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THE FORMATION OF UNUSUAL SULTONES DURING THE REARRANGEMENT REACTIONS OF BICYCLIC KETONES

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A wide variety of rearrangements and fragmentations have been observed in reactions of 1-methoxy-1,4-dihydro-1,4-ethenonaphthalene (1-methoxy-benzobarrelene) derivatives and the related 3,4-dihydro-1,4-ethenonaphthalen-2-(1H)ones (benzobarrelenones).[1] In our more recent work we have concentrated on the non-halogenated compounds,[2] some of which is reported now.

Rearrangement of 1-methoxy-2,9-dimethyl-1,4-dihydro-1,4-ethenonaphthalene[†] (1) in trifluoroacetic acid is unexceptional. The ketones (2) and (3) were isolated in 40 and 48% yield rapidly and the latter compound gave, on prolonged treatment, a ca. 1:1 equilibrium mixture of the ketones (3) and (4).

In sulphuric acid (96%) the compound (1) gave, in addition to the ketone (2) [isolated in 29% yield], a diastereomeric mixture of the diketones (5) [10% yield] and a more polar product [10% yield] which had a molecular formula $C_{14}H_{14}SO_4$ and was evidently a sultone. The diketones (5) and the sultone were also produced from the ketones (3) and (4) in 23 and 48% yields respectively. The diketones (5) also gave the sultone (10% yield). Although the compounds (5) have so far resisted all attempts to separate them completely [presumably due to easy epimerisation at C-2] their structures are established from the available spectral data and by an independent synthesis.

The mass spectrum of the diketones (5) was particularly informative and showed ions at m/e 216, 173, 158, 131, 103, 77, 51, and 43. Appropriate metastable transitions were observed and the base peak (m/e 158) corresponds to the expected McLafferty rearrangement product - with charge retention on the olefinic moiety - effectively the 2-methyl-naphth-1-ol ion. The oxidation of acetophenone with manganese (III) acetate in the presence of terminal olefins affords 4-alkyl-3,4-dihydronaphthalen-1-(2H)ones.[3] An analogous reaction using propiophenone, pent-1-ene-4-one, and manganese (III) acetate gave the ketones (5) in 10% yield.

[†] Satisfactory analytical and spectroscopic data were obtained for all of the new compounds described.

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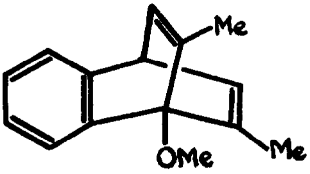
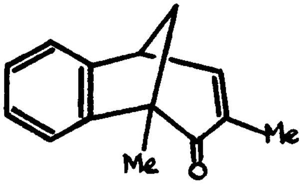
Spectral data for the sultone include ν_{max} 1695 (>C=0) and 1330 and 1155 ($C-SO_2-0-$) cm^{-1}; ^1H n.m.r. ($CDCl_3$), τ, 1.95 (1H, d x d), 2.3 - 2.75 (3H, m), 5.52 (1H, d, $|J|$= 14 Hz), 6.36 (1H, m), 6.55 (1H, d, $|J|$= 14 Hz), 6.96 - 8.0 (4H, m), and 8.6 (3H, s); ^{13}C n.m.r. ($CDCl_3$) δ24.4 (q), 41.4 (d), 43.6 (t), 46.5 (t), 50.1 (d x d), 60.0 (s), 96.2 (s), 126.9 (d), 127.9 (d), 128.1 (d), 129.0 (s), 135.2 (d), 149.3 (s), and 192.1 (s), indicated the structure (6). Construction of a scale molecular model suggested the stereochemistry shown, which was confirmed by a single crystal X-ray structure determination.‡



(1)



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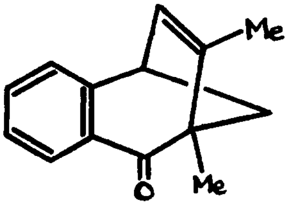

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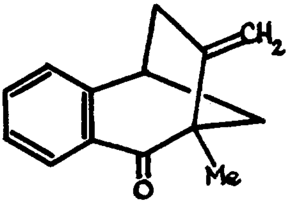

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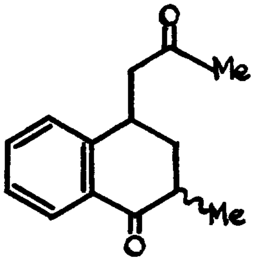

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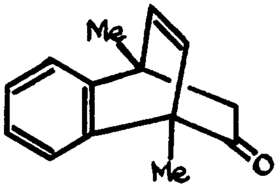
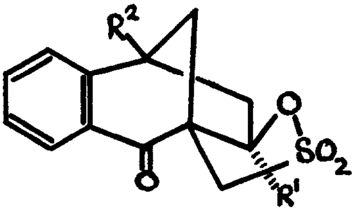
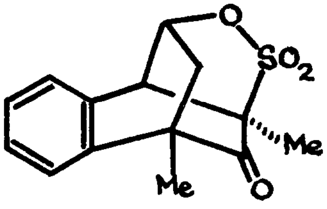


(7)



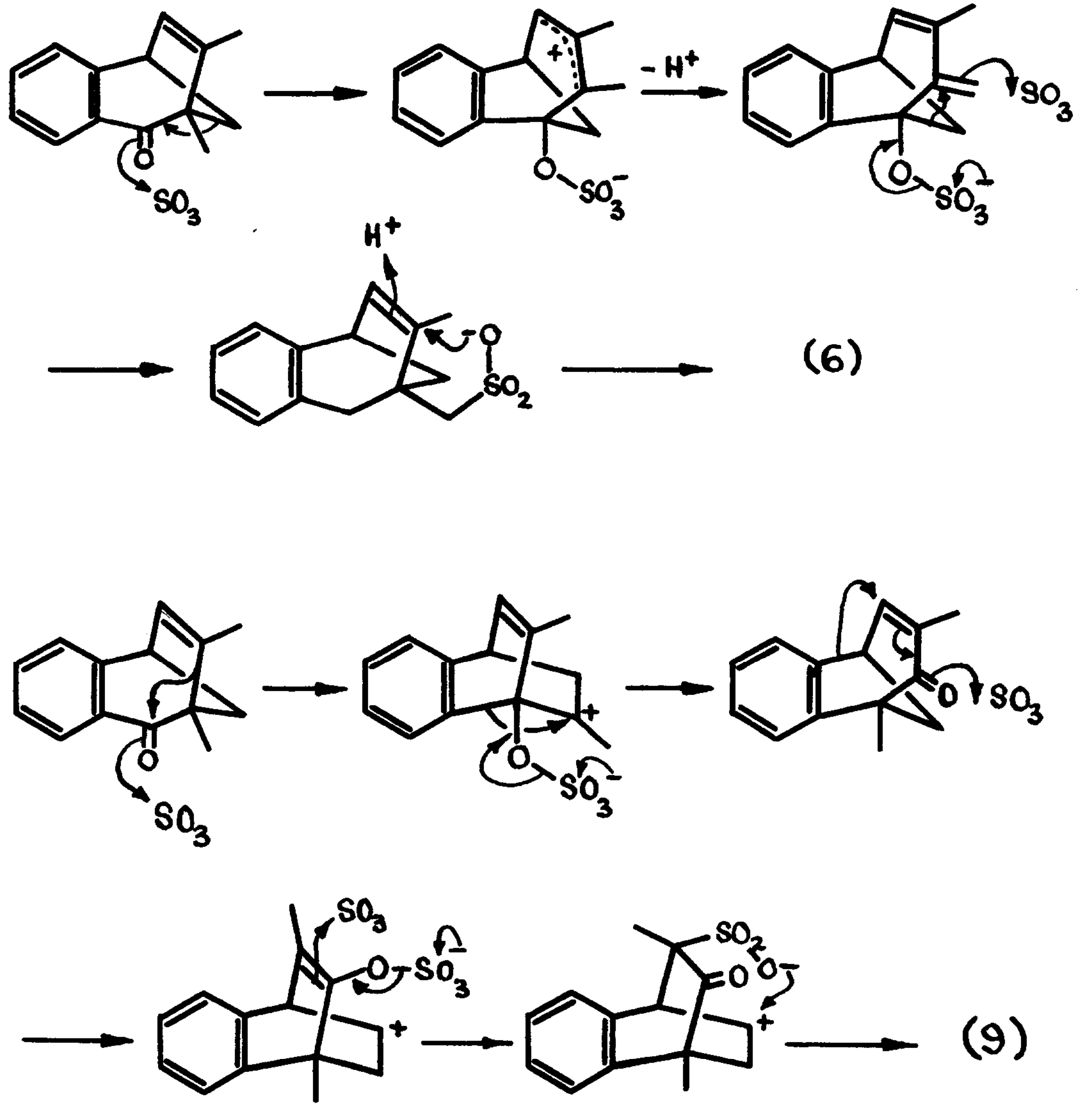
(6 ; R^1=Me , R^2= H)
(8 ; R^1=H , R^2=Me)



(9)

It is of interest to note that the ketone (7) affords the closely related sultone (8) in 59% yield, when it is treated with sulphuric acid.

‡ Crystal data and atomic co-ordinates for the sultones (6) and (9) are available from Dr.D.S.Brown.



SCHEME

These results suggest that sulphur trioxide, or more probably protonated sulphur trioxide, is the effective electrophile which directs these reactions. We therefore investigated the reactions of a number of the above compounds with the sulphurtrioxide-dioxan complex in methylene chloride. Although the compound (1) and the related 1-hydroxy-compound do not react in this system, the ketones (3) and (4) each give the sultone (6) in 48% yield. A new isomeric sultone was also produced in these reactions in ca. 40% yield which, on the basis of spectroscopic studies and mechanistic arguments, was tentatively assigned the structure (9). This has also been confirmed by X-ray crystallography.‡ Both of the sultones, (6) and (9), were stable in the presence of an excess of the sulphur-trioxide-dioxan complex. Remarkably, the α,β- unsaturated ketone (2) also gave the sultone (9) in 84% yield using the sulphur trioxide-dioxan complex in methylene chloride. Although the ketone (2) is apparently stable over prolonged periods of time (12 h) in sulphuric acid, the presence of free sulphur trioxide does result in the formation of small amounts of the compound (9).

The mechanistic sequences involved in the formation of the two types of sultone are evidently complex but can be rationalised, for example in the case of reactions involving the sulphur trioxide-dioxan complex, along the lines indicated in the Scheme.

The presence of a methyl group on a carbon atom α- to the carbonyl function is clearly an essential feature with respect to the formation of sultones of the type (6) and (8).

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