

⁶ Schmidt and Schmidbaur, *Angew. Chem.*, 1959, **71**, 220.

⁷ Sommer, Murch, and Mitch, *J. Amer. Chem. Soc.*, 1954, **76**, 1619.

⁸ Goyal, Saksena, and Saksena, *Agra Univ. J. Res. (Sci.)*, 1957, **6**, 23.

⁹ See, e.g., Wannagat, Schwarz, Voss, and Knauf, *Z. anorg. Chem.*, 1954, **277**, 73.

corresponding to that of the compound $\text{Si}(\text{NO}_3)_4 \cdot 2\text{C}_5\text{H}_5\text{N}$. The analogous reactions with silver nitrite and silver perchlorate also yielded products which produced precipitates on the addition of pyridine, but these were too unstable for reliable analytical figures to be obtained.

The infrared spectrum of the 2:1 addition compound of pyridine with silicon tetrani- trate may be compared with that of the analogous compound of pyridine with silicon tetrachloride.¹⁰ This suggested that bands at ~ 1600 and ~ 1280 cm^{-1} may be associated with the nitrate group.

Experimental.—Reagents were purified and dried by standard procedures.

Infrared spectra were obtained from mulls in Nujol and hexachlorobutadiene.

Preparation of the addition compound. Silver nitrate (4.0 g.) in acetonitrile (~ 20 ml.) at -40° was mixed with silicon tetrachloride (0.67 ml.) in ether (~ 20 ml.), also at -40° , and the whole was immediately cooled in liquid nitrogen and allowed to warm slowly until the silver chloride precipitate could be removed by use of a refrigerated centrifuge. A solution of pyridine (1.0 ml.) in ether (~ 20 ml.), cooled to -40° , was added to the above solution and the mixture allowed to warm to -30° . The precipitate, which carried down trace amounts of silver chloride, was rejected and, on cooling, a crystalline *adduct* appeared which was removed in a centrifuge, dried, and analysed (yield, 0.42 g., 16%) (Found: C, 27.3; H, 3.0; N, 18.0; Si, 6.5. $\text{C}_{10}\text{H}_{10}\text{N}_6\text{O}_{12}\text{Si}$ requires C, 27.7; H, 2.3; N, 19.3; Si, 6.7%). The bulk of the product was discarded and is not included in the yield. The compound slowly evolved oxides of nitrogen at room temperature, which no doubt accounts for the low nitrogen figure. The infrared spectrum (D.M.S. Index, A 135) showed the following bands: 3106w, 3030w, 2833w, 1616sh, 1605s, 1580s, 1490w, 1449m, 1282vs, 1220w, 1156m, 1075m, 1056w, 1020w, 906vs, 885sh, 871m, 820s, 777w, 750s, 732w, 690vs cm^{-1} .

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¹⁰ Hulme, Leigh, and Beattie, *J.*, 1960, 366.

828. *The Co-ordinative Power of Uranyl. Part IV.¹ The Heats of Solvation of the Bis(dibenzoylmethanato)uranyl Complex.*

By L. SACCONI and P. PAOLETTI.

PREVIOUS investigations have shown that uranyl complexes with β -diketones form solvates with water, ammonia, pyridine, and other donor molecules so that uranium tends to display a co-ordination number higher than six.^{1,2} For the solid adducts it has not been ascertained if all the extra molecules are co-ordinated directly to uranium or whether they are held, at least in part, by lattice forces.

Information on the strength, and consequently on the type, of bond may be obtained by calorimetric measurements. For this purpose Wendlandt *et al.*³ determined heats of solvation of a bis(acetylacetonato)uranyl complex with various solvate molecules. Calorimetric measurement of heats of formation of certain solvates of the bis(dibenzoylmethanato)uranyl complex are now reported.

Bis-(β -diketonato)uranyl complexes, whether anhydrous or solvated, dissolve easily in pyridine to intensely orange solutions. The solution obtained by dissolving the solvated complex in pyridine has a spectrum equal to that of a mixture of a solution of the anhydrous

¹ Part III, Sacconi, Caroti, and Paoletti, *J.*, 1958, 4257.

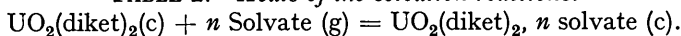
² Sacconi and Giannoni, *J.*, 1954, 2368, 2751; Comyns, Gatehouse, and Wait, *J.*, 1958, 4655.

³ Wendlandt, Bear, and Horton, *J. Phys. Chem.*, 1960, **64**, 1289.

TABLE 1. *Experimental heats of solution and other thermochemical data.*

No.	Process	Q (kcal.)
1	UO ₂ (dimet) ₂ (c) + 1760C ₅ H ₅ N (l)	6.79
2	UO ₂ (dimet) ₂ .H ₂ O (c) + 1760C ₅ H ₅ N (l)	3.24
3	UO ₂ (dimet) ₂ .2.5H ₂ O (c) + 1760C ₅ H ₅ N (l)	1.74
4	UO ₂ (dimet) ₂ .C ₅ H ₅ N (c) + 1759C ₅ H ₅ N (l)	-4.08
5	UO ₂ (dimet) ₂ .NH ₃ (c) + 95H ₂ O, 1760C ₅ H ₅ N (S)	-3.99
6	H ₂ O (l) + UO ₂ (dimet) ₂ , 1760C ₅ H ₅ N (S)	0.41
7	2.5H ₂ O (l) + UO ₂ (dimet) ₂ , 1760C ₅ H ₅ N (S)	1.03 ^a
8	NH ₃ .95H ₂ O (S) + UO ₂ (dimet) ₂ , 1760C ₅ H ₅ N (S)	49.99
9	95H ₂ O (l) + 1760C ₅ H ₅ N (l)	53.71
10	UO ₂ (acetac) ₂ (c) + 1760C ₅ H ₅ N (l)	4.05
11	UO ₂ (acetac) ₂ .H ₂ O (c) + 1760C ₅ H ₅ N (l)	0.82
12	H ₂ O (l) + UO ₂ (acetac) ₂ , 1760C ₅ H ₅ N (S)	0.42
13	NH ₃ (g) + 95H ₂ O (l)	8.26 ^b
14	H ₂ O (l) = H ₂ O (g)	-10.52 ^b
15	C ₅ H ₅ N (l) = C ₅ H ₅ N (g)	-9.66 ^c

(S) = solution. ^a Taken as 2.5 (Q, No. 6). "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards, Circular 500, 1952. ^c Andon, Cox, Herington, and Martin, *Trans. Faraday Soc.*, 1957, **53**, 1074.

TABLE 2. *Heats of the solvation reactions.*

Solvated complex	Combinations of Nos.	Q (kcal. mole ⁻¹)
UO ₂ (acetac) ₂ .H ₂ O	(10 + 12 - 11 - 14)	14.17 ± 0.10
UO ₂ (dimet) ₂ .H ₂ O	(1 + 6 - 2 - 14)	14.48 ± 0.20
UO ₂ (dimet) ₂ .2.5H ₂ O	(1 + 7 - 3 - 2.5 · 14)	32.38 ± 0.12
UO ₂ (dimet) ₂ .NH ₃	(1 + 13 + 8 - 9 - 5)	15.32 ± 0.74
UO ₂ (dimet) ₂ .C ₅ H ₅ N	(1 - 4 - 15)	20.53 ± 0.10

complex UO₂(dimet)₂ (dimet = dibenzoylmethanato) with a solution of the solvating molecule. This fact has allowed the use of pyridine as the solvent for the determination of the heats of solution, thus avoiding use of concentrated acids. The heats of solvation were calculated from the measured heats of solution in pyridine of the anhydrous complexes, solvated complexes, and solvate molecules respectively.

The calorimetric data obtained, and the necessary thermochemical data from the literature, are presented in Table 1. By combining these data, heats of formation (Table 2) of the solvates were obtained.

The heat of reaction between the bis(dibenzoylmethanato)uranyl complex and one mol. of water is 14.48 kcal. mole⁻¹, very close to those of the heats of addition of one mol. of water to uranyl nitrate or chloride dihydrate, which were found to be 13.3 and 14.4 kcal. mole⁻¹ respectively.⁴ Since it is generally recognised that in these compounds water is co-ordinated to the uranium,⁵ the results support the hypothesis that even in this bis-(β-diketonato)uranyl monohydrate water is attached directly by a U-O bond. The heat of reaction for the bis(acetylacetonato)uranyl complex with one mol. of water (14.17 kcal. mole⁻¹) is also very close to the above-mentioned values and in good agreement with that of Wendlandt *et al.*³ corrected for the heat of vaporisation of water (-13.74 kcal. mole⁻¹). The agreement between the heats of hydration of such different compounds is rather surprising when one considers that these heats differ from the bond strengths between the uranyl compounds and water by the difference ΔU between the lattice energies of either the anhydrous and the hydrated complex, or of the dihydrate and trihydrate of uranyl nitrate, respectively. In spite of the fact that very little is known of the lattice energies, particularly of non-ionic compounds, it appears that in the present cases the ΔU terms are either negligible or, at least, roughly equal.

⁴ Kapunstinskii and Baranova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1952, 1122 (*Chem. Abs.*, 1953, **47**, 4723).

⁵ Cf. Irving, *Quart. Rev.*, 1951, **5**, 208; Comyns, *Chem. Rev.*, 1960, **60**, 115.

The heat of addition of 2.5 mol. of water is 32.38 kcal. mole⁻¹ which is 2.2 times the heat of addition for only one mol. This seems to indicate that at least two of these water molecules are co-ordinated directly to the uranium.

The heat of solvation with one mol. of ammonia was found to be smaller than the heat of solvation with one mol. of pyridine. This is contrary to the usual order of basicity of the two ligands and also contrary to the findings for the corresponding solvates of the bis(acetylacetonato)uranyl complex. In fact, by making allowance for the heat of vaporisation of pyridine, the enthalpy changes for the addition of ammonia and pyridine to the bis(acetylacetonato)uranyl complex measured by Wendlandt *et al.*³ are $\Delta H_{\text{NH}_3} = -20.7$, $\Delta H_{\text{py}} = -18.32$ kcal. mole⁻¹.

Experimental.—The bis(diketonato)uranyl complexes and their solvates were prepared as described previously.^{1,2,3,6} The compounds were analysed for uranium gravimetrically after conversion into U₃O₈ at 900°. Nitrogen in the ammines and pyridinates was determined by the Dumas method. The pyridine was distilled over sodium in a Todd fractionating column.

The calorimeter, of the Oxford Pitzer type,⁷ was described in a previous paper.⁸ It was checked by determining the heat of solution of potassium chloride. In each experiment at least two electrical energy equivalents were determined; the reproducibility was usually better than 0.2%. The linear time-temperature relation was re-established 15–20 sec. after the bottle was opened. For each run the bottle was filled with a weighed amount of the uranyl complex (3–5 g.), water, or ammonia while the Dewar flask contained a weighed quantity (about 830 g.) of pyridine or a solution of the complex in pyridine. The accuracy of the weighings was ± 0.0002 g. for the solutes and ± 0.02 g. for the solvents. The heat values presented here are averages of at least three determinations. The experimental error was always <1.5%.

The spectra of the solutions 1 and 4; 2 and 6; 3 and 7; 5 and 8 (see Table 1) were measured in the 300–600 m μ range with a Beckman DU spectrophotometer. The spectra of each pair of solutions were found to be equal. All the solutions show three bands at 302, 338, and 402 m μ . The intensities vary slightly on passing from one solvated complex to another.

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FLORENCE, ITALY. [Received, January 30th, 1961.]

⁶ Biltz, *Z. anorg. Chem.*, 1904, **40**, 221.

⁷ Davies, Singer, and Staveley, *J.*, 1954, 2304.

⁸ Sacconi, Paoletti, and Ciampolini, *Ricerca sci.*, 1959, **29**, 2412.

829. *Suppression of 1,3-Diaxial Interaction in Methyl Reserpate during Alkaline Hydrolysis.*

By M. J. ALLEN.

THIS Note is an addendum to a previous publication¹ in which it was reported that methyl reserpate ($k = 1.39$) and methyl deserpidate ($k = 1.38$) underwent hydrolysis considerably faster than methyl isoreserpate ($k = 0.069$). This difference was attributed to the possibility that the conformation of the reserpate and deserpidate esters undergoing hydrolysis was such that all substitutions in ring E were axial. As a result it would be expected that a 1,3-diaxial interaction between the 18-hydroxyl and the 16-methoxy-carbonyl group would assist hydrolysis.

Further experimental evidence has been obtained which definitely confirms the effect of 1,3-diaxial interaction. Methyl reserpate 18-methyl ether² has been subjected to

¹ Allen, *J.*, 1960, 4904.

² Robison, Lucas, MacPhillamy, Barrett, and Plummer, *Experientia*, 1961, **17**, 14.

alkaline hydrolysis and the second-order rate constant obtained; this indicates that when the 18-hydroxyl is replaced by an 18-methoxyl group [structure (VII) cf. ref. 1] 1,3-diaxial interaction is considerably diminished.

Methyl reserpate 18-(tetrahydropyran-2-yl) ether² was also investigated. A spatial model of this compound shows that the only sterically unhindered configuration possible is that in which all substituents in ring E are equatorial [structure VI, cf. ref. 1]. This being the case, the rate of hydrolysis would be expected to be essentially the same as obtained for methyl isoreserpate.

Experimental.—The methyl and tetrahydropyran-2-yl ethers of methyl reserpate used were analytically pure; the alkaloids were supplied through the courtesy of Ciba Pharmaceutical Products, Inc. The alkaline dioxan solution used for the hydrolysis at $40^\circ \pm 0.5^\circ$ and the techniques used in the study were identical with those previously reported. The second-order rate constant was obtained from the equation

$$k = [2.303/t(a - b)] \log [b(a - x)/a(b - x)],$$

where a and b are the concentrations (in moles/l.) of the sodium hydroxide and the alkaloid, respectively, and t is the time (in minutes).

Methyl reserpate 18-methyl ether had $k = 0.346 \pm 0.013$; the 18-(tetrahydropyran-2-yl) ether had $k = 0.064 \pm 0.002$ l. mole⁻¹ sec.⁻¹.

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830. *The Structure of Sodium Hexafluoromolybdate(v).*

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ALTHOUGH much attention has been paid to the classification of complex fluorides from unit-cell dimensions,^{1,2} few structural determinations have been made. For quinquivalent ABF₆ compounds reported details are restricted to KRuF₆, RbRuF₆, and CsRuF₆,³ KOsF₆,⁴ KIrF₆,⁵ to KNbF₆ and KTaF₆,⁶ and NaSbF₆⁷ and KSbF₆.⁸

We here report a structure determination of sodium hexafluoromolybdate(v), NaMoF₆. This salt was chosen because the complex MoF₆⁻ ion is a regular octahedron in a simple environment, and hence the structure should provide a basis with which other structures and other properties of compounds in this part of the Periodic Table can be compared.

Experimental.—Sodium hexafluoromolybdate(v) was prepared by Hargreaves and Peacock's method.⁹ Powder samples for X-ray examination were sealed in thin-walled Pyrex capillaries under a vacuum. Photographs were taken with a 19 cm. cylindrical camera, using crystal reflected Cu-K_α radiation from a pentaerythritol monochromator. The multiple-film technique was used to obtain graded intensities, and duplicate films were examined with a Hilger microphotometer (type 451). Values of the integrated intensities in arbitrary units were obtained by measuring areas under the plotted photometer curves.

For any line on a powder photograph the intensity is given by:

$$I = \text{Constant} \cdot \frac{1 + \cos^2 2\alpha \cos^2 2\theta p''}{\sin^2 \theta \cos \theta} \cdot A \cdot F_{hkl}^2$$

¹ Cox, *J.*, 1956, 877.

² Wyckoff, "Crystal Structures," Interscience Publ., Inc., New York, Vol. I.

³ Weiss and Klemm, *Z. anorg. Chem.*, 1955, **279**, 74.

⁴ Hepworth, Jack, and Westland, *J. Inorg. Nuclear Chem.*, 1956, **2**, 79.

⁵ Westland, Ph.D. Thesis, Durham University, 1957.

⁶ Bode and Dohren, *Acta Cryst.*, 1958, **11**, 80.

⁷ Teufer, *Acta Cryst.*, 1956, **9**, 539.

⁸ Bode and Voss, *Z. anorg. Chem.*, 1951, **264**, 144.

⁹ Hargreaves and Peacock, *J.*, 1957, 4212.

where α is the angle of reflection in the monochromator and other symbols have their usual meaning.¹⁰ In calculating intensities the absorption correction was obtained from Bradley's values¹¹ (absorption coefficient = 220.4 cm.⁻¹). For the scattering factors the values of Berghuis *et al.*¹² were used for sodium and fluorine, and those of James and Brindley¹³ for molybdenum, quantities being taken for un-ionised atoms (cf. Gutmann and Jack¹⁴). The unit-cell dimension was calculated accurately by using the extrapolation function of Nelson and Riley.¹⁵

Observed X-ray reflections were indexed on a face-centred cubic unit cell, with side $a_0 = 8.194 \pm 0.002$ Å. The space group was assumed to be $Fm\bar{3}m$ (O_h^5 , No. 225), and good agreement between observed and calculated intensities was obtained by placing four molecules in the unit cell with atoms in the following positions: 4Mo in (a) at 0,0,0; 4Na in (b) at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; 24F in (e) at $\pm x, 0, 0$; $0, x, 0$; $0, 0, x$; where $x = 0.212 \pm 0.003$. The individual temperature factors, found by trial and error, were: $B_{Mo} = 2.7$; $B_{Na} = B_F = 4.7$ Å². Observed and calculated intensities are listed in Table 1. The structure is evidently closely related to that of NaSbF₆,⁷ and interatomic distances in both compounds are given in Table 2.

TABLE 1. *Relative intensities.*

Plane	I_c	I_o	Plane	I_c	I_o	Plane	I_c	I_o	Plane	I_c	I_o
111	402	405	422	104	145	620	98	88	731	31	} 84
200	629	587	333	3	} 177	533	36	49	553	47	
220	198	200	511	171		622	36	56	800	20	15
311	165	188	440	153	156	444	42	50	733	8	0
222	8	16	531	155	155	551	82	} 210	820	43	} 101
400	251	269	600	56	} 198	711	28		644	60	
331	37	79	442	132		640	102	} 117	822	23	} 55
420	370	362			642	102	660		28		

Some idea of the agreement between observed and calculated intensities can be obtained from the expression $\Sigma|I_o - I_c|/\Sigma I_o = 0.077$. The discrepancy factor $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ cannot be used because of the overlapping of the powder lines.

TABLE 2. *Dimensions (Å) of NaMoF₆ and NaSbF₆.*

	NaMoF ₆	NaSbF ₆ (ref. 7)
Unit cell size, a_0	8.194 ± 0.002	8.18(4)
M-F	1.74 ± 0.03	1.78
F-F	2.46 ± 0.03	2.52
Na-F	2.36 ± 0.03	2.31
x	0.212 ± 0.003	0.217

Discussion.—Sodium hexafluoromolybdate, like the hexafluoroantimonate, crystallises with a sodium chloride arrangement of sodium and regular MoF₆ groups. The observed Mo-F distance is shorter than either the sum of the ionic radii of Mo⁵⁺ and F⁻ (2.01 Å) or the sum of the covalent radii of Mo and F (2.08 Å). Notable too is the very short F-F distance which is about 0.26 Å shorter than the sum of the ionic radii (2.72 Å). Such values have been noted in the isostructural compound NaSbF₆, in KSbF₆, and in KOsF₆ and KIrF₆ where the shortest F-F distances are 2.48 Å and 2.47 Å respectively.

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¹⁰ International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, Vol. II, 1959, p. 237.

¹¹ Bradley, *Proc. Phys. Soc.*, 1935, **47**, 879.

¹² Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

¹³ James and Brindley, *Z. Krist.*, 1931, **78**, 470.

¹⁴ Gutmann and Jack, *Acta Cryst.*, 1951, **4**, 244.

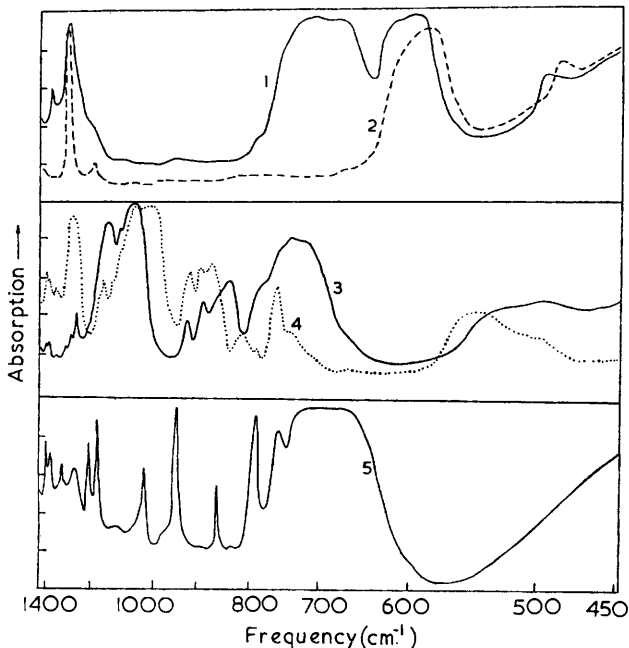
¹⁵ Nelson and Riley, *Proc. Phys. Soc.*, 1945, **57**, 160.

831. Structure of Phosphoryl Chloride-Boron Trichloride Complex.

By W. GERRARD, E. F. MOONEY, and H. A. WILLIS.

CERTAIN complexes of phosphoryl halides and metal halides (SnCl_4 , TiCl_4 , FeBr_2) were formulated by Sheldon and Tyree¹ showing oxygen as the donor atom [$\Delta\nu(\text{P}=\text{O})$ 55–90 cm^{-1} to lower frequency], whereas Greenwood and Wade² formulated the corresponding gallium compound as $[\text{POCl}_2]^+[\text{GaCl}_4]^-$. It was postulated³ that the boron trichloride complex had a similar constitution, $[\text{POCl}_2]^+[\text{BCl}_4]^-$ (I), with which we concur, on the basis of an infrared spectroscopic study.

If the complex were $\text{Cl}_3\text{P}=\text{O} \rightarrow \text{BCl}_3$ (II) as designated by Waddington and Klanberg,⁴ we should expect a considerable shift ($\sim 100 \text{ cm}^{-1}$) of the $\text{P}=\text{O}$ stretching mode to lower



Infrared spectra of (1) phosphoryl chloride-boron trichloride in Nujol mull, (2) phosphoryl chloride as film, (3) tri-n-propyl phosphate-boron trichloride as film, (4) tri-n-propyl phosphate as film, and (5) ethylammonium tetrachloroborate.

frequency, as found in the complexes POCl_3MX_4 ¹ and $(\text{PhO})_3\text{P}=\text{O},\text{BX}_3$.³ For structure (I) no more than a small shift is expected, because the phosphoryl-oxygen atom is now not a donor atom. In structure (II) the asymmetric B-Cl stretching bands would show a characteristic BCl_3 "envelope" which commences at 815 cm^{-1} ,⁵ whereas structure (I) would give the equally characteristic tetrachloroborate "envelope" commencing at 780 cm^{-1} .⁵ We prefer to consider the envelopes as diagnostic of the " BCl_3 " or " BCl_4 " structure, because the band system is in each case complex, being composed of the asymmetric B-Cl stretching mode (ν_3) and the combination from the symmetric B-Cl stretching and the B-Cl deformation modes ($\nu_1 + \nu_4$). Also both these bands show isotopic splitting from the ^{10}B Cl and ^{11}B Cl modes. Consequently, although it is difficult to locate

¹ Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775; 1959, **81**, 2290.

² Greenwood and Wade, *J.*, 1957, 1516.

³ Frazer, Gerrard, and Patel, *J.*, 1960, 726.

⁴ Waddington and Klanberg, *J.*, 1960, 2339.

⁵ Gerrard, Hudson, and Mooney, *J.*, 1960, 5168.

the band maxima with precision, there is no difficulty in locating the origin of the envelopes.

The spectrum (see Figures) obtained in the present work showed only a small shift of the P=O stretching frequency, which is in agreement with earlier observations,^{3,4} and shows the typical BCl₄ "envelope." These observations are consistent with structure (I). Waddington and Klanberg⁴ do not refer to a BCl "envelope" as such, but specify the ν_3 and $\nu_1 + \nu_4$ bands at 700 and 667 cm.⁻¹. From Table 4 of their paper⁴ these bands are consistent with the BCl₄ modes rather than the co-ordinated BCl₃ modes which are quoted as occurring at 757 and 715 cm.⁻¹.

Further evidence of the presence of the [POCl₂]⁺ ion is obtained from the P-Cl stretching frequencies, which now occur slightly higher (588 and 490 cm.⁻¹) than in phosphoryl chloride (578 and 483 cm.⁻¹); this is consistent with the change in hybridisation from the tetrahedral configuration of phosphoryl chloride to the planar configuration occurring in the [POCl₂]⁺ ion. This is analogous to the shifts of the B-Cl modes observed between the partially tetrahedral -BCl₃ in a co-ordination complex and the planar -BCl₂ in a boron dichloride. The 1190 cm.⁻¹ band assigned⁴ to the B-O stretching mode was not evident in the present work. The structure of phosphoryl chloride-boron trichloride can now be designated oxodichlorophosphorus tetrachloroborate (I).

Experimental.—The phosphoryl chloride-boron trichloride complex was prepared by the method of Frazer, Gerrard, and Patel³ and recrystallised from light petroleum (b. p. 30–40°) (Found: B, 4.1; Cl, 78.5. Calc. for BCl₃OP: B, 4.0; Cl, 78.6%). The spectra were recorded for Nujol mulls or liquid films between potassium chloride windows on Perkin-Elmer 137 spectrometers fitted with rock salt and potassium bromide optics; the calibration was checked by using polystyrene⁶ and 1,2,4-trichlorobenzene.

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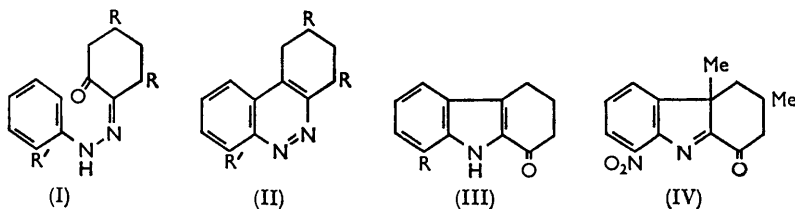
⁶ Plyler, Danti, Blaine, and Tidwell, *J. Res. Nat. Bur. Stand.*, 1960, **64**, 29.

832. Attempts to Prepare 1,2,3,4-Tetrahydro-9,10-diazaphenanthrenes from Cyclohexane-1,2-dione Monophenylhydrazones.

By ROSEMARY A. SOUTTER and MURIEL TOMLINSON.

MOORE¹ outlined a method for the conversion of cyclohexane-1,2-dione monophenylhydrazones (I) into tetrahydro-9,10-diazaphenanthrenes (II) by treatment with sulphuric acid: no exact conditions were described but he stated that the method is more convenient than the others available. We wanted nitro-compounds such as (II; R' = NO₂) for intermediates in the preparation of triazaphenanthrenes and so we decided to reinvestigate this method. Accordingly a wide range of conditions for this type of reaction was explored. Moore's claim that 3,5-dimethylcyclohexane-1,2-dione 2-phenylhydrazone (I; R = Me, R' = H) affords a high yield of 1,2,3,4-tetrahydro-1,3-dimethyl-9,10-diazaphenanthrene (II; R = Me, R' = H) with sulphuric acid was confirmed and we found that with polyphosphoric acid the yield was only 10%. Our yield of 1,2,3,4-tetrahydro-9,10-diazaphenanthrene (II; R = R' = H) from cyclohexane-1,2-dione monophenylhydrazone was even smaller than the 15% described by Moore: here with both sulphuric acid and polyphosphoric acid 1,2,3,4-tetrahydro-1-oxocarbazole (III; R = H) was the main product. The *o*-nitrophenylhydrazones of both cyclohexane-1,2-dione (I; R' = NO₂, R = H) and 3,5-dimethylcyclohexane-1,2-dione (I; R' = NO₂, R = Me) gave the corresponding tetrahydro-oxocarbazole (III; R = NO₂) and oxocarbolenine (IV) with polyphosphoric acid: with sulphuric acid the former (I; R' = NO₂, R = H) was converted into cyclohexane 1,2-dione bis-*o*-nitrophenylhydrazone but no pure compound was isolated from

¹ Moore, *Nature*, 1949, **163**, 918.



the latter (I; $R' = \text{NO}_2$, $R = \text{Me}$). It is therefore unlikely that this would form a suitable route for the preparation of the compounds we required.

Polymorphism was encountered in both the *o*-nitrophenylhydrazones.

Experimental.—*3,5-Dimethylcyclohexane-1,2-dione 2-phenylhydrazone.* A mixture of *cis*-3,5-dimethylcyclohexanone (12.5 g.) and ethyl formate (8 g.) in dry ether (20 ml.) was slowly added to sodium wire (2.3 g.) under ether. Next day any remaining sodium was destroyed with ethanol and the sodioformyldimethylcyclohexanone was dissolved in water (80 ml.). The aqueous layer was brought to pH 7 with acetic acid and immediately treated with a filtered solution of benzenediazonium sulphate [from aniline (8 g.) in water (25 ml.) and sulphuric acid (13 ml.)] which had been brought to pH 4–5 with 15% aqueous sodium hydroxide. The phenylhydrazone separated as a red oil which was extracted with chloroform. After removal of the solvent, the product (which solidified) was purified by chromatography in benzene on deactivated alumina, and 3,5-dimethylcyclohexan-1,2-dione 2-phenylhydrazone was obtained as red prisms (from methanol), m. p. 60–61° (Moore gives m. p. 58–59°) (Found: C, 73.1; H, 7.8. Calc. for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}$: C, 73.1; H, 7.8%). If the diazonium solution was neutral or alkaline the main product was 2,4-dimethyl-5,6-dioxoheptanoic acid 5-phenylhydrazone which formed yellow prisms, m. p. 130–133° (Found: C, 65.4; H, 7.3; N, 10.2. $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_3$ requires C, 65.2; H, 7.2; N, 10.1%). The latter product formed a *semicarbazone*, m. p. 201–204° (from aqueous alcohol) (Found: C, 58.4; H, 7.2; N, 20.6. $\text{C}_{16}\text{H}_{22}\text{N}_5\text{O}_3$ requires C, 57.7; H, 6.9; N, 21.1%).

Cyclohexane-1,2-dione o-nitrophenylhydrazone. (a) This was prepared, as above, from cyclohexanone (40 g.) and *o*-nitroaniline (46 g.) diazotised in sulphuric acid (135 ml.) and water (300 ml.). The diazonium solution (at pH 4–5) was filtered into the formylcyclohexane solution and *cyclohexane-1,2-dione o-nitrophenylhydrazone* separated as a mixture of yellow solid and red liquid which solidified completely in contact with alcohol. Chromatography in benzene–light petroleum (b. p. 60–80°) on deactivated alumina afforded first yellow needles, and then a mixture of these together with red prisms. Recrystallisation from ethanol, glacial acetic acid, or light petroleum gave mixtures of both types of crystal. The two forms were finally obtained as red prisms, m. p. 149–153°, and yellow needles, m. p. 130–134.5° (both from alcohol) [Found (prisms): C, 57.8; H, 5.2; N, 17.1; (needles) C, 57.8; H, 4.7. $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_3$ requires C, 58.3; H, 5.3; N, 17.0%]. With phenylhydrazine it gave *cyclohexane-1,2-dione o-nitrophenylhydrazone phenylhydrazone*, red prisms, m. p. 170–173° (from alcohol) (Found: C, 64.1; H, 5.6; N, 20.6. $\text{C}_{18}\text{H}_{19}\text{N}_5\text{O}_2$ requires C, 64.2; H, 5.7; N, 20.6%). When the coupling with *o*-nitrobenzenediazonium chloride was done at pH > 7 the main product was *cyclohexane-1,2-dione o-hydroxyphenylhydrazone* which formed brown prisms (from alcohol), m. p. 169° (decomp.) (Found: C, 66.0; H, 6.3; N, 12.8. $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$ requires C, 66.1; H, 6.5; N, 12.8%).

(b) A mixture of cyclohexane-1,2-dione (1.0 g.) and *o*-nitrophenylhydrazine (0.5 g.) in ethanol (30 ml.) was seeded with the above mono-*o*-nitrophenylhydrazone and the solvent was removed slowly without heating. Chromatography of the product, in benzene, on alumina gave, first, a little *cyclohexane-1,2-dione bis-o-nitrophenylhydrazone*, red needles, m. p. 181–184° (from alcohol), identical with that prepared from the mono-*o*-nitrophenylhydrazone and *o*-nitrophenylhydrazine (Found: C, 57.0; H, 4.8. $\text{C}_{18}\text{H}_{18}\text{N}_6\text{O}_4$ requires C, 56.6; H, 4.8%), and then a mixture of the needle and the prism form of the above mono-*o*-nitrophenylhydrazone.

3,5-Dimethylcyclohexane-1,2-dione 2-o-nitrophenylhydrazone was prepared from 2-formyl-3,5-dimethylcyclohexanone and *o*-nitrobenzenediazonium chloride. It formed orange prisms, m. p. 146° (the m. p. was not sharp and a yellow needle form had m. p. 112–113°) (Found: C, 61.1; H, 6.2; N, 15.4. $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_3$ requires C, 61.2; H, 6.2; N, 15.3%). With *o*-nitrophenylhydrazine in boiling alcohol containing a little hydrochloric acid it gave red needles

of the *bis-o-nitrophenylhydrazone*, m. p. 185—186° (from ethyl acetate) (Found: C, 58.7; H, 5.6; N, 20.4. $C_{20}H_{22}N_6O_4$ requires C, 58.5; H, 5.4; N, 20.2%).

Cyclisation of cyclohexane-1,2-dione monophenylhydrazone. (a) The hydrazone (2.0 g.) in sulphuric acid (6 ml.) was kept at 60° for 5 min. and then poured into ice-water. The resulting solution was made alkaline with aqueous ammonia and extracted with ether. The solid, recovered from the ether, afforded 1,2,3,4-tetrahydro-9,10-diazaphenanthrene (0.1 g.), yellow needles, m. p. 93—97° (from light petroleum) (Moore gives m. p. 98°).

(b) The phenylhydrazone (6.0 g.) was added to phosphoric acid (20 ml.; *d* 1.75) containing phosphorus pentoxide (24 g.), and the mixture was kept at 80° for 30 min. Dilution with water precipitated 1,2,3,4-tetrahydro-1-oxocarbazole, m. p. 160—164°, raised to 165° by recrystallisation from water; and from the filtrate (basified with ammonia) there was obtained 1,2,3,4-tetrahydro-9,10-diazaphenanthrene (0.3 g.), m. p. 98° (from light petroleum).

Cyclisation of 3,5-dimethylcyclohexane-1,2-dione 2-phenylhydrazone. (a) A solution, made by dissolving the hydrazone (5.0 g.) in concentrated sulphuric acid (15 ml.) at room temperature, was poured on ice, basified with aqueous ammonia, and extracted with ether. The yellow solid (3.5 g.), recrystallised from light petroleum (b. p. 60—80°), gave 1,2,3,4-tetrahydro-1,3-dimethyl-9,10-diazaphenanthrene, m. p. 109.5—111° (Moore gives 111°) (Found: C, 79.3; H, 7.6. Calc. for $C_{14}H_{16}N_2$: C, 79.2; H, 7.5%).

(b) The hydrazone (2.5 g.) in polyphosphoric acid (as above) kept at 80° for 5 min. gave the diazaphenanthrene (0.2 g.).

Cyclisation of cyclohexane-1,2-dione o-nitrophenylhydrazone. (a) A solution of the hydrazone (2 g.) in sulphuric acid (6 ml.) was diluted with ice-water, basified with aqueous ammonia, and extracted with ether. The solid recovered from the ether and chromatographed in benzene on deactivated alumina afforded cyclohexane-1,2-dione bis-*o*-nitrophenylhydrazone, m. p. 181—183°.

(b) The above sulphuric acid solution, kept at 100° for 5 min., gave 1,2,3,4-tetrahydro-8-nitro-1-oxocarbazole, needles, m. p. 195—197° (from alcohol) (Found: C, 62.7; H, 4.5; N, 11.9. $C_{12}H_{10}N_2O_3$ requires C, 62.6; H, 4.3; N, 12.2%).

(c) The hydrazone (2 g.) in phosphoric acid (13 ml.; *d* 1.75) with phosphorus pentoxide (15 g.) was heated to 100° and then decomposed with ice. 1,2,3,4-Tetrahydro-8-nitro-1-oxocarbazole (1.1 g.) was precipitated. Basification of the filtrate gave a little more of the same compound.

1,2,3,4-Tetrahydro-3,11-dimethyl-8-nitro-1-oxocarbazolenine. 3,5-Dimethylcyclohexane-1,2-dione 2-*o*-nitrophenylhydrazone (4.0 g.) with phosphoric acid (35 ml.; *d* 1.75) and phosphorus pentoxide (40 g.) was kept at 100° for 30 min. and the solution was then decomposed with ice. The brown solid so precipitated was extracted with chloroform, and the material thus extracted was chromatographed on deactivated alumina in benzene-light petroleum. The main product was 1,2,3,4-tetrahydro-3,11-dimethyl-8-nitro-1-oxocarbazolenine (0.7 g.) which separated from ethanol as orange plates, m. p. 156° (Found: C, 65.0; H, 5.3; N, 10.9. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.4; N, 10.8%).

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833. Some Derivatives of 2,7-Dihydroxynaphthalene.

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A DINITRO-DERIVATIVE of 2,7-dihydroxynaphthalene was described by Kaufler and Bräuer,¹ and a dinitro-derivative of 2,7-dimethoxynaphthalene by Fischer and Kern.² Both were assumed to be 1,8-dinitro-derivatives but since Wilson,^{3,4} and Cooke, Johnson, and Owen⁵ have shown that the dibromination of 2,7-dihydroxy- and 2,7-dimethoxy-naphthalene occurs mainly in the 1- and 6-positions, with a minor amount of 1,3-substitution, it appeared desirable to orient the nitro-compounds definitely.

¹ Kaufler and Bräuer, *Ber.*, 1907, **40**, 3269.

² Fischer and Kern, *J. prakt. Chem.*, 1916, **94**, 34.

³ Wilson, *Tetrahedron*, 1958, **3**, 236.

⁴ Wilson, *Tetrahedron*, 1960, **11**, 256.

⁵ Cooke, Johnson, and Owen, *Austral. J. Chem.*, 1960, **13**, 256.

The dinitro-2,7-dimethoxynaphthalene was readily obtained and reduced to the corresponding diamine,⁶ which had the properties of a typical 1,8-diamine as shown by its reaction with acetone and carbon disulphide.⁷ The previously assumed orientation is therefore proved. On the other hand it was not found possible to repeat the preparation of the dinitro-2,7-dihydroxynaphthalene. Under modified conditions a tetranitro-derivative was isolated, which could be converted into a tetranitro-2,7-dimethoxynaphthalene. Tetrasubstituted products were obtained also by the nitration of 1-bromo- and 1,6-dibromo-2,7-dihydroxynaphthalene and tribromo-2,7-dimethoxynaphthalene.

1-Chloro-2,7-dimethoxynaphthalene on nitration gave the same compound as that obtained by the chlorination of 2,7-dimethoxy-1-nitronaphthalene; it must, therefore, be the 1,8-derivative. Similarly, 1-bromo-2,7-dimethoxynaphthalene on nitration gave the same compound as given by 2,7-dimethoxy-1-nitronaphthalene on bromination; it must be the 1-bromo-8-nitro-derivative.

Experimental.—2,3-Dihydro-4,9-dimethoxy-2,2-dimethylperimidine. 1,8-Diamino-2,7-dimethoxynaphthalene (0.2 g.) was dissolved in boiling acetone (5 c.c.) and the solution left overnight. The *perimidine* crystallised as scarlet needles (0.18 g.), m. p. 271—273° (decomp.) (Found: C, 69.5; H, 6.9. $C_{15}H_{18}N_2O_2$ requires C, 69.8; H, 7.0%).

2,3-Dihydro-4,9-dimethoxy-2-thio*perimidine*. 1,8-Diamino-2,7-dimethoxynaphthalene (0.2 g.) was dissolved in ethanol (10 c.c.), and carbon disulphide (1 c.c.) was added. The mixture was boiled for 5 min. and on cooling the *perimidine* crystallised as golden plates, m. p. 218—220°, in almost quantitative yield (Found: C, 60.3; H, 4.6. $C_{13}H_{12}N_2O_2S$ requires C, 60.0; H, 4.6%).

Nitration of 2,7-dihydroxynaphthalene. The process of Kaufler and Bräuer¹ in our hands yielded only resin. Of the many modifications tried only the following led to a crystalline compound. Fuming nitric acid (10 c.c.) was added dropwise to the compound (2 g.) in acetic acid (100 c.c.). After about 1 hr. yellow crystals began to separate (sometimes very slight dilution was necessary to induce crystallisation). These, after recrystallisation from acetic acid, gave the *tetranitro-derivative* (0.5 g.) as needles, m. p. 227° (explosive decomp.) (Found: C, 35.6; H, 1.2. $C_{10}H_4N_4O_{10}$ requires C, 35.5; H, 1.2%). This was methylated, by methyl sulphate in boiling xylene solution in the presence of potassium carbonate, to a *tetranitro-2,7-dimethoxynaphthalene*, which crystallised from acetic acid as straw-coloured needles, m. p. 268° (Found: C, 39.1; H, 1.94. $C_{12}H_8N_4O_{10}$ requires C, 39.0; H, 2.17%).

Nitration of 1-bromo-2,7-dihydroxynaphthalene. Fuming nitric acid (1.5 c.c.) in acetic acid (1.5 c.c.) was added to the compound (1 g.) in acetic acid (10 c.c.). As crystallisation did not occur the mixture was poured into water, and the precipitate was crystallised from acetic acid. A *trinitro-derivative* was obtained as a yellow powder, m. p. 197° (decomp.) (Found: C, 31.8; H, 1.1. $C_{10}H_4BrN_3O_8$ requires C, 32.1; H, 1.1%).

Nitration of 1,6-dibromo-2,7-dihydroxynaphthalene. Prepared as for the 1-bromo-compound (above), the product (1.3 g. from 3 g.) was crystallised from acetone to give a crude *dinitro-derivative* as yellow crystals, m. p. 207° (decomp.) (Found: C, 30.1; H, 1.4. $C_{10}H_3Br_2NO_6$ requires C, 29.4; H, 1.0%). Further recrystallisation failed to raise the m. p. or improve the analytical figures.

Nitration of 1,3,6-tribromo-2,7-dimethoxynaphthalene. Fuming nitric acid (3 c.c.) in acetic acid (6 c.c.) was added to a warm suspension of the compound (1.5 g.) in acetic acid (15 c.c.). On cooling, the clear solution deposited red crystals, m. p. ca. 220°, which after recrystallisation from acetic acid gave the *mononitro-derivative* (0.3 g.) as red needles, m. p. 222—224° (Found: C, 30.9; H, 1.6. $C_{12}H_5Br_3NO_4$ requires C, 30.7; H, 1.7%).

1-Bromo-2,7-dimethoxy-8-nitronaphthalene. (a) Bromine (1 mol.) was added to a solution of 2,7-dimethoxy-1-nitronaphthalene² in hot chloroform. The mixture was boiled for a few minutes to expel hydrogen bromide, and then diluted with light petroleum. The product, after recrystallisation from acetic acid, formed prisms, m. p. 172—174° (Found: Br, 25.9; N, 4.3. $C_{12}H_{10}BrNO_4$ requires Br, 25.6; N, 4.5%).

(b) Concentrated nitric acid (0.5 c.c.) in acetic acid (1 c.c.) was added to a warm solution

⁶ Chakravarti and Pasupati, *J.*, 1937, 1859.

⁷ Klamann and Kramer, *Chem. Ber.*, 1960, **93**, 2320.

of 1-bromo-2,7-dimethoxynaphthalene (0.5 g.) in acetic acid (5 c.c.). The liquid almost immediately filled with pale yellow prisms, m. p. 165—172°, raised to 172—174° after one recrystallisation from acetic acid. Dr. D. M. W. Anderson kindly confirmed the identity of the infrared spectra of the two samples.

Interaction of 1-bromo-2,7-dimethoxy-8-nitronaphthalene with nitric acid. The compound was introduced slowly into fuming nitric acid, whereupon a permanganate colour developed initially. The resultant solution was poured into water, and the orange precipitate recrystallised from acetic acid to yield trinitro-2,7-dimethoxynaphthalene, m. p. 216°, alone or mixed with an authentic sample.² The bromine atom had been replaced by a nitro-group.

1-Chloro-2,7-dimethoxynaphthalene. Treatment of 2,7-dimethoxynaphthalene in chloroform with chlorine (1 mol.) led to a troublesome mixture of mono- and dichloro-derivatives. Sulphuryl chloride (3.8 g.) in chloroform (3 c.c.) was added dropwise to a solution of 2,7-dimethoxynaphthalene (5 g.) in chloroform (3.0 c.c.). The mixture was concentrated to small bulk and diluted with light petroleum to precipitate the impure dichloro-derivative (0.7 g.). The filtrate on further dilution yielded the almost pure 1-chloro-derivative, which formed needles (3.0 g.), m. p. 58—60°, from methanol (Found: C, 64.5; H, 5.1. C₁₂H₁₁ClO₂ requires C, 64.7; H, 4.9%).

1-Chloro-2,7-dimethoxy-8-nitronaphthalene. (a) Concentrated nitric acid (1 c.c.) in acetic acid (2 c.c.) was added to a warm solution of 1-chloro-2,7-dimethoxynaphthalene (1 g.) in acetic acid (10 c.c.). The solution immediately filled with a mass of needles, m. p. ca. 150°, which after recrystallisation from acetic acid gave the 8-nitro-derivative as yellow needles, m. p. 160—162° (Found: C, 54.3; H, 3.5. C₁₂H₁₀ClNO₄ requires C, 53.9; H, 3.7%). (b) Sulphuryl chloride (1 mol.) was added to 2,7-dimethoxy-1-nitronaphthalene in chloroform. The mixture was warmed and finally concentrated; the crystals (75%) which separated were identical with those obtained under (a).

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834. Reduction of Iodonitrobenzenes.

By BRIAN T. NEWBOLD.

In the present work, *o*-, *m*-, and *p*-iodonitrobenzene have been reduced with potassium hydroxide and ethanol. In early studies,¹ Gabriel reduced *m*-iodonitrobenzene and *p*-iodonitrobenzene with alcoholic potassium hydroxide and obtained the corresponding azoxybenzenes; he reported that alcoholic potassium hydroxide caused *o*-iodonitrobenzene to decompose easily with loss of iodine, and therefore doubted that 2,2'-di-iodoazoxybenzene could be prepared from *o*-iodonitrobenzene by this means. In the present study, attempts were made to reduce *o*-iodonitrobenzene in this way but the only product isolated was azoxybenzene in ~1% yield: this can be explained if the *o*-iodonitrobenzene decomposes with loss of iodine and the nitrobenzene obtained is then reduced to azoxybenzene. In studies of the reduction of *m*-iodonitrobenzene with alcoholic potassium hydroxide, the only product isolated was 3,3'-di-iodoazoxybenzene. Similar reduction of *p*-iodonitrobenzene gave 4,4'-di-iodoazoxybenzene as the main product, with some *p*-iodoaniline.

In other work, *o*-, *m*-, and *p*-iodonitrobenzene were reduced with zinc dust and sodium hydroxide, by essentially the method employed by Badger *et al.*² *o*-Iodonitrobenzene gave azobenzene in 66% yield, whereas *m*-iodonitrobenzene was reduced to 3,3'-di-iodoazobenzene and a small amount of azobenzene. In contrast, reduction of *p*-iodonitrobenzene gave only azobenzene, but in high yield (82%). The de-iodination could have occurred before or after formation of the azoxy-linkage. Cook and Jones³ reported that 2,2'-di-iodoazoxybenzene was converted into azobenzene by the mild reducing agent, sodium

¹ Gabriel, *Ber.*, 1876, **9**, 1405.

² Badger, Buttery, and Lewis, *J.*, 1953, 2143.

³ Cook and Jones, *J.*, 1939, 1311.

amalgam. We find that our reagent, zinc dust and sodium hydroxide, converts both 2,2'- and 4,4'-di-iodoazoxybenzene into azobenzene.⁴ Further work on this aspect is being carried out.

Experimental.—Reductions with potassium hydroxide and ethanol. (a) *o*-Iodonitrobenzene. To *o*-iodonitrobenzene (5 g.) in ethanol (60 ml.) was added potassium hydroxide (8 g.), and the mixture was refluxed for 30 min. Steam-distillation gave a yellow distillate which was acidified with hydrochloric acid and filtered. After cooling overnight, the filtrate gave a yellowish-brown residue, which yielded azoxybenzene, m. p. and mixed m. p. 33—33.5°, from aqueous ethanol (0.018 g., 1.1%). No amine was found when the acid filtrate was made alkaline with sodium hydroxide, and the residue yielded only tar.

(b) *m*-Iodonitrobenzene. *m*-Iodonitrobenzene (10 g.) in ethanol (100 ml.) was refluxed with potassium hydroxide (16 g.) for 1 hr. The mixture was then treated as above. No recovered *m*-iodonitrobenzene or *m*-iodoaniline was obtained. The residue left after steam-distillation was extracted with boiling benzene, and the extract cooled and evaporated to give 3,3'-di-iodoazoxybenzene (5.9 g., 60%) which recrystallized from ethanol-benzene as yellow needles, m. p. and mixed m. p. 120—121° (lit.,⁵ 120.5—121.5°).

(c) *p*-Iodonitrobenzene. Reaction as in (b) gave *p*-iodoaniline, needles (from aqueous ethanol), m. p. 62—62.5° (lit., m. p. 62.8°) (0.91 g., 10%) (acetyl derivative, m. p. 183—184°; lit., m. p. 183—184°). The residue left after steam-distillation was boiled with ethanol-benzene which extracted 4,4'-di-iodoazoxybenzene (6.1 g., 62%), plates (from benzene), m. p. and mixed m. p. 199—200° (lit., m. p. 198,⁵ 199.5°¹).

Reductions with zinc dust and sodium hydroxide. (a) *o*-Iodonitrobenzene. To *o*-iodonitrobenzene (5 g.) in ethanol (12 ml.) was added sodium hydroxide (3 g.) in water (3 ml.), and then zinc dust (7 g.) in small portions. The mixture was refluxed for 2 hr. Steam-distillation gave a distillate which on being acidified with hydrochloric acid and cooled overnight, gave an orange product, m. p. 67—69° (0.14 g.). The non-volatile residue was extracted with boiling ethanol several times to give an extract which, on cooling and dilution with water, yielded an orange product, m. p. 67—69° (0.86 g.). Both products were azobenzene (mixed m. p.; with peracetic acid gave azoxybenzene, m. p. and mixed m. p. 34—35°).

(b) *m*-Iodonitrobenzene. Reduction as above gave (from the steam-distillate) azobenzene, m. p. and mixed m. p. 68—70° (0.004 g., 0.26%), and (by extraction with ethanol-benzene) 3,3'-di-iodoazobenzene (from ethanol-acetic acid), m. p. and mixed m. p. 150—151° (lit.,¹ 150°) (1.68 g., 39%).

(c) *p*-Iodonitrobenzene. *p*-Iodonitrobenzene (10 g.) was reduced in the same way except that the mixture was not steam distilled. The residue was extracted with ethanol, and air was passed through the extract for several hours to oxidize any hydrazobenzene. Dilution of the extract with water gave azobenzene (2.50 g., 82%) that, recrystallized from ethanol-benzene, had m. p. and mixed m. p. 67—68°.

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⁴ Unpublished results.

⁵ Gore and Wheeler, *J. Amer. Chem. Soc.*, 1956, **78**, 2160.

835. *The Formation of a Substituted Biphenylene by an Ullmann Reaction.*

By J. F. CORBETT and P. F. HOLT.

FOR other work we required 2,2'-dibromo-4,4'-dimethyl-6,6'-dinitrobiphenyl. Yuan and Tsao¹ reported that treatment of 3-bromo-4-iodo-5-nitrotoluene with copper, in the absence of a solvent, gave 3-bromo-5-nitrotoluene as the only isolable product, but that in boiling nitrobenzene our desired biaryl was formed, though in poor yield.

Kornblum and Kendall² recommended dimethylformamide as solvent for Ullmann

¹ Yuan and Tsao, *J. Chinese Chem. Soc.*, 1935, **3**, 358.

² Kornblum and Kendall, *J. Amer. Chem. Soc.*, 1952, **74**, 5782.

reactions with reactive halides. Our experience with a variety of *o*-halogenonitro-compounds³ prompted us to use it for the present purpose. 3,4-Dibromo-5-nitrotoluene with copper bronze in refluxing dimethylformamide gave in 6 hours none of the biaryl but yielded 40% of a dimethyldinitrobiphenylene with a small quantity of 3-bromo-5-nitrotoluene. Similar treatment of 3-bromo-4-chloro-5-nitrotoluene, but with refluxing for 16 hr., gave only 6% of the biphenylene, and 85% of the starting material was recovered. By contrast, 3-bromo-4-iodo-5-nitrotoluene gave 58% of the biaryl, 2.5% of the biphenylene, and 3% of 3-bromo-5-nitrotoluene. The biphenylene must be either the 3,6-dimethyl-1,8-dinitro- or the 3,7-dimethyl-1,5-dinitro-compound.

The formation of a biphenylene under the conditions of the Ullmann reaction has not previously been reported, but Ward and Pearson⁴ recently obtained a small yield of 2,3:6,7-dibenzobiphenylene by the action of copper bronze on 2-bromo-3-iodonaphthalene in boiling dimethylformamide; they reported that similar treatment of *o*-bromiodobenzene gave only biphenyl. They suggested that a naphthylene intermediate was involved in the formation of their compound. The formation of a benzyne intermediate would explain the present results if it were assumed that its formation was slow compared with that of the biaryl by a normal Ullmann reaction, in the case of the more reactive iodo-compound, but fast in the case of the bromo- and chloro-compounds. In support it is noted that the biaryl is not an intermediate in the formation of the biphenylene derivative and that halogen atoms *meta*- to a nitro-group are normally unreactive under the conditions employed.² 2,5-Dibromonitrobenzene gives an excellent yield of 4,4'-dibromo-2,2'-dinitrobiphenyl under these conditions (unpublished work).

Experimental.—*Dihalogenonitrotoluenes.* 2-Bromo-4-methyl-5-nitroaniline,⁵ in acetic acid, was added to a solution of sodium nitrite (1.1 mol.) in sulphuric acid. The resulting solution was poured into a solution of cuprous chloride in hydrochloric acid, cuprous bromide in hydrobromic acid, or saturated aqueous potassium iodide. After $\frac{1}{2}$ hr., water was added and the crude product was filtered off and recrystallised from ethanol.

3-Bromo-4-chloro-5-nitrotoluene formed pale yellow needles (from ethanol), m. p. 60° (Found: C, 33.5; H, 2.1; Halogen, 45.7. $C_7H_5BrClNO_2$ requires C, 33.6; H, 2.1; Halogen, 46.0%).

3,4-Dibromo-5-nitrotoluene formed yellow blades (from ethanol), m. p. 65° (lit., m. p. 63—65°).

3-Bromo-4-iodo-5-nitrotoluene formed orange-yellow clusters (from ethanol), m. p. 78° (lit., m. p. 82—83°).

The Ullmann reactions. The following general method was employed. The 3-bromo-4-halogeno-5-nitrotoluene was refluxed with copper bronze (4 g.-atoms/mole) in dimethylformamide (15 ml. per g. of nitro-compound). The mixture was filtered while hot and the filtrate was concentrated and allowed to cool. The dimethyldinitrobiphenylene was filtered off and recrystallised from benzene. The dimethylformamide mother-liquor was poured into water, and the precipitate was filtered off, dried, and extracted with boiling benzene. The extract, on cooling, gave a further crop of the dimethyldinitrobiphenylene. The mother-liquor therefrom was evaporated and the residue was extracted with light petroleum to remove halogenonitrotoluenes. The extract was chromatographed on alumina, and the eluate set aside to crystallise. The material insoluble in light petroleum recrystallised from ethanol, to give 2,2'-dibromo-4,4'-dimethyl-6,6'-dinitrobiphenyl and/or an orange oil.

3,4-Dibromo-5-nitrotoluene (5.1 g.) gave, after 6 hours' refluxing, 3,6(7?)-dimethyl-1,8(5?) dinitrobiphenylene (0.97 g.) as bright yellow needles, m. p. 302° [Found: C, 62.1; H, 3.67; N, 10.4%; *M* (Rast), 293. $C_{14}H_{10}N_2O_4$ requires C, 62.2; H, 3.71; N, 10.4%; *M*, 270], λ_{max} . (log ϵ), 224 (4.6); 286 (4.0); 421 (3.93), and 3-bromo-5-nitrotoluene, m. p. and mixed m. p. 83° (lit., m. p. 83°).

3-Bromo-4-chloro-5-nitrotoluene (4 g.) gave the dimethyldinitrobiphenylene (0.12 g.) and the starting material (3.5 g.), m. p. and mixed m. p. 60°.

³ Corbett and Holt, *J.*, 1960, 3646, and unpublished work; Braithwaite and Holt, *J.*, 1959, 3025.

⁴ Ward and Pearson, *J.*, 1961, 515; Pearson, *Chem. and Ind.*, 1960, 899.

⁵ Carlin and Foltz, *J. Amer. Chem. Soc.*, 1956, 78, 1992.

3-Bromo-4-iodo-5-nitrotoluene (12.7 g.) gave, after 6 hr., the dimethyldinitrobiphenylene (0.12 g., 2.5%), 2,2'-dibromo-4,4'-dimethyl-6,6'-dinitrobiphenyl (4.5 g., 58%) m. p. 194—196° (lit., m. p. 195—196°), 3-bromo-5-nitrotoluene (0.25 g., 3%), m. p. 83°, and an orange oil.

THE UNIVERSITY, READING.

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836. *The Reduction of Alkyltriphenylphosphonium Halides with Lithium Aluminium Hydride.*

By S. T. D. GOUGH and S. TRIPPETT.

BAILEY and BUCKLER¹ have described the preferential removal of benzyl groups from benzylphosphonium salts by reduction with lithium aluminium hydride, *e.g.*, benzylethylmethylphenylphosphonium bromide gave ethylmethylphenylphosphine.² We have been concerned with the relative ease of removal of alkyl and phenyl groups from phosphonium salts, and have investigated the reduction with lithium aluminium hydride of alkyltriphenylphosphonium halides.

Reduction of alkyltriphenylphosphonium salts derived from primary alkyl halides, *i.e.*, $[\text{Ph}_3\text{P}\cdot\text{CH}_2\text{R}]^+\text{X}^-$, with lithium aluminium hydride in tetrahydrofuran gave alkyl-diphenylphosphines in 50—60% yield. In dibutyl ether, the yields were rather better. Reduction of the diphosphonium salt $[\text{Ph}_3\text{P}\cdot[\text{CH}_2]_4\cdot\text{PPh}_3]^{2+}2\text{Br}^-$ similarly gave the diphosphine $\text{Ph}_2\text{P}\cdot[\text{CH}_2]_4\cdot\text{PPh}_2$. This is the expected course of the reduction if, by analogy with the attack of hydroxide³ and alkoxide⁴ ions, the first stage in the reduction is attack by hydride ion, or its equivalent, on the positively charged phosphorus, with simultaneous or subsequent expulsion of that group most stable as the anion. The preferential removal of benzyl groups is also accommodated by this mechanism. However, reduction of phosphonium salts derived from secondary halides, *i.e.*, $[\text{Ph}_3\text{P}\cdot\text{CHRR}]^+\text{X}^-$, gave triphenylphosphine as the major product, and this is not consistent with the above simple mechanism.

Saunders and Burchman⁵ showed that reduction of methylenetriphenylphosphorane with lithium aluminium hydride gave methyldiphenylphosphine (28% isolated as the methiodide), and it seemed possible that alkylidenephosphoranes were intermediates in the reduction of alkyltriphenylphosphonium salts, particularly as the reaction mixtures had originally the characteristic red colour of Wittig reagents. That this was not so in the reduction of isopropyltriphenylphosphonium halides to triphenylphosphine was shown by the reduction of preformed isopropylidenetriphenylphosphorane, which gave isopropyl-diphenylphosphine. Similarly the benzylidenephosphorane could not be an intermediate in the reduction of benzyltriphenylphosphonium bromide, which gave 95% of triphenylphosphine, for reduction of preformed benzylidenetriphenylphosphorane gave benzyl-diphenylphosphine.

Experimental.—All experiments were carried out under oxygen-free nitrogen.

Reduction of ethyltriphenylphosphonium bromide with lithium aluminium hydride. Ethyltriphenylphosphonium bromide (20 g.) was added in 15 min. to a stirred, refluxing, suspension of lithium aluminium hydride (1.5 g.) in tetrahydrofuran (200 ml.), and the suspension refluxed overnight and cooled in ice. Methanol (20 ml.) was then added and the solvents were removed under reduced pressure. Distillation of the residue gave ethyldiphenylphosphine (6.2 g.), b. p. 129—132°/0.7 mm., characterised as the methiodide, m. p. (from chloroform—light petroleum) 182—183° (lit.,⁶ m. p. 181°) (Found: C, 50.7; H, 5.15. Calc. for $\text{C}_{15}\text{H}_{18}\text{IP}$: C, 50.6; H, 5.1%).

¹ Bailey and Buckler, *J. Amer. Chem. Soc.*, 1957, **79**, 3567.

² Bailey, Buckler, and Marktscheffel, *J. Org. Chem.*, 1960, **25**, 1996.

³ Bladé-Fort, VanderWerf, and McEwen, *J. Amer. Chem. Soc.*, 1960, **82**, 2396.

⁴ Grayson and Keough, *J. Amer. Chem. Soc.*, 1960, **82**, 3919; Parisek, McEwen, and VanderWerf, *ibid.*, 1960, **82**, 5503.

⁵ Saunders and Burchman, *Tetrahedron Letters*, 1959, No. 1, 8.

⁶ Michaelis and Link, *Annalen*, 1881, **207**, 193.

Similarly, methyltriphenylphosphonium bromide and iodide gave methyldiphenylphosphine (50–60%), b. p. 120–122°/0.15 mm., characterised as the methiodide, m. p. and mixed m. p. (from water) 242–243°; n-butyltriphenylphosphonium bromide gave n-butyldiphenylphosphine (54%), b. p. 140°/0.45 mm., characterised as the *methiodide*, m. p. (from chloroform–light petroleum) 172–173° (Found: C, 53.4; H, 5.6. C₁₇H₂₂IP requires C, 53.1; H, 5.75%); and tetramethylenebis(triphenylphosphonium) dibromide gave *tetramethylenebisdiphenylphosphine*, m. p. (from ethanol) 135–136° (Found: C, 78.4; H, 6.7. C₂₈H₂₈P₂ requires C, 78.8; H, 6.6%).

Triphenylphosphine, m. p. and mixed m. p. 79–80°, was the only product isolated on reduction of isopropyltriphenylphosphonium iodide (41%), s-butyltriphenylphosphonium iodide (63%), and benzyltriphenylphosphonium bromide (95%).

Reduction of isopropylidetriphenylphosphorane with lithium aluminium hydride. To a stirred suspension of isopropyltriphenylphosphonium iodide (10 g.) in tetrahydrofuran (150 ml.), ethereal 1.15N-butyl-lithium (22.4 ml.) was added, followed after 30 min. by lithium aluminium hydride (1.5 g.). The suspension was refluxed overnight, then cooled in ice, and methanol (20 ml.) was added. Removal of solvents and distillation of the residue gave isopropylidetriphenylphosphine (24%), b. p. 145–147°/0.5 mm., characterised as the *methiodide*, m. p. (from chloroform–light petroleum) 225–226° (Found: C, 51.9; H, 5.4. C₁₆H₂₀IP requires C, 51.9; H, 5.4%), and the phosphine oxide, m. p. and mixed m. p. 143°.

A similar reduction of benzylidetriphenylphosphorane gave benzylidetriphenylphosphine (31%), characterised as the methiodide, m. p. and mixed m. p. 241°.

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THE UNIVERSITY, LEEDS, 2.

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837. *The Electron Spin Resonance Spectrum of* *·CH(CO₂H)·CH₂·CO₂H in γ-Irradiated DL-Aspartic Acid Hydrochloride.*

By J. R. ROWLANDS.

THE analysis of the electron spin resonance spectrum of X- and γ-irradiated L-glutamic acid hydrochloride has shown the dominant species was a radical which exhibited hyperfine interaction with only three protons.^{1,2} Of these three protons, one had the properties which are characteristic of an α-proton,^{3,4} the other two showing only slight anisotropy and principal values typical of β-protons.^{4,5}

In glutamic acid hydrochloride there are two possible ways in which such a radical may be formed. A hydrogen may be lost from the end remote from the amino-group, or the amino-group itself may be lost. The first possibility was suggested by Lin, McDowell, and Rowlands¹ in a preliminary note on the nature of the radical. In aspartic acid hydrochloride, however, these two mechanisms would give rise to distinct species. Loss of hydrogen from the carbon not bonded to the amino-group leaves the radical ·CH(CO₂H)·CH(CO₂H)·NH₃⁺Cl⁻, whereas loss of the amino-group would give rise to the radical ·CH(CO₂H)·CH₂·CO₂H. We show below that the second of these mechanisms gives rise to the dominant species in γ-irradiated DL-aspartic acid hydrochloride.

A single crystal was grown from a concentrated hydrochloric acid solution, and subjected to 5 megarads of γ-irradiation of 1 Mev at the Spent Fuel Irradiation Unit, Harwell. The crystals are monoclinic, belonging to space group P2₁/c,⁶ the unit cell

¹ Lin, McDowell, and Rowlands, *J. Chem. Phys.*, in the press.

² Rowlands, unpublished work.

³ McConnell, Heller, Cole, and Fessenden, *J. Amer. Chem. Soc.*, 1960, **82**, 766; Ghosh and Whiffen, *Mol. Phys.*, 1959, **2**, 285; Atherton and Whiffen, *ibid.*, 1960, **3**, 1, 103.

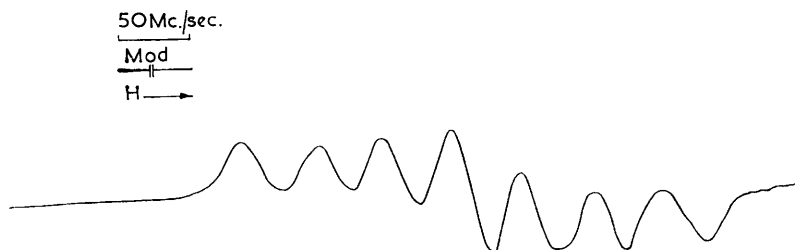
⁴ Pooley and Whiffen, *Mol. Phys.*, 1961, **4**, 81.

⁵ Heller and McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.

⁶ Dawson and Mathieson, *Acta Cryst.*, 1951, **4**, 475.

containing four molecules. The spectra were recorded at room temperature on a super-heterodyne electron spin resonance spectrometer, operating at 9000 Mc./sec. Measurements were made every 15° by rotating the crystal about three orthogonal axes, which included the crystallographic b -axis of the crystal.

As is the case in glutamic acid hydrochloride, more than one chemical species is produced by the irradiation. Heating the irradiated crystals removes, to a large extent, the second unidentified chemical species in both compounds. The present analysis refers to the dominant species after the irradiated DL-aspartic acid hydrochloride crystal had been heated for 5 hours at 165° .



Derivative of absorption spectrum of one orientation in which H_0 is perpendicular to b -axis.

The spectrum (Figure) obtained with the crystallographic b -axis perpendicular to the magnetic field contains seven lines, the central line having double the intensity of the remaining six. Analysis of the spectra obtained about the three axes was consistent with that of a radical showing the hyperfine interaction of three protons. One of these protons had the characteristic principal values and anisotropy of an α -proton, the other two showed the very little anisotropy typical of β -protons, and in the present analysis were assumed to be isotropic. The principal values of the α -proton tensor and the isotropic β -proton interactions are shown in the Table. Because of the overlapping species they are less accurate than those for the same chemical species in γ -irradiated succinic acid. However, the β -couplings of 116 and 68 Mc./sec. are somewhat different from the 100 and 80 Mc./sec. found for succinic acid,⁴ which is consistent with a rather greater angle of twist of the CH_2 group with respect to the free-radical plane in the aspartic acid host crystal. Since the detailed crystal structure is not known, no correlation can be made with the directions of the principal values of the α -proton tensor.

Coupling tensors in Mc/sec.

	Principal values	Isotropic component	Anisotropic component
H(α)	(-) 90 (-) 60 (-) 39	(-) 63	(-) 27 (+) 3 (+) 24
H ₁ (β)		+ 68	
H ₂ (β)		+ 116	

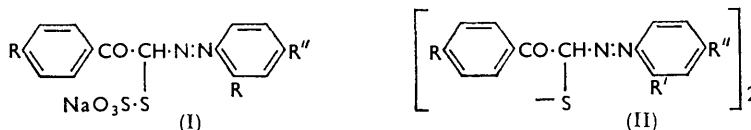
The radical is evidently formed by loss of the amino-group. In the assignment of the glutamic acid radical¹ this possibility was not considered. It now seems from the similarities in behaviour of the two compounds that it cannot be excluded.

The writer thanks Dr. D. H. Whiffen for helpful discussions and Miss B. Curran for running the spectra.

838. Condensation of Phenacyl Thiolsulphates with Diazonium Salts.

By BRIAN MILLIGAN and J. M. SWAN.

IN a search for further dyes rendered soluble by the $-S\cdot SO_3Na$ group,¹ we have coupled several diazonium salts with *S*-phenacyl and *S*-4-bromophenacyl thiolsulphate, obtaining in most cases the *S*- α -arylazophenacyl thiolsulphates (I).^{*} Most of these esters decompose readily in boiling water to the disulphides (II). In one case, (I; R = R' = H, R'' = CO₂Na), the thiolsulphate was unaffected by this treatment, but in another the thiolsulphate was so unstable that only the disulphide (II; R = Br, R' = H, R'' = NO₂) was obtained from the coupling reaction.



The α -arylazophenacyl thiolsulphates and some of the corresponding sulphonates were examined as dyes for wool, but showed little commercial promise.

Experimental.—*Sodium S*-4-bromophenacyl thiolsulphate. A mixture of 4-bromophenacyl bromide (14.5 g.) and sodium thiosulphate pentahydrate (13.0 g.) was heated under reflux in 50% aqueous ethanol (150 ml.) for 30 min. On cooling, the product (17.0 g., 98%) crystallized as colourless plates, m. p. 165° (decomp.) (Found: C, 28.5; H, 2.4; S, 18.8. C₈H₆BrNaO₄S₂ requires C, 28.9; H, 1.8; S, 19.2%).

Sodium S- α -phenylazophenacyl thiolsulphate. Aniline (0.93 g.) was diazotized in the usual way, and the resulting diazonium solution adjusted to pH 6 and added with stirring to a solution of sodium *S*-phenacyl thiolsulphate^{3,4} (2.54 g.) in *m*-phosphate buffer (pH 7; 50 ml.) at 0°. The pH of the mixture was maintained at 7 by addition of alkali. After 30 min. the product was filtered off. After rapid crystallization from water the yield was 3.15 g. (88%) (Found: C, 43.6; H, 3.6; N, 7.1; S, 16.6. C₁₄H₁₁N₂NaO₄S₂·2H₂O requires C, 42.6; H, 3.8; N, 7.1; S, 16.3%). The same product was obtained by using a large excess of diazonium salt.

The following compounds were prepared similarly in good yield:

Disodium S- α -(*o*-carboxyphenylazo)phenacyl thiolsulphate, yellow needles (from aqueous ethanol) (Found: C, 41.4; H, 2.9; N, 6.2; S, 14.8. C₁₅H₁₀N₂Na₂O₆S₂· $\frac{1}{2}$ H₂O requires C, 41.6; H, 2.6; N, 6.5; S, 14.8%); *sodium S*- α -(*p*-chlorophenylazo)phenacyl thiolsulphate, yellow needles (from ethanol) (Found: C, 42.5; H, 2.9; N, 7.0; S, 16.2. C₁₄H₁₀ClN₂NaO₄S₂ requires C, 42.8; H, 2.6; N, 7.1; S, 16.3%); *sodium S*-(4-bromo- α -phenylazo)phenacyl thiolsulphate, yellow plates, m. p. 206—209° (decomp.) (from ethanol) (Found: C, 36.4; H, 3.4; N, 5.8; S, 13.7. C₁₄H₁₀BrN₂NaO₄S₂·H₂O requires C, 36.9; H, 2.7; N, 6.1; S, 14.1%).

Reaction of 4-bromophenacyl thiolsulphate with *p*-nitrobenzenediazonium fluoroborate gave *di*-(4-bromo- α -*p*-nitrophenylazophenacyl) disulphide (II; R = Br, R' = H, R'' = NO₂), m. p. 204° (from acetic acid) (Found: C, 44.7; H, 2.6; S, 8.5. C₂₃H₁₈Br₂N₆O₆S₂ requires C, 44.3; H, 2.4; S, 8.5%).

Two other disulphides were prepared by heating aqueous solutions of the corresponding thiolsulphates on a steam bath for 30 min.: *di*-(α -phenylazophenacyl) disulphide, yellow prisms, m. p. 177° (from butan-2-ol) (Found: C, 65.8; H, 4.4; N, 10.6; S, 12.0. C₂₈H₂₂N₄O₂S₂ requires C, 65.9; H, 4.3; N, 11.0; S, 12.6%); *di*-(α -*p*-chlorophenylazophenacyl) disulphide, yellow prisms, m. p. 175° (decomp.) (from butan-2-ol) (Found: N, 9.4; S, 11.2. C₂₈H₂₀Cl₂N₄O₂S₂ requires N, 9.7; S, 11.1%).

Sodium α -*o*-carboxyphenylazoacetophenone- ω -sulphonate. This product, obtained by coupling

* These products can also be formulated as hydrazones.²

¹ Milligan and Swan, *Textile Res. J.*, 1961, **31**, 18.

² Wiley and Jarboe, *J. Amer. Chem. Soc.*, 1955, **77**, 403.

³ Baker and Barkenbus, *J. Amer. Chem. Soc.*, 1936, **58**, 262.

⁴ Milligan and Swan, *J.*, 1961, 1194.

o-carboxybenzenediazonium chloride with sodium acetophenone- ω -sulphonate,⁵ had m. p. 250—255° (decomp.) (from water) (Found: C, 44.7; H, 4.0; N, 6.8; S, 8.1. $C_{15}H_{11}N_2NaO_6S \cdot 2H_2O$ requires C, 44.3; H, 3.7; N, 6.9; S, 7.9%).

Sodium α -*p*-chlorophenylazoacetophenone- ω -sulphonate, prepared similarly, crystallized from water as yellow needles, m. p. 230° (Found: C, 45.8; H, 3.3; N, 7.4; S, 9.0. $C_{14}H_{10}ClN_2NaO_4S \cdot \frac{1}{2}H_2O$ requires C, 45.5; H, 3.0; N, 7.6; S, 8.7%). Parkes and Tinsley⁵ have described the free acid.

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⁵ Parkes and Tinsley, *J.*, 1934, 1861.

839. 3-Acetylidole.

By G. HART, D. R. LILJEGREN, and K. T. POTTS.

3-ACETYLINDOLE is prepared by the mild alkaline hydrolysis of 1,3-diacetylidole which is available from the reaction of indole with boiling acetic acid-acetic anhydride.¹ Under these conditions the formation of highly coloured, soluble by-products makes complete purification of the final product tedious and greatly diminishes the overall yield (*ca.* 44%).

These coloured impurities are probably aerial oxidation products of indole. The addition of a small amount of vinyl acetate to the reaction mixture and the omission of acetic acid completely eliminate the undesirable side reactions so that, from the resulting golden-yellow (a good indication of the completeness of the reaction) mixture, 3-acetylidole is isolated directly in consistent yields of 66%. Vinyl acetate probably does not react with the indole nucleus itself, as the addition of styrene has a similar effect. The simplest explanation is that these two compounds absorb all the oxygen from the solution and so prevent oxidation. This occurs by thermal polymerization of these vinyl monomers (reaction is at 130—136°) to free radicals that rapidly remove all traces of oxygen from solution.² This observation should be of use also in preventing undesirable oxidation in other indole systems.

Experimental.—Acetic anhydride should be purified by distillation. Adherence to the following conditions results in reproducible yields.

Indole (17.5 g.), acetic anhydride (160 ml.), and vinyl acetate (10 ml.) were heated together under reflux for 15—20 hr., the solution becoming golden-yellow. The solvent was removed, the last traces *in vacuo*. Ethanol (140 ml.) and 2*N*-sodium hydroxide (70 ml.) were added to the pale yellow, crystalline residue of 3-acetyl- and 1,3-diacetyl-indole. After a few minutes, the insoluble material was filtered off (3.68 g.; m. p. 233—234°) and identified as 1-3'-indolyl-1-3''-indolylidene-ethane by mixed m. p. determination and comparison of its infrared spectrum with that of an authentic specimen.¹ Addition of water to the filtrate precipitated 3-acetylidole that crystallized from ethyl acetate (charcoal) as very pale fawn columns (15.8 g., 66.5%), m. p. 190—191°. An analytical sample crystallized from a large volume of benzene as colourless needles, m. p. 190—191° (lit.,¹ m. p. 190°) (Found: C, 75.3; H, 5.7; N, 9.1. Calc. for $C_{10}H_9NO$: C, 75.5; H, 5.7; N, 8.8%). The infrared spectrum was identical with that of an authentic specimen.

Replacement of vinyl acetate by styrene gave the same overall effect. After the addition of the alkali, the insoluble material was extracted with warm benzene, the extract clarified (charcoal), and polystyrene (0.45 g.) precipitated with methanol. After further purification by partial precipitation from benzene solution, the infrared spectrum of this material was identical with that of authentic polystyrene. The residue from the benzene extract was

¹ Saxton, *J.*, 1952, 3592.

² Barnes, *J. Amer. Chem. Soc.*, 1945, **67**, 217; Barnes, Elofson, and Jones, *ibid.*, 1950, **72**, 210.

identified as 1-3'-indolyl-1-3''-indolyldiene-ethane. 3-Acetylindole was isolated in 66% yield as above.

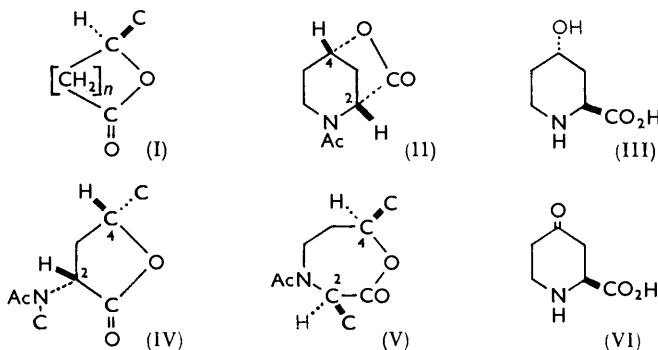
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840. Application of Hudson's Lactone Rule to Hydroxypipercolic Acids; an Anomaly.

By J. W. CLARK-LEWIS and P. I. MORTIMER.

ACCORDING to Hudson's lactone rule the molecular optical rotation difference (Δ value) for lactone *minus* hydroxy-acid is positive when lactones have the configuration (I; $n = 2$ or 3),¹ and this rule was recently cited by us² in confirmation of the absolute configuration of the (+)-*cis*-lactone (II) (Δ positive) obtained by the action of acetic anhydride on (–)-*trans*-4-hydroxy- L_s -pipercolic acid (III). Application of the rule here depends, however, upon arbitrary choice between the new rings created in forming the lactone, namely the five-membered ring (IV) and the seven-membered ring (V). Selection of the five-membered ring (IV), as proposed for bridged-ring lactones derived from certain carbocyclic hydroxy-acids,¹ would lead by the rule to the *cis*- L_s -configuration; but selection of the



seven-membered ring (V) leads to the *cis*- D_s -configuration (II). The latter configuration was assigned to the lactone (II) on other grounds,² so that in applying Hudson's lactone rule to *cis*-4-hydroxy- D_s -pipercolic acid it is evidently necessary to refer configuration to the nitrogenous ring. The present case therefore differs from *cis*-4-hydroxy- L_s -proline and *cis*-5-hydroxy- L_s -pipercolic acid³ as the configurations of these two acids, which also have positive Δ values, are correctly derived by reference to the non-nitrogenous ring.

Oxidation of (–)-*trans*-4-hydroxy- L_s -pipercolic acid (III) gives the oxo-acid (VI) which on reduction gives (–)-*cis*-4-hydroxy- L_s -pipercolic acid.^{2,4} L_s -Pipercolic acid is also formed⁴ during hydrogenation of the oxo-acid (VI), which supports the configurations assigned to the 4-hydroxypipercolic acids, and we conclude that Hudson's lactone rule is at present an unreliable guide to the configurations of bridged-ring lactones containing nitrogen.

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¹ Klyne, *Chem. and Ind.*, 1954, 1198.

² Clark-Lewis and Mortimer, *J.*, 1961, 189.

³ Witkop, *Experientia*, 1956, **12**, 372.

⁴ Vanderhaeghe and Parmentier, *J. Amer. Chem. Soc.*, 1960, **82**, 4414.