403. *The Protonation of Some Aminobenzothiazoles*

By C. H. Williams

The ultraviolet spectra of 4-, 5-, 6-, and 7-aminobenzothiazoles have been measured in water (Fig. 1), in 0·1N-sulphuric acid (Fig. 2), and in 20N-sulphuric acid (Fig. 3). Although significant spectral differences were observed for the amines in water, their spectra in dilute sulphuric acid were all very similar to that of benzothiazole.[1] In 20N-sulphuric acid the spectra of the amines corresponded to that of the benzothiazolium cation (Fig. 3). These observations are consistent with the view that in dilute acid formation of (I) occurs, and

[1] A. Cerniani and R. Passerini, *J.*, 1954, 2261.

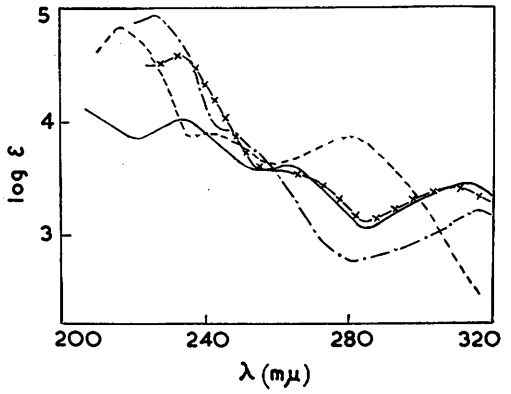


FIG. 1. Spectra in water of 4-(———), 5-(— · —), 6-(– – –), and 7-(— × — × —)-aminobenzothiazoles

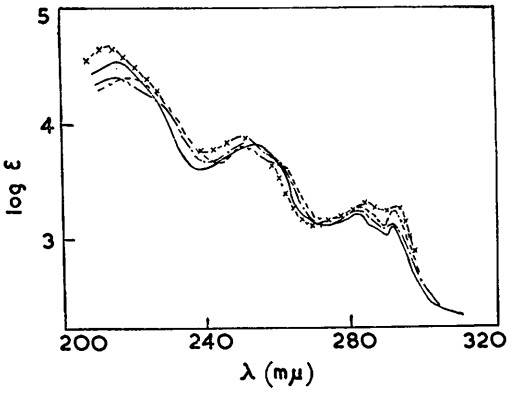


FIG. 2. Spectra in 0·1N-sulphuric acid of 4-(———), 5-(— · —), 6-(– – –) and 7-(— × —)-aminobenzothiazoles

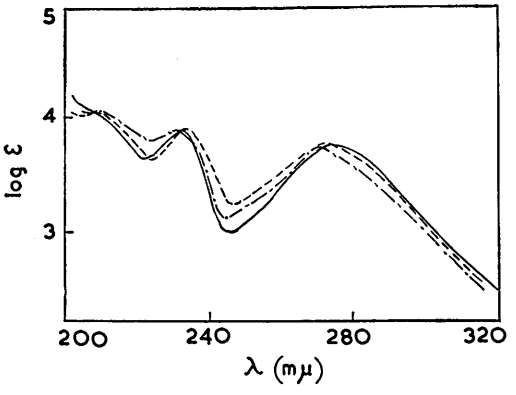
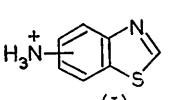


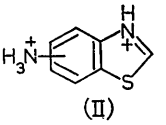
FIG. 3. Spectra in 20N-sulphuric acid of benzothiazole (– – –), and 4-(———) and 5-(— · —)-aminobenzothiazoles

Curves for 6- and 7-amino-derivatives were identical with the latter

that in more concentrated acid the dication (II) is formed. 6-Amino-7-bromobenzothiazole, in which the basic strength of the amino-group is presumably lowered by the bromine atom, also showed this behaviour.



(I)



(II)

This protonation sequence is the opposite of that which has been observed for many other *N*-hetero-aromatic amines.[2,3] The reasons for this are probably twofold. Firstly, benzothiazole itself is only a very weak base ($pK_a = 1{\cdot}2 \pm 0{\cdot}1$).[4] Secondly, in the aminobenzothiazoles, the type of base-strengthening resonance suggested by Albert *et al.*[5] for the aminoquinolines and analogous substances, cannot occur.

The author thanks Pfizer (Sandwich) Ltd. for financial support, and Dr. E. R. Ward, under whose supervision this work was carried out.

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[*Received, August 10th*, 1964.]

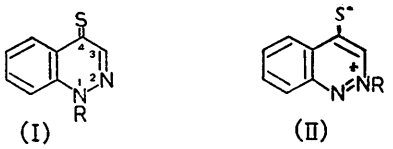
[2] M. J. Heam, R. A. Morton, and J. C. E. Simpson, *J.*, 1951, 3329.
[3] D. P. Craig and L. N. Short, *J.*, 1945, 419.
[4] A. Albert, R. Goldacre, and J. Phillips, *J.*, 1948, 2240.
[5] A. Albert and R. Goldacre, *J.*, 1946, 706.

404. *Ionization Constants of Heterocyclic Substances. Part VII.*[1] *Cinnolines*

By G. B. Barlin

The tautomeric equilibrium in mercapto-derivatives of numerous heteroaromatic systems has been investigated by comparing the ionization constants and ultraviolet spectra of the parent compound with those of the *N*- and *S*-methyl derivatives. It was found that in monoaza-systems [2] the tautomeric equilibrium favours forms in which the mobile hydrogen is on the nitrogen atom; and in diaza-systems [3] with two possible NH forms, the mobile hydrogen is attached principally to the nitrogen atom which is nearer the mercapto-group. This Note revises and extends the data on 4-mercaptocinnoline reported [3] in 1962 when only one *N*-methyl derivative of 4-mercaptocinnoline was available and was prepared from an *N*-methyl-4-hydroxycinnoline which has recently [4] been assigned another structure.

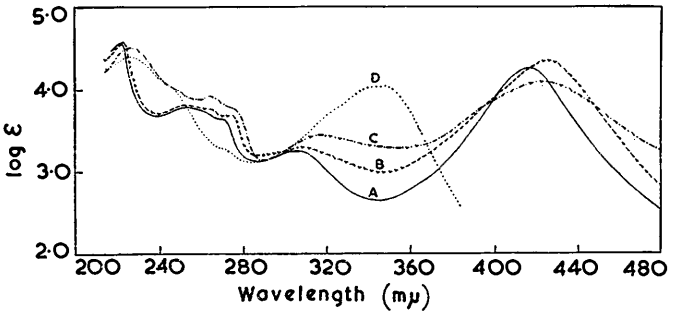
The ionization constants and ultraviolet spectra of all ionic forms of 4-mercapto-(and 4-hydroxy-)cinnoline and all its *N*- and *S*-methyl derivatives are now reported, and these results show clearly that the tautomeric form (I; R = H) with the hydrogen on



(I) (II)

$N_{(1)}$ is preferred to form (II; R = H) with hydrogen on $N_{(2)}$ or to that with it on the sulphur atom.

Ames and Kucharska [4] recently reported that methylation of 4-hydroxycinnoline with dimethyl sulphate and potassium hydroxide afforded a separable mixture of both *N*-methyl



Ultraviolet spectra of neutral molecules of: 4-mercaptocinnoline (A) at pH 4·0; 1,4-dihydro-1-methyl-4-thiocinnoline (B) at pH 1·0; the anhydro-base of 4-mercapto-2-methylcinnolinium hydroxide (C) at pH 7·0; 4-methylthiocinnoline (D) at pH 6·0; all in water at 20°

derivatives. They proved that the principal product (m. p. 163—165°, previously claimed by Schofield and Simpson [5] as the $N_{(1)}$-methyl derivative) was the anhydro-base of 4-hydroxy-2-methylcinnolinium hydroxide (oxygen analogue of II). Refluxing this

[1] Part VI, Barlin, *J.*, 1964, 2150.
[2] Albert and Barlin, *J.*, 1959, 2384.
[3] Albert and Barlin, *J.*, 1962, 3129.
[4] Ames and Kucharska, *J.*, 1963, 4924.
[5] Schofield and Simpson, *J.*, 1945, 512.

anhydro-base and phosphorus pentasulphide in benzene naturally gives the sulphur analogue (II), and not 1,4-dihydro-1-methyl-4-thiocinnoline as previously reported.[3] (This is the first recorded preparation of an anhydro-base of a mercapto-*N*-methylheterocycle from its oxygen analogue and phosphorus pentasulphide.)

The compound now known [4] to be 1,4-dihydro-1-methyl-4-oxocinnoline reacted readily with phosphorus pentasulphide in benzene to give 1,4-dihydro-1-methyl-4-thiocinnoline. An improved procedure for methylation of 4-hydroxycinnoline with a large excess of dimethyl sulphate is described.

Ultraviolet spectra of all ionic species of the $N_{(1)}$ methyl derivatives were measured after prior determination of pK_a values and are recorded with those of other reference compounds in the Table. The Table and Figure shows clearly that the spectrum of the

Physical properties

			Spectroscopy in water		
Cinnoline	Species [a]	pK_a (H_2O; 20°)	$\lambda_{max.}$ (mμ)	log ε	pH [g]
4-Hydroxy- [b]	0	—	207, 227, 234, 253, *261*, 284, 337, 352	4·49, 4·12, 4·11, 3·98, *3·89*, 3·35, 4·09, 4·01	5·0
	+	−0·35	205, 233, 249, *294*, 305, 338	4·25, 4·47, 4·08, *3·37*, 3·54, 3·76	−3·6
	−	9·27	211, 240, 336, *345*	4·48, 4·17, 4·02, *3·99*	11·5
$N_{(1)}$-Methyl	0		209, 233, 240, 256, *263*, 286, 344, *350*, *355*, 359	4·44, 4·16, 4·18, 3·92, *3·85*, 3·33, 4·13, *4·11*, *4·07*, 4·03	5·0
	+	−0·29 [d]	237, *254*, *298*, 308, 342	4·50, *3·95*, *3·31*, 3·52, 3·85	−2·34
$N_{(2)}$-Methyl [c]	0		212, *223*, 250, *265*, 347, 364	4·44, *4·16*, 4·02, *3·67*, 4·05, 4·06	7·0
	+	0·91	210, 241, *257*, 299, 309, 346	4·24, 4·47, *3·93*, 3·48, 3·54, 3·74	−3·0
O-Methyl [b]	0		*211*, 227, 293, 319, *328*	*4·30*, 4·59, 3·71, 3·69, *3·65*	7·0
	+	3·21	233, 254, *296*, 307, 338	4·50, 3·97, *3·53*, 3·71, 3·79	1·0
4-Mercapto [c]	0		*217*, 222, 252, 271, 305, 417	*4·46*, 4·56, 3·77, 3·63, 3·25, 4·27	4·0
	+	−1·83	211, 238, *248*, *288*, 295, 333, 369	4·10, 4·40, *4·24*, *3·36*, 3·37, 3·82, 4·02	−4·0
	−	7·09	221, 247, 275, 380	4·52, 3·82, 3·29, 4·13	9·5
$N_{(1)}$-Methyl	0		223, 252, *264*, 275, 308, 427	4·57, 3·83, *3·76*, 3·69, 3·30, 4·36	1·0
	+	−1·29 [e]	211, 239, *250*, 300, 336, 372, *386*	4·11, 4·36, *4·23*, 3·42, 3·82, 4·08, 3·99	−3·29
$N_{(2)}$-Methyl [c]	0		227, 265, *274*, 317, 424	4·51, 3·91, *3·79*, 3·45, 4·10	7·0
	+	−0·80	215, 244, 285, 333, *367*, 377	4·09, 4·49, 3·40, 3·68, *3·93* 3·95	−3·0
S-Methyl [c]	0		226, *246*, *271*, 349	4·41, *4·03*, *3·28*, 4·04	6·0
	+	3·13	219, 240, *256*, *281*, 385	4·26, 4·36, *3·90*, *3·23*, 4·18	0·0

[a] 0 Neutral species, + cation, − anion. [b] Ionization constant from Albert and Phillips, *J.*, 1956, 1294, and ultraviolet spectra from Albert and Barlin, *J.*, 1962, 3129. [c] Ionization constants and ultraviolet spectra from Albert and Barlin, *J.*, 1962, 3129. [d] The results were within ±0·02 unit when the pK_a was determined spectroscopically on 0·00002M-solutions at λ = 345 mμ. [e] The absorption due to the cation was found by extrapolation. The results were within ±0·1 units of the pK_a when it was determined spectroscopically on 0·00002M-solutions at λ = 250 mμ. [f] Shoulders and inflexions in italics. [g] pH Values below 0 have been obtained in solutions of sulphuric acid to which Hammett's acidity functions have been assigned.

neutral molecule of 4-mercaptocinnoline resembles that of the $N_{(1)}$-methyl derivative much more closely than those of the $N_{(2)}$- and *S*-methyl derivatives. Fine details of the spectrum of the mercapto-compound are retraced in that of the $N_{(1)}$-methyl derivative which has the expected small bathochromic shift.[2] Thus the tautomeric form with hydrogen on $N_{(1)}$ is favoured. Although the tautomer with the mobile hydrogen on $N_{(1)}$ likewise predominates in the neutral moleules of 4-hydroxycinnoline, methylation with dimethyl sulphate and potassium hydroxide yields principally the $N_{(2)}$ derivative.[4]

As with the monoaza-analogues,[2] the long-wavelength absorption band in the cation

of 4-mercaptocinnoline and its *N*-methyl derivatives occurs at a shorter wavelength than those of the neutral species, whereas that of the *S*-methyl derivative occurs at a longer wavelength.

Ionization Constants.—The conclusions drawn from a study of ultraviolet spectra were supported by measurement of ionization constants. In the Table it is seen that the basic pK_a of 4-mercaptocinnoline (and also that of the oxygen analogue) is closer to that of the $N_{(1)}$- than to that of the $N_{(2)}$-methyl derivative. Thus the $N_{(1)}$-H form is the principal contributor to the tautomeric mixture. Methylation at $N_{(1)}$ increases the pK_a slightly as has been found for analogous cases.[2,3]

Experimental.—Microanalyses were by Dr. J. E. Fildes and her staff. Solids for analysis were dried at 100° unless otherwise stated. M. p.s were taken in soda-glass capillaries. Paper chromatography (ascending) was carried out on Whatman No. 1 paper with (*a*) 3% ammonium chloride, and (*b*) butan-1-ol–5N-acetic acid (7 : 3) as solvent. Ionization constants were determined as previously described.[2]

Ultraviolet spectra were measured first on a Perkin-Elmer Spectracord model 4000 recording spectrophotometer and then $\lambda_{max.}$ and ε values were checked on a Hilger " Uvispek " manual instrument (by Mr. C. Arandjelovic).

Methylation of 4-hydroxycinnoline. A solution of 4-hydroxycinnoline (5 g.) in 4N-potassium hydroxide (120 ml.) was stirred at 50° while dimethyl sulphate (25 ml.) was added dropwise. The temperature rose to 70°, at which it was maintained for 30 min. and then the mixture was allowed to cool. The products were extracted with chloroform and separated as described by Ames and Kucharska [4] to give (*a*) the anhydro-base of 4-hydroxy-2-methylcinnolinium hydroxide (2·85 g.), m. p. 157·5—159° (lit.,[4] 163—165°) (Found, for sublimed material: C, 63·5; H, 5·3; N, 16·8. Calc. for $C_9H_8N_2O,\frac{1}{2}H_2O$: C, 63·9; H, 5·35; N, 16·6%), and (*b*) 1,4-dihydro-1-methyl-4-oxocinnoline (1·2 g.) which, crystallised from light petroleum (b. p. 60—80°), had m. p. 115—116° (lit.,[4] 114—116°).

1,4-*Dihydro*-1-*methyl*-4-*thiocinnoline.* 1,4-Dihydro-1-methyl-4-oxocinnoline (0·1 g.) and phosphorus pentasulphide (0·5 g.) in benzene (10 ml.) were refluxed for 1·5 hr., the solvent evaporated, water (10 ml.) added, and the solution extracted with chloroform. After drying (Na_2SO_4) the solvent was distilled and the orange-red residue recrystallised from light petroleum (b. p. 60—80°) to give 1,4-*dihydro*-1-*methyl*-4-*thiocinnoline* (0·085 g.; 77%) as orange-red needles, m. p. 143—144° (Found: C, 61·65; H, 4·70; N, 15·7; S, 18·1. $C_9H_8N_2S$ requires C, 61·35; H, 4·6; N, 15·9; S, 18·2%).

Chromatography in ammonium chloride gave a clear differentiation between this product and the anhydro-base of 4-mercapto-2-methylcinnolinium hydroxide.

Anhydro-base of 4-mercapto-2-methylcinnolinium hydroxide. This was prepared from the anhydro-base of 4-hydroxy-2-methylcinnolinium hydroxide (m. p. 157—159°, previously claimed [5] to be 1,4-dihydro-1-methyl-4-oxocinnoline) and phosphorus pentasulphide in benzene as described (in error) for 1,4-dihydro-1-methyl-4-thiocinnoline.[3] It had m. p. 184·5°.

I thank Mr. S. Truhly for experimental assistance.

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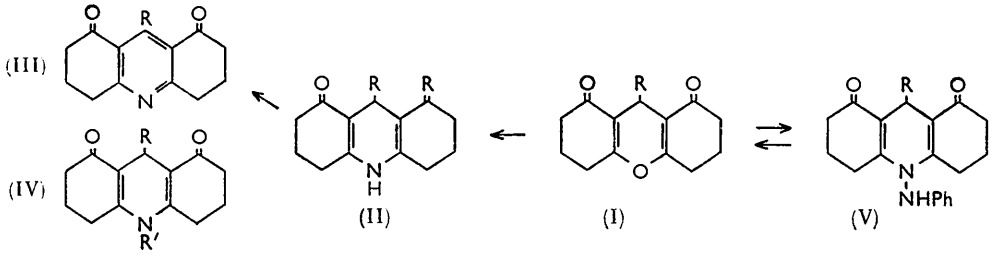
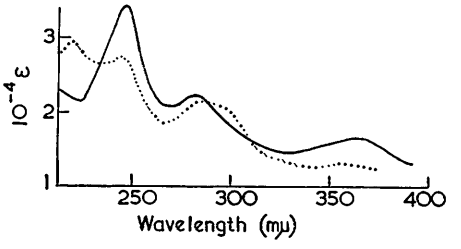
405. *Some Derivatives of Decahydro-1,8-dioxoacridine*

By H. Antaki

After synthesis [1] of 9-aryldecahydro-1,8-dioxoacridines by condensing aromatic aldehydes with cyclohexane-1,3-dione in presence of ammonium acetate we have extended the reaction to aromatic amines, obtaining 9,10-diaryl-1,8-dioxodecahydroacridines (IV) by this reaction in glacial acetic acid. With 2-aminopyridine and its 4-methyl derivative as the amine, only the 9-aryloctahydro-1,8-dioxoxanthen (I) was isolated. The latter is recovered unchanged after treatment with aromatic amines, indicating that the reaction does not proceed through the xanthen.



The xanthens (I) passed smoothly into the acridines (II) on treatment with ammonium acetate in glacial acetic acid, and 2,2′-arylidene-biscyclohexa-1,3-diene with aromatic amines gave the 9,10-diaryl derivatives (IV); oxidation with chromium trioxide gave the octahydroacridine (III). The 10-anilinoacridines (V) obtained by treatment with phenylhydrazine of the xanthen (I) readily reverted to the latter on reflux with ethanolic hydrochloric acid: 9-aryloctahydro- and 9-aryldecahydro-1,8-dioxoacridines and 9,10-diaryldecahydro-1,8-dioxoacridines were stable to acid treatment. Reduction of the 1,8-dioxo-group in the compounds (I), (II), and (IV) with thioglycollic acid [2] gave the corresponding 1,8-diols. Whereas the dihydroxy xanthen is rapidly oxidised in hot ethanol, acetic acid, or acetic



Ultraviolet absorption of deca- (——) and octa-hydro-9-*p*-nitrophenyl-1,8-dioxoacridine (– – –) in absolute alcohol

anhydride solution to the 1,8-diketone, the diol from the acridine (IV) is only oxidised in boiling acetic anhydride. Octahydroacridines have been prepared from 1,5-diketones [3] by the Stobbe–Volland synthesis.[4] The ultraviolet absorption spectra of the deca- and octa-hydroacridine (II and III; R = *p*-$NO_2 \cdot C_6H_4$) are shown in the Figure.

Experimental.—*1,2,3,4,5,6,7,8,9,10-Decahydro-9-p-nitrophenyl-1,8-dioxo-10-phenylacridine.* *p*-Nitrobenzaldehyde (3 g., 1 mol.), cyclohexane-1,3-dione (2·2 g., 1 mol.), and aniline (1·8 g., 1 mol.) in glacial acetic acid (100 c.c.) were refluxed for 1 hr. The solution was concentrated and diluted with water. The *product* crystallised, on cooling, in yellow prisms, m. p. 282°

[1] Antaki, *J.*, 1963, 4877.
[2] Bongartz, *Ber.*, 1888, **21**, 483.
[3] Colange, Dreux, and Delplace, *Bull. Soc. chim. France*, 1957, 447.
[4] Stobbe and Volland, *Ber.*, 1902, **35**, 3973.

(decomp.) (38%) (Found: C, 71·8; H, 5·6; O, 15·0; N, 6·2. $C_{25}H_{22}N_2O_4$ requires C, 72·4; H, 5·3; O, 15·4; N, 6·7%). The 10-β-*naphthyl derivative* formed yellow prisms, m. p. 297° (decomp.) (70%) (Found: C, 74·6; H, 5·2; O, 13·7; N, 6·1. $C_{29}H_{24}N_2O_4$ requires C, 75·0; H, 5·1; O, 13·8; N, 6·0%), and the 10-p-*chlorophenyl derivative* in yellow plates m. p. 300° (decomp.) (56%) (Found: C, 67·1; H, 4·9; O, 14·5; N, 6·3; Cl, 7·8. $C_{25}H_{21}ClN_2O_4$ requires C, 66·8; H, 4·6; O, 14·2; N, 6·2; Cl, 7·9%). The 10-o-*hydroxyphenyl derivative* crystallised in brown plates, m. p. >300° (47%) (Found: C, 68·9; H, 5·2; O, 18·4; N, 5·9. $C_{25}H_{22}N_2O_5$ requires C, 69·3; H, 5,1; O, 18·5; N, 6·2%).

1,2,3,4,5,6,7,8,9,10-*Decahydro*-9-p-*methoxyphenyl*-1,8-*dioxo*-10-*phenylacridine*. 2,2′-*p*-Methoxybenzylidinebiscyclohexa-1,3-dione (1 g., 1 mol.) and aniline (0·3 g., 1 mol.) in acetic acid (100 c.c.) were heated under reflux for 1 hr. The *product* separated, on cooling, from the concentrated solution in yellow prisms m. p. 267° (decomp.) (42%) (Found: C, 78·0; H, 6·1; O, 11·4; N, 3·2. $C_{26}H_{25}NO_3$ requires C, 78·1; H, 6·2; O, 12·0; N, 3·5%). The 10-p-*chlorophenyl derivative* formed yellow plates, m. p. 285° (decomp.) (Found: C, 71·7; H, 5·5; O, 10·9; N, 3·2; Cl, 7·6. $C_{26}H_{24}ClNO_3$ requires C, 71·9; H, 5·5; O, 11·0; N, 3·2; Cl, 8·1%) as did the o-*hydroxyphenyl derivative* (68%), m. p. 300°, (Found: C, 75·1; H, 5·4; O, 15·3; N, 3·1. $C_{26}H_{25}NO_4$ requires C, 75·3; H, 5·7; O, 15·4; N, 3·4%).

1,2,3,4,5,6,7,8-*Octahydro*-1,8-*dihydroxy*-9-p-*nitrophenylxanthen*. 10-Anilinodecahydro-9-*p*-nitrophenyl-1,8-dioxoacridine [1] (0·5 g.) in ethanol (150 c.c.) was saturated with hydrogen chloride and then heated under reflux for 30 min. with intermittent passage of a stream of hydrogen chloride. The solution, when concentrated and cooled, deposited the xanthen in white needles, m. p. 269° (decomp.). The xanthen (0·3 g., 1 mol.) and sodium thioglycollate (0·4 g., 4 mol.) in acetic acid (30 c.c.) were refluxed for 30 min. The 1,8-*diol* separated from the concentrated solution on dilution and cooling in white needles m. p. 210° (Found: C, 66·2; H, 5·5; O, 24·5; N 3·7. $C_{19}H_{21}NO_5$ requires C, 66·4; H, 6·1; O, 23·3; N, 4·0%).

1,2,3,4,5,6,7,8,9,10-*Decahydro*-1,8-*dihydroxy*-10-β-*naphthyl*-9-p-*nitrophenylacridine*. The acridine (IV; R = *p*-NO_2·C_6H, R′ = β-$C_{10}H_7$) (0·5 g., 1 mol.) and sodium thioglycollate (0·4 g., 4 mol.) were refluxed for 0·5 hr. The solution was concentrated, diluted, and cooled; the product separated in yellow prisms, m. p. 270° (decomp.) (Found: C, 74·0; H, 4·8; O, 13·3; N, 5·8. $C_{29}H_{28}N_2O_4$ requires C, 74·3; H, 5·1; O, 13·6; N, 5·9%).

1,2,3,4,5,6,7,8-*Octahydro*-9-p-*nitrophenyl*-1,8-*dioxoacridine*. To the decahydroacridine (II; R = *p*-NO_2·C_6H_4) (1 g., 1 mol.) in acetic acid (140 c.c.) and water (60 c.c.) at 70° chromium trioxide (0·7 g., 1 mol.) in 70% acetic acid (20 c.c.) was added. When the solution became pale brown it was diluted with water and cooled. The *product* separated in yellow prisms, m. p. >300° (64%) (Found: C, 67·5; H, 4·7; O, 18·6; N, 8·1. $C_{19}H_{16}N_2O_4$ requires C, 67·8; H, 4·7; O, 19·0; N, 8·3%). The 9-p-*methoxyphenyl derivative* formed yellow prisms, m. p. >300° (Found: C, 74·6; H, 5·7; O, 14·6; N, 4·2. $C_{20}H_{19}NO_3$ requires C, 74·7; H, 5·9; O, 14·9; N, 4·3%).

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406. DL-β-*Fluoren*-4-*ylalanine*

By D. C. MORRISON

THE series of aromatic amino-acids, fluoren-2- and -1-ylalanines,[1,2] has been extended by the similar preparation of the fluoren-4-yl isomer from ethyl fluorene-4-carboxylate. Lithium aluminium hydride reduction of the ester gave fluoren-4-ylmethanol, previously obtained from fluorene-4-aldehyde and the same reagent by Quelet and Barge.[3] The alcohol was transformed into the bromide which was then used to alkylate the sodium derivative of ethyl acetamidomalonate. The ester formed was hydrolysed and decarboxylated to the fluoren-4-ylalanine. The French workers prepared the corresponding acrylic and propionic acids.

[1] D. C. Morrison, *J. Org. Chem.*, 1959, **24**, 463.
[2] D. C. Morrison, *J. Org. Chem.*, 1960, **25**, 2055.
[3] R. Quelet and J. Barge, *Comptes. rendus.*, 1960, **251**, 1019.

The amino-acid, characterized as the *N*-benzenesulphonyl derivative, was generally similar to its 2- and 1-isomers, but more soluble. The infrared spectrum resembled that of the 1-isomer,[2] with strongest peaks at 3390, 1620, 1562, 1528, 1401, 739 cm.$^{-1}$ and a wide lower-intensity band at 3100—2600 cm.$^{-1}$. Assignments, where possible, are probably analogous to those listed for the 1-isomer.[2]

Experimental.—Fluorene-4-ylmethanol. Liquid ethyl fluorene-4-carboxylate was reduced as for the 2- and 1-isomers. A nearly quantitative yield of crude alcohol was obtained, which, recrystallized from ether and ether–light petroleum, formed large, glistening white crystals, m. p. 130—131° (lit.,[3] 129—130°).

Fluoren-4-ylmethyl bromide. Phosphorus tribromide (7 ml.) anhydrous benzene (30 ml.) was treated during 5 min. with 6 g. (0·031 mole) of the alcohol. Hydrogen bromide was evolved vigorously and a yellow-brown sludge formed. The mixture was left for several days at room temperature, then poured slowly on ice. The organic layer was separated, washed with water and dried, and the solvent removed at room temperature under vacuum. The *bromide* (7·5 g.; yield 94·5%) was recrystallized from ether–light petroleum and from light petroleum, and had m. p. 126—128°, depressed to 104—108° when mixed with the starting alcohol (Found: C, 65·0; H, 4·3. $C_{14}H_{11}Br$ requires C, 64·9; H, 4·25%).

Diethyl(fluoren-4-ylmethyl)acetamidomalonate. Sodium (0·293 g.; 0·0127 mole) in anhydrous absolute ethanol (100 ml.) was treated with ethyl acetamidomalonate (2·765 g.; 0·0127 mole) and the mixture warmed to dissolve the ester. The bromide (3·3 g.; 0·0127 mole) was added, and the liquid refluxed for 26 hr. Acetic acid (2 ml.) was added and most of the solvent distilled off. Water was introduced and the mixture steam-distilled for ½ hr. A viscous orange oil remained with the water and this began to crystallize in 1—2 days. After a week, the product was filtered off, washed, and dried (4·5 g.; yield 89·6%), recrystallized thrice from aqueous acetone (charcoal), and 5 times from ether. The *ester* formed white crystals, m. p. 130—130·5° (Found: C, 70·3; H, 6·3. $C_{23}H_{25}NO_5$ requires C, 69·9; H, 6·3%).

DL-β-*Fluoren-4-ylalanine.* The preceding ester (7·28 g.; 0·0184 mole), acetic acid (100 ml.) and concentrated hydrochloric acid (80 ml.) were refluxed for 4 days. Most of the solvents were distilled off and the residue was extracted by 6 portions of hot 2N-HCl, with filtration at 80° each time. The filtrates were boiled down for successive crops of the amino-acid hydrochloride, which were washed with 2N-HCl and dried (yield 3·5 g.; 65·7%). The salt was recrystallized from methanol–benzene but was not obtained analytically pure. The best sample discoloured above 190°, and fused at 218—232°.

The 3·5 g. of hydrochloride were digested with several portions of hot aqueous ammonia [1 : 1 v/v NH_4OH (*d* 0·88) : water] and filtered. The filtrates were heated with Norit and again filtered. The solution obtained was boiled down, 3 crops of amino-acid being taken (final volume 10 ml.). The yield of dried amino-acid was 2·64 g. (86·3% on hydrochloride). This *amino-acid* was recrystallized by boiling down its ammoniacal solution and cooling. After 5 treatments, a cream-white product was obtained. The best material discoloured at 215—220°, melting at 222—229° to a brown melt. This behaviour resembles that of the 1- and 2-isomers (Found: C, 75·7; H, 6·1. $C_{16}H_{15}NO_2$ requires C, 75·9; H, 5·9%).

N-*Benzenesulphonyl*-DL-β-*fluoren-4-ylalanine.* The hydrochloride (650 mg.) was dissolved in aqueous N-KOH (100 ml.) and the solution stirred with 2 ml. of benzenesulphonyl chloride in 50 ml. of ether. After 4·5 hr. the clear aqueous phase was separated and acidified with an excess of hydrochloric acid, giving a milky suspension which crystallized after a short time. This product was filtered next day, washed, and dried. The 500 mg. of acid was extracted with ether until no more was soluble and the solution boiled down for crystallization of the product. It was recrystallized from aqueous acetone (Norit) and purified through its potassium salt. The *acid* was regenerated and recrystallized from acetone–water and finally from ether–light petroleum. The best material had m. p. 226—230° (Found: C, 66·7; H, 4·9. $C_{22}H_{19}NO_4S$ requires C, 67·2; H, 4·8%).

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407. *Perfluoroalkyl Derivatives of Nitrogen. Part XIV.*[1] 1,1,1-*Trifluoroazomethane*

By A. H. Dinwoodie and R. N. Haszeldine

Trifluoronitrosomethane is stable in the presence of dilute aqueous acid, but is rapidly decomposed by dilute aqueous alkali to give trifluoronitromethane, hexafluoroazoxymethane, fluoride, carbonate, and nitrite.[2] The base hydrolysis of heptafluoronitrosopropane can be understood if nucleophilic attack occurs on nitrogen and on α-carbon.[3,4]

Nucleophilic attack on trifluoronitrosomethane by methylamine, now reported:

$$CH_3{\cdot}NH_2 + CF_3{\cdot}N{:}O \longrightarrow CF_3{\cdot}N(O^-){\cdot}\overset{+}{N}H_2{\cdot}CH_3 \xrightarrow[\text{(ii) } -H_2O]{\text{(i) H transfer}} CF_3{\cdot}N{:}N{\cdot}CH_3 \quad (57\%)$$

occurred rapidly at low temperature. Water and an unidentified solid were the only other products, together with traces of trifluoronitromethane and hexafluoroazoxymethane, the hydrolysis products of trifluoronitrosomethane.

1,1,1-Trifluoroazomethane has boiling point (2·6°) close to that of azomethane (2·0°; cf. $CF_3{\cdot}N{:}N{\cdot}CF_3$ b. p. −32·2°). The ultraviolet spectra of the vapour of these compounds: $CF_3{\cdot}N{:}N{\cdot}CF_3$,[5] $\lambda_{max.}$ 358 mμ (ε 1·74); $CF_3{\cdot}N{:}N{\cdot}CH_3$, $\lambda_{max.}$ 353 mμ (ε 3·58); $CH_3{\cdot}N{:}N{\cdot}CH_3$,[6] $\lambda_{max.}$ 338 mμ (ε 4·6), show the expected shift to the red on replacement of hydrogen by fluorine. The infrared spectrum of 1,1,1-trifluoroazomethane shows a band at 6·28 μ assigned to the N=N stretching vibration [cf. 6·34 μ for $CH_3{\cdot}N{:}N{\cdot}CH_3$ (Raman) [7]], and the characteristic CF_3 deformation triplet is at 13·75, 13·85, and 13·98 μ.

1,1,1-Trifluoroazomethane is decomposed by aqueous acid to give carbon dioxide, ammonium, and fluoride, and by aqueous base to give cyanate and fluoride. Azomethane is stable to aqueous base but is hydrolysed by acid to formaldehyde and methylhydrazine,[8] whereas hexafluoroazomethane is stable to aqueous acid,[9] but is decomposed by alcoholic potassium hydroxide.[5]

Photolysis of 1,1,1-trifluoroazomethane gives the compounds N_2, CHF_3, CH_4, C_2F_6, CF_3Me, and either $(CF_3)_2N{\cdot}NMe_2$ or $CF_3{\cdot}NMe{\cdot}NMe{\cdot}CF_3$:

$$CF_3{\cdot}N{:}N{\cdot}Me \longrightarrow CF_3{\cdot} + N_2 + CH_3{\cdot}$$
$$CF_3{\cdot} + CF_3{\cdot}N{:}N{\cdot}Me \longrightarrow CF_3H + CF_3{\cdot}N{:}N{\cdot}CH_2{\cdot}$$
$$CH_3{\cdot} + CF_3{\cdot}N{:}N{\cdot}Me \longrightarrow CH_4 + CF_3{\cdot}N{:}N{\cdot}CH_2{\cdot}$$
$$2CF_3{\cdot} \longrightarrow C_2F_6$$
$$CF_3{\cdot} + CH_3{\cdot} \longrightarrow CF_3Me$$

or

$$CF_3{\cdot}N{:}N{\cdot}Me \longrightarrow CF_3Me + N_2$$
$$CF_3{\cdot} + CF_3{\cdot}N{:}N{\cdot}Me \longrightarrow (CF_3)_2N{\cdot}\dot{N}{\cdot}Me \text{ or } CF_3{\cdot}\dot{N}{\cdot}N{\cdot}Me{\cdot}CF_3$$
$$CH_3{\cdot} + CF_3{\cdot}N{:}N{\cdot}Me \longrightarrow CF_3{\cdot}NMe{\cdot}\dot{N}{\cdot}Me \text{ or } CF_3{\cdot}\dot{N}{\cdot}NMe_2$$
$$(CF_3)_2N{\cdot}\dot{N}{\cdot}Me,\ CF_3{\cdot}\dot{N}{\cdot}NMe{\cdot}CF_3,\ CF_3{\cdot}NMe{\cdot}\dot{N}{\cdot}Me \text{ or } CF_3{\cdot}\dot{N}{\cdot}NMe_2 \xrightarrow{CH_3{\cdot} \text{ or } CF_3{\cdot}} (CF_3)_2N{\cdot}NMe_2 \text{ or } CF_3{\cdot}NMe{\cdot}NMe{\cdot}CF_3$$

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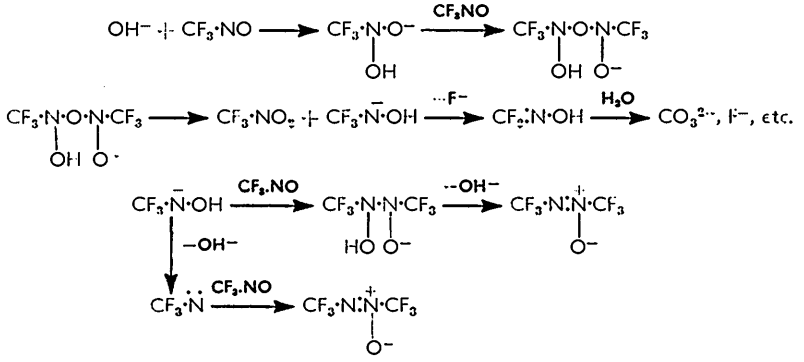
[1] Part XIII, A. H. Dinwoodie and R. N. Haszeldine, *J.*, 1965, 1681.
[2] J. Jander and R. N. Haszeldine, *J.*, 1954, 919.
[3] D. A. Barr and R. N. Haszeldine, *J.*, 1956, 3416.
[4] D. A. Barr and R. N. Haszeldine, *J.*, 1956, 3428.
[5] G. R. Porter, unpublished results. The ultraviolet spectrum reported by J. R. Dacey and D. M. Young, *J. Chem. Phys.*, 1955, **23**, 1302, shows a second maximum at 267·5 mμ caused by impurity trifluoroiodomethane.
[6] H. C. Ramsperger, *J. Amer. Chem. Soc.*, 1928, **50**, 123.
[7] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 357.
[8] J. Thiele, *Ber.*, 1909, **42**, 2575.
[9] O Ruff and W. Willenberg, *Ber.*, 1940, **73**, 724.

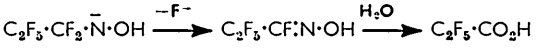
The boiling point of the 1,1- or 1,2-bistrifluoromethyldimethylhydrazine (67·9°) is close to that of tetramethylhydrazine (72·9°) [cf. $(CF_3)_2N{\cdot}N(CF_3)_2$, b. p. 32°].

The flow pyrolysis of 1,1,1-trifluoroazomethane at 560° gave 1,1-difluoroethylene as a major product, by dehydrofluorination of 1,1,1-trifluoroethane also isolated. Products arising by attack on the azo-group were not observed, but otherwise the pyrolysis resembled the photolysis.

The ease of nucleophilic attack by methylamine on trifluoronitrosomethane suggests that the conversion of the latter into trifluoronitromethane and hexafluoroazoxymethane by aqueous base could proceed as follows:



The formation of pentafluoropropionic acid from heptafluoronitrosopropane can be explained similarly, without postulating attack on the α-carbon: [3]



Since the work described in this Paper was completed, several Papers [10] have appeared, without experimental detail but recording boiling points, describing the preparation of $CF_3{\cdot}N{:}N{\cdot}C_2H_5$ and higher homologues, and mentioning the preparation of $CF_3{\cdot}N{:}N{\cdot}CH_3$. The photolysis of $CF_3{\cdot}N{:}N{\cdot}CH_3$ is considered to give $(CF_3{\cdot}NMe)_2$ b. p. 76°, but experimental detail is again lacking.[10] The Russian authors have also presented a similar,[11] and an alternative [12] scheme for the hydrolysis of trifluoronitrosomethane.

Experimental.—Preparation of 1,1,1-*trifluoroazomethane.* Trifluoronitrosomethane (2·950 g., 29·8 mmoles) and pure methylamine (0·924 g., 29·8 mmoles), sealed in a 500 ml. Pyrex tube and allowed to warm from −196° to room temperature, underwent a vigorous reaction as the amine liquified and gave a red-brown viscous liquid; no further reaction occurred when kept at 20°. Fractionation gave nitrogen (1·2 mmoles), carbon dioxide (1·1 mmoles), trifluoronitrosomethane (1·014 g., 10·26 mmoles, 34% recovery) (*M*, 98), 1,1,1-trifluoroazomethane (1·265 g., 11·14 mmoles, 57% yield), and water (0·304 g., 16·9 mmoles, 87% yield) (*M*, 20). Gas–liquid chromatography (30% dinonyl phthalate–Celite at 20°) removed traces of trifluoronitromethane (1%) and hexafluoroazoxymethane (2%) to give chromatographically pure 1,1,1-*trifluoroazomethane* (Found: C, 21·4; H, 2·6; N, 25·3%; *M*, 112. $C_2H_3F_3N_2$ requires C, 21·4; H, 2·7; N, 25·0%; *M*, 112), the vapour pressure of which over the range −33 to 0° is given by the

[10] S. P. Makarov, A. Ya. Yakubovich, V. A. Ginsberg, A. S. Filatov, M. A. Englin, N. F. Privezentseva, and T. Ya. Nikiforova, *Doklady Akad. Nauk, S.S.S.R.*, 1961, **141**, 357; V. A. Ginsberg, A. Ya. Yakubovich, A. S. Filatov, G. E. Zelenin, S. P. Makarov, V. A. Shpanskii, G. P. Kotelnikova, L. F. Sergienko, and L. L. Martynova, *ibid.*, 1962, **142**, 354.

[11] V. A. Ginsberg, A. Ya. Yakubovich, A. S. Filatov, V. A. Shpanskii, E. S. Vlasova, G. E. Zelenin, L. F. Sergienko, L. L. Martynova, and S. P. Makarov, *Doklady Akad. Nauk S.S.S.R.*, 1962, **142**, 88.

[12] A. Ya. Yakubovich, V. A. Ginsberg, S. P. Makarov, V. A. Shpanskii, N. F. Privezentseva, L. L. Martynova, B. V. Kir'yan, and A. L. Lemke, *Doklady Akad. Nauk S.S.S.R.*, 1961, **140**, 1352; V. A. Ginsberg, S. S. Dubov, A. N. Medvedev, L. L. Martynova, B. I. Tetel'baum, M. N. Vasil'eva, and A. Ya. Yakubovich, *ibid.*, 1963, **152**, 1104.

equation $\log_{10}p(\text{mm.}) = 7{\cdot}876 - 1377/T$, whence the b. p. is calculated as 2·6°, the latent heat of vaporisation is 6300 cal. mole^{-1}, and Trouton's constant is 22·9. The solid remaining in the reaction tube was extracted by 10% aqueous ethanol to give a red-brown, hygroscopic solid (1·308 g., 34% by weight), recrystallised from absolute ethanol to give a white crystalline solid (Found: C, 12·2; H, 5·8; N, 13·1%), m. p. 273—275°. An aqueous solution of the solid was acid to litmus and contained fluoride. The solid (0·3183 g.), heated under reflux with 30% aqueous sodium hydroxide (10 ml.) liberated 64% of the nitrogen in the solid as methylamine (0·060 g., 1·91 mmoles) (*M*, 31·6); fluoride and cyanate were then present.

1,1,1-Trifluoroazomethane shows bands in the infrared at 3·33m, 3·41m, 3·50m, 4·07w, 4·77m, 6·28m, 6·95s, 7·18s, 8·04vs, 8·17vs, 10·10s, 10·15s, 11·35m, 11·43m, 13·75s, 13·85s, and 13·98s.

Properties of 1,1,1-*trifluoroazomethane.* (*a*) *Stability to aqueous reagents.* 1,1,1-Trifluoroazomethane (0·20 g.), sealed in a 20 ml. tube with concentrated hydrochloric acid, (3 ml.), was completely decomposed after 24 hr. at 20°, with the formation of carbon dioxide and ammonium and fluoride ions. Aqueous 20% sodium hydroxide destroyed only 52% of the azo-compound after 16 hr. at 20°; complete breakdown had occurred after 10 days, and fluoride and cyanate were present.

(*b*) *Action of methylamine.* 1,1,1-Trifluoroazomethane (0·412 g., 3·68 mmoles) and methylamine (0·115 g., 3·72 mmoles), sealed in a 40 ml. Carius tube and warmed to room temperature, gave a solid (0·280 g., 94%), shown to be identical with that isolated as a by-product of the reaction of trifluoronitrosomethane with methylamine by m. p. and mixed m. p. (274°); 1,1,1-trifluoroazomethane (0·228 g., 2·02 mmoles; 55%) was recovered.

(*c*) *Pyrolysis.* The azo-compound was stable up to 210° in sealed Carius tubes. It was 48% destroyed after 24 hr. at 280° to give nitrogen (7%), carbon dioxide, and silicon tetrafluoride (19%), and a yellow-brown polymeric solid which remained on the walls of the tube. Pyrolysis of 1,1,1-trifluoroazomethane (0·693 g., 6·19 mmoles) at 1—2 mm., with a flow-rate of 3—4 ml./min. through an 8 mm. i.d. silica tube heated over 55 cm. to 560° gave (i) nitrogen (0·099 g., 3·51 mmoles; 57%) (*M*, 28) containing traces of methane, (ii) a mixture (0·238 g., 3·28 mmoles; 53%) (*M*, 72) shown by its infrared spectrum to consist mainly of 1,1-difluoroethylene with hexafluoroethane, 1,1,1-trifluoroethane and fluoroform also present, and (iii) 1,1,1-trifluoroazomethane (0·345 g., 3·08 mmoles, 49%).

(*d*) *Photolysis.* 1,1,1-Trifluoroazomethane (0·969 g., 8·65 mmoles) in a 57 ml. silica tube, irradiated for 36 hr. by a Hanovia S.250 lamp with the lower end of the tube masked to prevent irradiation of liquid products, gave nitrogen (0·110 g., 3·94 mmoles; 46%), fluoroform, 1,1,1-trifluoroethane, and carbon dioxide (0·039 g., 0·53 mmoles; 6%), and a less-volatile mixture (0·60 g., 62%) (*M*, 190) shown to contain three major and four minor components by gas–liquid chromatography (30% dinonyl phthalate–Celite column at 50°); the analysis and infrared spectrum of the separated largest component (*ca.* 25% yield) was consistent with either 1,1- or 1,2-bistrifluoromethyldimethylhydrazine (Found: C, 24·5; H, 3·1; N, 14·1%; *M*, 190. Calc. for $C_4H_6F_6N_2$: C, 24·5; H, 3·1; N, 14·3%; *M*, 196) b. p. (isoteniscope) 67·9°. Small amounts of a yellow, water-soluble solid formed on the walls of the tube.

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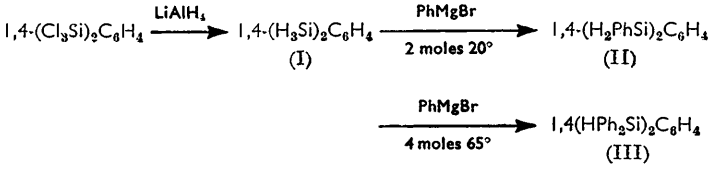
408. *Synthesis of Aryl-substituted* p-*Disilylbenzenes*

By D. Richard Anderson and J. M. Holovka

Although arylsilanes have been known for a long time,[1,2] a direct method of preparing *p*-disilylbenzenes has not been available. The difficulties encountered in the isolation of *p*-disilylbenzenes when a Grignard reagent and the appropriate chlorosilane [3] is used have led the authors to experiment with a Grignard reagent in conjunction with an aryl silane.[4,5] This Paper records a novel two-step synthesis of symmetrical aryl *p*-disilylbenzenes.



p-Disilylbenzene (I) was conveniently prepared by the reduction of *p*-bistrichlorosilylbenzene with lithium aluminium hydride. *p*-Bis(phenylsilyl)benzene (II) and *p*-bis(diphenylsilyl)benzene (III) were prepared from the reaction of compound (I) with the correct equivalent ratios of phenyl Grignard reagent when tetrahydrofuran was used as solvent. When sufficient Grignard reagent was available, the reaction temperature was of utmost importance because a change from room temperature to the boiling point of tetrahydrofuran (~60°) changed the reaction products from mono- to di-substituted on each silyl group.

Experimental.—p-*Disilylbenzene.* To a cooled slurry of lithium aluminium hydride (0·44 g., 0·12 mole) in anhydrous diethyl ether (900 ml.) was added *p*-bis(trichlorosilyl)benzene (242 g., 0·70 mole) at such a rate as to maintain the temperature below 20°. The mixture was allowed to warm to room temperature and was then heated to reflux for 2 hr. Light petroleum (b. p. 30—60°; 300 ml.) was added, stirred with the mixture, and decanted. The lower layer was extracted again with diethyl ether (300 ml.)–light petroleum (300 ml.). Moist ether was added to the lower layer until gas evolution ceased; then dilute hydrochloric acid was added. After extraction of the aqueous portion with light petroleum, the combined ether–petroleum fractions were washed twice with water and dried overnight ($MgSO_4$). Stripping of the solvents on a rotary evaporator and distillation of the residue yielded p-*disilylbenzene* (I) (61·8 g., 0·447 mole), b. p. 31°/10 mm., n_D^{25} 1·5243 (Found: C, 52·05; H, 7·2; Si, 40·3. $C_6H_{10}Si_2$ requires C, 52·1; H, 7·3; Si, 40·6%).

p-*Bis(phenylsilyl)benzene.* To a stirred solution of *p*-disilylbenzene (20 g., 0·14 ml.) tetrahydrofuran (50 ml.) was added the phenyl Grignard reagent, prepared from magnesium (7·9 g., 0·33 mole) and bromobenzene (47·1 g., 0·40 mole) in tetrahydrofuran. The temperature was always maintained below 20° during the addition of the Grignard reagent. After the solution was allowed to warm to room temperature, it was stirred for 16 hr., poured on to a mixture of crushed ice and dilute sulphuric acid, and extracted three times with diethyl ether. The combined ether fractions were washed twice with water and dried ($MgSO_4$). The solution was filtered and the solvent evaporated under vacuum. Vacuum distillation of the residue yielded the monophenyl-substituted *product* (17·6 g., 0·0606 mole), b. p. 148—155°/0·35 mm., n_D^{26} 1·6047 (Found: C, 74·6; H, 6·2; Si, 19·3%; *M*, 289. $C_{18}H_{18}Si_2$ requires C, 74·4; H, 6·2; Si, 19·3%; *M*, 290).

p-*Bis(diphenylsilyl)benzene.* To a stirred solution of *p*-disilylbenzene (20 g., 0·14 mole) in tetrahydrofuran (50 ml.) was added the phenyl Grignard reagent, prepared from magnesium

[1] Eaborn, " Organosilicon Compounds," Butterworth Scientific Publications, London, 1960.
[2] Westermark, *Acta Chem. Scand.*, 1954, **8**, 1830.
[3] Noltes and Van Der Kerk, *Rec. Trav. chim.*, 1960, **81**, 565.
[4] Gilman and Zeuch, *J. Amer. Chem. Soc.*, 1959, **81**, 5925.
[5] Gilman and Zeuch, *J. Amer. Chem. Soc.*, 1957, **79**, 4560.

(15·8 g., 0·66 mole) and bromobenzene (94·2 g., 0·6 mole) dissolved in tetrahydrofuran. The resulting solution was refluxed for 24 hr., and then poured on to a mixture of cracked ice and dilute sulphuric acid. The aqueous acid solution was extracted three times with ether. The ether extracts were washed twice with water and dried ($MgSO_4$). The solvent was removed on a rotating evaporator under vacuum. The non-distillable heavy oil was heated to 275°/0·3 mm. for several hours to removal all traces of solvents and starting materials. There was obtained the diphenyl-substituted *product* (45·3 g., 0·103 mole), n_D^{26} 1·6327 (Found: C, 80·5; H, 6·0; Si, 12·6%; *M*, 446. $C_{30}H_{26}Si_2$ requires C, 81·4; H, 5·9; Si, 12·7%; *M*, 443).

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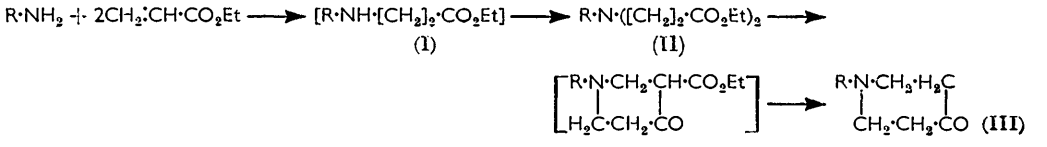
409. *The Preparation of* N-*t-Butyl*-4-*piperidone*

By J. B. ROBINSON and J. THOMAS

THE use of 4-t-butyl cyclohexane derivatives for the study of the conformations of substituted cyclohexanes has been reported by many workers.[1] The application of such methods to the study of the stereochemistry of piperidine derivatives has probably been neglected because of difficulties in the preparation of *N*-t-butyl-4-piperidone, an important intermediate in such studies. The preparation of this latter compound is now reported.

N-Alkyl-4-piperidones may be prepared by the following reaction sequence.



Ziering *et al.*[2] have reported the preparation of a series of di-(2-ethoxycarbonylethyl)-alkylamines (II; R = Pr^i, Bu^i, and Bu^s) in good yield by keeping the reactants for 1 week at room temperature in ethanol. Applying this method to the addition of t-butylamine to ethyl acrylate resulted in the isolation of the monoaddition product only 2-ethoxycarbonylethyl-t-butylamine (I; R = Bu^t). The monoaddition product was also obtained when the reaction time was 4 weeks, and when the reaction was carried out without solvent at 116° for 10 hr.

Attempts to prepare compound (II; R = Bu^t) by reacting compound (I; R = Bu^t) with ethyl β-chloropropionate in acetone in the presence of silver oxide were similarly unsuccessful.

The preparation was accomplished by refluxing compound (I; R = Bu^t) in ethyl acrylate for 96 hr. It was found that by varying the concentrations of the reactants the yield of the desired product (II; R = Bu^t) could be increased to about 27%. Attempts to improve the yield further lead to the formation of polymers and other side-products.

Attempts to cyclise compound (II; R = Bu^t) using sodium ethoxide in boiling xylene [3] gave a basic polymeric material as the only product. Formation of the hydrobromide of the basic polymer and crystallisation from ethanol yielded a small sample (0·5% yield) of *N*-t-butyl-4,4-diethoxypiperidine hydrobromide.[4]

Repetition of the Dieckmann cyclisation in boiling benzene [5] gave the desired product (III; R = Bu^t) in high yield after hydrolysis and decarboxylation.

[1] Winstein and Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 5562; Eliel, *J. Chem. Educ.*, 1960, **37**, 126, and refs. there cited.
[2] Ziering, Berger, Heineman, and Lee, *J. Org. Chem.*, 1947, **12**, 894.
[3] Fuson, Parham, and Reed, *J. Amer. Chem. Soc.*, 1946, **68**, 1239.
[4] R. E. Lyle, G. G. Lyle, and Adel, *J. Org. Chem.*, 1959, **24**, 342.
[5] Leonard, Fulmer, and Hay, *J. Amer. Chem. Soc.*, 1956, **78**, 3457.

Experimental.—*2-Ethoxycarbonylethyl-t-butylamine.* Ethyl acrylate (94 g.) and t-butylamine (34·5 g.) were mixed and placed in a screw-capped bottle, and the mixture heated at 116° (10 lb./sq. in.) for 10 hr. When the mixture had cooled, the excess of ethyl acrylate was distilled off, and the residual liquid fractionally distilled. *2-Ethoxycarbonylethyl-t-butylamine* was collected, b. p. 66°/2 mm.; 95—97°/20 mm. (65 g., 87%), n_D^{20} 1·4260 (Found: Equiv., 175. $C_9H_{19}NO_2$ requires Equiv., 173), $\nu_{max.}$ (liquid film) 1730 cm.$^{-1}$ (C = O); *2-ethoxycarbonyl-t-butylamine hydrochloride* m.p. 208·5—210° (from butanol) (Found: C, 46·25; H, 9·1. $C_7H_{16}ClNO_2$ requires C, 46·3; H, 8·8%).

Di-(2-ethoxycarbonylethyl)-t-butylamine. 2-Ethoxycarbonylethyl-t-butylamine (95 g.) was mixed with ethyl acrylate (200 ml.), and the mixture refluxed for 96 hr. The mixture was cooled and then fractionally distilled under reduced pressure. After a fore-run of 2-ethoxycarbonylethyl-t-butylamine (56 g.), the *di(2-ethoxycarbonylethyl)-t-butylamine* distilled, along with a solid by-product, at 143—146°/2·5 mm. The material was purified by dissolving it in ether and washing the ether solution with water (3 × 10 ml.). The bulked washings were then washed with ether (10 ml.) and then discarded. The bulked ether solution was dried ($MgSO_4$) and the ether distilled. The residual liquid was fractionally distilled when only one fraction was obtained, b.p. 118—120°/0·35 mm. (39·5 g., 27%) (Found: C, 61·4; H, 9·9%; Equiv., 273. $C_{14}H_{27}NO_4$ requires C, 61·7; H, 9·9%; Equiv., 273); $\nu_{max.}$ (liquid film) 1720 cm.$^{-1}$ (C=O).

N-*t-Butyl-4-piperidone.* Di-(2 *ethoxycarbonylethyl)-t-butylamine* (24 g.) in benzene (200 ml.) was added during 3 hr. to a suspension of sodium ethoxide [prepared from sodium hydride (6·5 g.) and absolute ethanol (2 ml.)] in boiling benzene (700 ml.). The mixture was refluxed for a further 3 hr. after the addition and then kept at room temperature overnight. The mixture was cooled in ice and glacial acetic acid (18 ml.) and then water (50 ml.) added. The aqueous phase was separated and retained. The benzene phase was extracted with 6N–HCl (4 × 70 ml.). The bulked acid extracts were heated on a steam-bath for 8 hr., the solution made alkaline with solid Na_2CO_3, and extracted with ether (4 × 100 ml.) and then with chloroform (3 × 100 ml.). The bulked organic extracts were dried ($MgSO_4$), the solvent distilled, and the residual liquid fractionally distilled to give N-*t-butyl-4-piperidone* b. p. 92—94°/9 mm. (8 g. 59%), $\nu_{max.}$ (liquid film) 1715 cm.$^{-1}$ (C=O); *hydrobromide salt*, m. p. 229—230° (decomp.), from isopropyl alcohol (Found: C; 45·7; H, 7·6. $C_9H_{18}BrNO$ requires C, 45·75; H, 7·6%); *picrate*, m. p. 201—202° (decomp.), from water (Found: C, 46·85; H, 5·2. $C_{15}H_{20}N_4O_8$ requires C, 46·9; H, 5·2%); *3,5-dibenzylidene* derivative,[6] m. p. 163—164° (Found: C, 83·2; H, 7·6. $C_{23}H_{25}NO$ requires C, 83·4; H, 7·55%), $\nu_{max.}$ (in Nujol) 1660 cm.$^{-1}$ (conjugated C=O). $\lambda_{max.}$ (in ethanol) 326 mμ (ε 34,300), 228 mμ (ε 16,100).

Department of Pharmacy, The University, Manchester. [*Received, June 23rd*, 1964.]

[6] McElvain and Rorig, *J. Amer. Chem. Soc.*, 1948, **70**, 1820.

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410. *Periodate Oxidation. Part VIII.* Oxidation Products from Methyl Pentopyranosides*

By G. J. F. Chittenden and R. D. Guthrie

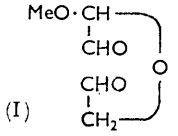
Jackson and Hudson [1] observed that the syrupy products from the periodate oxidation of an anomeric pair of methyl pentopyranosides had equal, but opposite specific rotations. Oxidation of the syrups with bromine water gave dibasic acids also of equal, but opposite rotation. Grosheintz [2] obtained similar results from lead tetra-acetate oxidations. Since the products were believed to be D- or L-methoxydiglycolaldehyde, *e.g.*, (I), this was reasonable, as the anomeric carbon atom was the only asymmetric centre in the molecule. However, there is very strong evidence that the oxidation products exist in the cyclic

* Part VII, R. L. Colbran and J. R. Holker, *J.*, 1963, 3347.

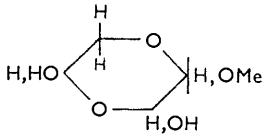
[1] E. L. Jackson and C. S. Hudson, *J. Amer. Chem. Soc.*, 1937, **59**, 994.
[2] J. M. Grosheintz, *J. Amer. Chem. Soc.*, 1939, **61**, 3379.

dioxan form (II) on the basis of their high specific rotations (±124°);[3] these are comparable with the values for the cyclic starting compounds, whereas known acyclic derivatives such as the borohydride reduction product of (II) have low specific rotations. Furthermore there are analogous crystalline oxidation products for which infrared evidence can be produced for the cyclic form.[4-6]

The cyclic forms (II) have three asymmetric centres and, therefore, the products from an anomeric pair of glycosides would not be expected to be mirror images, *i.e.*, have the same numerical specific rotation.

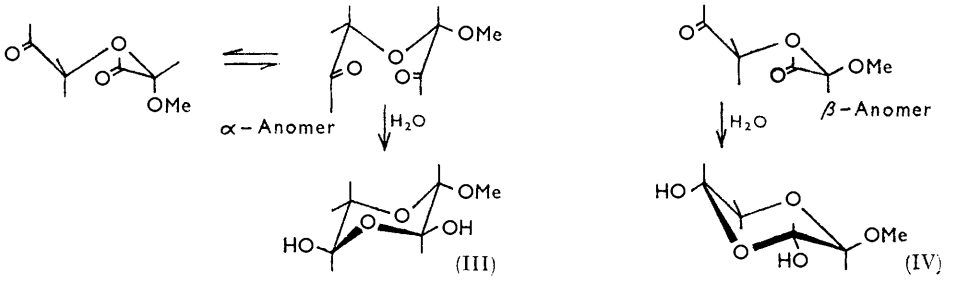


(I)



(II)

One of us has proposed a conformational change to account for this behaviour.[6] It was suggested that a conformational change occurs in one anomer (assuming a CA conformation [7]) so that the final cyclic products (III) and (IV) from α- and β-D-pentapyranosides are mirror images, as shown. Consider the α-anomer to undergo the conformational change:



The same argument would apply if the β-anomer had been considered. It is assumed that hydroxyl groups in the products are in an equatorial configuration though the same argument would apply for other configurations provided that it is the same in both anomers. No crystalline derivatives of a pair of periodate-oxidised anomers were then described in the literature to test the validity of this theory.

We have now prepared the crystalline di-*p*-nitrobenzoates of two pairs of anomeric pentosides, methyl α- and β-D-xylopyranosides and methyl α- and β-L-arabinopyranosides and find them not to be mirror-image pairs, thus invalidating the above theory. The derivatives from methyl α-D-xyloside and methyl α-L-arabinoside had m. p. 88·5—90·5° and showed specific rotations of +106 and −107°, respectively, whereas the derivatives from methyl β-D-xyloside and methyl β-L-arabinoside had m. p. 71—73° and specific rotations of +54·2 and −53·4°; measurement of the optical rotatory dispersion curves of the derivatives from methyl α- and β-D-xylosides in chloroform solution showed the α-anomer to a positive plain dispersion curve and the β-anomer to have a negative plain curve; the two curves were not mirror images.

All four compounds had almost identical infrared spectra with a strong ester band at 1750 cm.$^{-1}$ characteristic of the carbonyl stretching frequency of a hemialdal aryl ester.[8]

[3] I. J. Goldstein and F. Smith, *J. Amer. Chem. Soc.*, 1960, **82**, 3421.
[4] I. J. Goldstein, B. A. Lewis, and F. Smith, *J. Amer. Chem. Soc.*, 1958, **80**, 939.
[5] R. D. Guthrie and J. Honeyman, *J.*, 1959, 2441.
[6] R. D. Guthrie, *Adv. Carbohydrate Chem.*, 1961, **16**, 116.
[7] H. S. Isbell and R. S. Tipson, *J. Res. Nat. Bur. Stand.*, 1960, **64***A*, 171.
[8] R. D. Guthrie, *J.*, 1961, 2525.

The proton magnetic resonance spectra of the derivatives in deuterochloroform, although very similar, showed small, but definite differences.

To show that the oxidation products could also react in the dialdehyde form (cf. ref. 5), the bis-*p*-nitrophenylhydrazones of all four oxidation products were prepared.

Experimental.—Alumina was of type H, 100—200 mesh, supplied by Peter Spence Ltd. The identity of compounds was proved where necessary by mixed m. p. and infrared spectrometry. Optical rotations were measured for *NN*-dimethylformamide solutions.

Periodate oxidation of methyl pentopyranosides. The general procedure of Baer and Fischer [9] was followed, but the oxidation solution [from methyl pentopyranoside (0·81 g.)] was worked up as follows.

Barium chloride dihydrate (1·22 g.) and ethanol (150 ml.) were added to the oxidation solution. The precipitated inorganic salts were removed by filtration and evaporation of the filtrate gave a syrupy product mixed with a small amount of inorganic material. The syrup was extracted with chloroform (2 × 100 ml.) and acetone (50 ml.); the combined extracts were dried (Na_2SO_4) and evaporated *in vacuo* to give a clear glass, $[\alpha]_D^{21}$ ±124° (water).

Reaction of periodate-oxidised methyl pentopyranoside with p-*nitrobenzoyl chloride.* (*a*) *From methyl* α-D-*xyloside.* Periodate-oxidised methyl α-D-xyloside (0·69 g.) in dry pyridine (20 ml.) was treated with *p*-nitrobenzoyl chloride (2 g.) and mixture shaken at room temperature for 17 hr. Water (5 ml.) was added, the mixture stood for 10 min. and then poured into ice-cold saturated sodium hydrogen carbonate solution to give a sticky cream solid. Four recrystallisations from propan-1-ol gave the *di*-p-*nitrobenzoate*, m. p. 88·5—90·5°, $[\alpha]_D^{21}$ +106° (*c* 0·54) (Found: C, 50·5; H, 3·9; N, 6·2. $C_{19}H_{16}N_2O_{11}$ requires C, 50·9; H, 3·6; N, 6·2%).

(*b*) *From methyl* β-D-*xyloside.* Treatment of the oxidation product as in (*a*) gave the *di*-p-*nitrobenzoate*, m. p. 71·5—73°, $[\alpha]_D^{22}$ −53·4° (*c* 0·47) (Found: C, 50·6; H, 3·8; N, 6·1%).

(*c*) *From methyl* α-L-*arabinoside.* Treatment of the oxidation product as described in (*a*) gave the *di*-p-*nitrobenzoate*, m. p. 88—90°, $[\alpha]_D^{22}$ −107° (*c* 0·59) (Found: C, 51·3; H, 4·0; N, 5·9%).

(*d*) *From methyl* β-L-*arabinoside.* Treatment of the oxidation product as above gave the *di*-p-*nitrobenzoate*, m. p. 71—73°, $[\alpha]_D^{22}$ −54·2 (*c* 0·47) (Found: C, 51·4; H, 3·5; N, 6·1%).

Reaction of periodate-oxidised methyl pentopyranosides with p-*nitrophenylhydrazine.* (*a*) *From methyl* α-D-*xyloside.* The oxidation product (0·64 g.) was dissolved in ethanol (25 ml.), and water (5 ml.) and *p*-nitrophenylhydrazine (1·1 g., 1·75 mol.) were added; the mixture was heated at 60° for 10 min., cooled to room temperature, decolourised with charcoal, and the filtrate poured into ice–water (100 ml.) to give a yellow-orange solid. The product was collected, washed with water, and dried *in vacuo* (P_2O_5). Chromatography on alumina with benzene–ethanol (1 : 1) as eluant gave D-*methoxydiglycolaldehyde bis*-p-*nitrophenylhydrazone* (51%) m. p. 91—93° (decomp.), $[\alpha]_D^{21}$ −3·2 (*c* 0·58) (Found: C, 50·9; H, 4·6; N, 20·6. $C_{17}H_{18}N_6O_6$ requires C, 50·8; H, 4·5; N, 20·9%).

(*b*) *From methyl* β-D-*xyloside.* Reaction of the oxidation product as described above gave L-*methoxyglycolaldehyde bis*-p-*nitrophenylhydrazone*, m. p. 91—93° (decomp.), $[\alpha]_D^{21}$ +3·0° (*c* 0·62) (Found: C, 50·5; H, 4·6; N, 21·1%).

(*c*) *From methyl* α-L-*arabinoside.* Reaction of the oxidation product as described in (*a*) gave L-*methoxydiglycolaldehyde bis*-p-*nitrophenylhydrazone*, m. p. 90·5—92° (decomp.), $[\alpha]_D^{22}$ +3·2° (*c* 0·46) (Found: C, 50·5; H, 4·6%).

(*d*) *From methyl* β-L-*arabinoside.* Reaction of the oxidation product as described above gave D-*methoxydiglycolaldehyde bis*-p-*nitrophenylhydrazone*, m. p. 91—93° (decomp.), $[\alpha]_D^{21}$ −3·1° (*c* 0·57) (Found: C, 50·5; H, 4·5; N, 21·1%).

We thank Dr. A. F. Johnson for the optical rotatory dispersion measurements, Dr. A. Pidcock for determining the proton magnetic resonance spectra, and Imperial Chemical Industries Limited (Pharmaceuticals Division) for financial support (to G. J. F. C.).

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BRIGHTON, SUSSEX. [*Received, July 8th*, 1964.]

[9] H. H. Baer and H. O. L. Fischer, *J. Amer. Chem. Soc.*, 1959, **81**, 5184.

411. *Complex Halides of Transition Metals. Part I. Hexabromotungstates(v)*

By B. J. Brisdon and R. A. Walton

Interest has recently centred on the preparation and properties of complex halides of transition metals. Several complexes of the type, $M_2^{I}M^{IV}X_6$ (where M^{IV} = Mo or W, and X = Cl or Br) have recently been prepared,[1-3] and Chatt and his co-workers [4] described the salt $[Et_4N]^+[WCl_6]^-$. The latter complex contains a d^1 configuration and its spectral and magnetic properties would therefore be of interest. Several hexachlorovanadates(II) have also been prepared.[5]

We have prepared and characterised a series of substituted ethylammonium salts of the hexabromotungstate(v) ion. These complexes were precipitated as black crystals when chloroform solutions of tungsten(v) bromide and amine hydrobromide were heated together. All the salts were readily hydrolysed and were consequently handled under anhydrous conditions. They were soluble in acetone and methyl cyanide, but insoluble in non-polar solvents. Several complexes of tungsten(IV) bromide have been prepared,[3,6] *viz.*, WBr_4,2RCN, WBr_4,2py, and WBr_6^{2-}, but very few complexes of tungsten(v) bromide have been characterised, although several aminolysis and alcoholysis products are known.[7,8]

The infrared spectra of all except the tetraethylammonium salt showed broad bands at ~3150 and ~1600 cm.$^{-1}$, associated with the N–H stretching and bending modes, respectively. All the salts dissolved in methyl cyanide to give brown solutions; solutions of $[Et_4N]^+[WBr_6]^-$ in this solvent had molar conductivities of 108 and 132 ohm^{-1} cm.^{2} at concentrations of 7·16 and 1·06 moles/l., respectively. A typical 1 : 1 electrolyte, Et_4NBr, had Λ_m = 159 ohm^{-1} cm.^{2} at 25° for a concentration of 1·11 moles/l. Other workers [9] found similar values for 1 : 1 electrolytes in this solvent.

The reflectance spectra of the tetraethyl- and triethyl-ammonium salts were similar, and showed three broad and poorly resolved bands between 14,000 and 23,000 cm.$^{-1}$ (Table 1).

Table 1

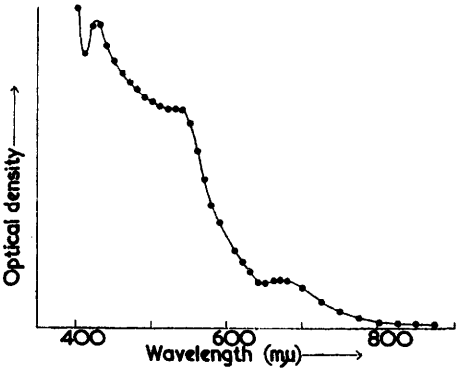
Visible spectra of hexabromotungstate complexes

Complex	Conditions	Peak positions (cm.$^{-1}$) (extinction coefficients in parentheses)
$[Et_4N]^+[WBr_6]^-$	Diffuse reflectance	~14,700sh; 18,900; ~22,700
	Methyl cyanide	14,900(73); 18,900(980); 23,500(2400)
$[Et_3NH]^+[WBr_6]^-$	Diffuse reflectance	~14,300sh; 18,200; 22,200

The spectrum of $[Et_4N]^+[WBr_6]^-$ in methyl cyanide (Table 1 and Figure) was almost identical with the diffuse-reflectance spectrum of this salt, suggesting that similar species are present in the solid and in solution. It is of interest that the hexabromotungstates(v) are stable in methyl cyanide solution, whereas tungsten(v) bromide is readily reduced by alkyl cyanides.[6] For a d^1 configuration in a field of octahedral (O_h) symmetry, one ligand-field band would be expected ($^2E_g \leftarrow {}^2T_{2g}$). A field of lower symmetry, for example D_{4h}, should result in the splitting of both upper (^2E_g) and ground ($^2T_{2g}$) terms, so that the transitions $^2A_{1g} \leftarrow {}^2B_{2g}$ and $^2B_{1g} \leftarrow {}^2B_{2g}$ are expected. The peaks at 14,900 and

[1] Edwards, Peacock, and Said, *J.*, 1962, 4643.
[2] Allen, Brisdon, Edwards, Fowles, and Williams, *J.*, 1963, 4649.
[3] Kennedy and Peacock, *J.*, 1963, 3392.
[4] Adams, Chatt, Davidson, and Gerratt, *J.*, 1963, 2189.
[5] Fowles and Walton, *J. Inorg. Nuclear Chem.*, 1965, in the press.
[6] Allen, Brisdon, and Fowles, *J.*, 1964, 4531.
[7] Brisdon and Fowles, *J. Less-Common Metals*, 1964, **7**, 102.
[8] Funk and Schauer, *Z. anorg. Chem.*, 1960, **306**, 203.
[9] Woodruff, Marini, and Fackler, *Inorg. Chem.*, 1964, **3**, 687.

18,900 cm.$^{-1}$ are tentatively assigned to these transitions; this asymmetry is possibly brought about by a Jahn–Teller distortion. The high intensity of the peak at 18,900 cm.$^{-1}$ may arise through the borrowing of intensity from the adjacent charge-transfer band at 23,500 cm.$^{-1}$. This latter band may be due to the transfer of charge from the metal to the bromine atoms. Transitions of the type, ligand (π) ⟶ metal, occur at much higher energy.[10] Jørgensen[11] predicted that for the "hypothetical" $MoCl_6^-$ ion, the $^2E_g \longleftarrow {}^2T_{2g}$ transition should occur about 30,000 cm.$^{-1}$, and Horner and



Visible spectrum of $[Et_4N]^+[WBr_6]^-$ in methyl cyanide

Tyree[12] observed a band at 24,100 cm.$^{-1}$ in a potassium chloride–molybdenum pentachloride melt, which they attribute to the $MoCl_6^-$ ion. In view of the accepted ligand-field order Cl > Br, a value of $D_q = 1890$ cm.$^{-1}$ for the WBr_6^- ion does not appear unreasonable.

The complexes $[Et_4N]^+[WBr_6]^-$ and $[EtNH_3]^+[WBr_6]^-$ had magnetic moments at 300°K of 1·28 and 1·23 B.M., respectively. It is apparent that spin–orbit coupling is responsible for lowering the magnetic moment below the spin-only value (1·73 B.M.), and is of the order expected for a third-row transition metal.

Experimental.—All experiments were carried out in a closed vacuum system.

Analytical methods. Tungsten was determined by ignition to the oxide at 800°, nitrogen by the Kjeldahl procedure, and bromine by the Volhard method after dissolution in sodium hydroxide and hydrogen peroxide solution. Valency-state determinations were made by dissolving the complex in standard potassium dichromate solution, and titrating the excess of the latter with iron(II) ammonium sulphate (Found for $[Et_4N]^+[WBr_6]^-$: valency state, 5·02).

TABLE 2

Hexabromotungstates(V)

	Found (%)			Calc. (%)		
Complex	Br	N	W	Br	N	W
$[Et_4N]^+[WBr_6]^-$	59·6	1·7	23·3	60·4	1·8	23·2
$[Et_3NH]^+[WBr_6]^-$	62·4	1·8	23·7	62·65	1·8	24·0
$[Et_2NH_2]^+[WBr_6]^-$	64·8	1·9	25·1	65·1	1·9	24·9
$[EtNH_3]^+[WBr_6]^-$	67·1	1·9	25·5	67·6	2·0	25·9

Materials. Tungsten(V) bromide was prepared by the action of bromine vapour (diluted with nitrogen) on tungsten metal powder at 1000° (Found: W, 31·2; Br, 68·1. Calc. for WBr_5: W, 31·5; Br, 68·5%).

[10] Jørgensen, *Mol. Phys.*, 1959, **2**, 309.
[11] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73.
[12] Horner and Tyree, *Inorg. Chem.*, 1963, **2**, 568.

Chloroform and methyl cyanide were dried by repeated distillation *in vacuo* from phosphoric oxide.

Preparation of hexabromotungstate(v) *salts.* Tungsten(v) bromide and the appropriate substituted ethylammonium bromide were sealed in ampoules in approximately 1 : 1 mole ratio, using chloroform as solvent. The contents of the ampoule were boiled for about 10 min.; on cooling, the hexabromotungstate salts separated as black crystals. They were washed several times with dry chloroform to remove unreacted tungsten(v) halide and amine hydrobromide.

Physical measurements. Visible spectra were measured by means of a Unicam S.P. 500 spectrophotometer equipped with a reflectance attachment, modified to make it suitable for measurements on compounds that reacted with air and moisture, and infrared spectra for Nujol mulls, with a Unicam S.P. 200 spectrophotometer. Magnetic susceptibilities were measured bythe Gouy procedure at room temperature only, and conductivities in specially adapted cells with a Phillips PR 9500 bridge at 25°.

We thank Dr. G. W. A. Fowles for providing facilities for the measurement of the spectral and magnetic properties.

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[*Received, July 8th*, 1964.]

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412. *Unstable Intermediates. Part XXIX. Sigma and Pi Radicals*

By M. C. R. Symons

Thomas [1] has recently reported the detection, by electron spin resonance spectroscopy, of free radicals obtained by oxidation of oximes with ceric salts. He postulated that these were iminoxy-radicals, $R_2C=NO$, formed by loss of hydroxyl hydrogen, and suggested that, in view of the large isotropic coupling constant to ^{14}N, the unpaired electron might be in an *s–p* hybrid orbital on nitrogen rather than a π-orbital. Similar radicals have been studied in static systems by Norman and his co-workers.[2]

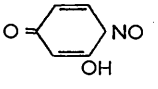
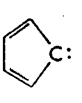
A radical formed by γ-radiolysis of dimethylglyoxime [3] has been assigned the structure HON=CMe–CMe=NO,[4] and the solid-state data were analysed to give more detailed information than can be obtained from the spectra of iminoxy-radicals in solution.

That the radicals under consideration are isostructural can be inferred from the near identity of the large isotropic coupling to ^{14}N (Table).

Electron spin resonance data for iminoxy-radicals, together with some parameters deduced therefrom

	A_{iso} (gauss)	a^2_{2s} (N)	a^2_{2pz}	*p* : *s* ratio	$\widehat{CNO}$
Iminoxy-radicals [1]	31·6 ± 2·4 [a]	0·058			
Dimethylglyoxime radical [3,4] ...	31·67	0·058	0·39	6·6	140°

[a] Mean of 7 results, but excluding that for the radical formulated as (I), for which A_{iso} (N) = 27·9 gauss.

(I)  (II) 

Analysis of the results for the radical obtained from dimethylglyoxime [4] showed that the unpaired electron was 44·8% on nitrogen, and that the *p*/*s* ratio for nitrogen was 6·6.

[1] J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 1446.
[2] B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc.*, 1964, 234.
[3] I. Miyagawa and W. Gordy, *J. Chem. Phys.*, 1959, **30**, 1590.
[4] M. C. R. Symons, *J.*, 1963, 1189.

On the assumption that this admixture arose from the C–N–O bond angle, this was estimated to be about 140°. This may be compared with the experimental and deduced [5] value of 134° for nitrogen dioxide.

Hence it was concluded that the unpaired electron is in a σ- rather than a π-orbital and that it is almost equally distributed between oxygen and nitrogen. This explains the fact that the isotropic hyperfine coupling to ^{14}N is almost constant for a wide range of iminoxy-radicals,[1,2,6] since the (*N*)*s*-character is determined by the bond angle and the amount of delocalisation on to oxygen, and is thus largely independent of the nature of the two R groups in $R_2C{=}NO$.

Further indication that the iminoxy-radicals are σ rather than π stems from the marked differences in hyperfine coupling attributed to the proton of RCH=NO for *syn*- and *anti*-isomers. Compared with results for vinyl radicals, $CH_2{=}\dot{C}H$, it seems that a proton *cis* to the unpaired electron gives the largest coupling (the reverse has been deduced theoretically for the vinyl radical [8]),* that both interactions are markedly reduced and that this reduction is far greater for the *syn*-isomer.[1] These changes may be rationalised qualitatively in terms of the 55% delocalisation on to oxygen and the greater degree of bending in the iminoxy-radicals.

The postulated structure is also in accord with the results of Gilbert *et al.*[2] who found relatively strong coupling to *ortho* protons when R was aryl, as, for example, in the anion from fluorenoneoxime (2·7*G*). This is readily understandable for radicals having about 55% of the unpaired electron in an in-plane orbital on oxygen, but would be hard to interpret if the unpaired electron were in the π-system.

It is not always obvious which alternative structure will be the ground state of a given radical, and in some instances it may well be that the alternative configurations $\ldots\sigma(\uparrow\downarrow)\,\pi\,(\uparrow)$ and $\ldots\pi(\uparrow\downarrow)\,\sigma\,(\uparrow)$ will, for a given bond angle, be relatively close. Such near equivalence is well illustrated by electron resonance results for triplet molecules such as (II) which have been satisfactorily [9] interpreted in terms of a structure $\ldots\pi(\uparrow)\,\sigma\,(\uparrow)$ Evidently the levels are so close that the pairing energy is greater than the σ–π splitting.

A change from $\pi(\uparrow\downarrow)\,\sigma\,(\uparrow)$ to $\sigma(\uparrow\downarrow)\,\pi\,(\uparrow)$ might be induced by suitable choice of substituent groups, or by a constraint on the relevant bond angle. For the radicals under consideration, substitution on the carbon attached to nitrogen or for aryl iminoxy-radicals, substitution in the ring would alter the π-level, whilst for radicals such as $RCO\dot{N}COR'$, the relative energies of the σ- and π-levels could well be sufficiently different for open chain and cyclic radicals such as succinimidyl that the order of levels is inverted. Further, for non-cyclic radicals the change from σ to π would take place before the energies were matched in the $\pi^2\sigma^1$ radical, since the equilibrium bond angle of the $\sigma^2\pi^1$ radical will be considerably reduced as a result of the influence of two σ-electrons. This generally deepens the σ-level relative to the π and hence would stabilise the $\sigma^2\pi^1$ configuration.

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* *Note added in Proof.*—However, the recent results of M. Bethoux, H. Lemaire, and A. Rassat (*Bull. Soc. chim. France*, 1964, 1985) suggest that Thomas's assignment may be wrong.

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413. *The Reaction between Tetra-aryltins and Some Non-metal Fluorides*

By D. W. A. Sharp and J. M. Winfield

Tetra-alkyl- and tetra-aryl-tins react with halides in some cases to transfer an alkyl or an aryl group and in others to form rather ill-defined dialkyl- or diaryl-tin(II) compounds, which appear to undergo thermal decomposition to alkyl or aryl radicals. Thus, boron trifluoride reacts with tetramethyltin to give trimethyltin fluoroborate and methyl boron difluoride,[1] and organotin derivatives have been used in the preparation of vinyl and perfluorovinyl boron fluorides.[2] As examples of the second type of reaction, tetra-n-butyltin reacts with boron tribromide to give butane, but-1-ene, *cis*- and *trans*-but-2-ene, and stannous bromide as well as the expected n-butylboron dibromide,[3] whilst tetramethyltin reacts with aluminium trichloride to give dark red organotin(II) compounds, which undergo thermal decomposition to give ethyl radicals.[4]

These reactions have been extended in the present work to include the interaction of some tetra-aryltins and non-metal fluorides. Boron trifluoride and phosphorus pentafluoride react with tetraphenyltin to give phenylboron difluoride and phenylphosphorus tetrafluoride, respectively. The solid products appear to be triphenyltin fluoroborate and hexafluorophosphate, but they are mixed with some unreacted tetraphenyltin, even when excess of fluoride is used, and cannot be purified. When heated, the fluoroborate and hexafluorophosphate undergo thermal decomposition to triphenyltin fluoride. Arsenic pentafluoride is reduced almost quantitatively to arsenic trifluoride by tetraphenyltin, the other product being a brown gummy material. Phenylarsenic derivatives were not identified amongst the products.

The weaker Lewis acids sulphur tetrafluoride, silicon tetrafluoride, and phosphonitrilic fluoride trimer react similarly to aluminium chloride [4] and benzene, and red-brown gummy materials are produced. Under the fairly extreme conditions necessary to initiate the reaction, it appears that the organotin(II) polymers are unstable and give phenyl radicals, which abstract hydrogen from other phenyl groups. A small amount of triphenyltin fluoride was isolated from each of the reactions, indicating that a straight transfer of phenyl groups may occur, but that any volatile organo-derivatives that are formed are unstable under the conditions used; fluorobenzene was not identified as a product of any of the reactions. If phosphorus pentafluoride containing a trace of hydrogen fluoride was allowed to react with tetraphenyltin the products were benzene and red-brown gummy materials; this indicates that the products are very much dependent upon the purity of the reactants.

The reaction between tetraphenyltin and non-metal fluorides provides a ready method of converting tetraphenyltin to triphenyltin fluoride. In a similar reaction, tetrakispentafluorophenyltin may be converted to trispentafluorophenyltin fluoride by the action of sulphur tetrafluoride. The other product is a red or yellow liquid, which it has not been possible to identify. Boron trifluoride did not react with tetrakispentafluorophenyltin under the conditions used.

Experimental.—Reactions were carried out in a 25 ml. stainless steel bomb which was thoroughly cleaned and dried before each experiment. Tetraphenyltin (from Pure Chemicals Ltd.) and tetrakispentafluorophenyltin (kindly given by Dr. R. D. Peacock) were transferred

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[2] F. E. Brinckman and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6218; H. D. Kaesz, S. L. Stafford, and F. G. A. Stone, *ibid.*, 1959, **81**, 6336.
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[4] G. A. Razuvaev, N. S. Vyazankin, Yu. I. Dergunov, and O. S. D'Yachkovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1960, **132**, 364; G. A. Razuvaev, N. S. Vyazankin, Yu I. Dergunov, and N. N. Vyshynskii, *Zhur. obshchei Khim.*, 1961, **31**, 1712.

to the bomb in a glove-box. Fluorides were prepared by normal methods, purified *in vacuo*, and condensed into the bomb.

Reactions of tetraphenyltin. Tetraphenyltin (2·7 g.) was treated with boron trifluoride (6 g.) for 40 hr. at 140°. The volatile products were unchanged boron trifluoride and phenylboron difluoride (Found: C, 60·4; H, 4·3; F, 27·2%; *M*, 126. Calc. for $C_6H_5BF_2$: C, 57·3; H, 4·0; F, 30·2%; *M*, 126), which were further characterised by their infrared and nuclear magnetic resonance spectra. The solid residue showed two broad infrared bands in the 1000—1100 cm.$^{-1}$ region, a region characteristic of fluoroborates,[5] but this product could not be separated from unchanged tetraphenyltin. When the residue was heated, boron trifluoride was evolved and the solid product was mainly triphenyltin fluoride (Found: C, 57·5; H, 4·7. Calc. for Ph_3SnF: C, 58·6; H, 4·1%) mixed with a small amount of unchanged tetraphenyltin. The identity of these two products were checked further by *X*-ray powder photography.

Tetraphenyltin (2·0 g.) was treated with phosphorus pentafluoride (4·0 g.) for 20 hr. at 135°. The volatile products were unchanged phosphorus pentafluoride and phenylphosphorus tetrafluoride (Found: C, 40·0; H, 2·9; F, 40·5; P, 16·4. Calc. for $C_6H_5F_4P$: C, 39·2; H, 2·7; F, 41·3; P, 16·9%), which were further characterised by infrared and nuclear magnetic resonance spectroscopy. The solid residue showed strong spectral bands at 909 and 877 cm.$^{-1}$; a hexafluorophosphate species would be expected to absorb in this region.[6] Unchanged tetraphenyltin and triphenyltin fluoride were identified after the solid residue had been heated and extracted.

The reaction between tetraphenyltin and phosphorus pentafluoride containing traces of hydrogen fluoride as impurity gave benzene as the main product (*M*, found 80·0. Calc. for C_6H_6: *M*, 78·0).

Tetraphenyltin (1·9 g.) was heated with arsenic pentafluoride (3·0 g.) for 18 hr. at 120°. The volatile product was arsenic trifluoride (1·5 ml.) (Found: *M*, 133. Calc. for AsF_3: *M*, 132). The identification was confirmed by infrared and nuclear magnetic spectroscopy. The solid residue was dark brown and was not identified.

Tetraphenyltin (0·9 g.) was heated with sulphur tetrafluoride (4·0 g.) for 18 hr. at 115°. The volatile products were unchanged sulphur tetrafluoride and benzene (0·1 g.) (Found: *M*, 78·7. Calc. for C_6H_6: *M*, 78·0). The residue was pink; some triphenyltin fluoride was identified in the residue. The reaction between tetraphenyltin and sulphur tetrafluoride did not occur at temperatures below 100°; the use of higher temperatures gave the same products as at 115°. The presence of thionyl fluoride did not affect the reaction.

Tetraphenyltin (1·5 g.) was heated with silicon tetrafluoride (5·0 g.) for 48 hr. at 140°. The volatile products were unchanged silicon tetrafluoride and benzene (50 mg.) (Found: *M*, 78·4. Calc. for C_6H_6: *M*, 78·0). The residue contained unchanged tetraphenyltin and triphenyltin fluoride. Reaction between silicon tetrafluoride and tetraphenyltin did not occur at 110°.

Phosphonitrilic fluoride trimer (1·5 g.) (kindly given by Dr. N. Paddock) was heated with tetraphenyltin (1·6 g.) for 18 hr. at 110°. The volatile product contained unchanged phosphonitrilic fluoride trimer and benzene (identified by infrared and nuclear magnetic resonance spectroscopy).

Reactions of tetrakispentafluorophenyltin. Tetrakispentafluorophenyltin (1·1 g.) was heated with sulphur tetrafluoride (5·0 g.) for 22 hr. at 130°. The volatile product was unchanged sulphur tetrafluoride and an unidentified material containing C_6F_5 groups. The solid product was unchanged tetrakispentafluorophenyltin, which was sublimed at 150° to leave *trispentafluorophenyltin fluoride* (Found: C, 33·2; F, 47·1; Sn, 19·4. $C_{18}F_{16}Sn$ requires C, 33·9; F, 47·6; Sn, 18·6%). This substance decomposes on heating in air at about 300°, and is not attacked when refluxed with alcoholic potassium hydroxide.

Boron trifluoride did not react with tetrakispentafluorophenyltin during 65 hr. at 130°.

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414. *Reactivity of Co-ordinated Oxalate. Part IV.*[1] *The Racemisation of Sodium Trisoxalatorhodium*(III)

By A. L. Odell, R. W. Olliff, and F. B. Seaton

Slow racemisation of potassium trisoxalatorhodium(III) was first noticed by Werner,[2] who reported that it racemised much more slowly than the corresponding chromium complex. Recent studies of the aquation [3] and ligand-exchange [4] reactions have shown that the rhodium complex is not as inert as has been generally supposed. Acid-catalysed racemisation of the chromium complex [5,6] is faster than either aquation [7] or ligand exchange,[1] and, by analogy with this, the rate of acid-catalysed racemisation of the rhodium(III) complex, should be readily measurable. As part of our studies [1,7,8] of the reactivity of co-ordinated oxalate, we have measured this rate and found this prediction to be true.

Experimental.—The complex was prepared by dissolving hydrated rhodium(III) oxide in a solution of sodium hydrogen oxalate and allowing the complex to crystallise as bright orange efflorescent crystals. Resolution was achieved by way of the strychnine salt.[2]

Optical rotations were measured with a Shimadzu QR50 spectrophotometer with polarometric attachment, at a wavelength of 480 mμ. A typical run is shown in Table 1.

Table 1

A typical set of observations of the racemisation of sodium trisoxalatorhodium(III)

[Complex] = 0·0025M; [$HClO_4$] = 0·21M; temp. = 56·3°

Time (hr.) ...	0	0·85	1·58	3·45	4·78	6·18	7·78	9·17	10·66	21·48
Obs. rotn. ...	1·15°	1·03	0·94	0·79	0·665	0·56	0·505	0·42	0·365	0·145

The plot of the logarithm of the rotation against time was linear, and, from the slope, the first-order rate constant, $k_1 = 2{\cdot}03 \times 10^{-2}$ hr.$^{-1}$, was obtained.

Results and Discussion.—Racemisation in the pH region 2—6 was found to be very slow. However, as with potassium trisoxalatochromium(III),[6] a marked acid catalysis was observed below pH 2, as detailed in Table 2. It is seen that the rate of racemisation increases

Table 2

Acid-dependence of the rate of racemisation of sodium trisoxalatorhodium(III) at 44·6° [ionic strength = 3·0 (sodium perchlorate)]

[$HClO_4$] (M)	0·149	0·297	0·596	1·04	1·25	1·49	1·79
10^2k_1 (hr.$^{-1}$)	1·03	2·03	7·23	18·1	26·0	31·3	45·8

at a rate greater than the stoicheiometric acidity, a result similar to that obtained for the chromium complex.[5]

Absorption spectra measured before and after several runs showed that less that 1% of aquation had occurred during the run.[3]

Increasing the ionic strength of the solutions by addition of sodium perchlorate had little effect on the rate of racemisation. This is also found for the chromium complex.[5]

Measurements at 36·8, 44·6, and 56·3° enabled the activation energy to be obtained

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from the Arrhenius equation as 20 ± 1 kcal. mole^{-1}, with $\log_{10} A = 13{\cdot}7 \pm 0{\cdot}7$, in 0·596M-perchloric acid at an ionic strength of 3·0. Potassium trisoxalatochromium(III) racemises in 1·0M-perchloric acid with an activation energy of 17·6 kcal. mole^{-1}, and $\log_{10} A = 9{\cdot}97$.[5] Although these data are not directly comparable, they may be compared by adjusting the data on the rhodium complex to 1·0M-perchloric acid, by using the acid-dependence of the rate as set out in Table 2. The data are then (for $[H^+] = 1M$):

$CrOx_3^{3-}$	$\Delta E_A = 17{\cdot}6$ kcal. mole^{-1}	$\log_{10} A = 9{\cdot}97$
$RhOx_3^{3-}$	20	14·1

It would appear that the difference in the rate of racemisation of the rhodium(III) complex, compared with the chromium(III) complex, is associated with changes in both the activation energy and the frequency factor. Ligand-field studies [8] have indicated that the activation energy should be about 20 kcal. mole^{-1} greater for the rhodium(III) than for the chromium(III) complex, but it is generally much closer, because of increased covalent bonding in rhodium complexes.[8] The different values of $\log_{10} A$ for the two complexes are possibly associated with different degrees of protonation.

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415. *Spiro*[3,3]*heptane*

By BORIS WEINSTEIN, A. H. FENSELAU, and J. G. THOENE

ALTHOUGH derivatives of spiro[3,3]heptane have been accessible for many years from the reaction of pentaerythritol tetrabromide with sodiomalonic ester, the parent hydrocarbon in this series is apparently an unknown compound. We here record the first synthesis of spiro[3,3]heptane. Spiro[3,3]heptane-2-carboxylic acid [1] was converted in the presence of iodine and lead tetra-acetate [2] into 2-iodospiro[3,3]heptane. Reduction of the iodide with lithium and t-butyl alcohol [3] gave the desired spiro[3,3]heptane.

Experimental.—*2-Iodospiro*[3,3]*heptane.* For best results the carbon tetrachloride was freshly distilled and the lead tetra-acetate was dried overnight *in vacuo* with the aid of phosphorus pentoxide. Spiro[3,3]heptane-2-carboxylic acid (12·92 g.) was added dropwise under a nitrogen atmosphere to a stirred, refluxing, irradiated (tungsten lamp) solution of lead tetra-acetate (47·0 g.) in carbon tetrachloride (1·2 l.). After 10 min. a saturated solution of iodine (21·0 g.) in carbon tetrachloride (300 ml.) was introduced during 2 hr. Simultaneously, carbon tetrachloride was continuously distilled from the reaction flask, was collected by the use of a condenser with a side arm, and was recycled in the form of a saturated iodine solution. On being cooled and filtered, the violet liquid was evaporated and was chromatographed on neutral alumina in pentane. Distillation of the pink liquid (43°/0·3 mm.) and re-chromatography gave *2-iodospiro*[3,3]*heptane*, n_D^{25} 1·5421, $\lambda_{max.}$ (in cyclohexane) (log ε), 258 (2·91) (Found: C, 38·0; H, 5·1; I, 57·0. $C_7H_{11}I$ requires C, 37·9; H, 5·0; I, 57·15%).

Spiro[3,3]*heptane.* Lithium wire (1·12 g.) was added portionwise during 15 min. to a stirred solution of 2-iodospiro[3,3]heptane (8·94 g.) in t-butyl alcohol (6·0 g.) and anhydrous tetrahydrofuran (175 ml.) under a nitrogen atmosphere. On cautious warming of the mixture to 75° for 2 min. an exothermic reaction ensued which continued without appreciable abatement for 1 hr. The solution was refluxed for another hour, kept overnight, then was poured on to

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ice, and the organic phase was extracted with ether. The residual liquid, recovered from the ether, was washed with cold, concentrated sulphuric acid, and was distilled to yield colourless *spiro*[3,3]*heptane* (2·05 g.) b. p., 96—97°, n_D^{10} 1·4405, spectrometer [Found: C, 87·2; H, 12·42%; *M* (mass spectrometer), 96. C_7H_{12} requires C, 87·4; H, 12·6%; *M*, 96].

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416. *Nitration of Some Substituted* 1,4-*Dimethoxybenzenes*

By W. F. GUM, jun., M. R. W. LEVY, and M. M. JOULLIÉ

THE reaction of fuming nitric acid and 4-amino-2,5-dimethoxytoluene in acetic anhydride yields 2-acetamido-5-methyl-*p*-benzoquinone instead of the expected nitro-derivative. A similar reaction was reported by Kohn and Guttman [1] who found that 2,5-dibromo-1,4-dimethoxybenzene was converted into the corresponding dibromoquinone by fuming nitric acid whilst 2,6-dibromo-1,4-dimethoxybenzene yielded a dinitro-compound under the same conditions. Thus, it appeared that demethylation and subsequent oxidation of substituted 1,4-dimethoxybenzenes by nitric acid was typical of a structure having certain electron-donating substituents in the 2- and 5-positions. To test this trend, the three possible isomers of diacetamido-1,4-dimethoxybenzene were prepared and their nitration was studied. Both 2,3- and 2,6-diacetamido-1,4-dimethoxybenzene gave the expected mononitro-derivatives. 2,5-Diacetamido-1,4-dimethoxybenzene was oxidised to the corresponding quinone, under the same conditions, confirming what had been previously observed. These results show that nitric acid and certain 2,5-disubstituted 1,4-dimethoxybenzenes thus yield the corresponding quinones.

Experimental.—2-*Acetamido-5-methyl*-p-*benzoquinone*. Concentrated nitric acid (1·7 ml.; *d* 1·4) was added dropwise with stirring to a solution of 4-amino-2,5-dimethoxytoluene [2] (2·7 g.) in acetic anhydride (50 ml.). The temperature was maintained below 15° until crystals began to form at which time it was allowed to rise to 30°. The mixture was poured into water to yield a precipitate. Crystallisation from 50% ethanol yielded the quinone (78%), m. p. 181—182° (lit.,[3] 175°) (Found: C, 60·2; H, 5·2; N, 7·9. Calc. for $C_9H_9NO_3$: C, 60·3; H, 5·0; N, 7·8%), $\nu_{max.}$ (KBr) 1695 and 1670 (C=O), 1645, 1500, and 1270 (NHAc), 1610 (C=C) 1435 and 1365 (Me_3), 870, and 850 cm.$^{-1}$ (CH).

A solution of the quinone (6 g.) in ethanol (40 ml.) was reduced in a Parr hydrogenator using platinum dioxide catalyst (20 mg.). The catalyst was removed by filtration and the volume of the solution reduced. The crystals formed were reacted with fused sodium acetate and acetic anhydride for 1 hr. The solution was poured on to ice to yield 2-*acetamido-5-methylhydroquinone diacetate* m. p. 162—165° (from benzene) (Found: C, 58·7; H, 5·5; N, 5·2. $C_{13}H_{15}NO_5$ requires C, 58·8; H, 5·7; N, 5·2%).

Preparation of 2,3- *and* 2,5-*diacetamido*-1,4-*dimethoxybenzene*. These compounds were obtained from the selective reduction of a mixture of 1,4-dimethoxy-2,3- and -2,5-dinitrobenzenes which was formed when 1,4-dimethoxybenzene was nitrated.[4] This mixture (6 g.) was dissolved in acetic anhydride (150 ml.). To this solution was added 10% palladium-on-carbon (0·5 g.) and the solution was then hydrogenated in a Parr apparatus. After the theoretical amount of hydrogen had been taken up, the catalyst was filtered off and the solution concentrated to 70 ml. to yield a white crystalline precipitate of the 2,3-diacetamido-compound (58%), m. p. 213—215° (lit.,[5] 203—213°), $\nu_{max.}$ (KBr) 1655, 1520, and 1260 (NHAc), 1430 and 1365 (Me) and 800 cm.$^{-1}$ (CH). No 2,5-diacetamido-analogue could be isolated from this reaction.

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[2] P. Mamalis, J. Green, S. Marcinkiewicz, and D. McHale, *J.*, 1959, 3350.
[3] G. B. Barlin and N. V. Riggs, *J.*, 1954, 3125.
[4] F. E. King, N. G. Clark, and P. M. H. Davis, *J.*, 1949, 3012.
[5] L. Weinberger and A. R. Day, *J. Org. Chem.*, 1959, **24**, 1451.

When the same nitration mixture was hydrogenated in 2-ethoxyethanol and treated with anhydrous hydrogen chloride a mixture of 2,3- and 2,5-diamino-1,4-dimethoxybenzene dihydrochlorides was obtained. The mixture of dihydrochlorides (9·5 g.) was dissolved in water (200 ml.) and added slowly to 10% potassium carbonate solution (60 ml.). To this solution was added acetic anhydride (24 ml.) and 100 ml. of an aqueous solution containing 27 g. of sodium acetate. The reaction was exothermic and stirring was continued until white crystals began to form. The solid formed was removed by filtration to yield 8% of *2,5-diacetamido-1,4-dimethoxybenzene*, m. p. 289—292° (from ethanol–water) (Found: C, 57·2; H, 6·3; N, 11·0. $C_{12}H_{16}N_2O_4$ requires C, 57·2; H, 6·3; N, 11·1%), $\nu_{max.}$ (KBr) 1650, 1540, 1255 (NHAc), 1455 and 1360 (Me), and 845 cm.$^{-1}$ (CH). Concentration of the filtrate to one-half its original volume yielded an additional white precipitate which was filtered to yield 43% of a compound which was proven by comparison of infrared spectra to be 2,3-diacetamido-1,4-dimethoxybenzene. The yield of the latter closely parallels that of Weinberger and Day's [5] who prepared it by a similar procedure.

2,6-Diacetamido-1,4-dimethoxybenzene. This compound was prepared from hydroquinone by a five-step synthesis,[6] m. p. 199—200° (lit.,[6] 194·5—196·5°), $\nu_{max.}$ (KBr) 1660, 1530, 1270 (NHAc), 1460 and 1360 (Me), and 860 cm.$^{-1}$ (CH).

Nitration of the isomeric diacetamido-1,4-dimethoxybenzenes. The 2,3-diacetamide-compound was nitrated according to the procedure of Weinberger and Day [5] to yield the corresponding mononitro-derivative (58%), m. p. 262—263° (lit.,[5] 265—268°). A similar procedure was followed for the 2,5-diacetamido-compound. A solution of this compound (0·8 g.) in glacial acetic acid (50 ml.) was treated with concentrated nitric acid (3 ml.) and concentrated sulphuric acid (3 ml.) at room temperature.

The solution set aside for ½ hr., poured into ice–water, and neutralised to yield yellow crystals (89%), m. p. 312—315° (decomp.) (lit.,[7] decomposition above 300° without melting) (Found: C, 53·7; H, 4·2; N, 12·6. Calc. for $C_{10}H_{10}N_2O_4$ C, 54·0; H, 4·5; N, 12·6%), $\nu_{max.}$ (KBr) 1685 (C=O), 1645, 1480, and 1265 (NHAc), 1600 (C=C), 1435 and 1360 (Me), and 870 cm.$^{-1}$ (CH).

A solution of the 2,6-diacetamido-compound (1·4 g.) in glacial acetic acid (100 ml.) was treated with concentrated nitric acid (3 ml.) and concentrated sulphuric acid (3 ml.) at room temperature. The mixture was stirred for 1 hr., poured into ice–water, and neutralised to yield *2,6-diacetamido-1,4-dimethoxy-3-nitrobenzene* (31%), m. p. 214·5—215·5° (Found: C, 48·4; H, 5·2; N, 14·3. $C_{12}H_{15}N_3O_6$ requires C, 48·4; H, 5·1; N, 14·1%).

All infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer.

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417. *A By-product from the Preparation of Dehydroacetic Acid—Fleischmann's "Pyrone-lactone"*

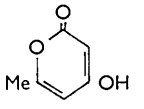
By A. K. Kiang and (Mrs.) S. F. Tan

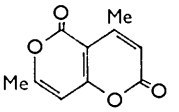
In the preparation of dehydroacetic acid by the self condensation of ethyl acetoacetate in the presence of a trace of anhydrous sodium hydrogen carbonate,[1] we have isolated, in about 10% yield, a colourless crystalline product, $C_{10}H_8O_4$, m. p. 215—216°, from the residue remaining after dehydroacetic acid had been distilled off at 120—140°/2 mm. The compound was isolated by distillation of the residue at 140—180°/2 mm. and recrystallised from benzene [Found: C, 62·6; H, 4·5%; *M* (Rast), 194. $C_{10}H_8O_4$ requires C, 62·5; H, 4·2%; *M*, 192].

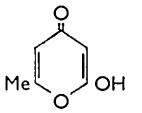
[1] Arndt, *Org. Synth.*, **1940**, **20**, 26.

The compound is identical with the " pyrone-lactone " prepared [2] by condensing triacetic lactone with ethyl acetoacetate or ethyl β-aminocrotonate under acid conditions. The identity has been established by comparison of m. p.'s and infrared spectra of our product and its monobromo- and mononitro-derivatives with those of the " pyrone-lactone " and the same derivatives.

In acid solution triacetic lactone has been shown from spectral studies to exist in the α-pyrone form (I).[3] That the same product is obtained when it reacts with ethyl acetoacetate or ethyl β-aminocrotonate shows that the reaction must involve esterification of the phenolic hydroxyl group followed by removal of water and ammonia at the reactive β-position. Thus, the compound would be expected to have structure (II).


(I)


(II)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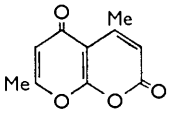

(IV)

Based on the reactions of mononitro-" pyrone-lactone," Fleischmann [2] favoured structure (IV) which would have resulted from the γ-pyrone form (III) of triacetic lactone. Praill and Whitear [4] re-examined the chemical properties and light-absorption of Fleischmann's compound, and stated that these were more consistent with structure (II). However, they did not provide any data.

Our observations are in agreement with the dilactone structure (II). The compound is sparingly soluble in 10% aqueous sodium carbonate solution but dissolves on heating to give a yellow solution; it does not form salts with hydrogen chloride or with picric acid; it does not form an adduct with maleic anhydride; and potentiometric and conductometric titrations in aqueous alcohol at room temperature show that one mole reacts with two equivalents of sodium hydroxide. The ultraviolet and the infrared spectra show only the characteristic absorptions of α-pyrones: [3] $\lambda_{max.}$ (in EtOH) 280 and 335 mμ (log ε 3·895 and 3·90); $\nu_{max.}$ (in Nujol) 1760, 1740, 1635 and 1540 cm.$^{-1}$.

Fleischmann reported that the dilactone gave only a monobromo-derivative. We have also prepared a *dibromo-derivative*, m. p. 258—259° (from benzene) (Found: C, 34·2; H, 1·95; Br, 46·1. $C_{10}H_6Br_2O_4$ requires C, 34·3; H, 1·7; Br, 45·7%).

It is difficult to account for the formation of the dilactone in the sodium hydrogen carbonate catalysed condensation of ethyl acetoacetate. A possible explanation is that hydrolysis of some dehydroacetic acid has taken place to triacetic lactone which then condenses with the excess acetoacetate. We have found that, by refluxing triacetic lactone, ethyl acetoacetate, and a trace of sodium hydrogen carbonate for 30 min., the dilactone is obtained in 48% yield. We have also obtained the dilactone in 18% yield by heating triacetic lactone with ethyl β-aminocrotonate, in the presence of a trace of sodium hydrogen carbonate in an oil-bath at 115—120° for 10 min.; reaction took place with evolution of ammonia; absence of sodium hydrogen carbonate lowered the yield to about 13%.

The authors thank Miss Sai Ing Tan for technical assistance, and Mrs. H. K. Tong for microanalysis.

CHEMISTRY DEPARTMENT, UNIVERSITY OF SINGAPORE. [*Received, September 4th,* 1964.]

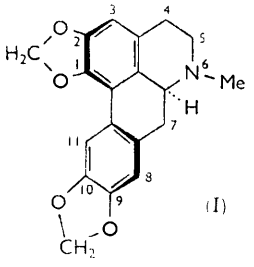
[2] Fleischmann, *J.*, 1907, **91**, 250.
[3] Bu'Lock and Smith, *J.*, 1960, 502.
[4] Praill and Whitear, *Proc. Chem. Soc.*, 1961, 112.

418. *New Aporphine Alkaloids from* Neolitsea pulchella

By (Miss) W. H. Hui, S. N. Loo, and (in part) H. R. Arthur

The alcohol extract of the leaves of *Neolitsea pulchella* yields three new alkaloids: neolitsine ($C_{19}H_{17}O_4N$) (a new aporphine), neolitsinine ($C_{18}H_{23}O_3N$), and the isomeric pulchelline ($C_{18}H_{23}O_3N$).

As shown in a recent review,[1] several of the aporphine alkaloids possess one methylenedioxy-group, but neolitsine is the first isolated to possess two such groups. The ultraviolet absorption suggested that it was an aporphine. Since it gave a positive Labat test and did not contain phenolic or methoxyl groups, it was concluded that there were two methylenedioxy-groups; there were also characteristic infrared bands at 2760 and 940 cm.$^{-1}$. The molecular weight was confirmed to be 323 by mass spectrometry; an intense (M − 1) base peak and an (M − 43) peak typical of aporphines with an *N*-methyl function were observed [1] and the presence of this group was confirmed in the n.m.r. spectrum. The optical rotatory dispersion curve corresponded to that of a 1,2,9,10-tetrasubstituted aporphine with absolute configuration as shown in (I).[2] Thus, the methylenedioxy-groups were fixed in the 1,2- and 9,10-positions; this was confirmed by the ultraviolet spectrum in ethanol which showed maxima at 310 and 284 mμ (log ε 4·11 and 3·9) characteristic of a 1,2,9,10-tetrasubstituted aporphine.[2] In the n.m.r. spectrum the methylenedioxy-groups appeared as two doublets centred at τ 4·04, 4·17 (1,2-substituted group),[1] and a singlet at τ 4·05 (9,10-substituted group). Signals for the three aromatic hydrogens were at τ 2·43 (11-H), and 3·32, 3·57 (3-H and 8-H).[1] A signal at τ 7·53 showed the presence of the *N*-Me group.



(I)

Neolitsine formed salts but it would not undergo demethylenation either with phloroglucinol and acids or with aluminium chloride in hydrocarbon solvents.

Neolitsinine ($C_{18}H_{23}O_3N$) has one methoxyl and one methylimino-group, two active hydrogens, one phenolic hydroxyl, and one non-phenolic hydroxyl, and the isomeric pulchelline ($C_{18}H_{23}O_3N$) has one phenolic and one non-phenolic hydroxyl. Their structures are being investigated.

Two other *Neolitseae* have been investigated: *N. involucrata* for its seed, fruit-coat, and kernel fats,[3] and nine alkaloids, including boldine, roemerine, laurolitsine, and litsericine, have been isolated from *N. sericea*.[4]

Experimental.—Analyses were by the microanlytical laboratories of the universities of Melbourne and Singapore. M. p.s were taken on a Kofler hot-stage apparatus. Alumina was B.D.H. analysis grade. Light petroleum had b. p. 60—80°. Infrared spectra were taken on a Perkin-Elmer model 137 Infracord spectrophotometer. N.m.r. spectra were taken on a Varian Associates A60 spectrometer system in deuterochloroform. Optical rotatory dispersion determinations were made in methanol solution. Optical rotations are for chloroform solutions.

Isolation of alkaloids. Dried leaves (5·5 kg.) were extracted with cold ethanol, and the combined extracts concentrated under reduced pressures to 1 l. treated with sodium carbonate to give pH 8, and extracted with chloroform. The aqueous solution (F) was treated with sodium carbonate to give pH 10·5, and the chloroform extract (X) was treated with N-sodium hydroxide. The sodium hydroxide layer, on acidification with hydrochloric acid and extraction with chloroform, gave residue (E) in the chloroform, and residue (D) in the aqueous layer after treatment with sodium carbonate. The chloroform layer from (X) was treated with 2N-hydrochloric acid, yielding (C) after basification of the aqueous layer with sodium hydroxide; the

[1] M. Shamma and W. A. Slusarchyk, *Chem. Rev.*, 1964, **64**, 59.
[2] C. Djerassi, K. Mislow, and M. Shamma, *Experientia*, 1962, **18**, 53.
[3] B. G. Gunde and T. P. Hilditch, *J.*, 1938, 1610.
[4] T. Nakasato and S. Nomura, *J. Pharm. Soc. Japan*, 1959, **79**, 1267.

chloroform part was treated with sodium hydroxide, the chloroform evaporated, and the residue dissolved in 10% acetic acid, solid potassium iodide added, and the solution filtered. This formed a precipitate which was filtered off, dissolved in sodium hydroxide solution, and extracted with chloroform (A). The filtrate was basified with sodium hydroxide, and yielded (B) on chloroform extraction.

Residues (A) (25 g.), (C) (6 g.), and (E) (30 g.) contained neolitsine. Residue (C) was dissolved in benzene (200 ml.) and applied to a column of alumina (200 g.). Elution with benzene gave a yellow oil followed by crystals (5 g.) which yielded *neolitsine*, m. p. 149—150° (from acetone), $[\alpha]_D$ +56·5 (*c* 1·57) (Found: C, 70·6; H, 5·5; N, 4·3; OMe, 0·0. $C_{19}H_{17}NO_4$ requires C, 70·6; H, 5·3; N, 4·3; 1OMe, 9·6%); it gave a positive Labat test, and in methanol it formed a *picrate*, m. p. 186° (decomp. from ethanol) (Found: C, 54·5; H, 4·1; N, 10·1. $C_{19}H_{17}NO_4,C_6H_3N_3O_7$ requires C, 54·4; H, 3·6; N, 10·1%). With methyl iodide in acetone, neolitsine formed a *methiodide*, m. p. 221—224° (from ethanolic acetone) (Found: C, 50·7; H, 4·9; I, 25·4; N, 2·6. $C_{20}H_{20}O_4IN,CH_3OH$ requires C, 50·7; H, 4·8; I, 25·55; N, 2·8%). With concentrated hydrochloric acid in ethanol the base formed a *hydrochloride* which, after recrystallization from ethanol, charred at 219° (or 221° *in vacuo*).

Residue (A) (25 g.) yielded neolitsine (10 g.) after crystallization from benzene and then from light petroleum. Residue (E) (30 g.) was triturated with warm water, and ammonia was added to give pH 8—9. The alkaline solution was extracted with chloroform, from which solution, after drying, a black residue (15 g.) was obtained. This was dissolved in chloroform–benzene (1 : 9) (150 ml.) and applied to a column of alumina (300 g.). Elution with benzene gave a yellow oil followed by crystals (11 g.) which on recrystallization from acetone yielded neolitsine.

Residue (D) (40 g.) contained neolitsinine and pulchelline. Aqueous solution (F) contained neolitsinine. Residue (D) (40 g.) was dissolved in chloroform (300 ml.) and applied to a column of alumina (300 g.). Elution with chloroform gave yellow amorphous material (30 g.) which was dissolved in chloroform–benzene (1 : 1) and applied to a column of alumina (300 g.). Elution with benzene gave a yellow oil. Elution with ethyl acetate–benzene (1 : 1) gave crystals of *pulchelline*, m. p. 189° (0·4 g.) (from acetone), $[\alpha]_D$ +80·1° (*c* 0·81) [Found: C, 71·7; H, 7·8; N, 5·1%; *M* (mass spectrometry), 301. $C_{18}H_{23}NO_3$ requires C, 71·7; H, 7·8; N, 4·7%; *M*, 301]. Further elution with the same solvent gave crystals (10 g.) which on recrystallization from acetone gave *neolitsinine*, m. p. 214—215°, $[\alpha]_D$ +94·7 (*c* 2·31) [Found: C, 72·1; H, 7·9; N, 5·0; OMe, 10·7%; *M* (mass spectrometry), 301. $C_{18}H_{23}NO_3$ requires C, 71·7; H, 7·8; N, 4·7; OMe, 10·3%; *M*, 301].

Aqueous solution (F) was brought to pH 10·5 with sodium carbonate and the procedure of extraction as for the solution of pH 8 was applied. In the residue corresponding to residue (D) neolitsinine (5 g.) was obtained. The aqueous solution (F) after removal of neolitsinine was treated in an attempt to isolate quaternary bases, but none was obtained.

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Hong Kong. [*Received, September 7th*, 1964.]

419. *Isolation of Crystalline 3-O-α-D-Galactopyranosyl-L-arabinose from a Polysaccharide found in* Watsonia * *Corm-sacs*

By D. H. SHAW, A. M. STEPHEN, and (in part) A. O. FULLER

DURING structural investigations of the complex polysaccharide [1] found in the dormant season in *Watsonia* corm-sacs, the disaccharide 3-*O*-α-D-galactopyranosyl-L-arabinose was isolated in unusually high yield. Upon refrigeration of a portion of this compound in methanol solution, crystals, m. p. 156·5—157·5°, were deposited slowly. Analysis of the dried (at 100° *in vacuo*) material proved this to be the anhydrous disaccharide. The scarcely measurable downward mutarotation $[\alpha]_D^{20}$ +202° ⟶ +198° indicated a preponderance of the β-anomeric form; the equilibrium value is somewhat higher than those reported [2,3] for earlier preparations of the syrupy disaccharide. Application of Hudson's rules of isorotation [4] showed that the reducing end of the disaccharide consisted of arabinopyranose. A second portion of the syrup in methanol yielded a crystalline material, which showed differences in its infrared spectrum [5,6] and its *X*-ray powder-diffractogram due, probably, to the appearance of a second crystalline phase chemically the same as the first.

This disaccharide has been isolated before in the form of two hepta-*O*-methyl derivatives (from arabic acid),[7] and, in low yield, as a syrup from gum arabic Turc. variety [2] and from the gum exudate of *Acacia cyanophylla* stems.[3] Identification of the disaccharide obtained from *Watsonia* corms was achieved by means of (i) quantitative estimation of the sugars released upon hydrolysis; (ii) formation of the phenylosazone; (iii) degradation of the disaccharide to give 2-*O*-α-D-galactopyranosyl-L-erythritol; [8] and (iv) methylation of the disaccharide to give a crystalline product identical with that obtained in a corresponding manner from *A. cyanophylla* gum,[3] followed by gas–liquid chromatography of its methanolysate.[9]

The significance of the recovery of 3-*O*-α-D-galactopyranosyl-L-arabinose in characterising one of the major structural units of *Watsonia* corm-sac polysaccharide will be discussed in a later Paper. It appears from a recent examination in this laboratory of the hydrolysates of numerous plant gums derived from several species of *Acacia*, as well as from other sources in widely differing taxa, that the α1 ⟶ 3-linkage between galactose and arabinose is uncommon. Evidence for a β1 ⟶ 3-linkage has likewise been reported rarely, *e.g.*, for *Anogeissus* [10] and *Albizzia* [11] gums.

Experimental.—Conventional solvent systems were used in paper chromatography (all v/v): (*a*) butan-1-ol–ethanol–water (4 : 1 : 5, upper layer), (*b*) ethyl acetate–acetic acid–formic acid–water (18 : 3 : 1 : 4), (*c*) ethyl acetate–pyridine–water (10 : 4 : 3), and (*d*) toluene–ethanol–water (270 : 30 : 1). Paper ionophoresis was for 4 hr. at 10v/cm. and 15 mA in borate [12] at pH 9·2. R_{gal} and M_g values express rates of movement relative to galactose and glucose, respectively. Gas–liquid chromatographic separations were achieved with a 4-ft. column of

* Identification of the source material as *Watsonia pyramidata* (Andr.) Stapf was kindly undertaken by Dr. A. V. Hall, Bolus Herbarium, University of Cape Town.

[1] D. H. Shaw and A. M. Stephen, *S. African Ind. Chemist*, 1964, 65.
[2] J. K. N. Jones, *J.*, 1953, 1672.
[3] A. J. Charlson, J. R. Nunn, and A. M. Stephen, *J.*, 1955, 269.
[4] C. S. Hudson, *J. Amer. Chem. Soc.*, 1909, **31**, 66; 1916, **38**, 1566.
[5] J. W. White, jun., C. R. Eddy, J. Petty, and N. Hoban, *Analyt. Chem.*, 1958, **30**, 506.
[6] S. A. Barker, E. J. Bourne, R. Stephens, and D. H. Whiffen, *J.*, 1954, 3468.
[7] F. Smith, *J.*, 1939, 744.
[8] A. J. Charlson, P. A. J. Gorin, and A. S. Perlin, *Canad. J. Chem.*, 1957, **35**, 365.
[9] G. O. Aspinall, *J.*, 1963, 1676.
[10] G. O. Aspinall, B. J. Auret, and E. L. Hirst, *J.*, 1958, 4408; G. O. Aspinall and T. B. Christensen, *J.*, 1961, 3461.
[11] D. W. Drummond and Elizabeth Percival, *J.*, 1961, 3908.
[12] cf. A. B. Foster, *J.*, 1953, 982.

ethylene glycol succinate [13] on 80—100 mesh Gas Chromosorb W at 166°, and the use of a thermal conductivity detector. A Philips model P.W. 1050 *X*-ray diffractometer was used (Co-$K\alpha$ and Cu-$K\alpha$ radiation) to obtain spacings in the crystalline materials. Specific rotations were, in general, measured on aqueous solutions.

Isolation of the disaccharide. A jelly-like polysaccharide was excised from the sacs present in *Watsonia* corms collected near Cape Town in February and March 1964; 216 g. of crude air-dried material was recovered from 790 corms. Slow addition of ethanol (75 l.) to the extremely viscous solution obtained by homogenising the polysaccharide in water (25 l.) caused the precipitation of the bulk of the solid material (150 g.) as a stringy mass. Numerous tests indicated that the precipitate was essentially homogeneous. Acid hydrolysis of a sample showed the component sugars to be D-galactose, L-arabinose, and D-xylose, which were characterised in the usual way. The vacuum-dried polysaccharide (30 g.) having $[\alpha]_D^{20}$ −80° (*c* 0·3) was heated in 0·01N-sulphuric acid (1 l.) at 90° for 7 hr.; trial hydrolyses had indicated that this was the most suitable preliminary treatment for obtaining the disaccharide component R_{gal} 0·52, 0·78, and 0·76 in solvents *a*, *b*, and *c* (chromatographically indistinguishable from 3-*O*-α-D-galactopyranosyl-L-arabinose prepared from *A. cyanophylla* gum [3]). The solution was neutralised ($BaCO_3$), filtered, washed with water, concentrated below 40° to 100 ml., and poured slowly with stirring into methanol (400 ml.). The resulting precipitate (5·25 g.) was separated, and the filtrate was concentrated *in vacuo* to a syrup (21·7 g.); this was shown by paper chromatography to contain arabinose, traces of galactose and xylose, the disaccharide, a slower-moving oligosaccharide, and residual material immobile in solvent *a*. L-Arabinose (1·83 g.), which crystallised spontaneously from the syrup, was removed by filtration, and the remaining sugar components were fractionated on a charcoal–Celite column (85 × 4 cm.).[14] The disaccharide (5 g.), which was eluted with 6% aqueous ethanol, was a chromatographically pure (solvents *a*, *b*, and *c*) syrup, and had $[\alpha]_D^{18}$ +182° (*c* 5·2), M_g 0·75. The oligosaccharides eluted with higher concentrations of ethanol, as well as the solid insoluble in 80% aqueous methanol (mentioned above), were all shown subsequently to give rise to more (potentially 2·8 g.) of this same disaccharide upon continued mild acid hydrolysis. All sugar assays were performed by adapting the phenol–sulphuric acid method.[15]

A portion (1·5 g.) of the syrupy disaccharide was dissolved in hot methanol and, after removal of some insoluble material by filtration, was kept for 2 months at 0°. The crystalline deposit was separated, washed with methanol, and dried at 100° *in vacuo*, yielding 3-O-α-D-*galactopyranosyl*-L-*arabinose*, m. p. 156·5—157·5°, $[\alpha]_D^{20}$ +202° (7 min.) ⟶ +198° (50 min., constant; *c* 1·08) (Found: C, 42·3; H, 6·1. $C_{11}H_{20}O_{10}$ requires C, 42·3; H, 6·45%). Dr. E. A. K. Middlemost, Department of Geology, described the product as " an aggregate of fibrolamellar structure, all but extremely thin pieces of which are opaque to cloudy. Extinction is parallel to the long axis of the fibres; refractive index 1·52 for the long direction. Double refraction is moderate. The crystals are length slow." A second portion (1·5 g.) of the disaccharide in hot methanol was seeded with a crystal of the above product and stored at 0° for 1 week; microscopic aggregates (1 g., after being dried at room temperature *in vacuo* for 3 hr.), m. p. 156·5—157·5° (undepressed on admixture with the first preparation), were obtained, $[\alpha]_D^{20}$ +198° (equil. value reached within 2 min.; *c* 0·99) (Found: C, 42·3; H, 6·6%). Infrared spectra of the two crystalline preparations, in Nujol and in potassium chloride discs, showed $\nu_{max.}$ in the 750—1200 cm.$^{-1}$ region as follows: 773w, 817s, 849w, 865vw, 898m, 923w, 949m, 972sh, 995s, 1007vw, 1020w, 1037w, 1047sh, 1058w, 1080s, 1109m, 1144vs (peak intensities relative to the general contour of the spectrum). In addition, the second preparation absorbed very weakly at 796 cm.$^{-1}$. Peak heights varied somewhat from one spectrum to the next, as has been observed [5] with disaccharide samples having different degrees of crystallinity. Absorption at 849 cm.$^{-1}$ indicated β-anomer (of L-arabinopyranose) in both batches.[6]

Hydrolysis of a sample of the disaccharide gave D-galactose and L-arabinose in the molar ratio 1·1 : 1 (by estimation of the sugars after separation on a filter-paper sheet, and measurement of their optical rotations).

Phenylosazone formation and oxidation. A phenylosazone, m. p. 235°, $[\alpha]_D^{20}$ +81° (*c* 0·32 in pyridine–ethanol, 7 : 3), was prepared from the syrupy disaccharide by following the procedure

[13] E. Klein and C. J. Barker, jun., *Textile Research J.*, 1961, **31**, 486.
[14] R. J. Whistler and D. F. Durso, *J. Amer. Chem. Soc.*, 1950, **72**, 677.
[15] M. Dubois, K. A. Gilles, J. K. Hamilton, P. A. Rebers, and F. Smith, *Analyt. Chem.*, 1956, **28**, 350.

adopted by earlier workers [16] for 3-*O*-β-D-xylopyranosyl-D-xylosazone. The compound was shown to be homogeneous by paper chromatography in solvent *d*,[17] and it gave an ultraviolet absorption spectrum characteristic [18] of a disaccharide phenylosazone. On admixture with the phenylosazone (m. p. 234°) of a disaccharide (having identical R_{gal} values in *a*, *b*, and *c*) isolated recently from carboxyl-reduced *A. cyanophylla* gum by Dr. A. J. Charlson in this laboratory, there was no depression of the m. p. 235°. The infrared spectra and *X*-ray powder-diffractograms of the two phenylosazones were identical. Hydrolysis of the phenylosazone (from *Watsonia*) yielded galactose as the only sugar; oxidation of another sample (4·8 mg.) with periodate in aqueous ethanol (10 ml.) gave no precipitate of mesoxalic dialdehyde 1,2-bisphenylhydrazone, but yielded 1 mol. each of formaldehyde and formic acid.[19]

Lead tetra-acetate degradation. The disaccharide (100 mg.) was converted by lead tetra-acetate oxidation (for 15 min. at 18° in acetic acid) and sodium borohydride reduction into 2-*O*-α-D-galactopyranosyl-L-erythritol [8] (14 mg., after recrystallisation from ethanol), m. p. and mixed m. p. 153°, $[\alpha]_D^{20}$ +143° (*c* 1·2), R_{gal} 0·71, 0·82 (solvents *a* and *c*). The infrared spectra of this preparation and of the authentic sample were identical.

Methylation of the disaccharide. Methylation of the disaccharide (300 mg.) yielded a syrup (243 mg.), which crystallised rapidly; recrystallisation three times from petroleum (b. p. 60—80°) yielded needles, m. p. 89° and mixed m. p. (with a sample of the hepta-*O*-methyl derivative from *A. cyanophylla* gum) 85—86°, $[\alpha]_D^{20}$ +164° (*c* 0·86) (Found: OMe, 51·5. Calc. for $C_{18}H_{34}O_{10}$; OMe, 52·9%). Methanolysis of the methylated disaccharide gave the methyl glycosides of 2,3,4,6-tetra-*O*-methylgalactose and of 2,4-di-*O*-methylarabinose, characterised by their gas–liquid chromatographic retention times.[9,20]

X-Ray powder-diffractograms of the crystalline disaccharide and of the derived phenylosazone (*with* Dr. A. O. FULLER, *Department of Geology*). (i) *Disaccharide.* The product (dried at 100°) of the first crystallisation from methanol was well crystallised as indicated by the large ratio of peak height to width. The *d*-spacings (in Å) were as follows (peak intensities: vs = very strong, m = moderate, w = weak, vw = very weak): 13·3s, 10·5s, 8·36w, 6·64m, 4·96vw, 4·80vw, 4·65m, 4·40vs, 3·95vw, 3·81m, 3·39w, 3·34w, 3·15w, 3·04w, 2·82w. Crystals (dried at room temperature) of the same m. p. and mixed m. p., obtained from the second portion of same syrupy disaccharide, had all the *d*-spacings listed above and, in addition, *d*-spacings as follows: 8·19w, 6·56s, 6·19m, 4·85m, 4·53m, 4·20m, 3·65w. No change in the pattern resulted after the second crystalline product had been heated at 100° *in vacuo* for 3 hr.

(ii) *The phenylosazone.* The phenylosazone, m. p. 235°, of the disaccharide from *Watsonia* was well crystallised, with *d*-spacings (in Å): 21·5vs, 16·30vw, 11·15w, 8·22s, 7·46m, 6·24m, 5·66w, 5·26m, 4·69w, 4·49vw, 4·31m, 4·06vw, 3·97m, 3·66vw, 3·50vw, 3·28vw, 3·19vw, 2·98vw. Identical spacings were found for the phenylosazone, m. p. 234°, prepared from disaccharide recovered from reduced *A. cyanophylla* gum.

We are indebted to the South African C.S.I.R. for an assistantship (held by D. H. S.), to the Staff Research Fund of the University of Cape Town for financial support, and to Dr. A. J. Charlson and Dr. A. S. Perlin for their co-operation in obtaining reference samples.

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SOUTH AFRICA. [*Received, September 14th*, 1964.]

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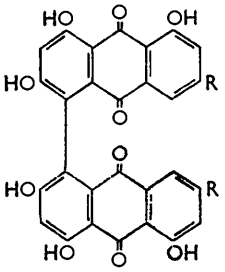
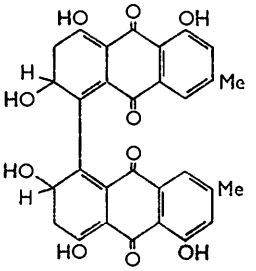
420. *Chemistry of Fungi. Part II.*[1] *Constituents of Three* Endothia *Species*

By Lindsay H. Briggs and P. W. Le Quesne

The fungi *Endothia parasitica*, which causes chestnut blight, and *E. fluens* owe their orange-yellow colour to 1,1'-bisanthraquinone derivatives.[2] Two further pigmented species, *E. longirostris* and *E. tropicalis*, are found as saprophytes on New Zealand trees. Their colouring matters, and that of the type species, *E. gyrosa*,[3] have now been shown to be of the same kind. Whereas *E. gyrosa* (Clinton's strain) produced skyrin (I; R = R' = Me) and rugulosin (II), similarly to the closely related *E. fluens*, the pigment of *E. longirostris*



(I)



(II)

and *E. tropicalis* consisted only of skyrin. From one culture of *E. longirostris* skyrinol ("Pigment C,"[2c] R = R' = CH_2·OH) was also obtained, insufficient for complete characterisation.

Experimental.—The analysis was performed by Dr. A. D. Campbell and associates, University of Otago, New Zealand. Light petroleum refers to the fraction of b. p. 40—60°. May and Baker's heavy magnesium carbonate was used. *Endothia longirostris* and *E. tropicalis* were collected by Miss J. M. Dingley, Plant Diseases Division of the Department of Scientific and Industrial Research, Mt. Albert, Auckland, while *E. gyrosa* was obtained from the Centraalbureau voor Schimmel-cultures, Baarn, The Netherlands.

Cultures. The fungi were grown in 1-l. Erlenmeyer flasks, on 20% potato suspension in water, enriched with 3% glucose added as a 45% solution with the inoculum, which was prepared by finely cutting dextrose–agar slope cultures. The flasks were kept at 20° in the light for 30—50 days.

Extraction of E. longirostris. The dried, ground mycelium (55 g.) was extracted (Soxhlet) successively with light petroleum (400 ml.; 25 hr.), acetone (4 × 400 ml.; 36 hr.), and methanol (400 ml., 48 hr.). The pale yellow light-petroleum extract contained no hydroxyanthraquinones but had absorption maxima at 402, 452, and 482 mμ, suggesting the presence of a β-carotene derivative [cf. cryptoxanthin, $\lambda_{max.}$ (in hexane) at 425, 451, and 483 mμ].[4] Concentration of the red acetone extract gave crystalline D-mannitol, m. p. 165—166° (1% yield), identified by direct comparison and by preparation of the acetate, m. p. 123·5—124·5°. The acetone extract and the acetone-soluble fraction of the methanol extract were combined and chromatographed on heavy magnesium carbonate. Elution of the single magenta band with acetone containing a

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[2] (*a*) S. Shibata, W. Tanaka, G. Chihara, and H. Mitsuhashi, *Pharm. Bull.* (*Japan*), 1953, **1**, 302; (*b*) S. Shibata, T. Murakami, O. Tanaka, G. Chihara, and M. Sumimoto, *ibid.*, 1955, **3**, 274; (*c*) S. Shibata, M. Takido, and T. Nakajima, *ibid.*, 1955, **3**, 286; (*d*) S. Shibata, M. Takido, A. Ohto, and T. Kurosu, *ibid.*, 1957, **5**, 573.

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little acetic acid (5 drops; 100 ml.) gave a red solution which was evaporated to dryness and the residue chromatographed on a calcium hydrogen phosphate column using light petroleum–acetone–water (20 : 10 : 1) [2a] as eluant. The eluted single light orange band on concentration and crystallisation from glacial acetic acid gave skyrin (I; R = R′ = CH_3), as orange-brown rods, which did not melt below 300°. It was identified by colour tests,[2b] infrared spectrum, and *X*-ray powder photograph, with an authentic specimen. Skyrin hexa-acetate, prepared from acetic anhydride and pyridine, had a variable melting point, depending on the solvents used for crystallisation and the glass of the capillaries. Material crystallised from acetone–methanol melted in acid-washed Pyrex capillaries at 312—315°, while in normal glass capillaries the melting point varies between 258 and 296° [2b] (Found: C, 63·45; H, 3·9. Calc. for $C_{42}H_{30}O_{16}$: C, 63·8; H, 3·8%).

Extraction of E. tropicalis. The dried, ground mycelium (22·9 g.) was extracted successively with light petroleum, acetone, and methanol, as described for *E. longirostris*. The light-petroleum extract contained no colouring matter, but the acetone extract, after separation of mannitol (315 mg., 1·4%) and chromatography as above, gave skyrin (36 mg.).

The acetone-soluble fraction of the methanol extract gave, on treatment similar to the above, a red crystalline pigment (4 mg.), which did not melt below 360°. It had similar chemical properties and spectra to those of skyrin, but a different *X*-ray powder pattern. It dissolves in sodium hydrogen carbonate solution, and is considered to be skyrinol (" Pigment C ") [2c] (I; R = R′ = CH_2·OH). This compound was also initially obtained in small quantity from a culture of *E. longirostris*, but later cultures yielded only skyrin, as determined by the n.m.r. spectrum of the acetylated pigment.

Extraction of E. gyrosa. The dried, ground mycelium (62·2 g.) was extracted as described above. The light-petroleum extract contained an insignificant amount of colouring matter, but the acetone extract (2·2 l.), after removal of mannitol (77 mg., 0·12%), was concentrated to 150 ml. and kept at 0° for 5 days. Golden-yellow crystals were deposited, which on recrystallisation from ethanol gave rugulosin (II), m. p. 291·5—293° (decomp.) (4·80 g., 7·6%), identified by colour reactions, spectra, direct comparison with authentic material, and preparation of the hexabenzoate, m. p. 222—224° (decomp.). The remaining acetone extract was evaporated nearly to dryness, and, after the addition of acetone (120 ml.), was rapidly boiled and filtered. The dark orange crystalline precipitate recovered from the concentrated acetone extract was recrystallised from glacial acetic acid to give skyrin (654 mg., 1·1%), identified as above. Insignificant colouring matter remained in the extract. The acetone-soluble portion of the methanol extract was shown by chromatography to contain very small amounts of skyrin and rugulosin.

We thank Miss J. M. Dingley for assistance with the cultures, Professor S. Shibata for authentic samples of bisanthraquinone derivatives, and Mr. R. L. Sinclair for *X*-ray powder photographs. Assistance is gratefully acknowledged from the Chemical Society, the Rockefeller Foundation of New York, the Australian and New Zealand Association for the Advancement of Science, and the New Zealand Universities Research Grants Committee. One of us (P. W. Le Q.) is grateful for a Research Fund Fellowship and a Duffus Lubecki Scholarship.

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421. *The Platinum-catalysed Oxidation of Some 6-Deoxyhexopyranosides*

By J. S. Brimacombe, M. C. Cook, and (in part) L. C. N. Tucker

The isolation of numerous unusual branched-chain, deoxy-, and amino-sugars from antibiotics (reviews by Berry [1] and Dutcher [2]) has promoted widespread interest in their synthesis, and the value of keto-sugars as intermediates has been demonstrated.[3,4] Numerous carbohydrate components of antibiotics are 6-deoxyhexose derivatives, and we have therefore examined the platinum-catalysed oxidation of various 6-deoxyhexopyranosides as a route to useful keto-intermediates.

Non-catalytic methods of oxidation of carbohydrate secondary hydroxyl groups (review by Theander [5]) generally require protection of other hydroxyl groups in order to effect oxidation at a particular site. Heyns and his co-workers (review by Heyns and Paulsen [6]) and others [7] showed that the catalytic oxidation of cyclitols and pentopyranosides is selective and preferentially affects axial hydroxyl groups; protection of other secondary hydroxyl groups in the molecule is not required, although protection of the primary hydroxyl group is necessary with hexopyranosides. The selectivity of oxidation can be explained if a dehydrogenation mechanism occurs, with cleavage of the carbon–hydrogen bond, since equatorial hydrogen atoms will be more reactive.

Thus, as expected, methyl 6-deoxy-β-D-allopyranoside yields methyl 6-deoxy-β-D-*ribo*-hexopyranosid-3-ulose since the preferred C1 conformation has an axial C-3 hydroxyl group. Reduction of the keto-sugar with sodium borohydride gave a mixture of methyl 6-deoxy-β-D-glucopyranoside and methyl 6-deoxy-β-D-allopyranoside, thereby confirming the location of the carbonyl function. Catalytic oxidation of methyl α-L-fucopyranoside (methyl 6-deoxy-α-L-galactopyranoside) gave methyl 6-deoxy-α-L-*xylo*-hexopyranosid-4-ulose, with reaction occurring at the only axial hydroxyl group in the preferred 1C conformation.[8] While this work was in progress, similar results were reported by Heyns *et al.*[9] for some 6-substituted galactopyranosides.

As predicted [10] benzyl α-L-rhamnopyranoside (benzyl 6-deoxy-α-L-mannopyranoside), which has an axial C-2 hydroxyl group in the 1C conformation, was catalytically oxidised to yield benzyl 6-deoxy-α-L-*arabino*-hexopyranosidulose. The location of the carbonyl group was established by reduction and acidic hydrolysis to a mixture of 6-deoxy-L-glucose and L-rhamnose (identified by paper chromatography). Methyl 6-deoxy-α-D-glucopyranoside, the C1 conformation of which has equatorial hydroxyl groups, was almost completely resistant to catalytic oxidation. Similar observations have been made with scylloinositol [11] and methyl β-D-xylopyranoside,[7,12] although in the latter case partial oxidation occurs on prolonged treatment, presumably through the less stable 1C form.

Experimental.—Paper chromatography was performed on Whatman No. 1 paper using butan-2-one saturated with water as the mobile phase.[13] Thin-layer chromatography was

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[3] W. G. Overend, *Chem. and Ind.*, 1963, 342, and references cited therein.
[4] J. S. Brimacombe and M. J. How, *J.*, 1963, 3886.
[5] O. Theander, *Adv. Carbohydrate Chem.*, 1962, **17**, 223.
[6] K. Heyns and H. Paulsen, *Adv. Carbohydrate Chem.*, 1962, **17**, 169.
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performed on Silica-gel (Merck) using benzene–ether (4 : 1 v/v) as the mobile phase; the separated components were detected with vanillin–perchloric acid reagent.[14]

Methyl 6-deoxy-β-D-ribo-hexopyranosid-3-ulose. A rapid stream of oxygen was bubbled for 4·5 hr. at room temperature through a solution of methyl 6-deoxy-β-D-allopyranoside [15] (0·81 g.) in water (25 ml.) containing platinum (0·6 g.; prepared by reduction of the oxide [6]). The catalyst was filtered off, the filtrate reduced in volume to *ca.* 10 ml., and the keto-sugar absorbed on to Amberlite IRA-400 (HSO_3^-). The resin and solution were placed in a glass column and the resin washed with water (500 ml.) and then with water containing an increasing concentration of acetone (100 ml. each of 5, 10, and 20%) to desorb the keto-sugar. Evaporation of the acetone washings gave a semicrystalline material (0·18 g.) which on recrystallisation from ethanol–ether gave the *product* (0·15 g.), m. p. 142—144°, $[\alpha]_D^{20}$ −74° (*c* 1·2 in water) (Found: C, 48·1; H, 6·4. $C_7H_{12}O_5$ requires C, 47·7; H, 6·9%).

Location of the carbonyl function. A solution of sodium borohydride (0·6 g.) in water (6 ml.) was added dropwise to a cooled (5°) solution of the foregoing product (0·12 g.) in water (4 ml.); a stream of carbon dioxide was bubbled through the mixture to maintain a pH 8—9. After 1 hr., the solution was shaken with Amberlite IR-120(H^+) to remove sodium ions, the filtered solution concentrated, and boric acid removed from the solid residue by repeated evaporation with methanol. Paper chromatograms of the resultant syrup (0·12 g.) revealed two components indistinguishable in their mobilities from methyl 6-deoxy-β-D-allopyranoside and methyl 6-deoxy-β-D-glucoside. A solution of the syrup (0·12 g.) in water (3 ml.) was applied to a column of Dowex-1 (OH^-) (2·7 × 25 cm.) [16] and the resin eluted with de-ionised water; fractions (5 ml.) were collected automatically. Examination of the fractions by paper chromatography showed that only a partial separation of the glycosides was achieved. Evaporation of fraction 44 and recrystallisation of the residue from ethyl acetate gave methyl 6-deoxy-β-D-glucopyranoside (3 mg.), m. p. 130—131°, alone or in admixture with an authentic sample (see later). Fractions 51—53 were combined, and on evaporation gave a syrup (12 mg.) which after recrystallisation from ethyl acetate had m. p. 89—90°, alone or in admixture with methyl 6-deoxy-β-D-allopyranoside.[15] Acidic hydrolysis of the intermediate fractions gave two components, the chromatographic properties of which were indistinguishable from those of 6-deoxy-D-glucose and 6-deoxy-D-allose.

Methyl 6-deoxy-α-L-xylo-hexopyranosid-4-ulose. This compound was prepared in 26% yield from methyl α-L-fucopyranoside [17] (1·4 g.) using the oxidation procedure described herein. The *product*, $[\alpha]_D$ −160° (*c* 1·2 in water), was obtained as a chromatographically pure syrup which showed a characteristic carbonyl band at 1740 $cm.^{-1}$ in its infrared spectrum (Found: C, 47·8; H, 6·7. $C_7H_{12}O_5$ requires C, 47·7; H, 6·9%). Recovery and re-cycling of unoxidised material afforded additional quantities of the keto-sugar.

Reduction of the product (0·25 g.) with sodium borohydride gave a syrupy product mixture (0·18 g.) which was separated on Dowex-1(OH^-) [16] as described above. Evaporation of fractions 29—36 gave a syrup (48 mg.) which after crystallisation from ethyl acetate had m. p. 157—159°, alone or in admixture with methyl α-L-fucopyranoside.[17] The syrup (88 mg.), obtained on evaporation of fractions 40—48, did not crystallise but was indistinguishable on paper chromatograms from methyl 6-deoxy-α-D-glucopyranoside. Acetylation of the syrup in the usual manner gave methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-L-glucopyranoside, m. p. 73—75°; the infrared spectrum of the acetylated glycoside was indistinguishable from that of the D-enantiomorph, m. p. 75—76° (see later).

Benzyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranoside. A solution of L-rhamnose (18·7 g.) in benzyl alcohol (100 ml.) was saturated with hydrogen chloride during 30 min. and was thereafter shaken at room temperature for 40 hr. Water was then added and the mixture extracted several times with ether. Evaporation of the ether extracts gave a syrup (13 g.), which was dissolved in pyridine (35 ml.), cooled (0°), and treated with acetic anhydride (22 ml.). After standing at room temperature overnight, the reaction mixture was poured into cold (5°) water (300 ml.) and the aqueous solution was extracted with chloroform (3 × 200 ml.). The chloroform extracts were washed successively with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water, and dried ($MgSO_4$). After filtration, the chloroform was removed, to give

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[15] P. A. Levene and J. Compton, *J. Biol. Chem.*, 1936, **116**, 169.
[16] P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley, *J.*, 1963, 5350.
[17] S. B. James and F. Smith, *J.*, 1945, 746.

a syrup which was shown by chromatography, to contain several components. After reacetylation (as above), on pouring the reaction mixture into cold water a solid precipitated. This was filtered off, washed with water, and recrystallised from ethanol, to give the *product* (14·8 g.), m. p. 110°, $[\alpha]_D^{20}$ −73° (*c* 1 in chloroform) (Found: C, 60·2; H, 6·4. $C_{19}H_{24}O_8$ requires C, 60·0; H, 6·4%).

Benzyl α-L-*rhamnopyranoside.* A stream of dry ammonia was passed for 45 min. through a cooled (0°) solution of the foregoing compound (1 g.) in dry methanol (12 ml.). After standing for 20 hr. at room temperature, the solution was evaporated and the last traces of ammonia were removed by repeated evaporation with methanol. The resulting syrup was crystallised from propan-2-ol–ether, to give the *product* (0·16 g.), m. p. 76°, $[\alpha]_D^{20}$ −63° (*c* 1 in water) (Found: C, 61·1; H, 6·9. $C_{13}H_{18}O_5$ requires C, 61·4; H, 7·1%).

Subsequent deacetylations were carried out using a catalytic amount of sodium in dry methanol in the usual manner. After the removal of sodium ions with Amberlite IR-120 (H^+), the solution was concentrated to a syrup which crystallised on seeding with the product obtained previously.

Benzyl 6-*deoxy*-α-L-arabino-*hexopyranosidulose.* This compound, $[\alpha]_D^{20}$ −97° (*c* 2 in water), was obtained in 26—30% yield from benzyl α-L-rhamnopyranoside (1·7 g.) using the oxidation procedure described herein. The syrupy *product* was chromatographically pure and showed a characteristic carbonyl band at 1750 cm.$^{-1}$ in its infrared spectrum (Found: C, 61·6; H, 6·2. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·4%).

The location of the carbonyl group was determined by reduction with sodium borohydride (see above) and hydrolysis of the glycoside mixture with N-sulphuric acid at 95° for 4 hr. Examination of the neutralised ($BaCO_3$) hydrolysate by paper chromatography showed two components which were indistinguishable in their chromatographic properties from L-rhamnose and 6-deoxy-D-glucose.

Preparation of the anomeric methyl 6-*deoxy*-D-*glucopyranosides.* 6-Deoxy-α-D-glucose [18] (1·83 g.) was refluxed in a 2% solution of hydrogen chloride in methanol (50 ml.) for 8 hr., and the neutralised (Ag_2CO_3) and filtered solution concentrated to a syrup. The syrupy glycoside mixture was dissolved in water (5 ml.) and chromatographed on Dowex-1 (OH^-) (3 × 36 cm.) [16] as described herein; 25 ml. fractions were collected automatically. Fractions 12 and 13 were combined and evaporated to a syrup which crystallised slowly and on recrystallisation from ethyl acetate gave methyl 6-deoxy-α-D-glucopyranoside (0·55 g.), m. p. 90—94°, $[\alpha]_D$ +154° (*c* 0·24 in water) (lit.,[19] m. p. 98—99° for the compound prepared by a different procedure). Fractions 15 and 16 were combined and evaporated to a solid which on recrystallisation from ethyl acetate gave methyl 6-deoxy-β-D-glucopyranoside (0·3 g.), m. p. 130—131°, $[\alpha]_D^{23}$ −51° (*c* 1 in water) {lit.,[20] m. p. 131—132°, $[\alpha]_D^{20}$ −55° (*c* 8·6 in water), for the compound prepared in another way}.

Methyl 2,3,4-*tri*-O-*acetyl*-6-*deoxy*-α-D-*glucopyranoside.* Acetic anhydride (0·18 ml.) was added to a cooled (0°) solution of methyl 6-deoxy-α-D-glucopyranoside (48 mg.) in dry pyridine (0·25 ml.), and, after 20 hr., water was added to the mixture. The aqueous solution was extracted with ether (3 × 50 ml.), and the combined extracts washed with 2N-hydrochloric acid, water, sodium hydrogen carbonate solution, and water, and dried (K_2CO_3). Concentration of the filtered extract gave a syrup which was crystallised from light petroleum (b. p. 40—60°) to give the product (30 mg.), m. p. 75—76° (lit.,[21] 77—78° for the compound prepared by a different procedure).

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422. *Alkylation of the Aromatic Nucleus. Part XII.*[1] *Isopropylation*

By K. M. Davies and W. J. Hickinbottom

Alkylation of toluene, isopropylbenzene, and t-butylbenzene by the thermal decomposition of isopropyl toluene-*p*-sulphonate in an excess of the hydrocarbon gives products containing a high proportion of *m*-dialkylbenzene. When phenol or anisole are similarly alkylated no *meta*-isomer is formed, the product consisting entirely of *o*- and *p*-isomers. With fluorobenzene, *o*- and *p*-fluorobenzenes are formed almost exclusively; the *m*-isomer is no more than 4% of the product.

These results are in agreement with the previous conclusions [2] that *meta*-substitution is a characteristic of the further alkylation of the monoalkylbenzenes and that it is determined not so much by the activity of the substituting group [3] as by the nature of the monosubstituted benzene undergoing alkylation.

Experimental.—Isopropyl toluene-*p*-sulphonate was obtained as an oil, n_D^{21} 1·5040, from propan-2-ol and toluene-*p*-sulphonyl chloride in pyridine (lit.,[4] n_D^{20} 1·5065).

Alkylations were brought about by heating the sulphonic ester with a five-fold excess of the monosubstituted benzene until the reaction was complete. Propene was evolved in all such alkylations; it was collected in a cold trap and identified by its dibromide, b. p. 144—145°, n_D^{20} 1·5195, and the addition compound with 2,4-dinitrophenylsulphenyl chloride, m. p. and mixed m. p. 76—77·5° (lit.,[5] 75—76°).

The alkylation product was isolated in the usual way, and the proportion of isomers determined by vapour-phase chromatography. When the resolution was not satisfactory, the estimations were made from the infrared spectrum. The results are summarised in the Table.

	Conditions of alkylation		Yield	Isomer distribution in product			
	Hr.	Temp.	(%)	*o*-	*m*-	*p*-	Ref.
Toluene	5	Reflux	38	44	19	37	*a*
				42	58 †		*b*
Isopropylbenzene	5	125°	62	16	31	53	*c*
t-Butylbenzene	15	125		—	51	49	*c*
	5	125		—	41	59	
Phenol	5	125—140	34	53	0	47	*d*
Anisole	5	130	40	51	0	41	*d*
Fluorobenzene	24	Reflux	34	44	4	53	*f*
				45	55 †		*b*

a, Infrared, using peaks, 13·2 and 13·77 μ for *ortho*; 12·88 and 14·22 μ for *meta*; 12·29 μ for *para*. *b*, Vapour phase chromatography; 10% Reoplex on Celite (60—70 mesh) at 75°. *c*, Vapour phase chromatography; 10% Reoplex on Celite (60—70 mesh) at 100°. *d*, Vapour phase chromatography; 15% Apiezon on Celite (100—120 mesh) at 125°. *e*, The values have been corrected for the presence of *m*- and *p*-di-t-butylbenzene and some cumene. *f*, Infrared, using peaks, 13·3 μ for *ortho*; 12·82 μ for *meta*, and 12·05 for *para*. † Total of *m*- and *p*-.

The product from the isopropylation of t-butylbenzene contained not only *m*- and *p*-isopropyl-t-butylbenzenes but some isopropylbenzene and appreciable amounts of *m*- and *p*-di-t-butylbenzenes. *p*-Di-t-butylbenzene was isolated pure, m. p. and mixed m. p. 78—79°;

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dinitro-derivative, m. p. and mixed m. p. 191—192°. It was shown that when *p*-isopropyl-t-butylbenzene was heated in t-butylbenzene with anhydrous toluene-*p*-sulphonic acid for 5 hr., *m*- and *p*-di-t-butylbenzenes were formed; no *m*-isopropyl-t-butylbenzene could be detected.

Reference compounds required for the identification of the products were prepared by standard methods, and their constants agreed with those in the literature.

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