NOTES.

849. *The Reaction of Sulphur Hexafluoride with Sodium.*

By H. C. Cowen, F. Riding, and E. Warhurst.

We have recently measured the rate of reaction of sodium atoms with sulphur hexafluoride by the Polanyi diffusion flame technique. The reaction was very fast, and the extremely large bimolecular velocity constant at 247°, $2{\cdot}23 \times 10^{13}$ c.c. mole^{-1} sec.$^{-1}$, seems completely inconsistent with the widespread view that sulphur hexafluoride is extraordinarily inert towards attack by sodium. The origin of this view lies in the work of Moissan and Lebeau (*Compt. rend.*, 1900, **130**, 865, 984); unfortunately, these authors give very few details. However, the usual conclusion (see, for example, Sidgwick, " The Chemical Elements and their Compounds," Oxford, Vol. II, 1950, p. 944) seems to be that a clean sodium surface is completely unaffected by sulphur hexafluoride except at temperatures very close to the boiling point of sodium (880° at 1 atm.). We have heated sodium in sulphur hexafluoride and obtained results which do not confirm this earlier view.

The sulphur hexafluoride was very pure. It was prepared and purified by Imperial Chemical Industries Limited, General Chemicals, Runcorn, whom we thank for the gift of this compound. The gas was stated to contain about 10 parts per million of water and of hydrolysable fluorides and less than 1 part per million of disulphur decafluoride.

A thick film of sodium was deposited *in vacuo* on the side of a Pyrex tube, and sulphur hexafluoride was then admitted at room temperature to a pressure of 10 mm. No decrease of pressure was observed nor was the bright surface of the sodium tarnished on standing. As the temperature was raised the pressure began to drop at 200—250°, and during a period of 8 min., in which time the temperature rose to about 300°, the pressure rapidly fell to less than 0·1 mm. The sodium surface was largely covered with a brownish incrustation. A second experiment with 235·5 mm. of gas showed that at 300° the reaction came to a stop after only 10 mm. of gas had been absorbed, the sodium surface being very heavily covered with incrustation. A third experiment showed that at 500° the reaction was accompanied by a chemiluminescence of the sodium D line.

We believe that these experiments show conclusively that a clean sodium surface reacts rapidly with sulphur hexafluoride at about 250°, and think that, on theoretical and general grounds, this result is much more likely than the previous view. The relevant thermochemical data show that the gas-phase reaction $SF_6 + Na \longrightarrow SF_5 + Na^+F^-$ is exothermic to an extent of about **37** kcal. The reaction with a sodium surface would be even more exothermic. In the light of the interpretation of the sodium " flame " reaction in terms of potential-energy curves (Evans and Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11), together with general experience over a very wide field of halide reactivities towards sodium atoms, it would be expected that such a high exothermicity would involve a fast reaction rate and a low activation energy, as we have found. In contrast to this type of reaction in which a sodium atom approaches the molecule and " picks off " a fluorine atom, there is a type of reaction, for example hydrolysis (and possibly oxidation), which necessitates the attack of the sulphur atom by the other reactant. For this type, because of the geometry of the molecule, in which the sulphur atom is completely surrounded by fluorine atoms, extreme inertness is to be expected, and has been found experimentally in a number of cases. The very great difference in behaviour shown by sulphur hexafluoride with regard to these two types of reaction is an excellent example of the highly specific nature of chemical reactivity.

The most plausible explanation of the chemiluminescence is that one of the five stages

$$SF_n + Na \longrightarrow SF_{n-1} + Na^+F^- \quad (n \leqslant 5)$$

is exothermic to an extent greater than 49 kcal., the energy required to excite the D line.

THE UNIVERSITY, MANCHESTER.

[*Received, June 26th,* 1953.]

850. *The Dipole Moment of Acetone in the Liquid, Dissolved, and Gaseous States.*

By A. D. BUCKINGHAM and R. J. W. LE FÈVRE.

ACETONE has been used to test empirical equations of Barclay and Le Fevre (*J.*, 1950, 556) and Buckingham and Le Fèvre (*J.*, 1952, 1932), $\mu_{C_6H_6}$ and μ_{gas} being taken as 2·74 and 2·83—3·02 D, respectively. Tables 1 and 2 show the sources from which these values were drawn. The absence of a reliable figure for the distortion polarisation made redeterminations desirable.

TABLE 1. *Determinations of* μ_{gas}.

μ, D	Results calc. from	No. of temps. used	Authors
2·97	Measurements of ε at 100°	1	Hojendahl, " Studies of Dipole Moment," Kobenhavn, 1928.
2·83—3·02	Individual $(\varepsilon - 1)T°$	3	Stuart, *Z. Physik*, 1928, **51**, 490.
2·85	Individual polarisations	5	Zahn, *Physik. Z.*, 1932, **33**, 686.
2·95	$P = 6 + 53650/T$	2	Ramaswamy, *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 108.

TABLE 2. *Determinations of* $\mu_{C_6H_6}$.

Temp.	Polarisation expressed as	No. of solns. examined	μ, D	Authors
18°	${}_{\infty}P_{A+O} = 156·8$	3	2·72	Hassel and Naeshagen [1]
18	${}_{\infty}P_{A+O} = 164·2$	3	2·78	Hassel and Uhl [2]
22	${}_{\infty}P_{O} = 157·2$	5	2·74	Wolf and Gross [3]
20	${}_{\infty}P_{E+A+O} = 176$	Not stated	2·74	Müller [4]

[1] *Z. physikal. Chem.*, 1929, *B*, **4**, 217. [2] *Ibid.*, 1930, *B*, **8**, 187. [3] *Ibid.*, 1931, *B*, **14**, 305. [4] *Physik. Z.*, 1933, **34**, 689.

Present Work.—Measurements on acetone vapour were made with the apparatus used for the bromomethanes (*J.*, 1953, 3432), except that the cell, having been dismantled and repolished, had a new carbon dioxide standardisation equation after reassembly. For solutions in benzene the arrangements shown in " Dipole Moments," Methuen, 3rd Edn., 1953, Fig. 17, were used. Essential observations are in Tables 3 and 4.

TABLE 3. *Polarisations of acetone vapour.*

T, °K	$(\delta C/p)^{C_3H_6O*}_{p=0}$	P	$P_{calc.}$	p, range in cm.	No. of obsns.	T, °K	$(\delta C/p)^{C_3H_6O*}_{p=0}$	P	$P_{calc.}$	p, range in cm.	No. of obsns.
363·0	117·5	158·8	159·1	4—11	7	429·3	87·0	136·0	137·3	11—40	13
370·2	113·8	156·4	156·3	3—10	9	578·3	53·3	107·0	106·7	7—19	7
406·1	97·0	144·6	144·1	5—11	8	588·8	51·5	104·9	105·1	6—37	13
412·2	94·8	143·1	142·3	3—17	11						

* Standardising equation : $(\delta C/p)^{CO_2}_{p=0} = 0{\cdot}667 + 1730/T$.

TABLE 4. *Solutions of acetone in benzene*, t = 25°.

10^6w_2	0	9539	10,889	17,537	17,592	21,799	37,348	44,180	53,973
ε_{12}	2·2725	2·4131	2·4331	2·5272	2·5293	2·5887	2·8142	2·9212	3·0652
d_{12}	0·87378	0·87282	0·87269	0·87202	0·87204	0·87160	0·87010	0·86941	0·86858

From Table 3 we obtain by the method of least squares the Debye equation : $P = 18{\cdot}4(\pm 1{\cdot}7) + 51057(\pm 707)/T$, whence $\mu_{gas.} = 2{\cdot}89 \pm 0{\cdot}02$ D. From Table 4, the mean $\alpha\varepsilon_1$ is 14·63, while $\beta = (d_{12} - d_1)/w_2d_1$ shows a slight dependence on w_2; it is given by $\beta = -0{\cdot}117 + 0{\cdot}109w_2$. Accordingly, ${}_{\infty}P_2$ is 181·9 ± 1·2 c.c., and since ${}_{D}P = 18{\cdot}4 \pm 1{\cdot}7$ c.c., $\mu_{C_6H_6}$ follows as $2{\cdot}83 \pm 0{\cdot}02_5$D (standard errors have been quoted throughout).

Discussion.—The following predictions of $\mu_{C_6H_6}/\mu_{gas}$ are obtained by using equations (1)—(4), given by Buckingham and Le Fèvre (*loc. cit.*); in addition, their expressions (5)—(7), inclusive, are applied to liquid acetone. The required constants for 25° are $A = 5{\cdot}15, B = 6{\cdot}54, C = 3{\cdot}80$, exp $x^2 = 0{\cdot}754, \zeta = 0{\cdot}32, M_2 = 58{\cdot}08, d_2 = 0{\cdot}7863, n_D{}^2 = 1{\cdot}8400, n^2{}_{eff.} = 1{\cdot}995, \varepsilon = 19{\cdot}11$, and $\mu_{liq.} = 1{\cdot}48$ D :

Equation used	(1)	(2)	(3)	(4)	Value observed $0{\cdot}98 \pm 0{\cdot}01_5$
$\mu_{C_6H_6}/\mu_{gas}$, calc.	0·93	0·96	0·92	0·96	
Equation used	(5)	(6)	(7)	*	Value observed $2{\cdot}89 \pm 0{\cdot}02$ D
μ_{gas}, calc., D	2·96	2·96	2·86	2·93	

The value marked with an asterisk has been derived from the equation ${}_0P = (\varepsilon - n^2)[\varepsilon + (n^2 - \varepsilon)A]^2M/\varepsilon(2\varepsilon + n^2)[1 + (n^2 - 1)A]^2d$ developed by Buckingham (*Austr. J. Chem.*, 1953, **6**, 93, eqn. 20) on the assumption that the liquid consists of uniformly polarised ellipsoids each one of which is surrounded by a continuum having the " macroscopic " dielectric constant of the fluid in bulk.

In view of the uncertainties underlying the " shape-factors " exp x^2 and ζ, the forecasts are regarded as satisfactory.

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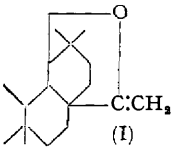
851. *The Infra-red Absorption of Vinyl Ethers.*

By G. D. MEAKINS.

ALTHOUGH the infra-red spectra of several unsubstituted vinyl ethers, $CH_2{:}CH{\cdot}OR$, are available in the literature (" Catalogue of Infra-red Spectrograms," S. P. Sadtler, Philadelphia), there appear to be few data on such ethers containing substituents in the vinyl group. Most of the few known examples [*e.g.*, *cis*- and *trans*-but-1-enyl butyl ether (Hall, Philpotts, Stern, and Thain, *J.*, 1951, 3341), dihydropyran (see, *e.g.*, Bader, *Helv. Chim. Acta*, 1953, **36**, 215)] contain substituents at the β-carbon atom, and thus represent only one of the possible substituted types. The compounds now reported cover a more varied range; the preparation and ultra-violet spectra of the samples used have already been described (Eglinton, Jones, and Whiting, *J.*, 1952, 2873).


(I)

The spectra were recorded on a Perkin–Elmer double-beam spectrometer (sodium chloride prism), liquid films of various thicknesses being used. In the Table the intensities of the bands (w = weak, m = medium, s = strong) are given as guides to the appearance of the spectra. Only the most prominent bands in the 1000—650 cm.$^{-1}$ region are listed.

	Wave-length range (cm.$^{-1}$)					
	3150—3050	1700—1580	1000—650			
(*a*) *n*-Butyl vinyl ether	3120 w	1650 sh	964 m	811 ms	—	—
	3050 w	1633 m	—	—	—	—
	—	1611 s	—	—	—	—
(*b*) 2-Ethoxyhex-1-ene	3150 w	1655 s	958 m	—	793 m	—
	—	1592 m	—	—	—	—
(*c*) Tetrahydro-2-methylenefuran	3115 w	1669 s	—	895 m	796 s	—
	—	1590 w	—	882 m	—	—
	—	—	—	875 m	—	—
(*d*) " Triterpene vinylidene ether " *	—	1664 s	981 m	—	792 s	—
	—	1583 w	—	—	—	—
(*e*) Dihydropyran	3063 m	1644 s	929 m	889 m	749 m	—
	—	—	—	835 m	727 m	—
(*f*) 1 : 2-Dihydrofuran †	3120 w	1630 s	—	—	715 m	699 m
(*g*) 1-Ethoxybut-1-en-3-yne	3095 w	1631 s	948 m	879 m	733 m	—
	3070 w	—	—	—	—	—
(*h*) 4 : 5-Dihydro-2-methylfuran	3107 w	1677 s	958 m	891 m	717 m	—
	—	—	925 m	—	—	—

* Examined as a mull in Nujol. Partial formula (I) (*J.*, 1951, 2698).

† Data kindly supplied by Professor C. L. Wilson and Dr. D. Aten (personal communication). They have independently examined compounds (*b*), (*c*), and (*h*); their results are in general agreement with those reported here.

From the results it can be seen that linkage of an oxygen atom to a double bond affects the positions and intensities of the bands normally associated with the unsaturated system (for olefinic absorption see Sheppard and Simpson, *Quart. Reviews*, 1952, **6**, 1). *n*-Butyl vinyl ether (*a*), and other compounds $CH_2{:}CH{\cdot}OR$ (Sadtler, *op. cit.*) have shoulders at approximately 3120 cm.$^{-1}$, and strong bands at about 1610, 960, and 810 cm.$^{-1}$ (The 1610-cm.$^{-1}$ band is accompanied by at least one medium-intensity band or shoulder between 1650 and 1620 cm.$^{-1}$.) The 3120-cm.$^{-1}$ band and the absorption around 1610 cm.$^{-1}$ can be assigned to the olefinic carbon–hydrogen and carbon–carbon stretching modes, respectively. The hydrogen stretching bands are thus moved by *ca.* 40 cm.$^{-1}$ to higher frequency from the normal vinyl position ($\sim$3080 cm.$^{-1}$). This may explain the appearance of two olefinic hydrogen bands in butyl vinyl ether; in most hydrocarbons the saturated carbon–hydrogen stretching absorption envelops all but the highest-frequency vinyl stretching band. The double-bond stretching bands are, as expected, intensified by the introduction of oxygen, but the frequencies are little affected (vinyl $\sim$1640 cm.$^{-1}$).

While the origin of the bands at 960 and 810 cm.$^{-1}$ is not so obvious, it is probable that they represent displaced olefinic out-of-plane bending frequencies (normally 990 and 910 cm.$^{-1}$ for vinyl groups). The regular occurrence of these bands in compounds $CH_2{:}CH{\cdot}OR$, their relative intensities (960-cm.$^{-1}$ band weaker than the 810-cm.$^{-1}$ band), and their disappearance on substitution of the vinyl group support this suggestion.

With the substituted types similar effects are observed in the displacement of the olefinic carbon–hydrogen stretching bands, and the intensification of the carbon–carbon stretching bands. In some of the compounds the latter bands appear as single peaks (cf. unsubstituted ethers above). The frequencies of the double-bond peaks are slightly higher than those of their hydrocarbon analogues, and the positions of the bands vary in the usual way with structural change. Thus in tetrahydro-2-methylenefuran (*c*) and the " triterpene vinylidene ether " (*d*) (terminal methylene groups exocyclic to five-membered rings) the frequencies are higher than in the corresponding acyclic compound 2-ethoxyhex-1-ene (*b*), and the frequency in dihydropyran (*e*) is greater than that in 1 : 2-dihydrofuran (*f*) (double bonds in six- and five-membered rings respectively) (cf. discussion by Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402). The effect of increased substitution is shown by comparison of (*e*) and (*h*), while in (*g*) conjugation accounts for the low frequency.

Assignments of the out-of-plane hydrogen bending bands are less certain. Compounds (*b*), (*c*), and (*d*) (with terminal methylene groups) have strong bands at 795 cm.$^{-1}$ which probably correspond to the olefinic bending (normally at 890 cm.$^{-1}$ in analogous hydrocarbons). It may be noted that the methylene wagging in 1 : 1-difluoroethylene, which is somewhat similar to this type of vinyl ether, occurs at 803 cm.$^{-1}$ (Smith, Nielsen, and Claassen, *J. Chem. Phys.*, 1950, **18**, 326). In *cis*- and *trans*-but-1-enyl butyl ether the bending vibrations (720—690 cm.$^{-1}$, and 960 cm.$^{-1}$ for related olefins) probably occur at 730 and 933 cm.$^{-1}$ respectively (Hall *et al.*, *loc. cit.*). If these assignments are correct, then the band of the *trans*-disubstituted olefinic group, like those of the vinyl and terminal methylene groups, is displaced to lower frequency by the linkage to oxygen, while the *cis*-group band is not appreciably affected. On this basis the olefinic bending bands of (*e*), (*f*), and (*g*) would be at 727, 715 (or 699) and 733 cm.$^{-1}$ respectively. (From its method of preparation—addition of ethanol to diacetylene under basic conditions—the last compound could be a mixture of *cis*- and *trans*-isomers. However, the absence of strong absorption between 1000 and 800 cm.$^{-1}$ appears to indicate a mainly *cis*-configuration.) Alternatively the *cis*-olefinic bands could have been displaced to below 650 cm.$^{-1}$, in which case the bands mentioned may be associated with skeletal or methylene modes.

It has not been found possible to identify with certainty the carbon–oxygen stretching bands. It is well known that the positions of these skeletal bands depend on structural factors such as ring size (see, *inter al.*, Barrow and Searles, *J. Amer. Chem. Soc.*, 1953, **75**, 1175). However, each of the compounds studied has one medium or strong band in the range 1275—1200 cm.$^{-1}$, and another between 1075 and 1020 cm.$^{-1}$. These ranges are close to those suggested by Tschamler and Leutner (*Monatsh.*, 1952, **83**, 1502) for the carbon–oxygen stretching frequencies in unsaturated ethers.

THE UNIVERSITY, MANCHESTER, 13. [*Received, July 24th*, 1953.]

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852. *The Reactions of Metallic Salts of Acids with Halogens. Part IV.* Synthesis of Perfluoro-nitroso- and -nitro-compounds.*

By R. N. HASZELDINE and J. JANDER.

THE first synthesis of perfluoroalkyl nitroso-compounds involved the conversion of the corresponding polyfluoroiodoalkane into the free radical, followed by reaction with nitric oxide (Haszeldine, *J.*, 1953, 2075) :

$$CF_3\cdot[CF_2]_n\cdot I \xrightarrow{Hg,\ h\nu} CF_3\cdot[CF_2]_n\cdot \xrightarrow{NO} CF_3\cdot[CF_2]_n\cdot NO$$

and one route to the corresponding nitro-compounds was to oxidise the nitroso-compounds. The use of iodo-compounds can now be avoided by reaction of the silver salt of the corresponding carboxylic acid with nitrosyl chloride :

$$\begin{tikzcd} CF_3\cdot[CF_2]_n\cdot CO_2Ag \arrow[r, "NOCl"] & AgCl + CF_3\cdot[CF_2]_n\cdot CO\cdot O\cdot NO \quad \text{(I)} \arrow[d, "Heat"] \\ & CF_3\cdot[CF_2]_n\cdot NO + CF_3\cdot[CF_2]_n\cdot NO_2 + CO_2 \text{ etc.} \end{tikzcd}$$

The reaction is of the type described in Parts I—III* for chlorine, bromine, or iodine. Thus with silver trifluoroacetate, an addition compound, probably (I; $n = 0$), is first formed at $-10°$, and when heated decomposes into carbon dioxide, oxides of nitrogen, trifluoronitrosomethane, and trifluoronitromethane; the last compound is formed by oxidation of the nitroso-compound, or possibly by reaction of the trifluoromethyl radical with dinitrogen tetroxide. Hexafluoroethane is also formed, suggesting that free radicals are involved in the decomposition of (I; $n = 0$). Chlorotrifluoromethane (b. p. $-80°$), formed by reaction of silver trifluoroacetate with chlorine, is the other main by-product and, like hexafluoroethane (b. p. $-79°$), cannot easily be removed from the nitroso-compound (b. p. $-86°$) by distillation. The thermal and chemical stability of chlorotrifluoromethane and hexafluoro-

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* Parts I, II, and III, *J.*, 1952, 584, 993, 4259.

ethane are such, however, that these compounds play no part in any subsequent reactions of the nitroso-compound, and can readily be removed by distillation from the products of such reactions which usually boil appreciably higher (unpublished work). The advantages of the method are that a ready source of the reactive trifluoronitrosomethane is made available without the use of iodine, mercury, or ultra-violet light, and that substantial quantities of the nitroso-compound can be prepared in a short time.

Experimental.—Silver trifluoroacetate, prepared as described earlier (Part I, *loc. cit.*), was thoroughly dried *in vacuo*, and stored over phosphoric anhydride in the dark. Nitrosyl chloride was redistilled and stored *in vacuo* in absence of light.

Reaction of silver trifluoroacetate with nitrosyl chloride. Nitrosyl chloride (12·5 g., 0·19 mole) was condensed into a 500-ml. conical flask fitted with a reflux water-condenser connected *via* rubber tubing to two traps cooled in liquid oxygen. The flask was cooled in liquid oxygen, and silver trifluoroacetate (5·5 g., 0·025 mole) was added slowly. The flask and contents were then warmed to −10° and shaken vigorously to produce a yellow solid mass from which the excess of nitrosyl chloride was distilled by raising the temperature to 5°. Some chlorotrifluoromethane was formed at this stage. The reaction vessel was then placed behind a safety screen and the lower edge of the flask was heated gently by a *small* flame. (N.B. If the flask is heated rapidly a vigorous, almost explosive, reaction spreads through the solid, and most of the product is lost.) The rate of thermal decomposition can be followed by the evolution of gas, and should be controlled carefully for best results. The mixture is finally heated strongly. The products were distilled *in vacuo* through a trap cooled to −140°. The fraction which passed through was deep blue, and was shaken with ice-cold 20% aqueous sodium hydroxide for 4 min. to remove carbon dioxide and traces of oxides of nitrogen, then redistilled to give trifluoronitrosomethane (*ca.* 0·4 g., 16%; identified by comparison of its infra-red spectrum with that of a pure specimen prepared earlier), chlorotrifluoromethane (*ca.* 0·3 g.), and hexafluoroethane (*ca.* 0·2 g.). The fraction which had condensed in the trap cooled to −140° was shaken with mercury to remove dinitrogen tetroxide, then repeatedly distilled *in vacuo* to give trifluoronitromethane (0·37 g., 13%), identified by comparison of its infra-red spectrum with that of a pure sample; a third compound is at present unidentified. Silver trifluoroacetate (1·2 g.) was recovered unchanged after the reaction.

Infra-red spectra. These were measured on a Perkin–Elmer Model 21 Spectrometer with rock-salt optics. Trifluoronitrosomethane is characterised by the N=O stretching vibration at 6·25 μ, and trifluoronitromethane by the asymmetrical stretching vibration at 6·13, 6·18 μ (doublet) and the symmetrical stretching vibration at 7·78 μ (cf. $CClF_2{\cdot}CF_2{\cdot}NO_2$ which has corresponding bands at 6·18 and 7·85 μ; Haszeldine, *J.*, 1953, 2525).

We are indebted to Professor H. J. Emeléus, F.R.S., for his interest and one of us (J. J.) to the British Council for a British Council Scholarship for Germany, during the tenure of which this work was carried out.

University Chemical Laboratory, Cambridge. [*Received, July 24th*, 1953.]

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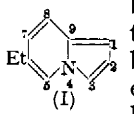
853. 6-*Ethylpyrrocoline.*

By G. R. Clemo, B. W. Fox, and Richard Raper.

One of us (G. R. C.) described the degradation of strychnine with potassium hydroxide under mild conditions (*J.*, 1936, 1695) and a fraction was obtained as a picrate, m. p. 192°, insoluble in cold acetone, from which a colourless, sweet smelling oil, $C_{10}H_{11}N$, b. p. 90°/1 mm., designated "base B," was obtained. It was reduced by the addition of eight atoms of hydrogen to give "perhydro base B," a strong base $C_{10}H_{19}N$, which easily formed salts. It was suggested that base B was either an ethyl- or a dimethyl-pyrrocoline, and that on reduction an octahydropyrrocoline was formed.

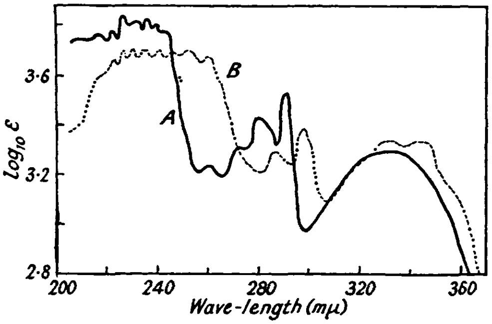


(I)

The perhydro-base B was shown to differ from 1- and 2-ethyloctahydropyrrocoline (Clemo and Metcalfe, *J.*, 1937, 1518) and from 6-ethyl- and 1 : 7-dimethyl-octahydropyrrocoline (Clemo, Fletcher, Fulton, and Raper, *J.*, 1950, 1140). Ochiai and Tsuda (*Ber.*, 1934, **67**, 1011) prepared 2 : 3-dimethylpyrrocoline and 2 : 3-dimethyloctahydropyrrocoline, Tschichibabin (*Ber.*, 1927, **60**, 1617) prepared 2 : 4-dimethylpyrrocoline (but recorded no picrate or reduction product), but these too were different from the compounds from strychnine.

6-Ethylpyrrocoline (I) has now been prepared from 5-ethyl-2-methylpyridine by Borrows and Holland's method (*J.*, 1947, 672). It is unstable, has the characteristic properties of pyrrocolines, and readily forms a crystalline picrate, soluble in cold acetone and decomposing rapidly in air. It thus also differs from base B. Reduction over platinum oxide gave 6-ethyloctahydropyrrocoline, identical with that described by Clemo, Fletcher, Fulton, and Raper.

Experimental.—6-*Ethylpyrrocoline*-2-*carboxylic acid.* 5-Ethyl-2-methylpyridine (Frank, Blegen, Deerborn, Myers, and Woodward, *J. Amer. Chem. Soc.*, 1946, **68**, 1368) (purified through the picrate, m. p. 164°) (6·8 g.), ethyl bromopyruvate (Borrows and Holland, *loc. cit.*) (11·0 g.) and ethanol (45 ml.) were refluxed for 1 hr. and set aside for 4 days. Th yellow solution rapidly became deep brown-red. The ethanol was distilled off at reduced pressure, and the syrupy residue diluted with water (20 ml.). The coloured impurities were extracted with chloroform, sodium hydrogen carbonate was added until effervescence ceased, and the liberated 5-ethyl-2-methylpyridine was extracted with ether. The brown aqueous solution was treated with an excess of sodium hydrogen carbonate (5 g.), and the solution kept on a water-bath for 1 hr., then cooled and acidified with dilute hydrochloric acid. 6-*Ethylpyrrocoline*-2-*carboxylic acid* separated as a buff-coloured powder (2·4 g., 23%) and recrystallized from alcohol as almost colourless plates, m. p. 182—183° (Found : C, 69·7; H, 6·2; N, 7·8. $C_{11}H_{11}O_2N$ requires C, 69·7; H, 5·8, N, 7·4%). Light absorption : Max. at 2250—2600 (ε 5670), 2870 (ε 5172), 2975 (ε 5295), 3310 (ε 5230), and 3440 Å (ε 5230) (see Fig.).



Ultra-violet absorption of :
A, 6-*ethylpyrrocoline.*
B, 6-*ethylpyrrocoline*-2-*carboxylic acid.*

6-*Ethylpyrrocoline* (cf. Diels and Alder, *Annalen*, 1932, **498**, 16). 6-Ethylpyrrocoline-2-carboxylic acid (2 g.) and freshly prepared quicklime (6 g.) were triturated and dry-distilled at atmospheric pressure, and at as low a temperature as possible. A dark brown oil passed over, which was dissolved in ether (10 ml.), dried ($MgSO_4$), and fractionally distilled. 6-*Ethylpyrrocoline* (0·9 g., 59%) (Found : C, 82·8; H, 8·15; N, 9·8. $C_{10}H_{11}N$ requires C, 82·75; H, 7·6; N, 9·7%) is a colourless oil, b. p. 124—126°/18 mm., which darkens in air and dissolves in ether or chloroform to give a faintly fluorescent solution, becoming bright blue in a few hr. It gives the usual indole-like colours with the pine shaving and the Ehrlich reaction. Light absorption : Max. at 2250—2400 (ε 5800), 2800 (ε 5350), 2910 (ε 5480), and 3320 Å (ε 5172) (see Fig.).

A picrate, brown needles, m. p. 152—155° (decomp.) (base B gives a picrate, m. p. 192°) from ether, decomposed quickly and was very soluble in cold acetone and in ethanol.

6-*Ethyloctahydropyrrocoline.* 6-Ethylpyrrocoline (0·4 g.) in glacial acetic acid (20 ml.) was shaken with platinic oxide and hydrogen at 100 lb./sq. in. at room temperature overnight, hydrogen (300 ml., 4 mols.) being absorbed. The solvent was removed, the residue treated with potassium carbonate solution and extracted with ether, and the extract dried ($MgSO_4$) and distilled. 6-*Ethyloctahydropyrrocoline* (0·35 g.), a colourless oil, b. p. 80—85°/18 mm.

(Found: C, 78·5; H, 12·5. Calc. for $C_{10}H_{19}N$: C, 78·4; H, 12·4%), gave a picrate, m. p. 176° (after three recrystallizations from ethanol), not depressed by admixture with an authentic specimen (Found: C, 69·7; H, 6·2. Calc. for $C_{10}H_{19}N,C_6H_3O_7N_3$: C, 69·8; H, 5·8%). The methiodide, colourless needles (from acetone–ether), m. p. 221—222°, and the picrolonate, m. p. 185°, prisms from methanol, agreed in properties with those recorded by Clemo, Fletcher, Fulton, and Raper (*loc. cit.*).

Ultra-violet absorption measurements were made in ethanol purified according to Bladon, Henbest, and Wood (*J.*, 1952, 2738) and with a Hilger "Uvispec" spectrophotometer.

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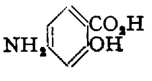
854. *Pyrimidines. Part VII.* Some Pyrimidine Analogues of 4-Aminosalicylic Acid.*

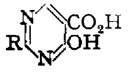
By J. F. W. McOmie and I. M. White.

4-Aminosalicylic acid (I) was first introduced into the chemotherapy of tuberculosis by Lehmann (*Lancet*, 1946, **250**, 14); of the many related compounds since investigated, however, none has proved superior (*e.g.*, Erlenmeyer *et al.*, *Helv. Chim. Acta*, 1948, **31**, 988; Doub *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 903). The present paper describes the preparation of some pyrimidine analogues of 4-aminosalicylic acid, none of which possesses antitubercular activity. After the completion of this work, some pyridine analogues were described by Fox (*J. Org. Chem.*, 1952, **17**, 547). 3-Hydroxypyridine-4- and 4-hydroxypyridine-3-carboxylic acid were inactive, but 3-aminopyridine-4-carboxylic acid and its methyl ester had approximately half the antitubercular activity of nicotinamide and of 4-aminosalicylic acid in mouse infections (Fox, *ibid.*, p. 542).

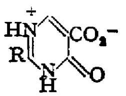
The 4-hydroxypyrimidine-5-carboxylic acids (II; R = SH, SMe, H, NH_2, OH, and Me) bear a formal resemblance to 4-aminosalicylic acid (I), although in neutral solution the pyrimidine acids probably exist as zwitterions and in the form of pyrimidones (*e.g.*, III). For convenience, they are named as derivatives of the structure (II). The pyrimidines studied are all known compounds, but some of them have been prepared by new and better methods (see Experimental).



(I)



(II)



(III)

The acids (II; R = SH, SMe, NH_2, OH) and the ethyl esters of (II; R = SH, NH_2, OH, Me, SEt) were examined for antitubercular activity by the chick-embryo test. The compounds were all inactive except 4-hydroxy-2-mercaptopyrimidine-5-carboxylic acid which, however, was inactive when tested in mice. The following related compounds were also inactive in the chick-embryo test: 4-hydroxy-2-mercapto-, 2-methylthio-, and 2 : 4-dimercaptopyrimidine, whereas 5-amino-2-ethylthio-4-hydroxypyrimidine (Boarland and McOmie, *J.*, 1952, 4942) was active.

Experimental.—*4-Hydroxy-2-mercaptopyrimidine-5-carboxylic acid.* Ethyl 4-hydroxy-2-mercaptopyrimidine-5-carboxylate (2·5 g.) (Ballard and Johnson, *J. Amer. Chem. Soc.*, 1942, **64**, 794) and 20% sulphuric acid (50 c.c.) were boiled for 1½ hr. and then cooled. Two recrystallisations of the product (2·1 g.) from water gave the pure acid, m. p. 288—289° (decomp.). Johnson and Ambler (*J. Amer. Chem. Soc.*, 1911, **33**, 982) recorded m. p. 246—247° (decomp.).

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* Part VI, *J.*, 1953, 3129

The *ammonium* salt, prepared by dissolving the acid in warm ammonia solution, cooling, and acidifying with acetic acid, had m. p. 308—310° (decomp.) (Found : C, 32·0; H, 3·7; N, 22·1; S, 16·8. $C_5H_7O_3N_3S$ requires C, 31·8; H, 3·7; N, 22·2; S, 16·9%).

4-Hydroxy-2-methylthiopyrimidine-5-carboxylic acid. A solution of 4-hydroxy-2-mercaptopyrimidine-5-carboxylic acid (4·2 g.) and sodium hydroxide (5·0 g.) in water (130 c.c.) was shaken vigorously with methyl sulphate (8·0 g.) for 2½ hr. Acidification with hydrochloric acid gave the 2-methylthio-compound (2·2 g., 48%), m. p. 234—235° (decomp.). Wheeler, Johnson, and Johns (*Amer. Chem. J.*, 1907, **37**, 404) recorded m. p. 235°.

Ethyl 4-hydroxy-2-methylthiopyrimidine-5-carboxylate. A mixture of methyl sulphate (3·2 g.), ethyl 4-hydroxy-2-mercaptopyrimidine-5-carboxylate (5·0 g.), and sodium hydroxide (1·75 g.) in water (150 c.c.) was stirred for 1 hr. The solution was filtered, acidified with hydrochloric acid, and concentrated under reduced pressure. The solid which separated on cooling was recrystallised from water giving the pure ester (1·6 g., 30%), m. p. and mixed m. p. 134—136° (Todd, Fletcher, and Tarbell, *J. Amer. Chem. Soc.*, 1943, **65**, 350).

4-Hydroxypyrimidine-5-carboxylic acid. Ethyl 4-hydroxy-2-mercaptopyrimidine-5-carboxylate (5·0 g.) in water (200 c.c.) was heated under reflux with Raney nickel sludge (25 g.) for 4 hr., with stirring. After filtration, the green solution was evaporated to dryness and the residue recrystallised thrice from water (charcoal) giving needles of 4-hydroxypyrimidine-5-carboxylic acid (0·5 g., 14%), m. p. 236—237° (decomp.). Ballard and Johnson (*loc. cit.*) give m. p. 238°.

No pure sulphur-free compounds could be isolated from the attempted desulphurisation of the acids (II; R = SH and SMe) or of the ethyl ester of the latter.

Uracil-5-carboxylic acid. Finely powdered ethyl 4-hydroxy-2-mercaptopyrimidine-5-carboxylate (4·0 g.) was added in portions to a boiling solution of 10% nitric acid (54 c.c.) during ½ hr. The solution was concentrated and the solid (2·9 g., 83%), m. p. 284—285° (decomp.), collected. Recrystallisation from water gave uracil-5-carboxylic acid, m. p. 288—290° (decomp.). Wheeler, Johnson, and Johns (*loc. cit.*) recorded m. p. 278° (decomp.).

Ethyl 2-amino-4-hydroxypyrimidine-5-carboxylate. This was prepared by Mitter and Palit's method (*J. Indian Chem. Soc.*, 1925, **2**, 61); the m. p., after two recrystallisations from glacial acetic acid, was found to be 303—304° (decomp.; rapid heating) (Found: C, 45·6; H, 5·0. Calc. for $C_7H_9O_3N_3$: C, 45·9; H, 5·0%), whereas Mitter and Palit recorded m. p. 285°.

The authors thank Mr. G. E. Davies of Imperial Chemical (Pharmaceuticals) Ltd., for the bacteriological tests. One of them (I. M. W.) thanks the University of Bristol for a Graduate Scholarship.

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855. *Reduction of 4-Methyl-3-nitroacetophenone.*

By O. L. BRADY and P. E. HALSTEAD.

IN an attempt to obtain pure 4-ethyl-2-nitro- or 2-amino-4-ethyl-toluene in good yields 4-methyl-3-nitroacetophenone has been reduced by the reactions: $NO_2{\cdot}C_6H_3Me{\cdot}COMe \longrightarrow NO_2{\cdot}C_6H_3Me{\cdot}CHMe{\cdot}OH \longrightarrow NO_2{\cdot}C_6H_3Me{\cdot}CHMeCl \longrightarrow NO_2{\cdot}C_6H_3Me{\cdot}CH{:}CH_2 \longrightarrow C_6H_3MeEt{\cdot}NH_2$, but only a 12% yield was obtained, which was no better than Brady and Day (*J.*, 1934, 114) obtained by Clemmensen reduction. Electrolytic reduction with an amalgamated cadmium cathode under varying conditions was unsuccessful, as also was heating the hydrazone or azine of 4-methyl-3-nitro- or 3-amino-4-methyl-acetophenone with sodium ethoxide under pressure; but Rinkes (*Rec. Trav. chim.*, 1945, **64**, 205) has, subsequent to our work, obtained a 75% yield of 2-amino-4-ethyltoluene by reducing 3-amino-4-methylacetophenone with hydrazine hydrate at 200°.

Experimental.—*1-(4-Methyl-3-nitrophenyl)ethanol.* 4-Methyl-3-nitroacetophenone was heated under reflux for 1 hr. with aluminium *iso*propoxide in *iso*propyl alcohol; the water was run out of the condenser and the heating continued until the acetone had escaped and then the excess of *iso*propyl alcohol was distilled off. After cooling, the solid was heated with 2N-sulphuric acid, the liberated oil extracted with ether, and the extract washed with alkali, dried, and evaporated. The brownish oil remaining did not crystallise after 5 months but when distilled under reduced pressure (b. p. 205—210°/70 mm.) crystallised after some months in a desiccator. Later preparations, undistilled, solidified in 24 hr. when seeded. 1-(*4-Methyl-3-nitrophenyl)ethanol* was obtained from light petroleum in pale yellow crystals, m. p. 52·5°; very soluble in most organic solvents (Found: C, 59·7; H, 6·1. $C_9H_{11}O_3N$ requires C, 59·8 H, 6·1%).

1-(*3-Amino-4-methylphenyl)ethanol.* The foregoing alcohol (7·5 g.) in ethanol (25 c.c.) was boiled under reflux for 2 hr. with reduced iron (10 g.) and concentrated hydrochloric acid (0·5 c.c.), filtered and evaporated. The solid obtained was extracted (Soxhlet) with light petroleum; after evaporation and crystallisation from light petroleum the *amine* was obtained, having m. p. 75° and becoming brown in air (Found: C, 71·7; H, 8·5. $C_9H_{11}ON$ requires C, 71·5; H, 8·7%).

4-Ethyl-2-methylaniline. 1-(4-Methyl-3-nitrophenyl)ethanol (16 g.) was dissolved in thionyl chloride (25 c.c.) and excess of the latter removed at 120°. The product was distilled at 18 mm. and the fraction boiling at 165° collected and distilled twice at 0·2 mm.; 1-(*4-methyl-3-nitrophenyl)ethyl chloride* was thus obtained as a yellow oil, b. p. 113°/0·2 mm. (Found: Cl, 17·2. $C_9H_{10}O_2NCl$ requires Cl, 17·8%). This chloride was boiled under reflux with excess of pyridine; after 3 hr., light brown crystals separated, of which a portion was collected and crystallised from water and found to be 1-1′-(*4-methyl-3-nitrophenyl)ethylpyridinium chloride*, m. p. 201° (Found: Cl, 12·0. $C_{14}H_{15}O_2N_2Cl$ requires Cl, 12·8%). The halogen was ionisable and was determined with silver nitrate. After a further 6 hr.' refluxing the liquid was decanted into a large excess of dilute hydrochloric acid. Extraction with ether and evaporation gave a liquid which decolorised cold acid permanganate rapidly and was free from chlorine. Distillation under reduced pressure gave *4-methyl-3-nitrostyrene* as a pale yellow liquid, b. p. 70°/0·2 mm. (Found: C, 65·4; H, 5·7. $C_9H_9O_2N$ requires C, 66·2; H, 5·5%).

The solid pyridinium chloride remaining was repeatedly refluxed with fresh pyridine and further small amounts of styrene were obtained, but the total yield was poor (only about 25% of the ethyl chloride used). The styrene (2 g.) was reduced in ethanol at room temperature with hydrogen at 5 atm. and Adams platinum oxide (0·1 g.). After filtration and evaporation 4-ethyl-2-methylaniline (1·6 g.) was obtained as a liquid which was identified by conversion into the acetyl derivative, m. p. 137°, and comparison with that compound prepared by Brady and Day from *p*-ethyltoluene.

Hydrazines and azines. The following hydrazones were prepared with excess of hydrazine hydrate, and the azines from these by the action of hydrochloric acid; the azine of the amino-ketone was precipitated from its solution in hydrochloric acid by ammonia.

4-Methyl-3-nitro-, orange plates, m. p. 86° (Found: C, 55·8; H, 5·6. $C_9H_{11}O_2N_3$ requires C, 56·0; H, 5·7%), and *3-amino-4-methyl-acetophenone hydrazone*, silvery plates, m. p. 116° (Found: C, 66·5; H, 7·6. $C_9H_{13}N_3$ requires C, 66·3; H, 8·0%). *4-Methyl-3-nitro-*, yellow needles, m. p. 198° (Found: C, 60·7; H, 4·9. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1%), and *3-amino-4-methyl-acetophenone azine*, colourless, m. p. 168° (Found: C, 73·4; H, 7·5. $C_{18}H_{22}N_4$ requires C, 73·5; H, 7·5%). All were crystallised from light petroleum.

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856. *Chemistry of the Platinum Metals. Part III.* Lattice Constants of some Chloropalladates, Bromopalladates, and Bromoplatinates.*

By A. G. Sharpe.

Ketelaar and von Walsem (*Rec. Trav. chim.*, 1938, **57**, 964) found potassium, rubidium, cæsium, and ammonium chloro- and bromo-palladates to be isomorphous with potassium chloroplatinate. In their values for the lattice constants of these compounds, however, two curious features may be noticed. First, that of ammonium bromopalladate (9·95 Å) is much closer to that of the potassium salt (9·92 Å) than to that of the rubidium salt

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* Part II, *J.*, 1953, 197.

(10·25 Å). Secondly, there is little difference between the values given for ammonium bromopalladate and ammonium chloropalladate (9·90 Å), though the values for cæsium chloro- and bromo-palladate (10·16 and 10·64 Å, respectively) show the expected large difference resulting from the replacement of chlorine by bromine.

The lattice constants of these chloro- and bromo-palladates have therefore been re-determined, with samples whose purity has been checked by adequate chemical analysis (Ketelaar and von Walsem give no analytical data). Because of the possibility of solid-solution formation [see, *e.g.*, Sharpe, *J.*, 1950, 3444; Busch, Galloni, and Haitz, *Anal. Asoc. Quim. Argentina*, 1951, **39**, 55 (*Chem. Abs.*, 1952, **46**, 314)], this precaution appears particularly desirable when only a partial investigation of the structure is made. Data have also been obtained for the corresponding bromoplatinates: that for the potassium salt is in moderate agreement with the value of 10·21 Å given by Busch *et al.* (*loc. cit.*); the other compounds have not been investigated previously.

The results obtained are summarised below, together with the most recent data for the analogous chloroplatinates. Only for potassium and cæsium chloropalladates and cæsium bromopalladate do they agree well with those of Ketelaar and von Walsem. They do, however, show the customary regular variation among salts of alkali metals and similarity between palladium and platinum compounds.

Lattice Constants (±0·01 Å).

(Values in parentheses are those of Ketelaar and von Walsem, *loc. cit.*; values quoted for chloroplatinates are those of Engel, *Z. Krist.*, 1935, **90**, 341.)

K_2PdCl_6	9·74(9·74)	Rb_2PdCl_6	9·87(9·99)	Cs_2PdCl_6	10·18(10·16)	$(NH_4)_2PdCl_6$	9·84(9·90)
K_2PtCl_6	9·73	Rb_2PtCl_6	9·88	Cs_2PtCl_6	10·19	$(NH_4)_2PtCl_6$	9·83
K_2PdBr_6	10·25(9·92)	Rb_2PdBr_6	10·38(10·25)	Cs_2PdBr_6	10·62(10·64)	$(NH_4)_2PdBr_6$	10·33(9·95)
K_2PtBr_6	10·27	$RbPtBr_6$	10·41	Cs_2PtBr_6	10·63	$(NH_4)_2PtBr_6$	10·37

Experimental.—Potassium tetrachloropalladite (Found: Pd, 32·5. Calc. for K_2PdCl_4: Pd, 32·6%), palladium-free sodium chloroplatinate, "AnalaR" potassium and ammonium halides, and Kahlbaum rubidium and cæsium halides were used as starting materials. A solution of sodium chloropalladate was obtained by precipitating palladium as palladous oxide with sodium carbonate, purifying the oxide by reprecipitation, dissolving it in hydrochloric acid, and warming the solution with sodium chlorate. The sparingly soluble potassium, rubidium, cæsium, and ammonium salts were precipitated on addition of the appropriate chloride; they were washed with chlorine water, alcohol, and ether. Treatment with even cold water causes the liberation of some chlorine from these compounds, and recrystallisation was impossible. Decomposition was effected by reduction with warm hydrazine sulphate solution: the precipitated palladium was dissolved in the minimum quantity of aqua regia and determined as the dimethylglyoxime derivative; chloride was determined as silver chloride [Found, for the K salt: Pd, 26·8; Cl, 53·3. Calc. for K_2PdCl_6: Pd, 26·9; Cl, 53·6. Found, for the Rb salt: Pd, 21·4; Cl, 43·6. Calc. for Rb_2PdCl_6: Pd, 21·8; Cl, 43·4. Found, for the Cs salt: Pd, 18·1; Cl, 36·2. Calc. for Cs_2PdCl_6: Pd, 18·3; Cl, 36·3. Found, for the NH_4 salt: Pd, 29·6; Cl, 59·7. Calc. for $(NH_4)_2PdCl_6$: Pd, 30·0; Cl, 59·8%].

Bromopalladates were made by dissolving palladous oxide in hydrobromic acid and warming the solution with the alkali metal bromide and bromine; crystals separated when the solutions were cooled to 0°. Analyses were made by methods similar to those used for the chloropalladates [Found, for the K salt: Pd, 15·9; Br, 72·5. Calc. for K_2PdBr_6: Pd, 16·1; Br, 72·2. Found, for the Rb salt: Pd, 14·0; Br, 63·6. Calc. for Rb_2PdBr_6: Pd, 14·1; Br, 63·3. Found, for the Cs salt: Pd, 12·3; Br, 56·2. Calc. for Cs_2PdBr_6: Pd, 12·5; Br, 56·3. Found, for the NH_4 salt: Pd, 17·5; Br, 77·0. Calc. for $(NH_4)_2PdBr_6$: Pd, 17·2; Br, 77·0%].

Bromoplatinates were obtained from sodium bromoplatinate (Part I, *J.*, 1950, 3444) and alkali metal bromides. They were recrystallised from water, and platinum was determined by thermal decomposition [Found, for the K salt: Pt, 25·9. Calc. for K_2PtBr_6: Pt, 25·9. Found, for the Rb salt: Pt, 22·8. Calc. for Rb_2PtBr_6: Pt, 23·0. Found, for the Cs salt: Pt, 20·7. Calc. for Cs_2PtBr_6: Pt, 20·7. Found, for the NH_4 salt: Pt, 27·6. Calc. for $(NH_4)_2PtBr_6$: Pt, 27·4%].

X-Ray powder photographs were taken with Cu-K_α radiation, a 19-cm. camera being used; samples were filled into Pyrex capillaries, which were sealed with warm picein wax. Lattice constants were evaluated by the method of Henry, Lipson, and Wooster ("The Interpretation of *X*-Ray Diffraction Photographs," Macmillan, 1951, p. 191).

Grateful acknowledgment is made to Messrs. Johnson, Matthey, and Company, Limited, for the loan of compounds of palladium and platinum.

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857. *The Mesomorphic Transition Points of the* p-n-*Alkoxybenzoic Acids. A Correction.*

By G. W. GRAY and BRYNMOR JONES.

IN an attempt to correlate mesomorphism and structure more precisely, several homologous series of mesomorphic compounds have recently been examined. Comparison of these results with those published for the *p*-*n*-alkoxybenzoic acids has revealed some discrepancies between the melting and transition points reported for the latter. Bennett and Brynmor Jones (*J.*, 1939, 420) prepared the methyl to decyl, dodecyl, and hexadecyl ethers, and Weygand and Gabler (*Z. physikal. Chem.*, 1940, **46**, *B*, 270) the propyl to decyl ethers. Substantial differences were evident for the transition points of the heptyl, octyl, nonyl, and decyl ethers, and a re-examination of thirteen *p*-*n*-alkoxybenzoic acids has been made. The new constants agree with those reported by Weygand and Gabler. No variation is found for the dodecyl ether, or the well-known methyl and ethyl ethers. Bennett and Jones (*loc. cit.*) state that the hexadecyl ether melts at 100° to a smectic state, which changes to a nematic melt at 131°, and at 133° becomes isotropic. The nematic–smectic transition is described as very difficult to detect. The reported m. p. of 100° has now been found to be too high by some 15°, and the ether shows no nematic phase. When the isotropic liquid is cooled, characteristic smectic bâtonnets appear, and these coalesce to a focal-conic structure. The octadecyl ether, which has been prepared for the first time, is also purely smectic. The revised constants for the *p*-*n*-alkoxybenzoic acids are tabulated below.

	Temp. of transition to			Phase length of	
Alkyl group	smectic	nematic	isotropic	smectic	nematic
Methyl	—	—	184°	—	—
Ethyl	—	—	196	—	—
Propyl	—	145°	154	—	9°
Butyl	—	147	160	—	13
Pentyl	—	124	151	—	27
Hexyl	—	105	153	—	48
Heptyl	92°	98	146	6°	48
Octyl	101	108	147	7	39
Nonyl	94	117	143	23	26
Decyl	97	122	142	25	20
Dodecyl	95	129	137	34	8
Hexadecyl	85	—	132·5	47·5	—
Octadecyl	102	—	131	29	—

When these values are plotted against the number of carbon atoms in the alkyl chain the transition points relating to the change mesomorphic to isotropic fall on two curves, one relating to the ethers with an odd number of carbon atoms in the alkoxy-group, the other to those with an even number. The five smectic–nematic transition points all lie on one smooth curve.

It is likely that the errors in the constants as quoted by Bennett and Jones (*loc. cit.*) arose from the method used in the determinations. This involved a repeated heating and cooling of the material, which was mounted by melting it between a glass slide and a cover slip. Repeated heating of a single specimen has now been shown to cause substantial decomposition of these acids, and so makes the transitions difficult to observe. Moreover, the temperature of each transition was measured by a thermometer mounted close to the slide, which was contained in a glass tube to serve as an air-jacket. A careful check on this procedure has shown that the values are liable to substantial error. However, no variations have been noted in the values which they quote for the polymorphic transitions, but these changes may be less affected by partial decomposition.

Experimental.—All m. p.s are corrected for exposed stem.

Preparation of p-n-*alkoxybenzoic acids.* These acids, prepared by alkylation of *p*-hydroxybenzoic acid (Brynmor Jones, *J.*, 1935, 1874), were crystallised twice from each of the solvents, glacial acetic acid, ethyl alcohol, and benzene.

Observation of transition temperatures. Preliminary measurements of the solid–mesomorphic, smectic–nematic, and mesomorphic–isotropic transitions were made in a wide melting-point capillary heated in a well-stirred paraffin-bath. A specimen was then melted on a microscope slide and a cover slip pressed down on the liquid to obtain a thin section of the material. This was inserted in a specially constructed heating instrument (details of which will be published elsewhere) mounted on the stage of the microscope. In this electrically heated block, the sample could be observed continuously under carefully controlled temperature conditions. Any change (solid–solid, solid–mesomorph, etc.) was easily seen : the temperature was recorded on a standardised thermometer.

With the exception of the hexadecyloxy- and octadecyloxy-benzoic acids, the appearances of the solid and mesomorphic states of this series of acids were found to be as described by Bennett and Jones (*loc. cit.*).

p-*Hexadecyloxybenzoic acid* (solid–85°–smectic–132·5°–isotropic). This *acid* (Found : C, 76·4; H, 10·5. $C_{23}H_{38}O_3$ requires C, 76·25; H, 10·5%) exhibits no polymorphism, and melts to a characteristic smectic state consisting of well-defined focal–conics of high double refraction. No further change occurs on heating it until the isotropic liquid is reached. When the sample is cooled, the smectic phase reappears.

p-*Octadecyloxybenzoic acid* (solid–102°–smectic–131°–isotropic). This *acid* (Found : 76·95; H, 10·8. $C_{25}H_{42}O_3$ requires C, 76·9; H, 10·8%) is qualitatively identical in behaviour with the hexadecyloxy-acid.

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858. N-*Alkylation of Nitriles in Presence of Silver Sulphate.*

By J. CAST and T. S. STEVENS.

CANNON, GREBBER, and HSU (*J. Org. Chem.*, 1953, **18**, 516) report that nitriles react with alkyl halides and aluminium chloride, thus :

$$\mathrm{RCl + AlCl_3 \longrightarrow R^+\,AlCl_4^-}$$

$$\mathrm{R^+ + R'{\cdot}CN \longrightarrow R'{\cdot}C{\vdots}\overset{+}{N}R \longleftrightarrow R'{\cdot}\overset{+}{C}{:}NR \xrightarrow{H_2O} R'{\cdot}CO{\cdot}NHR}$$

We have encountered a similar reaction between nitriles and diphenylmethyl bromide in presence of silver sulphate :

$$\mathrm{CHPh_2Br + Ag^+ \longrightarrow CHPh_2^+ + AgBr}$$

$$\mathrm{CHPh_2^+ + Me{\cdot}CN \longrightarrow Me{\cdot}C{\vdots}\overset{+}{N}{\cdot}CHPh_2 \longleftrightarrow Me{\cdot}\overset{+}{C}{:}N{\cdot}CHPh_2 \xrightarrow{H_2O} Me{\cdot}CO{\cdot}NH{\cdot}CHPh_2}$$

Experimental.—Silver sulphate was freshly precipitated, washed with water, acetone, and ether, and thoroughly dried. Acetonitrile was repeatedly distilled over phosphoric oxide.

Diphenylmethyl bromide (1 g.) was dissolved in benzene (10 c.c.) and acetonitrile (1·3 c.c.); addition of silver sulphate (2 g.) caused immediate reaction, with production of silver bromide, which was completed by warming until the supernatant liquid remained clear. The filtered liquid was washed with water, the benzene evaporated, and the residue extracted with ligroin (b. p. 90—120°). The extract yielded on concentration *N*-diphenylmethylacetamide (0·34 g.), identical (mixed m. p.) with a specimen prepared from diphenylmethylamine (Found : C, 79·7; H, 6·8; N, 5·8. Calc. for $C_{15}H_{15}ON$: C, 80·0; H, 6·6; N, 6·2%). By crystallisation from methanol, the material insoluble in ligroin afforded bisdiphenylmethyl ether (0·04 g.), m. p. 106—107°.

When in a parallel experiment acetonitrile was replaced by propionitrile (1·8 c.c.), *N*-diphenylmethylpropionamide (Davies, Ramsay, and Stove, *J.*, 1949, 2633) was obtained (0·43 g.)

and identified as before (Found: C, 80·0; H, 7·1; N, 6·0. Calc. for $C_{16}H_{17}ON$: C, 80·3; H, 7·1; H, 5·9%). Bisdiphenylmethyl ether (0·06 g.) was also isolated.

Acetamide is alkylated in the same way—replacement of the nitrile by 1·0, 0·2, and 0·1 g. of amide led respectively to yields of 0·48, 0·27, and 0·14 g. of diphenylmethylacetamide—but the original result cannot be attributed to the alkylation of amide present in the carefully purified nitrile.

We thank the Department of Scientific and Industrial Research for a maintenance grant (to J. C.).

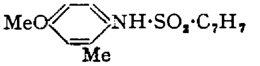
THE UNIVERSITY, SHEFFIELD, 10. [*Received, August 14th,* 1953.]

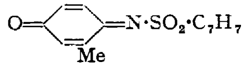
859. *2-Methyl-*p*-benzoquinone 1-Toluene-*p*-sulphonimide.*

By F. BELL.

THE production of the 3-nitro-derivative from 2-acetamido-5-methoxytoluene is an uncertain process and the main product is always the 4-nitro-derivative (MacMillan, *J.*, 1952, 4019). Since the toluene-*p*-sulphonamido-group is more powerfully directive than the acetamido-group it appeared that 5-methoxy-2-toluene-*p*-sulphonamidotoluene (I) might readily furnish the desired 3-nitro-derivative. This proved not to be so, as the compound passed very easily with nitric acid under a variety of conditions into the quinone imide (II), the constitution of which was proved by its severance to *p*-toluquinone and toluene-*p*-sulphonamide. Analogous compounds have been obtained by Adams and Looker (*J. Amer. Chem. Soc.*, 1951, **73**, 1145) by the oxidation of the arylsulphonyl derivatives of *p*-aminophenols with lead tetra-acetate, and Saunders and Watson (*Biochem. J.*, 1950, 629) have described the enzymic oxidation of 4-methoxy-2 : 6-dimethylaniline to 2 : 6-dimethyl-*p*-benzoquinone.

(I)





(II)

Rather surprisingly, treatment of 4-toluene-*p*-sulphonamidophenetole with dilute nitric acid led to the 3-nitro-derivative without production of any quinone. Uyeyangi, similarly, has described the conversion of *p*-toluene-*p*′-sulphonamidoanisole into the 3-nitro-derivative (*Ann. Rept. Takeda Res. Lab.*, 1949, **8**, 22).

Experimental.—*5-Methoxy-2-toluene-*p*-sulphonamidotoluene,* from 2-amino-5-methoxytoluene, crystallised from ethanol in large prisms, m. p. 95° (Found: C, 61·4; H, 5·5. $C_{15}H_{17}O_3NS$ requires C, 61·8; H, 5·8%). When this (10 g.) was warmed with nitric acid (10 c.c.; *d* 1·4) and water (100 c.c.) on a steam-bath the resultant oil rapidly solidified (about ½ hr.). The product (6·2 g.) was crystallised from benzene and gave *2-methyl-*p*-benzoquinone 1-toluene-*p*-sulphonimide* (II) as orange-red prisms, m. p. 149° (Found: C, 60·4; H, 4·4. $C_{14}H_{13}O_3NS$ requires C, 61·1; H, 4·7%). The quinone crystallised in large prisms from acetic acid but the m. p. then became much less sharp. Crystallisation of the crude, moist product from acetic acid led to complete decomposition into *p*-toluquinone, m. p. 69°, and toluene-*p*-sulphonamide, m. p. and mixed m. p. 137° (acetyl derivative, m. p. 139°). Dissolution of the quinone in acetic anhydride containing one drop of sulphuric acid led to a compound, insoluble in sodium hydroxide, which crystallised from ethanol in colourless needles, m. p. 178—180° (Found: C, 57·5; H, 5·0; S, 7·1. $C_{20}H_{21}O_7NS$ requires C, 57·3; H, 5·0; S, 7·6%). It appears to be 4 : *5-diacetoxy-*N*-acetyl-2-methyl-*N*-toluene-*p*-sulphonylaniline.*

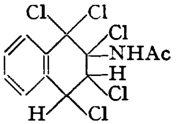
p-Toluene-*p*′-sulphonamidophenetole with dilute nitric acid, as above, gave an oil which hardened to a plastic mass on cooling. This on crystallisation from ethanol gave yellow needles, m. p. 93°, of 3-nitro-4-toluene-*p*-sulphonamidophenetole (Reverdin and Roethlistberger, *Helv. Chim. Acta*, 1922, **5**, 301, give 95°), readily hydrolysed by dissolution in cold sulphuric acid to 4-amino-3-nitrophenetole, red prisms, m. p. 113°

HERIOT-WATT COLLEGE, EDINBURGH. [*Received, August 14th,* 1953.]

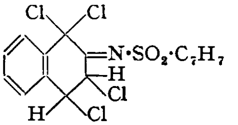
860. *The Chlorination of Arylamine Derivatives by Sulphuryl Chloride.*

By F. Bell.

Several papers have dealt with the interaction of aromatic compounds with sulphuryl chloride in the presence of various catalysts (see, *e.g.*, Wynne, *J.*, 1892, **61**, 1042; Silberrad, *J.*, 1921, **119**, 2029; 1925, **127**, 1724; Kharasch, *J. Amer. Chem. Soc.*, 1939, **61**, 2142, 3432) but the very variety of compounds obtained has militated against the use of this reagent as a nuclear chlorinating agent. It is now found that by addition of sulphuryl chloride to certain compounds, with subsequent removal of the excess of reagent and crystallisation of the residue, a number of derivatives, otherwise difficult of access, can be obtained in high yield.



(I)



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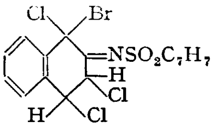


(III)

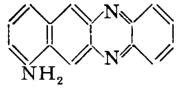
By this method the undermentioned results were obtained: (*a*) 1-Chloro-2-acetonaphthalide gave (I), converted by thermal decomposition into 1 : 3 : 4-trichloro-2-acetonaphthalide, m. p. and mixed m. p. 220°. (*b*) 2-Toluene-*p*-sulphonamidonaphthalene and its 1-chloro-derivative gave (II), m. p. and mixed m. p. 164°. (*c*) 1-Bromo-2-toluene-*p*-sulphonamidonaphthalene gave (III), m. p. and mixed m. p. 179°. (*d*) 1-Toluene-*p*-sulphonamidonaphthalene gave the 2 : 4-dichloro-derivative, m. p. and mixed m. p. 193°. (*e*) Phenacetin gave 4-acetamido-2 : 5-dichlorophenetole, m. p. 164° [base, m. p. 65°, which yielded the *toluene*-p-*sulphonyl* derivative, prisms, m. p. 150°, from acetic acid or chloroform (Found: C, 50·9; H, 3·7. $C_{15}H_{15}O_3NCl_2S$ requires C, 50·0; H, 4·2%)]. (*f*) 4-Toluene-*p*-sulphonamidophenetole gave an equal weight of material, m. p. 142—145°, which only after repeated crystallisation gave the 2 : 5 dichloro-derivative, m. p. 150° (above), and a small amount of a compound, m. p. 161°, not further examined. (*g*) *p*-Toluene-*p*′-sulphonamidotoluene gave mainly a tetrachloro-derivative, alternatively obtained in 20% yield by use of chlorine in acetic acid, and a small amount of the more soluble 3-chloro-derivative, which formed rhombs, m. p. 103—105°, from ethanol (Found: C, 56·0; H, 4·3 Calc. for $C_{14}H_{14}O_2NClS$: C, 56·8; H, 4·7%) (Schuloff, Pollak, and Riess, *Ber.*, 1929, **62**, 1849, give m. p. 103°). The *tetrachloro*-derivative crystallised from acetic acid in prisms, m. p. 183—185° (Found: C, 42·3; H, 3·3; Cl, 35·4. $C_{14}H_{11}O_2NCl_4S$ requires C, 42·1; H, 2·8; Cl, 35·6%). (*h*) 2-Methoxy-1-acetonaphthalide underwent vigorous and prolonged action with sulphuryl chloride, and the residue after removal of excess of reagent was a pale green resinous mass. On addition of warm ethanol the product immediately became yellow and soon gave a deep-red solution which on cooling deposited red crystals, m. p. 170—180°. Recrystallised from acetic acid these gave 3 : 4-dichloro-1 : 2-naphthaquinone as deep-red plates, m. p. 182°, which sublimed without decomposition (Zincke, *Ber.*, 1886, **19**, 2499, gives m. p. 184°). (*i*) 2′ : 4′-Dichlorotoluene-*p*-sulphonanilide was unchanged. (*j*) 2-Methoxy-1-toluene-*p*-sulphononaphthalide and 1-bromo-2-acetonaphthalide gave uncrystallisable products.

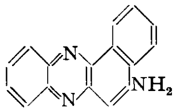
Heriot-Watt College, Edinburgh. [*Received, August* 14*th*, 1953.]

861. *The Reaction of* o-*Nitroaniline with* 1-*Naphthylamine.*

By J. W. Cook and Leon Hunter.

By heating a mixture of *o*-nitroaniline and 1-naphthylamine with zinc chloride at 150°, Wohl and Lange (*Ber.*, 1910, **43**, 2186) obtained an aminobenzophenazine, m. p. 294°. They advanced no evidence of its structure, nor did they assign one, but in reporting this work Allen and Webster ("Six-membered Heterocyclic Nitrogen Compounds with Four Condensed Rings," Interscience Publishers, Inc., New York, 1951, p. 39) ascribed to the compound the formula (I). This seemed improbable as it implies 2 : 3-addition to a naphthalene nucleus and reaction in the unsubstituted ring of 1-naphthylamine, both of which are unlikely. Of various possible structures, that of 3-amino-1 : 2-benzophenazine (II) seemed to us the most probable, and we have confirmed this structure for the compound.

(I) 

 (II)

The ring system present was established by deamination to 1 : 2-benzophenazine, m. p. 140° (Kehrmann and Mermod, *Helv. Chim. Acta*, 1927, **10**, 62, give m. p. 142°); the alternative 2 : 3-benzophenazine has m. p. 233° (Hinsberg, *Annalen*, 1901, **319**, 261). Fischer and Hepp (*Ber.*, 1890, **23**, 845), who prepared 3-amino-1 : 2-benzophenazine (II) from 4-phenylazo-1-naphthylamine and *o*-phenylenediamine, gave its m. p. as 264°, but this was corrected by Kehrmann (*Ber.*, 1894, **27**, 3342) to 294°. A sample of (II), prepared by Fischer and Hepp's method, was found to be identical with the aminobenzophenazine prepared as described by Wohl and Lange (*loc. cit.*).

Experimental.—1 : 2-*Benzophenazine.* The aminobenzophenazine prepared from *o*-nitroaniline (2·8 g.), 1-naphthylamine (2·8 g.), and zinc chloride (8·2 g.) (Wohl and Lange, *loc. cit.*) was purified by vacuum-sublimation and crystallisation from xylene and then ethanol. It formed golden-yellow needles, m. p. 289—291° (uncorr.) (Found: C, 78·3; H, 4·7; N, 16·95. Calc. for $C_{16}H_{11}N_3$: C, 78·3; H, 4·5; N, 17·1%). Light absorption in ethanol: $\lambda_{max.}$ 4650, 3090, 2750, 2520, 2380 Å; log ε = 4·05, 4·49, 4·37, 4·4, 4·43.

The sparingly soluble hydrochloride of this amine, suspended in hydrochloric acid, reacted only partly when treated with sodium nitrite at −5°; the amine (0·1 g.) was therefore diazotised with nitrosylsulphuric acid in pyridine and the diazonium compound reduced with cold hypophosphorous acid, as described by Cook and Moffatt (*J.*, 1951, 2489) for an analogous case. A benzene solution of the crude reaction product was purified by chromatography on alumina and yielded 1 : 2-benzophenazine, m. p. 140—143°.

Authentic 3-*amino*-1 : 2-*benzophenazine.* This was prepared by Fischer and Hepp's method (*loc. cit.*) and purified by vacuum-sublimation and then crystallisation from ethanol. It had m. p. 289—291° (uncorr.), alone or mixed with the compound prepared according to Wohl and Lange. Light absorption in ethanol: $\lambda_{max.}$ 4660, 3090, 2730, 2520, 2370 Å; log ε = 4·04, 4·5, 4·4, 4·45, 4·48.

University of Glasgow.

[*Received, August* 18*th*, 1953.]

862. *The Adsorption Method of Measuring Surface Areas.*

By R. M. Barrer, N. Mackenzie, and D. MacLeod.

Recently (*J.*, 1952, 1736) we derived various B.E.T.-type equations to be used as extrapolation formulæ for measuring monolayer values, v_m, and surface areas. Several corrections necessary in the equations of Table 1 (p. 1737) are given below. These corrections do not alter the v_m values derived, but change the affinity constants, C, in small whole-number ratios.

Isotherm B : replace $2C$ in numerator and denominator by C.
Isotherm C : replace iC in numerator and denominator by C.
Isotherm D : replace the first 1 in the denominator by 2.
Isotherm F : replace the first 1 in the denominator by i.
Isotherm G : replace iC in numerator and denominator by C.

The corresponding linear plots are then easily written. Also, equation 3 should read

$$\frac{v}{v_m} = y\,\mathrm{d}\ln\left(1 + Cyg + \frac{Cy^2g}{m_1} + \ldots . + \frac{Cy^ig}{m_1m_2 \ldots . m_{i-1}} + \ldots .\right)$$

where $C = a_1/b_1$, not b_1/a_1 as accidentally given in our paper.

Aberdeen University, Old Aberdeen.
[*Received, August* 21*st*, 1953.

863. *The Preparation and Deamination of* 4 : 4′-*Diamino*-3 : 3′-*dinitrodiphenyl.*

By C. C. Barker and F. D. Casson.

Despite the earlier interest of 4 : 4′-diamino-3 : 3′-dinitrodiphenyl in connection with the stereochemistry of diphenyl (cf. Cain, Coulthard, and Micklethwait, *J.*, 1912, **101**, 2298), no satisfactory preparation has been described. 4 : 4′-Diacetamidodiphenyl has been converted into 4 : 4′-diacetamido-3 : 3′-dinitrodiphenyl by fuming nitric acid at 0° (Strakosch, *Ber.*, 1872, **5**, 236; Brunning and Witt, *Ber.*, 1887, **20**, 1024; Cain *et al.*, *loc. cit.*); we find that this procedure gives a product of variable m. p. and that 4 : 4′-diacetamido-3 : 3′-dinitrodiphenyl is unstable in fuming nitric acid at 0°. Nitration in sulphuric acid gives unidentified, low-melting products. On the other hand, nitration in acetic anhydride–nitric acid at −12° gives 4 : 4′-diacetamido-3 : 3′-dinitrodiphenyl in 97·5% yield.

Deamination of the tetrazonium salt, prepared from 4 : 4′-diamino-3 : 3′-dinitrodiphenyl and nitrosylsulphuric acid (cf. Hodgson and Walker, *J.*, 1933, 1620), requires much ethanol, but the alternative use of hypophosphorous acid is unsatisfactory.

Difficulties in the reduction of 3 : 3′-dinitrodiphenyl, which were encountered by Dennett and Turner (*J.*, 1926; 481), are overcome by the use of iron pin dust and hydrochloric acid in 85% ethanol, the overall yield of 3 : 3′-diaminodiphenyl from 4 : 4′-diacetamidodiphenyl amounting to 75%.

Experimental.—4 : 4′-*Diacetamido*-3 : 3′-*dinitrodiphenyl.* 4 : 4′-Diacetamidodiphenyl (m. p. 323—324°; 50·0 g.) was added during 6 min. to a mechanically-stirred mixture of nitric acid (95%; 500 c.c.) and acetic anhydride (120 c.c.), maintained at −12°(±2°) by intermittent external cooling with solid carbon dioxide. After a further minute, the solution was poured on ice–water, giving 4 : 4′-diacetamido-3 : 3′-dinitrodiphenyl (65·0 g.), m. p. 318—321°, raised to 324—325° on recrystallisation from nitrobenzene (Cain *et al.*, *loc. cit.*, give m. p. 310°) (Found : N, 15·2. Calc. for $C_{16}H_{14}O_6N_4$: N, 15·6%).

4 : 4′-*Diamino*-3 : 3′-*dinitrodiphenyl.* 4 : 4′-Diacetamido-3 : 3′-dinitrodiphenyl (65·0 g.; m. p. 318—321°) was added to a mixture of concentrated sulphuric acid (260 c.c.) and water (65 c.c.), and heated at 100° for 30 min. The solution was then poured into water, and the precipitate washed with water, dilute ammonia solution, and water, and dried, giving 4 : 4′-diamino-3 : 3′-dinitrodiphenyl (45·2 g.), m. p. 275° (from aniline) (Cain *et al.*, *loc. cit.*, give m. p. 275°).

3 : 3′-*Dinitrodiphenyl.* Sodium nitrite (24·0 g.), added to concentrated sulphuric acid (239 c.c.) at 10°, was dissolved at 70°. Powdered 4 : 4′-diamino-3 : 3′-dinitrodiphenyl (44·0 g.) was added at 10°, the solution stirred for 1 hr., acetic acid (239 c.c.) added at 10°, and the mixture stirred for 15 min.; a drop added to ethanol then gave a buff precipitate devoid of red colour. This solution was added to ethanol (1600 c.c.) at 10°, and cuprous oxide (12·0 g.) added, the sudden frothing which occurred being controlled by vigorous agitation. When a sample gave no colour with alkaline chromotropic acid, water (1500 c.c.) was added, giving 3 : 3′-dinitrodiphenyl (41·5 g.) as a buff, crystalline precipitate, m. p. 196—198°. This product contained compounds of copper, and traces of impurities which could not be removed by crystallisation. Sublimation at 200°/10^{-3} mm. gave a 92% recovery of yellow crystals, m. p. 200°.

3 : 3′-*Diaminodiphenyl.* Ethanol (85%; 285 c.c.), concentrated hydrochloric acid (15 c.c.), iron pin dust (40 g.), and unpurified 3 : 3′-dinitrodiphenyl (24·0 g.) were stirred and refluxed for 24 hr. Sodium carbonate (8·5 g.) was then added and refluxing continued for 30 min.; the iron sludge was removed and washed with hot ethanol. The combined filtrates were evaporated to dryness and the residue distilled under reduced pressure giving 3 : 3′-diaminodiphenyl (14·5 g.), b. p. 205—215°/10^{-3} mm., m. p. 92—94° (Emde, *Chem. Zentr.*, 1915, II, 278, gives m. p. 93·5°).

UNIVERSITY COLLEGE, HULL.

[*Received, August* 25*th*, 1953.]

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864. *Cleavage of Steroid Epidioxides with Lithium Aluminium Hydride.*

By G. F. LAWS.

THE use of dehydroergosterol as a starting material in the partial synthesis of cortisone has led various workers (Bergmann and Stevens, *J. Org. Chem.*, 1948, **13**, 10; Bladon, Clayton, Greenhalgh, Henbest, Jones, Lovell, Silverstone, Wood, and Woods, *J.*, 1952, 4883) to consider the readily obtained 5α : 8α-epidioxide as a means of modifying the reactivity of the conjugated triene system. In a parallel investigation, the author was concerned with a convenient method of rupture of the epidioxide bridge.

Dehydroergosterol epidioxide, on prolonged heating with lithium aluminium hydride in ethereal solution, gave the known ergosta-7 : 9(11) : 22-triene-3β : 5α-diol (Windaus, Auhagen, Bergmann, and Butte, *Annalen*, 1930, **477**, 268), characterised as the acetate. Under the same conditions, ergosterol epidioxide gave ergosta-7 : 22-diene-3β : 5α-diol (Clayton, Henbest, and Jones, *J.*, 1953, 2015), together with some ergosterol. The constitution of the latter diol was confirmed by its oxidation with mercuric acetate to the above mentioned triene.

Experimental.—$[\alpha]_D$ are in $CHCl_3$, ultra-violet absorption spectra in EtOH.

Cleavage of dehydroergosterol acetate epidioxide. The epidioxide (2 g.), m. p. 169—170°, $[\alpha]_D$ +87° (*c*, 1·9) (Windaus and Linsert, *Annalen*, 1928, **465**, 148; Bladon *et al.*, *J.*, 1952, 4887), was dissolved in dry ether (100 ml.). An extract of powdered lithium aluminium hydride (1 g.) in dry ether (100 ml.) was added, and the solution kept under reflux overnight. Excess of reducing agent was then destroyed with ethyl acetate, and the solution worked up in the usual way. The product, after acetylation in pyridine–acetic anhydride at room temperature overnight, was chromatographed on alumina. Elution with 9 : 1 benzene–ether gave, as plates (from methanol), 3β-acetoxy-ergosta-7 : 9(11) : 22-trien-5α-ol (0·7 g.), m. p. 219—220° [undepressed on admixture with a sample obtained by the method of Windaus, Auhagen, Bergmann, and Butte (*loc. cit.*) of m. p. 219—220° $[\alpha]_D$ +48° (*c*, 1·3)], $[\alpha]_D$ +48° (*c*, 2·1), $\lambda_{max.}$ 244 mμ (ε 15,300).

Cleavage of ergosterol epidioxide. Egosterol epidioxide, m. p. 178—179°, $[\alpha]_D$ −36° (*c*, 1·6) (1·25 g.), was dissolved in dry ether (50 ml.). An extract of powdered lithium aluminium hydride (1 g.) in dry ether (50 ml.) was added, and the solution refluxed for 2 days. Working up, followed by acetylation and chromatography as before, gave two components : (i) eluted with 1 : 3 light petroleum (b. p. 40—60°)-benzene, plates (from methanol) (0·4 g.), m. p. 170—171°, undepressed on admixture with ergosteryl acetate, $[\alpha]_D$ −80° (*c*, 2·1), $\lambda_{max.}$ 271 and 281 mμ (ε 10,200); and (ii) eluted wih 9 : 1 benzene-ether, 5α-hydroxyergosta-7 : 22-dien-3β-yl acetate (0·75 g.) as needles (from methanol), m. p. 230—232°, $[\alpha]_D$ ±0° (*c*, 2·0) (Found : C, 78·45; H, 10·2. Calc. for $C_{30}H_{48}O_3$: C, 78·9; H, 10·6%). By alkaline hydrolysis ergosta-7 : 22-diene-3β : 5α-diol was obtained as needles (from methanol), m. p. 237—238°, $[\alpha]_D$ +0·5° (*c*, 2·1) (Found : C, 80·6; H, 10·8. Calc. for $C_{28}H_{46}O_2$: C, 81·1; H, 11·2%). Clayton, Henbest, and Jones (*loc. cit.*) give m. p. 228—233°, $[\alpha]_D$ +2°, for the monoacetate, and m. p. 227—234°, $[\alpha]_D$ +1°, for the diol.

Action of mercuric acetate on 5α-hydroxyergosta-7 : 22-dien-3β-yl acetate. The diene (200 mg.) was dissolved in chloroform (10 ml.), and a solution of mercuric acetate (700 mg.) in acetic acid (15 ml.) added at 20°. Mercurous acetate separated during 2 days at room temperature. The product formed plates (from methanol), m. p. 217—218°, $\lambda_{max.}$ 244 mμ (ε 16,000), undepressed on admixture with 5α-hydroxyergosta-7 : 9(11) : 22-trien-3β-yl acetate.

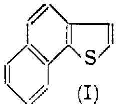
The author acknowledges with thanks financial assistance from the Nuffield Foundation. He is indebted to Professor D. H. R. Barton for guidance and encouragement.

BIRKBECK COLLEGE, LONDON, W.C.1. [*Received, September 4th*, 1953.]

865. 6 : 7-*Benzothionaphthen.*

By W. CARRUTHERS.

THE isolation of the hitherto unknown 6 : 7-benzothionaphthen (I) from a coal-tar fraction by Kruber and Raeithel (*Chem. Ber.*, 1953, **86**, 366) prompts us to record the preparation of this compound from 6 : 7-benzothioindoxyl (II). Reduction of (II) with zinc dust and acetic acid (cf. Bezdrik, Friedländer, and Koeniger, *Ber.*, 1908, **41**, 227) yielded a mixture consisting apparently of 6 : 7-benzothionaphthen (I) and a dihydro-derivative. Dehydrogenation of this mixture by sulphur (cf. Hansch, *J. Amer. Chem. Soc.*, 1947, **69**, 2908) afforded pure (I). Desulphurisation with Raney nickel yields 2-ethylnaphthalene, and the quinone (III) was obtained on oxidation with chromium trioxide.



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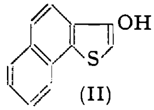

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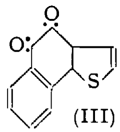

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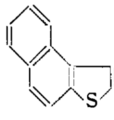

(IV)

4 : 5-Benzothionaphthen (IV) (Mayer, *Annalen*, 1931, **488**, 259; Kruber and Raeithel, *loc. cit.*) was prepared similarly from 4 : 5-benzothioindoxyl. In this case, however, dehydrogenation of the mixed product obtained on reduction was by chloranil in boiling xylene (Dost and Van Nes, *Rec. Trav. chim.*, 1951, **70**, 403), since sulphur caused decomposition.

Experimental.—6 : 7-*Benzothionaphthen.* Zinc dust (5 g.) was added to a solution of 6 : 7-benzothioindoxyl (2 g.) in acetic acid (50 c.c.) and the mixture boiled for 5 hr. Further small amounts of zinc were added from time to time. Excess of zinc was filtered off and washed with acetic acid, and the combined filtrates were diluted with water and extracted with benzene. The extract was washed with dilute sodium hydroxide and water, dried, and evaporated, and the residue distilled as a colourless oil at 130°/0·2 mm. (1·2 g.) (Found : C, 77·8; H, 4·9%). This material (550 mg.) was dehydrogenated by sulphur (110 mg.) at 260° for 2 hr. The dark reaction mass was extracted with benzene, and the product distilled at 120°/0·2 mm. (air-bath temp.) as a colourless oil which gradually solidified (350 mg.). After further purification through the picrate, 6 : 7-benzothionaphthen was obtained as colourless prisms (from methanol), m. p. 27—28° (lit., 25·2°) (Found : C, 78·2; H, 4·3. Calc. for $C_{12}H_8S$: C, 78·2; H, 4·4%). The picrate separated from ethanol in fine yellow needles, m. p. 143—144° (Found : N, 10·4. Calc. for $C_{18}H_{11}O_7N_3S$: N, 10·2%) (Kruber and Raeithel, *loc. cit.*, describe the picrate as brown-red needles, m. p. 145—146°).

Oxidation of 6 : 7-benzothionaphthen as described by Kruber and Raeithel (*loc. cit.*) yielded the 4 : 5-quinone, crystallising from ethanol in fine red needles, m. p. 218—219° (lit., 217—218°). The azine formed yellow needles (from ethanol), m. p. 222—223° (lit., 222—223°).

Desulphurisation to 2-ethylnaphthalene. A solution of 6 : 7-benzothionaphthen (0·15 g.) in ethanol (10 c.c.) was boiled with Raney nickel (1·5 g.) for ½ hr. After filtration and evaporation, 2-ethylnaphthalene was obtained as a colourless oil, b. p. 60°/0·2 mm. (air-bath temp.) (Found : C, 92·5; H, 7·5. Calc. for $C_{12}H_{12}$: C, 92·25; H, 7·75%). The picrate formed yellow needles (from ethanol), m. p. 74—75°, not depressed when mixed with an authentic specimen of 2-ethylnaphthalene picrate.

4 : 5-*Benzothionaphthen.* 4 : 5-Benzothioindoxyl (2 g.), when reduced as was its isomer (but for 6 hr.), gave a red gum (1·5 g.) which was distilled as a yellow oil at 150°/0·2 mm. (air-bath temp.). No pure product could be obtained by crystallisation of this material. It (350 mg.) was dehydrogenated with chloranil (500 mg.) in boiling xylene (6 c.c.) for 8 hr. The cooled mixture was diluted with a little benzene, insoluble material filtered off, and the extract washed with dilute sodium hydroxide and with water. Evaporation yielded a dark gum from which 4 : 5-benzothionaphthen (110 mg.) was obtained by chromatography on alumina from benzene solution. It crystallised from *cyclo*hexane as colourless plates, m. p. 112° (lit. : 108—109°, 112—113°) (Found : C, 78·3; H, 4·2%). The picrate formed orange-red needles (from ethanol), m. p. 146—147° (lit., 147—148°).

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866. 2 : 3- *and* 2 : 5-*Diaminoquinol Diethyl Ether.*

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The above ethers, required as intermediates for the preparation of new metal-complexing agents, have been prepared by catalytic hydrogenation of the nitration product of quinol diethyl ether. Attention is drawn to the ease of separation of the isomers based on the difference in solubility of the hydrochlorides in ethanol, and to the extreme ease with which the 2 : 5-isomer undergoes atmospheric oxidation compared with the stability of the 2 : 3-isomer. Only a monohydrochloride of the 2 : 3-diamine has been obtained (contrast Nietzki and Rechberg, *Ber.*, 1890, **23**, 160).

Experimental.—2 : 3- *and* 2 : 5-*Diaminoquinol diethyl ether.* A mixture (200 g.) of 2 : 3- and 2 : 5-dinitroquinol diethyl ether (Nietzki, *Annalen*, 1882, **215**, 149), ethanol (1 l.), and Raney nickel (50 g.) were shaken with hydrogen in a stainless steel autoclave at 100 atm. pressure. The temperature rose to 70° and the hydrogen consumption was approximately theoretical. The solution was decanted and the catalyst extracted (Soxhlet) with industrial alcohol. The combined solutions were concentrated by distillation (steam-bath), variable amounts of ammonia resulting from deamination during reduction being noticed at this stage. The amine residues were distilled, the bulk at 140—150°/0·5 mm., leaving a tarry residue, which, if not removed complicated the subsequent separation. Efficient separation could not be achieved by distillation but the following simple procedure was found to be effective. The amines were dissolved in the minimum of hot dry industrial alcohol, and a saturated solution (at −30°) of hydrogen chloride in the same solvent added, until a large excess of hydrochloric acid was present. The precipitate (233 g.) was filtered off. All procedures up to this stage were carried out under nitrogen. The mixture of hydrochlorides was refluxed with dry industrial alcohol (1 l.), and the hot solution filtered. The residue (65 g.) consisted almost entirely of the hydrochloride of the 2 : 5-isomer. The filtrate, on cooling, deposited the hydrochloride of the 2 : 3-isomer as clusters of small white needles (125 g.) which could be entirely freed from traces of the 2 : 5-isomer by two further recrystallisations from industrial alcohol. 2 : 3-*Diaminoquinol diethyl ether* had m. p. 78—79°, b. p. 174—176°/6 mm., and became discoloured only after several weeks' exposure to air (Found: C, 61·25; H, 8·0; N, 14·3. $C_{10}H_{16}O_2N_2$ requires C, 61·2; H, 8·2; N, 14·1%). The *monohydrochloride* had m. p. 225° (decomp.) (Found: C, 51·25; H, 7·1; N, 11·7; Cl, 15·4. $C_{10}H_{17}O_2N_2Cl$ requires C, 51·6; H, 7·3; N, 12·0; Cl, 15·3%). The hydrochloride of the 2 : 5-isomer was fairly pure as obtained but could be further purified by precipitation from aqueous solution with hydrogen chloride. 2 : 5-*Diaminoquinol diethyl ether* was extremely sensitive to atmospheric oxidation and neither melting point nor analysis could be obtained. The *dihydrochloride* (long white needles from hydrochloric acid) decomposed at about 280° (Found: C, 44·7; H, 6·7; N, 9·95; Cl, 25·3. $C_{10}H_{18}O_2N_2Cl_2$ requires C, 44·6; H, 6·7; N, 10·4; Cl, 26·4%). The following acetyl and benzoyl derivatives were prepared by suspending acetic anhydride and benzoyl chloride, respectively, in an aqueous solution of the amine hydrochloride and slowly adding dilute sodium hydroxide to the well-stirred mixture. In the case of the 2 : 5-isomer other preparative methods caused extensive decomposition. The acetyl derivative of the 2 : 3-isomer was unsuitable for characterisation.

2 : 3-*Dibenzamidoquinol diethyl ether*, m. p. 185·5—186° (from ethyl alcohol) (Found: C, 71·3; H, 6·1; N, 7·0. $C_{24}H_{24}O_4N_2$ requires C, 71·3; H, 5·9; N, 6·9%). 2 : 5-*Diacetamidoquinol diethyl ether*, m. p. 266° (from ethylene glycol) (Found: C, 60·1; H, 7·05; N, 9·6. $C_{14}H_{20}O_4N_2$ requires C, 60·0; H, 7·1; N, 10·0%). 2 : 5-*Dibenzamidoquinol diethyl ether*, m. p. 215—215·5° (from amyl alcohol) (Found: C, 71·6; H, 5·9; N, 6·65.

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