Reaction of Dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanide with Aromatic Aldehydes

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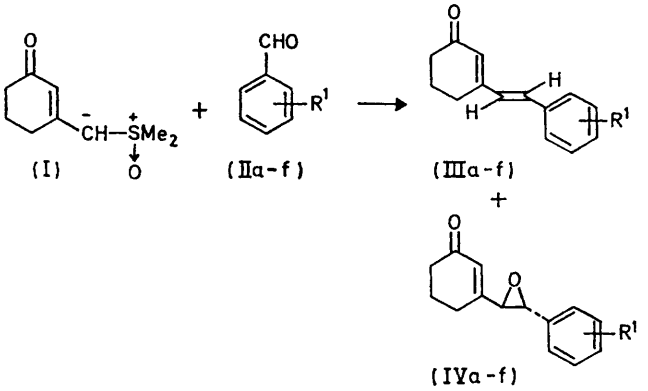
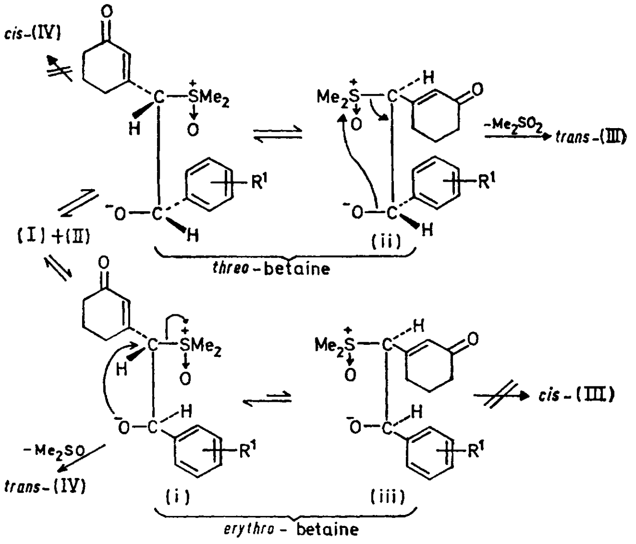
Summary Reaction of dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanide with aromatic aldehydes gave a mixture of *trans*-olefin and *trans*-oxiran.

STUDIES on the reactions of carbonyl compounds with ylides have shown that phosphonium ylides give the olefin[1] but sulphonium and oxosulphonium ylides give the oxiran.[2] We now report that the reaction of an oxosulphonium ylide stabilised by a 3-oxocyclohex-1-enyl group, with aromatic aldehydes, gives a mixture of olefin and oxiran.



Dimethyloxosulphonio-(3-oxocyclohex-1-enyl)methanide (I)[3] was treated with *p*-nitrobenzaldehyde (IIa) in dry THF under reflux for 28 h. Concentration of the mixture *in vacuo* followed by preparative t.l.c. (alumina–benzene) gave a 20% yield of *trans*-1-(*p*-nitrophenyl)-2-(3-oxocyclohex-1-enyl)ethylene (IIIa) (m.p. 122—122·5°) and a 16% yield of *trans*-2-(*p*-nitrophenyl)-3-(3-oxocyclohex-1-enyl)oxiran (IVa) (m.p. 131·5—132·5°). The structure of (IIIa) was confirmed by direct comparison with an authentic sample.[4] The structure of (IVa) was assigned from analytical and spectral data [ν_{max} ($CHCl_3$) 1670 cm^{-1}; λ_{max} (EtOH) 220 nm (log ϵ 4·09); *m/e* 259 (M^+); τ ($CDCl_3$) 1·72 (2H, d, *J* 8·5), 2·49 (2H, d, *J* 8·5), 3·78 (1H, bs), 5·98 (1H, d, *J* 2·0[5]), 6·51 (1H, d, *J* 2·0[5]), and 7·4—8·1 (6H, m) and a small vicinal coupling constant (*J* 2·0 Hz[5]) of oxiran ring protons show the *trans*-configuration]. The reaction of other aromatic aldehydes (IIb—f) with (I) gave the *trans*-olefins (IIIb—f) and *trans*-oxirans (IVb—f). The reaction of (I) and (II) could be explained by a pathway in which decomposition of the initially formed *erythro*-betaine (i)† gives *trans*-(IV). However, when this decomposition is retarded,[6] (i) is in rapid equilibrium with *threo*-betaine, which undergoes a Wittig-type reaction through (ii) to give *trans*-(III). In fact, equimolecular amounts of dimethylsulphone and *trans*-(IIId) were isolated in the reaction of (I) and (IId). The conversion of (ii) into *trans*-(III) is accelerated by stabilisation of the conjugated olefin product, and *cis*-olefin formation from (i) is restricted by steric interference between cyclohexenone and benzene rings in (iii).

Aldehydes (II)	Products	
R^1	% yield of (III)	% yield of (IV)
a; *p*-NO_2	20	16
b; *p*-OMe	11	9
c; H	19	trace
d; *p*-Cl	19	„
e; *o*-OMe	20	„
f; *o*-Cl	39	„



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† As proposed in phosphonium ylides,[1] we also assume the initial formation of *erythro*-betaine in oxosulphonium ylides.

[1] H. O. House, 'Modern Synthetic Reactions', Benjamin, California, 1972, p. 682; M. Schlosser, *Topics in Stereochemistry*, 1970, **5**, 1.

[2] H. O. House 'Modern Synthetic Reactions', Benjamin, California, 1972, p. 709; E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 867, 3782; A. W. Johnson, V. J. Hruby, and J. L. Williams, *ibid.*, 1964, **86**, 918; A. W. Johnson and R. T. Amel, *J. Org. Chem.*, 1969, **34**, 1240; H. König and H. Metzger, *Chem. Ber.*, 1965, **98**, 3733.

[3] Y. Tamura, T. Miyamoto, T. Nishimura, J. Eiho, and Y. Kita, *J.C.S. Perkin I*, 1974, 102; the ylide (I) readily reacted with a variety of enones to give the corresponding vinyl cyclopropanes (Y. Tamura, T. Miyamoto, H. Kiyokawa, and Y. Kita, *ibid.*, in the press).

[4] Y. Tamura, T. Miyamoto, and H. Taniguchi, *Chem. and Ind.*, submitted.

[5] A. J. Speziale and D. E. Bissing, *J. Amer. Chem. Soc.*, 1963, **85**, 3878.

[6] C. R. Johnson, C. W. Schroeck, and J. R. Shanklin, *J. Amer. Chem. Soc.*, 1973, **95**, 7424 and references therein.