ferential refractometry. The two components in the disaccharide region were separated by PC ($R_{ribitol}$ 0.13 and 0.86). NMR of the fast component (6 mg) showed, *inter alia*, a signal at δ 5.03, $J_{1,2}$ 1.5 Hz, assigned to the anomeric proton. The component showed $[\alpha]_{589}^{25}$ −28° (*c* 0.6, water) and $[\alpha]_{589}^{25}$ −80°, $[\alpha]_{578}^{25}$ −83°, $[\alpha]_{546}^{25}$ −102°, $[\alpha]_{436}^{25}$ −204°, and $[\alpha]_{365}^{25}$ −417° (*c* 0.2, 0.037 M sodium molybdate at pH 5.5). The oligosaccharide (2 mg) in dimethyl sulfoxide (1 ml) was treated with 2 M sodium methylsulfinyl anion in dimethyl sulfoxide (1 ml) for 4 h at room temperature and methyl iodide (1 ml) was added under external cooling with ice. The solution was diluted with chloroform (5 ml) and extracted with water (6 × 2 ml). The chloroform phase on GLC-MS gave a single peak with the MS expected [5] for fully methylated 1-*O*-β-D-ribofuranosylribitol, and showing, *inter alia*, the following ions: 45(63), 55(6), 59(23), 71(36), 74(5), 75(11), 83(5), 87(5), 88(6), 89(17), 99(7), 101(100), 102(7), 103(5), 111(6), 115(7), 133(2), 143(8), 145(3), 175(4), 177(1), 191(4) and 207(1).

The fully methylated disaccharide was hydrolysed with 0.25 M sulfuric acid (0.5 ml) at 100 °C for 16 h, reduced ($NaBH_4$), acetylated and analysed by GLC-MS. Two components, with MS corresponding to 1-*O*-acetyl-2,3,4,5-tetra-*O*-methylribitol and 1,4-di-*O*-acetyl-2,3,5-tri-*O*-methylribitol, were obtained.

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A Photolytic Study of Ethoxy(diphenylmethylene)sulfonium Ion and Hydroxy(diphenylmethylene)sulfonium Ion. Alkylation of Benzophenone, Thiobenzophenone and Thiobenzophenone-*S*-oxide

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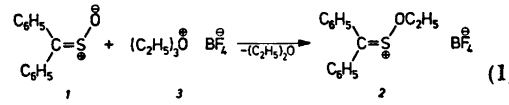
In connection with our investigations on the photolytic transformation of sulfines (thiocarbonyl-*S*-oxides) into the thermally unstable oxathiiranes,[1] we have studied the photolysis of thiobenzophenone-*S*-oxide (*1*) in concentrated sulfuric acid. In addition, with the aim of eventually obtaining more stable derivatives, we have examined the photochemistry of the hitherto unknown ethoxy(diphenylmethylene)sulfonium tetrafluoroborate (*2*).

Compound *2* is prepared by heating a mixture of *1* and triethyloxonium tetrafluoroborate in the solid state; it is analyzed as described in the experimental section. The yellow, crystalline, highly hygroscopic compound exhibits a UV absorption maximum at 369 nm ($\varepsilon = 1.77 \times 10^4$ M^{-1} cm^{-1}).



(1)

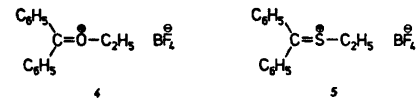
On hydrolysis of *2*, elemental sulfur is formed along with benzophenone in greater than 90 % yield. In analogy with the acid catalyzed hydrolysis of *1* reported by Strating *et al.*[2] the hydrolysis may be formulated as shown in eqn. 2.

(2)

Compound *2* may be dealkylated to the starting sulfine in 25 % yield with triphenylphosphine in methylene chloride.

When *1* was dissolved in concentrated sulfuric acid an orange solution was obtained. The absorption bands of *1* [3] were replaced by a band with maximum at 364 nm ($\varepsilon = 1.59 \times 10^4$ M^{-1} cm^{-1}), close to that of *2* indicating protonation of *1* at oxygen. Cautious addition of water (cooling) afforded *1* in quantitative yield.

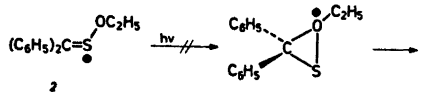
The ethyl salts of benzophenone (*4*) [4] and thiobenzophenone (*5*) were prepared and analyzed in the same way as *2*. In both cases yellow highly hygroscopic products were obtained exhibiting UV absorption maxima at 337 and 384 nm for *4* and *5*, respectively.



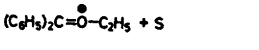
4 *5*

Photolytic reactions of hydroxy(diphenylmethylene)sulfonium ion and ethoxy(diphenylmethylene)sulfonium ion. A 10^{-4} M solution of *1* in concentrated sulfuric acid was irradiated ($\lambda = 360$ nm) at room temperature for 3 h. No significant change in concentration was observed during this time. This is in striking contrast to the rapid transformation of *1* in ethanol upon photolysis under similar conditions.[1] The reasons for this apparent inactivity are not known but one explanation may be a photolytic deprotonation (in analogy with the below mentioned dealkylation of *2*) followed by reprotonation.[5]

When a 10^{-4} M solution of *2* in methylene chloride was irradiated ($\lambda = 370$ nm) and the conversion followed by UV spectroscopy, an apparently complicated transformation took place. Benzophenone was observed as the end product in 75 % yield. Formation of compound *4* was not observed which rules out a mechanism involving an *O*-alkylated oxathiirane (eqn. 3) analogous to the photolytic rearrangement of sulfines [1] (eqn. 4). Compound *4* is stable under the prevailing conditions.



2 (3)



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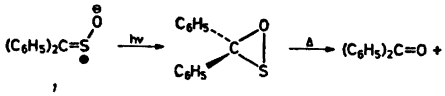
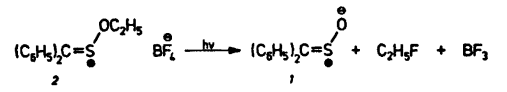


1 (4)

A sample of *2* in methylene chloride showed no decomposition when stored in the dark for several days.

On irradiation of *2* monitored with IR spectroscopy, formation of benzophenone was also observed. Weak absorptions at 1105 and 1005 cm^{-1} characteristic of *1* [3] might correspond to a steady state concentration of this compound. By monitoring the reaction by NMR, new signals were observed at δ 1.39 (t) and 4.15(q). These are well within the region reported for ethyl fluoride.[6] The formation of this compound was further demonstrated by use of GLC-MS. From the NMR data ethyl fluoride was estimated to be formed in almost quantitative yield. It is inferred from these experiments that the photochemical reaction of *2* as the primary step most probably is dealkylation with formation of ethyl fluoride and *1* (eqn. 5). The latter, which is photochemically active was observed in small concentrations only as it undergoes a facile transformation into benzophenone and sulfur [1] (eqn. 4).



2 *1* (5)

Experimental. IR spectra in methylene chloride were recorded on a Perkin-Elmer 337 Grating Infrared Spectrophotometer, UV spectra on a Pye Unicam SP-800, and ^{1}H NMR spectra on a Varian A-60A spectrometer. GLC-MS analysis was carried out on a Varian Aerograph model 2700 in combination with a Finnigan 1015 S/L mass spectrometer on a 2 m, 3 mm column with 3 % SE-30 (J. J.'s Chromatography Ltd.) on chromosorb W 80/100 mesh (Johns-Manville Products Corp.). Irradiations were performed with a Bausch and Lomb SP-200 mercury point source equipped with monochromator (typical bandwidth 20 nm).

Alkylation procedure. Approximately 2 mmol of the compound to be ethylated (*ca.* 5 % excess) was mixed with triethyloxonium tetrafluoroborate and heated in the solid state to melting of the mixture. After cooling, the tetrafluoroborates were obtained on digestion with dry ether. Yields around 50 % were obtained. Because of their highly hygroscopic nature elemental analysis could not be performed. However, equivalent weights were determined by titration with sodium hydroxide after hydrolysis according to eqn. 2. *O-Ethyl thiobenzophenone-S-oxide.* M.p. 80 – 85 °C (closed tube), equiv. weight 329 ± 3, calc. 330. NMR (CH_2Cl_2): δ 4.76 (CH_2, q), 1.59 (CH_3, t). The shift of the methylene protons are well within the range where $-OCH_2-$ signals are normally found.[7] *O-Ethyl benzophenone* M.p. (closed tube) 113.5 – 115 °C, equiv. weight 292 ± 3, calc. 298. *S-Ethyl thiobenzophenone.* Oil, equiv. weight 316 ± 3, calc. 314.

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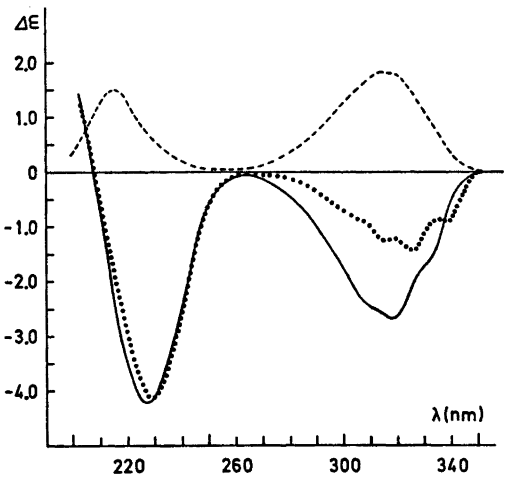

Fig. 1. CD curves of methyl dihydroketo-picrotoxinate (*3*, ——), methyl keto-β-picrotoxinate (*4*, · · ·) and methyl dihydroketo-β-picrotoxinate (*5*, - - -) in methanol.

Studies on Orchidaceae Alkaloids. 41.* The Configuration at C-4 in δ-Nobilonine and Dihydroketopicrotoxinic Acid

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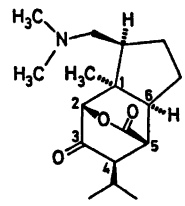
In a previous communication [1] we reported on a determination of the absolute configuration of the dendrobine alkaloids. The assignment was based on a comparison of the circular dichroism (CD) curve of δ-nobilonine (*1*) with that of dihydroketopicrotoxinic acid (*2*), derived from picrotoxinin for which the absolute configuration was known. As the two CD curves show negative Cotton effects at ~315 nm, a 4*R* configuration in *1* was suggested.

To gain further evidence concerning the configuration at C-4 in *1* and *2*, the picrotoxinin derivatives *3*, *4*, and *5* have now been synthesised and their CD curves recorded. In *4* and *5* an epimerisation at C-4 is impossible due to the ether linkage between C-6 and



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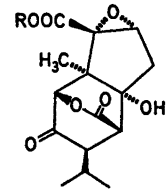
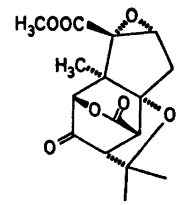


2:R=H
3:R=CH_3



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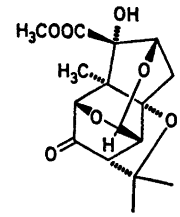

5

C-12. Compounds *1*, *2* and *3*, which have the same chromophore as *4*, exhibit negative Cotton effects at ~315 nm which are almost twice that of *4*. This large difference in amplitude indicates that the isopropyl groups in *1*, *2* and *3* make a significant negative contribution to the Cotton effect associated with the $n \rightarrow \pi^*$ transitions of the C-3 carbonyl group. Hence *1* and *2* have the 4*R* configuration.

The CD curves of *4* and *5* show Cotton effects at ~315 nm of about the same magnitude

* For Paper 40 in this series, see Ref. 1.