A Tertiary α-Ketol Enol-sulphite as a Source for the Dipolar Favorsky Intermediate

By J. LEVISALLES,* E. ROSE and I. TKATCHENKO

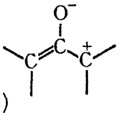
(*Laboratoire de Chimie Organique, Faculté des Sciences, 54-Nancy, France*)†

TURRO *et al.*[1] have described cyclo-addition reactions of 2,2-dimethylcyclopropanone. Because of the unusual π-structure of the dipolar intermediate (I), resulting from the disrotatory opening of cyclopropanone, both (4 + 2)π and (2 + 2)π cycloadditions occur.[1] We report the transient formation of a dipolar intermediate such as (I), by a reverse (2 + 2)π cycloaddition, and its reactions.

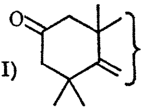
During a study of steroidal α-ketols,[2] dehydration (thionyl chloride–pyridine) of the ketol (II) (4,4-dimethylcholest-5-ene series) gave instead of the expected enone (III) the cyclic hydroxy-enol sulphite (IV), m.p. 118°. The structure (IV) was supported by the following reactions.‡ (1) With sodium methoxide in methanol (1 hr.; 40°), the ketol (II) was regenerated; (2) in hexane (30 min.) sulphur dioxide and the enone (III), m.p. 112—114° were obtained; (3) in furan (48 hr.) both the enone (III) and the adduct (V), m.p. 114—116° were formed; (4) with methanol (35 hr.; 40°) the methoxy-ketones (VIa) and (VIb), m.p. 87° and 114° were isolated; and (5) in ether with dry sodium methoxide (1 hr.) (IV) gave an oily mixture of methyl esters, in which the ester (VII) must be the major component; lithium aluminium hydride reduction of the mixture gives as the major component, alcohol (VIIIa), m.p. 128—130°.

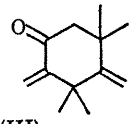
These reactions are those expected from a dipolar intermediate of type (I), *i.e.* (IX), which could be formed by a (2 + 2)π cycloelimination reaction. This elimination is the reverse of the cycloaddition[1a] of 2,2-dimethylcyclopropanone and sulphur dioxide. As (I) is also the intermediate postulated by several authors[3] for the Favorsky reaction,[4] the formation, from (IX) of enone (III), methoxy-ketones (VIa) and (VIb), and ester (VII), is easily understood. It thus seems that type (I) intermediates can be generated thermally from compounds other than cyclopropanones.

(I)

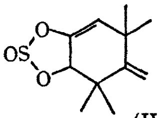


(II)

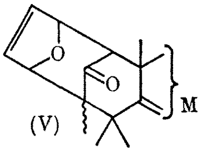




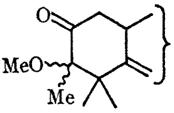
(III)



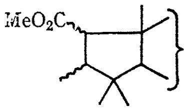
(IV)



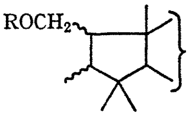
(V)



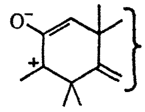
(VIa) α - Me, β - OMe
(VIb) α - OMe, β - Me



(VII)



(VIIIa) R=H
(VIIIb) R=Ac



(IX)

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† Research team associated with C.N.R.S.

‡ All structures assigned are supported by i.r., u.v., and n.m.r. spectra.

[1] (a) N. J. Turro, S. S. Edelson, J. R. Williams, and T. R. Darling, *J. Amer. Chem. Soc.*, 1968, **90**, 1926; (b) N. J. Turro and J. R. Williams, *Tetrahedron Letters*, 1969, 321.

[2] S. Huneck, J. Levisalles, and I. Tkatchenko, *Bull. Soc. chim. France*, 1967, *p.* 3140; J. Alais, J. Levisalles, and I. Tkatchenko, in the press.

[3] A. W. Fort, *J. Amer. Chem. Soc.*, 1962, **84**, 4979; R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 1963, 129; *J. Chem. Soc.*, 1965, 2009; J. G. Aston and J. D. Newkirk, *J. Amer. Chem. Soc.*, 1951, **73**, 3900; J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1954, 1201; H. O. House and W. F. Gilmore, *J. Amer. Chem. Soc.*, 1961, **83**, 3972, 3980.

[4] R. Jacquier, *Bull. Soc. chim. France*, 1950, 835; B. Tchoubar, *ibid.*, 1955, 1363; A. S. Kende, *Org. Reactions*, 1960, **11**, 261.