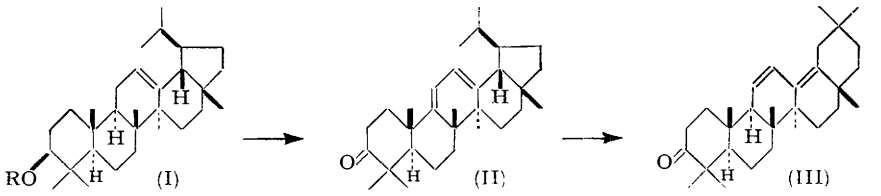
NOTES.

91. *Triterpenoids. Part XLVI.* The Conversion of Ursa-9(11) : 12-dien-3-one into Oleana-11 : 13(18)-dien-3-one.*

By J. I. SHAW, F. S. SPRING, and ROBERT STEVENSON.

THE conversion of three dienes derived from α-amyrin into a β-amyrin derivative, and other arguments, led Beaton, Spring, Stevenson, and Strachan [1] to propose the formula (I; R = H) for α-amyrin. The most readily available of the three compounds converted into an oleanane isomer, namely, ursa-9(11) : 12-dien-3β-yl acetate,[2] on treatment with hydrochloric–acetic acid mixture gave only 10% of pure oleana-11 : 13(18)-dien-3β-yl



acetate,[1] probably owing partly to the instability of the 3β-acetoxy-group under the strongly acid conditions where secondary reactions, such as contraction of ring A, intervene. This important argument is now supported by conversion of ursa-9(11) : 12-dien-3-one (II) into oleana-11 : 13(18)-dien-3-one (III) in 65% (crude) and 30% (pure) yield.

* Part XLV, *J.*, 1955, 3992.

[1] Beaton, Spring, Stevenson, and Strachan, *J.*, 1955, 2610.
[2] Ruzicka, Jeger, and Redel, *Helv. Chim. Acta*, 1943, **26**, 1235.

The preparation [3] of ursa-9(11) : 12-dien-3-one from ursa-9(11) : 12-dien-3β-ol has been improved by replacing chromic–acetic acid by the chromic acid–pyridine complex [4] as oxidising agent, oxidation of the conjugated diene system being thereby lessened; [5] a purer product is then obtained.

Experimental.—Rotations were measured in $CHCl_3$ and ultraviolet absorption spectra in EtOH solutions. Grade II alumina was used for chromatography.

Ursa-9(11) : 12-*dien*-3-*one* (II). Chromium trioxide (2·0 g.) in pyridine (20 c.c.) was added to a solution of ursa-9(11) : 12-dien-3β-ol (2·0 g.) in pyridine (20 c.c.), and the mixture kept at room temperature for 18 hr. with occasional shaking. A solution of the product, isolated in the usual manner, in benzene was filtered through alumina, the filtrate evaporated, and the residue crystallised from chloroform–methanol to give ursa-9(11) : 12-dien-3-one (1·3 g.) as needles, m. p. 164—166°, $[\alpha]_D$ +411°, +414° (*c*, 1·7, 1·0), $\lambda_{max.}$ 2820 Å (ε 10,200) (Found : C, 85·1; H, 11·15. Calc. for $C_{30}H_{46}O$: C, 85·2; H, 11·0%). It gives a red brown colour with tetranitromethane. Jacobs and Fleck [3] give m. p. 133—134°, $[\alpha]_D$ +412° (in pyridine), and Spring and Vickerstaff [3] give m. p. 135—137° for this compound. The oxime crystallised from chloroform–methanol as needles, m. p. 249—250° (decomp.), $\lambda_{max.}$ 2060 and 2820 Å (ε 4700 and 9400) (Found : C, 82·6; H, 10·9. Calc. for $C_{30}H_{47}ON$: C, 82·3; H, 10·8%). Jacobs and Fleck [3] give m. p. 233—235° and Spring and Vickerstaff [3] give m. p. 236°.

Oleana-11 : 13(18)-*dien*-3-*one* (III). Chromium trioxide (280 mg.) in acetic acid (5 c.c.) was added to oleana-11 : 13(18)-dien-3β-ol (1·0 g.) in acetic acid (600 c.c.) at 30°, and the mixture kept at room temperature for 50 hr. *Oleana*-11 : 13(18)-*dien*-3-*one* isolated in the usual way and chromatographed on alumina, crystallised from chloroform–methanol as needles, m. p. 236—240°, $[\alpha]_D$ −48·5° (*c*, 0·8), $\lambda_{max.}$ 2420, 2500, and 2600 Å (ε 28,200, 32,400, and 21,100) (Found : C, 85·2; H, 10·8. $C_{30}H_{46}O$ requires C, 85·2; H, 11·0%). It gives a red-brown colour with tetranitromethane. The *oxime* crystallised from chloroform–methanol as needles, m. p. 279—280° (decomp.), $\lambda_{max.}$ 2420, 2510, and 2600 Å (ε 29,200, 32,000, and 20,700) (Found : C, 82·1; H, 10·9. $C_{30}H_{47}ON$ requires C, 82·3; H, 10·8%).

Conversion of ursa-9(11) : 12-*dien*-3-*one* (II) *into oleana*-11 : 13(18)-*dien*-3-*one* (III). Ursa-9(11) : 12-dien-3-one (360 mg.) was heated with concentrated hydrochloric acid (5 c.c.) in acetic acid (30 c.c.) at 100° for 60 hr., with addition of hydrochloric acid (5 c.c.) after 24 and 48 hr. Concentration of the solution yielded needles (340 mg.), a solution of which in benzene was filtered through alumina (5 g.). The filtrate was evaporated and the solid (280 mg.) dissolved in light petroleum (b. p. 60—80°) and filtered through alumina (5 g.). The eluate (240 mg.) was crystallised twice from chloroform–methanol, to give oleana-11 : 13(18)-dien-3-one (110 mg.) as needles, m. p. and mixed m. p. 236—238°, $[\alpha]_D$ −48° (*c*, 1·0), $\lambda_{max.}$ 2430, 2510, and 2600 Å (ε 25,400, 28,500, and 18,400).

We thank the Department of Scientific and Industrial Research for a Maintenance Award (to J. I. S.).

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[3] Jacobs and Fleck, *J. Biol. Chem.*, 1930, **88**, 137; Spring and Vickerstaff, *J.*, 1937, 249.
[4] Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 222.
[5] Cf. Beaton, Shaw, Spring, Stevenson, and Strachan, *J.*, 1955, 2606.

92. *The Effect of Dissolved Oxygen on the Diamagnetic Susceptibility of Organic Liquids.*

By C. M. FRENCH and D. HARRISON.

EGGLESTON, EVANS, and RICHARDS [1] pointed out that many of the values recorded in the literature for the magnetic susceptibilities of organic liquids may be in error by as much as 1·7% because of the presence of dissolved oxygen. In view of the bearing of this on the interpretation of the considerable amount of earlier magnetochemical data, the present authors have investigated the matter further.

The existence and approximate magnitude of the effect can be demonstrated in the

[1] Eggleston, Evans, and Richards, *J.*, 1954, 941.

following way, without the use of specially designed susceptibility tubes. The susceptibility of a liquid which has been in contact with air for some time is first measured by the normal Gouy method. Air is then removed by bubbling pure dry hydrogen through the liquid for 2 hr. Then the liquid is driven directly, under hydrogen pressure, into the susceptibility tube used for the first measurement. The tube is tightly stoppered and the magnetic measurement repeated. The difference in forces observed in this way for benzene corresponds to a change in molar susceptibility of 0·40 unit, quite close to the value (0·46) obtained by Eggleston *et al.* by their degassing technique. It was found that the hydrogen-saturated liquid could be left in the susceptibility tube for several hours without appreciable change in susceptibility due to replacement of hydrogen by air. The method might therefore be capable of development into an accurate method for measuring air-free liquids without the use of specially designed tubes. By the same method, we have observed changes in molar susceptibility of 0·40 for acetone, 0·59 for ethyl methyl ketone, and 0·77 for diethyl ketoxime, showing that the effect is not restricted to hydrocarbons. In all cases, when the hydrogen-saturated liquid was shaken with air for 5 min., the susceptibility returned to its original value.

For various reasons we do not believe that the matter is as serious as suggested by Eggleston *et al.* In the first place, the values quoted above are derived from differences in absolute susceptibilities (X* − X) calculated by means of the equations :

$$F = \alpha(\mathrm{X}d - \kappa_{\mathrm{air}}); \quad F^* = \alpha(\mathrm{X}^*d - \kappa_{\mathrm{air}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where F and F^* are the forces in mg. on similar cylindrical specimens of air-saturated and air-free liquid, d the density of the liquid, κ_{air} the volume susceptibility of air, and α a constant determined by the cross-sectional area of the specimen and the magnetic field strengths at its upper and lower ends. (All susceptibility values are expressed in -10^{-6} c.g.s. units.) The necessity of determining α directly is usually avoided by measuring also the force (F_{b}mg.) on a similar specimen of benzene. Under normal conditions of working, this benzene will be practically air-saturated, if organic liquids do in fact absorb air as rapidly as indicated by the spectrophotometric measurements of Eggleston *et al.* The susceptibility χ (which is not in general the same as X, and may therefore be termed the relative susceptibility) is calculated by means of the equation :

$$\chi = (\chi_{\mathrm{b}} - \kappa_{\mathrm{air}}/d_{\mathrm{b}}) \, . \, Fd_{\mathrm{b}}/F_{\mathrm{b}}d + \kappa_{\mathrm{air}}/d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where χ_{b} is an assumed value for the susceptibility of air-saturated benzene. For a similar determination with only air-free liquids, the susceptibility χ^* is calculated from the equation :

$$\chi^* = (\chi_{\mathrm{b}}^* - \kappa_{\mathrm{air}}/d_{\mathrm{b}}) \, . \, F^*d_{\mathrm{b}}/F_{\mathrm{b}}^*d + \kappa_{\mathrm{air}}/d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If for χ_{b} and χ_{b}^* the corresponding absolute susceptibilities X_{b} and $\mathrm{X}_{\mathrm{b}}^*$ are used, the differences ($\chi^* - \chi$) and (X* − X) are identical. In practice, a value of 0·702 is usually taken for the specific susceptibility of benzene, irrespective of the air content, *i.e.*, $\chi_{\mathrm{b}} = \chi_{\mathrm{b}}^* = 0{\cdot}702$. Under these conditions, it can easily be shown that $\chi^* - \chi < \mathrm{X}^* - \mathrm{X}$; thus from equation (1), the difference in absolute susceptibilities of air-saturated and air-free liquids is given by the equation

$$F - F^* = \alpha(\mathrm{X}d - \mathrm{X}^*d) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\therefore \quad \mathrm{X} - \mathrm{X}^* = (F - F^*)/\alpha d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Subtracting equation (3) from (2) we have :

$$\chi - \chi^* = \frac{1}{d}\left[\frac{F}{F_{\mathrm{b}}}(\chi_{\mathrm{b}}d_{\mathrm{b}} - \kappa_{\mathrm{air}}) - \frac{F^*}{F_{\mathrm{b}}^*}(\chi_{\mathrm{b}}^*d_{\mathrm{b}} - \kappa_{\mathrm{air}})\right] \quad . \quad . \quad . \quad . \quad (6)$$

But from (1),

$$F_b = \alpha\,(\chi_b d_b - \kappa_{air});\quad F_b^* = \alpha(\chi_b^* d_b - \kappa_{air})$$

if the values taken for χ_b and χ_b^* are the absolute susceptibilities, X_b and X_b^*.

Then $$(\chi_b d_b - \kappa_{air})/F_b = (\chi_b^* d_b - \kappa_{air})/F_b^* = 1/\alpha$$

$\therefore$ from (6) $$\chi - \chi^* = F/\alpha d - F^*/\alpha d$$
$$= X - X^*$$

In practice, the same value (0·702) is taken for χ_b irrespective of air content, *i.e.*, $\chi_b = \chi_b^* = 0{\cdot}702$. Since presumably this is the absolute susceptibility X_b of air-saturated benzene,

$$(\chi_b d_b - \kappa_{air}) = (\chi_b^* d_b - \kappa_{air})$$
$$= F_b/\alpha$$

Under these conditions, equation (6) becomes

$$\chi - \chi^* = \frac{F_b}{\alpha d}\left[\frac{F}{F_b} - \frac{F^*}{F_b^*}\right]$$
$$= X - X^* + \frac{F_b F^*}{\alpha d}\left(\frac{1}{F_b} - \frac{1}{F_b^*}\right)$$

Now α, F_b, and F_b^* are negative, and since we are dealing here with diamagnetic liquids F^* is also negative, and F_b^* is numerically greater thab F_b; the last term will thus be positive. Since χ^* is greater than χ, this can be rewritten :

$$\chi^* - \chi = X^* - X - \frac{F_b F^*}{\alpha d}\left(\frac{1}{F_b} - \frac{1}{F_b^*}\right)$$

i.e., $$(\chi^* - \chi) < (X^* - X)$$

For instance, in the case of acetone, $\chi^* - \chi$ is 0·0025, compared with a value of 0·0069 for $X^* - X$. This indicates that, with the normal method of measurement and calculation, the effect is much less serious than at first appeared likely. A similar reduction was shown for the other liquids studied. Looked at in another way, the effect of dissolved air in the liquid being measured is compensated, to some extent, by the presence of air in the standard liquid (benzene) used. In this discussion it is assumed that all measurements are made at the same temperature, otherwise the position is complicated by variation both in the amount of dissolved oxygen and in its paramagnetic susceptibility. It is likely that much of the earlier work on the variation of the susceptibility of diamagnetic liquids with temperature is invalidated by the presence of significant amounts of dissolved oxygen.

Much of the discussion in magnetochemical work on organic compounds is concerned with susceptibility increments between pairs of liquids. It would seem reasonable to suppose that in many cases both liquids will contain a certain amount of dissolved air; hence the error in the increment will be considerably less than that in either of the individual susceptibility values.

In conclusion, two points, not specifically considered by Eggleston *et al.*, must be mentioned. Since the magnetic force on a particular liquid specimen depends both on its specific susceptibility (χ) and its density (d), it is conceivable that the observed changes in F might be due to alteration in d, χ remaining constant. It is not easy to test this by direct experiment, but, in the case of benzene, our observed value of $F - F^*$ corresponds to a density difference of 0·006 on the assumption that $\chi = \chi^*$. It appears unlikely that simple replacement of one dissolved gas by another, or even complete removal of dissolved

gas, should cause a change in density of this magnitude. Nevertheless, the possibility that change in density might have a small effect on the observed value of $F - F^*$ cannot be entirely ruled out. A further point is that if the oxygen actually reacts with the liquid to give a trace of diamagnetic product, the effect on χ should be negligible. This is probably the case with aliphatic aldehydes (but not with ketones, as the present results show), and may explain, at least in part, the fact that these compounds have consistently higher susceptibilities (numerically)[2] than the isomeric ketones.

QUEEN MARY COLLEGE, MILE END ROAD, LONDON, E.1. [*Received, May 4th*, 1955.]

[2] Angus, Llewelyn, and Stott, *Trans. Faraday Soc.*, 1955, **51**, 241.

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93. *Studies in Aromatic Nucleophilic Substitution. Part V.* The Influence of the Solvent.*

By C. W. L. BEVAN and G. C. BYE.

IN the reactions of amines with halogenonitrobenzenes (cf. Chapman and Parker [1]) it is almost certainly true that the greater reactivity of activated aromatic fluoro- than of corresponding chloro-compounds is partly due to a high degree of solvation of the incipient fluoride ion.[2] This would be predicted on Hughes and Ingold's theory of solvent action,[3] but this theory would also predict a very much smaller solvent effect in reactions between a neutral molecule and an ion, so that differences in rate comparable to those found by Chapman and Parker [1] between replacement of fluoride and chloride ion from corresponding activated positions in an aromatic nucleus by ions such as the methoxide ion [4] are not explicable on this basis alone. However, it was of interest to see whether increasing the ionising power of the solvent did cause a large divergence of reactivity ratios, k_F/k_{Cl}. In halogenonitrobenzenes, k_F/k_{Cl} is $\sim 10^3$ and it is not possible to choose completely analogous compounds which react with methoxide ion in methanol at comparable rates. Thus, although reaction with *p*-fluoronitrobenzene is conveniently measured, that with *p*-chloronitrobenzene takes place only at such high temperatures that attack by alkali on the glass vessels would invalidate the results obtained in aqueous alcohol. The compounds chosen for comparison were *o*-fluoronitrobenzene and 1-chloro-2 : 4-dinitrobenzene and the ionising power of the solvent was increased by the addition up to 20% of water to methanol.[5] It was shown that in no case was the production of phenol (owing to the equilibrium $OMe^- + H{\cdot}OH \rightleftharpoons Me{\cdot}OH + OH^-$) greater than $5 \pm 1\frac{1}{2}\%$. This is in accord with Caldin and Long's results.[6]

The results obtained, together with certain data from the literature, are assembled in Table 1. They show that increasing the ionising power of the solvent by the addition of water causes a slight increase in the bimolecular rate constants. The rate for the fluoro-compound increases by 36%, and that of the chloro-compound by 14% on the addition of 20% by weight of water. This increase is contrary to expectation [7] and the difference between fluoride- and chloride-ion displacement produced by increasing the ionising power of the solvent does not seem sufficient for solvation effects to account for the large absolute difference in rate of displacement. The apparent discrepancy in Riklis's results (Table 1) may be due to (*a*) attack by alkali on the glass and (*b*) the fact that *o*-chloronitrobenzene is reduced in absolute alcoholic solution, particularly above 70°.

* Parts I—IV, *J.*, 1951, 2340; 1953, 655; 1954, 3091; 1956, 254.

[1] Chapman and Parker, *J.*, 1951, 3301.
[2] Cf. Musgrave, *Quart. Rev.*, 1954, **8**, 354.
[3] Hughes and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 608.
[4] Bevan, *J.*, 1951, 2340; Miller, Beckwith, and Leahy, *J.*, 1952, 3550.
[5] Cf. Hughes, Ingold, Cooper, Dhar, MacNulty, and Woolf, *J.*, 1948, 2043.
[6] Caldin and Long, *Nature*, 1953, **171**, 583.
[7] Cf. Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.

TABLE 1. *Effect of addition of water on the methoxylation of halogenonitrobenzene in methanol (k_2 in l. sec.$^{-1}$ mole^{-1}).*

Substituents	MeOH (% by wt.)			Substituents	MeOH (% by wt.)		
o-Fluoronitro	100	90	80	1-Chloro-2 : 4-dinitro	100	90	80
$k_2 \times 10^4$ (28·18°)	1·78 [d]	2·02	2·35	$k_2 \times 10^3$ (14·95°) ...	9·40	10·2	10·7
E (kcal.)	19·93 [d]	—	19·52	E (kcal.)	17·43 [a]	—	17·30
$\log_{10} B$	10·71 [d]	—	10·53	$\log_{10} B$	11·26 [a]	—	11·16
o-Dinitro [b]	100	90	80	*o*-Chloronitro [c]	100	90	80
$k_2 \times 10^5$ (25°)	7·0	7·7	8·2	$k_2 \times 10^3$ (80°)	4·45	4·17	3·57

[a] Miller *et al.*, *J.*, 1952, 3552; [b] Lobry de Bruyn and Steger, *Rec. Trav. chim.*, 1899, **18**, 41; [c] Riklis, *J. Gen. Chem.* (*U.S.S.R.*), 1947, **17**, 1511; [d] Bevan and Bye, *J.*, 1954, 3091.

TABLE 2. *k_2 (l. sec.$^{-1}$ mole^{-1}) for reaction of halides with* OMe^- *in aqueous methanol.*

o-Fluoronitrobenzene

	80% MeOH			90% MeOH
Temp.	28·18°	40·00°	51·49°	28·18°
k_2	$2·35 \times 10^{-4}$	$8·06 \times 10^{-4}$	$2·44 \times 10^{-3}$	$2·02 \times 10^{-4}$

1-Chloro-2 : 4-dinitrobenzene

	80% MeOH			90% MeOH	100% MeOH
Temp.	4·98°	14·95°	25·00°	14·95°	14·95°
k_2	$3·66 \times 10^{-3}$	$1·072 \times 10^{-2}$	$2·99 \times 10^{-2}$	$1·02 \times 10^{-2}$	$9·40 \times 10^{-3}$

TABLE 3. *Determination of rate constants, k_2 (l. sec.$^{-1}$ mole^{-1}).*

Reaction of 1-chloro-2 : 4-dinitrobenzene with sodium methoxide in 80% methanol +20% water. Initially, [Halide] $\approx$ 0·019M, [NaOMe] $\approx$ 0·034M. Temp. 14·95°.

(*a*) Concns. in ml. of 0·01527N-NaOEt per 5·00 ml. of sample.

t (min.)	0	20·0	23·0	26·0	29·2	32·1	35·0	38·0	41·0	45·1	49·1	51·0	∞
[NaOMe] ...	11·27	9·20	8·98	8·80	8·59	8·42	8·26	8·16	7·98	7·81	7·60	7·59	5·02
[Halide]	6·25	4·18	3·96	3·78	3·57	3·40	3·24	3·14	2·96	2·79	2·58	2·57	0·00
$10^2 k_2$	—	1·09	1·09	1·07	1·08	1·08	1·08	1·05	1·07	1·06	1·09	1·05	—

Mean $k_2 = 1·07 \times 10^{-2}$.

(*b*) Concns. in ml. of 0·01491N-$AgNO_3$ per 5·00 ml. of sample.

t (min.)	0	13·0	18·2	20·0	22·0	25·1	28·1	31·0	35·0	39·3	44·1	∞
[NaOMe] ...	11·46	10·0	9·56	9·41	9·27	9·03	8·86	8·68	8·46	8·26	8·03	5·17
[Halide]	6·29	4·83	4·39	4·24	4·10	3·86	3·69	3·51	3·29	3·09	2·86	0·00
$10^2 k_2$	—	1·07	1·07	1·07	1·07	1·08	1·07	1·07	1·07	1·06	1·07	—

Mean $k_2 = 1·07 \times 10^{-2}$.

Experimental.—Materials. *o*-Fluoronitrobenzene was prepared as by Bevan and Bye.[8]

1-Chloro-2 : 4-dinitrobenzene. An "AnalaR" specimen was crystallised from absolute ethanol to constant m. p. 51·0°.

Kinetic methods were as in previous papers of this series except that for the experiment in Table 3 (*b*) chloride ion was determined potentiometrically. Details of runs are given in Tables 2 and 3. The results in the latter Table establish the exact equivalence of the rate of loss of alkalinity and the rate of production of chloride ions.

In those methoxylations carried out in 80% methanol the yield of the corresponding phenol, which appeared to imcrease with temperature, was determined colorimetrically at the highest temperature used in studying the kinetics of these reactions. Standard solutions of the pure phenol, 1%, 2%, 3%, etc., were made up in a solvent of the composition used in rate measurements and containing an amount of sodium methoxide corresponding to its infinity concentration. "Infinity" tubes from runs were compared with these and in no case was the yield of phenol greated than 5%.

One of us (G. C. B.) thanks the Council of University College, Exeter, for a Scholarship, during the tenure of which this work was carried out.

UNIVERSITY COLLEGE, EXETER.
UNIVERSITY COLLEGE, IBADAN, NIGERIA.

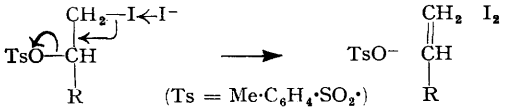
[*Received, June 27th*, 1955.]

[8] See ref. *d*, Table 1.

94. *The Action of Sodium Iodide on Methyl* 4 : 6-O-*Benzylidene*-3-*deoxy*-3-*iodo*-2-O-*toluene*-p-*sulphonyl*-α-D-*glucoside.*

By F. H. Newth.

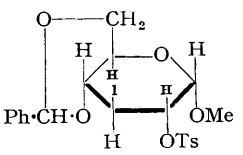
The reaction of di-toluene-*p*-sulphonates of terminal 1 : 2-glycols with sodium iodide in acetone leads to the formation of unsaturated products. Foster and Overend [1] suggest that the primary toluene-*p*-sulphonyloxy-group in ·CH(OTs)·CH_2·OTs first undergoes direct replacement by iodide and the resulting 1-deoxy-1-iodo-2-toluene-*p*-sulphonate is then attacked by iodide ion through the concerted mechanism :

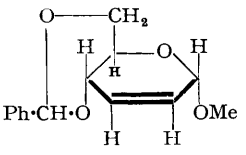


rather than to give a vicinal di-iodide which then undergoes elimination of iodine as postulated by Bladon and Owen.[2] Foster and Overend's evidence is that 3 : 6-anhydro-1-deoxy-1-iodo-4 : 5-*O*-*iso*propylidene-2-*O*-toluene-*p*-sulphonyl-D-mannitol, although stable when heated alone in acetone, undergoes elimination with sodium iodide more readily than does 3 : 6-anhydro-4 : 5-*O*-*iso*propylidene-1 : 2-di-*O*-toluene-*p*-sulphonyl-D-mannitol, and that the reaction is effected also by anions other than iodide.

While there are no steric requirements in these acyclic compounds, in a cyclic compound it is self-evident that the iodine atom must be *trans* to the vicinal toluene-*p*-sulphonyloxy-group for ionic elimination to occur. Such a compound is methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo-2-*O*-toluene-*p*-sulphonyl-α-D-glucoside (I).[3] This derivative has been treated with sodium iodide in acetone at 100° and after 10 min. sodium toluene-*p*-sulphonate, iodine, and methyl 4 : 6-*O*-benzylidene-2 : 3-didehydro-2 : 3-dideoxy-α-D-glucoside (II)[4, 5]

(I)





(II)

were formed quantitatively. The remarkable facility of this reaction provides support for Foster and Overend's formulation of elimination. Whether the yet unknown methyl 4 : 6-*O*-benzylidene-2 : 3-di-*O*-toluene-*p*-sulphonyl-α-D-mannoside could give an intermediate isomeric with (I) in the D-glucose or D-altrose series would depend upon the ability of iodide to replace either toluene-*p*-sulphonyloxy-group; it is significant that methyl 4 : 6-*O*-benzylidene-2 : 3-di-*O*-toluene-*p*-sulphonyl-α-D-glucoside is unaffected by sodium iodide in acetone.

The very easy elimination shown by (I) suggests that, in that compound, the iodide and the toluene-*p*-sulphonyloxy-group are to a substantial extent situated axially in the boat conformation of the pyranoside ring [6] (C1, 1C interconversion is not possible because of the *trans* ring junction at $C_{(4)}$:$C_{(5)}$), a condition which would be favoured by electrostatic repulsion and steric interaction between the two groups.

Experimental.—Methyl 4 : 6-O-*benzylidene*-3-*deoxy*-3-*iodo*-2-O-*toluene*-p-*sulphonyl*-α-D-*glucoside.* This derivative, m. p. 136°, was obtained from methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo-α-D-glucoside.[3]

Reaction of methyl 4 : 6-O-*benzylidene*-3-*deoxy*-3-*iodo*-2-O-*toluene*-p-*sulphonyl*-α-D-*glucoside with sodium iodide in acetone.* The derivative (100 mg.) was heated in acetone (5 ml.) containing

[1] Foster and Overend, *J.*, 1951, 3452.
[2] Bladon and Owen, *J.*, 1950, 598.
[3] Newth, Richards, and Wiggins, *J.*, 1950, 2356.
[4] Richards, *J.*, 1954, 4511.
[5] Bolliger and Prins, *Helv. Chim. Acta*, 1946, **29**, 1061.
[6] Newth, *J.*, 1956, 441.

sodium iodide (100 mg.) at 100°. Considerable reaction was apparent after 2 min. and heating was continued for 10 min. Sodium toluene-*p*-sulphonate weighed 34 mg. (96%), and iodine was equivalent to 3·55 ml. of 0·1N-thiosulphate (45 mg.; 98%). Acetone was evaporated and the aqueous portion was extracted with chloroform. This extract, when dried (Na_2SO_4) and evaporated, provided a crystalline residue (44 mg.) of methyl 4 : 6-*O*-benzylidene-2 : 3-didehydro-2 : 3-dideoxy-α-D-glucoside, m. p. 117—119°. After recrystallising from ethanol it had m. p. 119—120°, $[\alpha]_D^{20}$ +129° (*c* 0·66 in $CHCl_3$). Richards [4] gives m. p. 119·5—120°, $[\alpha]_D^{26}$ +129°.

Methyl 4 : 6-*O*-benzylidene-2 : 3-di-*O*-toluene-*p*-sulphonyl-α-D-glucoside did not react with sodium iodide in acetone at 100° during 24 hr.

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95. *The Conversion of Bulbocapnine into Morphothebaine.*

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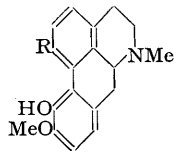
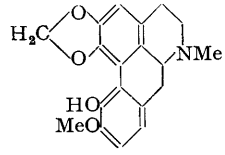
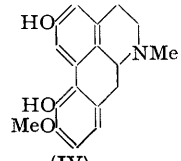
THE alkaloid *iso*thebaine is of interest since synthesis by any of the well-established routes leading to aporphines has not been possible and also because there is a difference of opinion as to whether its structure is really that given by the formula (I). Schlittler and Müller [1] degraded *O*-methyl*iso*thebaine to 3 : 4 : 5-trimethoxyphenanthrene which was synthesised by Pschorr and Koch's method.[2] However, Kiselev and Konovalova [3] obtained a trimethoxyphenanthrene picrate by the same degradative procedure but said that it depressed the melting point of 3 : 4 : 5-trimethoxyphenanthrene picrate prepared from morphenol.[4]



(I) : R = OMe
(II) : R = OH



(III)



(IV)

We have examined the fission with sodium and liquid ammonia of the methylenedioxy-group in bulbocapnine which we expected to afford morphothebaine (IV) and possibly the aporphine (II) which could then be converted into *iso*thebaine with diazomethane. However, the only phenolic product which could be isolated from the limited amount of bulbocapnine at our disposal was identical in all respects with morphothebaine prepared from thebaine.[5]

Experimental.—Bulbocapnine (400 mg.) was dissolved in ether (50 ml.) and liquid ammonia (500 ml.), and small pieces of sodium were added until the blue colour persisted for 1 hr. After the ammonia had been allowed to evaporate, the residue was taken up in water, and the alkaline solution extracted with chloroform which yielded unchanged bulbocapnine (130 mg.), m. p. 204° after one crystallization from ethanol. Excess of carbon dioxide was bubbled through the alkaline solution which was then extracted with chloroform to afford, after crystallization from ethanol, morphothebaine (165 mg.), m. p. and mixed m. p. 196—197° (Found : C, 72·4; H, 6·7; N, 4·8. Calc. for $C_{18}H_{19}O_3N$: C, 72·7; H, 6·5; N, 4·7%). The infrared spectrum was identical with a sample prepared from thebaine. Morphothebaine (30 mg.) was the only product which could be isolated from the crystallisation mother-liquors.

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[1] Schlittler and Müller, *Helv. Chim. Acta*, 1948, **31**, 1119.
[2] Pschorr and Koch, *Annalen*, 1912, **391**, 40.
[3] Kiselev and Konovala, *J. Gen. Chem.* (*U.S.S.R.*), 1949, **19**, 148.
[4] Vongerichten and Dittmer, *Ber.*, 1906, **39**, 1718.
[5] Howard, *Ber.*, 1884, **17**, 527.