Reaction of Ozone with Vinyl Sulphides. Reactions Retaining Hydrocarbon Chains

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Summary Ozone reacts with vinyl sulphides and gives, with thiopinacolone and thiocamphor derivatives, products containing unmodified hydrocarbon chains; however, with 4-alkylthio-2,6-dimethylhept-3-ene the classical reaction of cleavage of the double bond has been observed.

OZONOLYSIS remains one of the most efficient methods to cleave carbon–carbon double bonds and a mechanism for this reaction has been proposed and tested by Criegee.[1,2] However, in a number of cases, the outcome of this reaction may be very different and can result in oxygenated compounds which retain their hydrocarbon chains unchanged.[1] In the case of tetracyanoethylene this even leads to no reaction at all.[3]

Büchi[4] has recently studied the ozonolysis of vinylsilanes and has observed a number of abnormal reactions (α-siloxy-dioxetans and/or α-silylperoxy-ketones have been obtained). We here report preliminary results on the behaviour of the vinyl sulphides (**1**), (**3**), and (**6**)† towards ozone. For this study a solution of the vinyl sulphides (**1**), (**3**), and (**6**) (4 g) in pyridine–methylene chloride[5] was ozonized, to the point of saturation, at −70 °C. Three types of reaction took place.

Thus, ozonization of the methylthio- (**1a**) and ethylthiobut-1-ene (**1b**) gave the aldehydes (**2a**), b.p. 85 °C at

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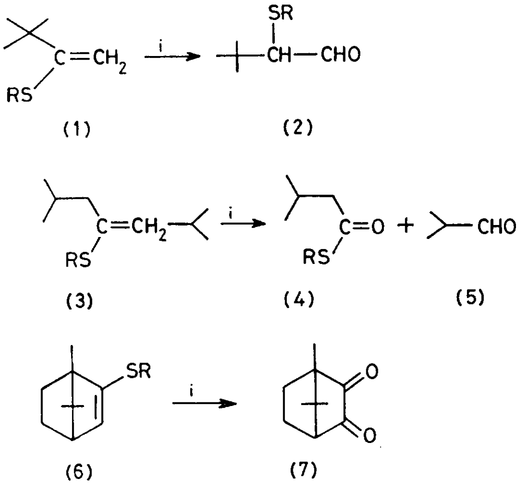
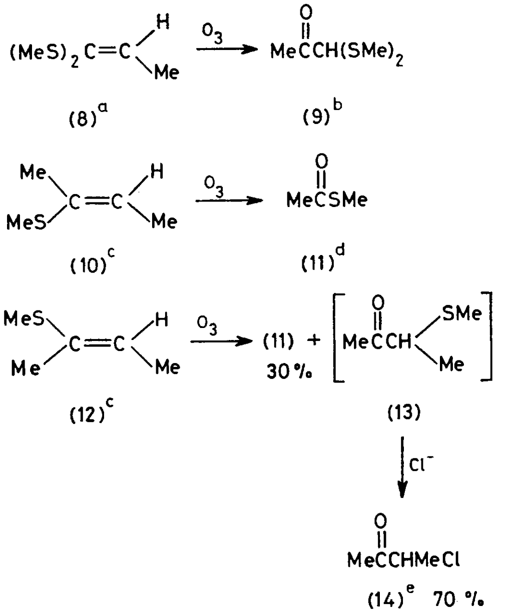
† The vinyl sulphides (**1**), (**3**), and (**6**) were obtained by the reaction, in Me_2SO–NaH, of an alkyl iodide with the appropriate thioketone, in 75—80% yield. All the sulphides are easily made which determined our choice to a certain extent (see D. Paquer, *Internat. J. Sulfur Chem.*, 1972, **7**, 269). Compounds (**3a**) and (**3b**) were obtained as mixtures of *ca.* 90% *Z*- and *ca.* 10% *E*-isomers.

20 mmHg, and (**2b**), b.p. 90 °C at 20 mmHg, respectively, in *ca.* 55% yield.‡ In contrast, ozonization of the methylthio- (**3a**) and ethylthio-hept-3-ene (**3b**) led to classical double bond cleavage to give the thioesters (**4a**) (70% yield; b.p. 50 °C at 20 mmHg) and (**4b**) (80%; b.p. 108 °C at 100 mmHg), respectively, together with isobutyric aldehyde (**5**), which distilled over with the methylene chloride solvent, but which was readily identified by i.r. spectroscopy. The third type of reaction was shown by the thiocamphor derivatives (**6a**) and (**6b**), ozonization of which gave camphorquinone (**7**) in *ca.* 65% yield following recrystallization from pentane.



a; R = Me
b; R = Et
Reagents: i, O_3, C_5H_5N–CH_2Cl_2.

From these results it appears that the presence of a hydrogen atom *cis* to the alkylthio group is necessary for the 'abnormal reactions' which retain an unmodified carbon chain to be observed; double bond cleavage is always observed when this structural feature is lacking. The reactions of (**8**), (**10**), and (**12**) confirm this hypothesis.



[a] J. M. Beiner and A. Thuiller, *Compt. rend.*, 1972, **274C**, 642. [b] ν_{CO} (CCl_4) 1700 cm^{-1}; δ (CCl_4) 2·03 (6H, s), 2·26 (3H, s), and 4·20 (1H, s). [c] J. M. Beiner, D. Lecadet, D. Paquer, and A. Thuillier, *Bull. Soc. chim. France*, 1973, 1983. [d] E. E. Reid, 'Organic Chemistry of Bivalent Sulfur,' vol. IV, Chemical Publishing Co., New York, 1962. [e] *Cf.* E. M. Kosower, W. J. Cole, G. S. Wu, D. E. Cardy, and G. Meisters, *J. Org. Chem.*, 1963, **28**, 630. Our identification of (**14**) was based on comparison with an authentic sample synthesized independently by an unambiguous route.

(*Received*, 1*st June* 1978; *Com.* 560.)

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‡ Yields correspond to the weight of product isolated after distillation or recrystallization. G.l.c. of the crude product showed the absence of products other than those noted. Products were identified by i.r. and n.m.r. spectroscopy; *e.g.* compound (**2a**) showed ν_{CO} (CCl_4) 1700 cm^{-1}; δ (CCl_4) 1·10 (9H, s), 1·90 (3H, s), 2·55 (1H, d), and 9·15 (1H, d, *J* 6·6 Hz), and compound (**4a**) ν_{CO} (CCl_4) 1680 cm^{-1}; δ (CCl_4) 0·93 (6H, d), 2·23 (3H, s), and 2·33 (3H, m) (*cf.* J. P. Idoux, *J. Org. Chem.*, 1973, **38**, 4239).

[1] R. Criegee and G. Schroder, *Chem. Ber.*, 1960, **93**, 689.
[2] R. Criegee, *Chem.-Ztg.*, 1975, **99**, 138.
[3] R. Criegee and P. Gunther, *Chem. Ber.*, 1963, **96**, 1564.
[4] G. Büchi and H. Wuest, *J. Amer. Chem. Soc.*, 1978, **100**, 294.
[5] J. M. Conia and P. Leriverend, *Compt. rend.*, 1960, **250**, 1078.