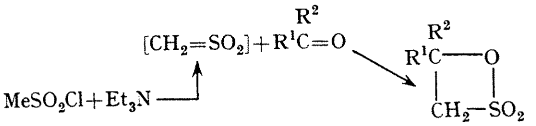
Reaction of Sulphene with Highly Halogenated Ketones

By JOHN R. NORELL

(*Phillips Research Center, Phillips Petroleum Company, Bartlesville, Oklahoma* 74003)

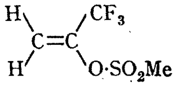
Summary β-Sultones are formed from the cycloaddition of sulphene with hexahalogenoacetones; however, 1,1,1-trihalogenoacetones do not give the expected adduct but instead yield the novel 1-trihalogenomethylvinyl methanesulphonates.

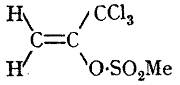
INTEREST[1-3] in sulphene cycloadditions to carbonyl compounds prompts us to report the cycloaddition of sulphene with highly halogenated ketones. In the three ketones, R^1COR^2, where $R^1 = R^2 = CCl_2F$, $R^1 = R^2 = CF_2Cl$, and $R^1 = CCl_2F$, $R^2 = CClF_2$, cyclic sultones† are formed in good yield.‡ No olefinic linkages are observed in the i.r., and the n.m.r. spectra exhibit singlets at δ *ca.* 5·1 p.p.m. in all three adducts (methylene protons).



With 1,1,1-trifluoroacetone, which contains hydrogen atoms α to the carbonyl group, the expected 4-ring sultone was not obtained, but instead the novel 1-trifluoromethylvinyl methanesulphonate (**1**) was isolated [75% yield, b.p. 54° (4·5 mm.), n_D^{20} 1·3806] on reaction with equimolar quantities of the ketone, triethylamine, and methane sulphonyl chloride (Et$_2$O, 10°). Similarly, with 1,1,1-trichloroacetone, (**2**) is obtained (13%) as a distillable liquid (b.p. 86°/0·3 mm.) but solidifies on cooling (m.p. 36—38°).

(1)

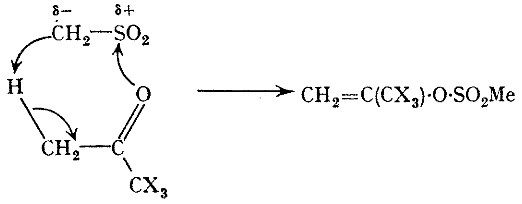




(2)

Unlike the cyclic adducts, the vinyl sulphonates exhibit bands in the i.r. at 1660 cm.$^{-1}$ for (**1**) and 1640 cm.$^{-1}$ for (**2**) (C=CH$_2$ stretch) and both (**1**) and (**2**) show absorbances at 3110 cm.$^{-1}$ (=CH$_2$ asymmetric stretch); all these are characteristic of terminal vinyl groups.[4] In addition the sulphone bands are at 1160 and 1350 cm.$^{-1}$ for both adducts. For (**1**), the calculated n.m.r. spectrum for an ABX$_3$ system (computer program NMRIT) was in close agreement with that obtained experimentally (CD$_3$·SO·CD$_3$). The following parameters were observed: δ_H (Me$_4$Si internal standard) = 6·00, H$_A$; 5·94, H$_B$ (J_{AB} −4·9 ± 0·1,§ J_{AX} 0·0 ± 0·1, J_{BX} 1·4 ± 0·1 Hz.); δ 3·52 (CH_3, 3:2, methyl : vinyl); ^{19}F n.m.r. −5·73 p.p.m. (d) (from CF$_3$CO$_2$H). Assignments of the chemical shifts and corresponding coupling constants of either vinyl protons cannot be made, although it is likely that J_{BX} is a *trans* coupling constant.[6] A simple AB system is shown for (**2**) (neat) as no coupling with chlorine can occur: H$_A$, δ 5·96; H_B, 5·57, and H$_{Me}$, 3·32 p.p.m. (J^{gem}_{AB} 4·5 Hz.) with integral ratios of 2:3 for vinyl : methyl protons. For **1**, *m/e* (rel. intensity, fragment): 79 (100, CH$_3$SO$_2^+$), 69 (54, CF$_3^+$), 190 (3, M^+), 121 (3,CH$_2$=COSO$_2$CH$_3$). If the adduct were cyclic, the *m/e* peak at 79 would probably not be significant.

The vinyl sulphonates may arise *via* two possible pathways, both of which require at least one hydrogen atom α to the carbonyl function. The most obvious route is attack of the sulphonyl chloride or sulphene on the enol form, CH$_2$=C(OH)CX$_3$, of the trihalogenoacetone. An intriguing possibility involving a cyclic transition state can also be rationalized.



Interestingly, even though pentafluoroacetone contains an α hydrogen atom, a low yield of an adduct was obtained (b.p. 64—65·5° : 3·5 mm, n_D^{20} 1·3729) and n.m.r. indicated that the β-sultone was the major product δ 6·25 (t, –CHF$_2$, J_{HF} 53 Hz.[7]) 4·97 p.p.m. (ring CH_2, J_{AB} 15 Hz) instead of a 3·3 p.p.m. singlet only, as expected for the CH$_3$SO$_3^-$ group.

I thank Dr. James Randall for interpretation of the n.m.r. spectra of the vinyl sulphonates.

(*Received, September* 11*th*, 1969; *Com.* 1378.)

---

† All adducts isolated gave satisfactory elemental analyses and spectral data consistent with the structures assigned.

‡ Recently Truce and Liu (ref. 1) independently reported the reaction of hexahalogenoacetones and chloral with sulphene. The boiling points and refractive indices of our products are in good agreement with those of theirs.

§ The sign of the geminal coupling constant could not be determined although it appears likely it is negative (ref. 5).

[1] W. E. Truce and L. K. Liu, *Chem. and Ind.*, 1969, **457**.
[2] D. Borrnmann and R. Wegler, *Chem. Ber.*, 1966, **99**, 1245.
[3] F. I. Luknitskii and B. A. Vovsi, *Doklady Akad. Nauk S.S.S.R.*, 1967, **173**, 1327.
[4] K. Nakanishi, "Infrared Absorption Spectroscopy—Practical," Holden-Day, San Francisco, 1962, p. 24.
[5] T. Schaefer, *Canad. J. Chem.*, 1962, **40**, 1.
[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," vol. 2, Pergamon, London, 1966, p. 913.
[7] D. D. Elleman, L. C. Brown, and D. Williams, *J. Mol. Spectroscopy*, 1961, **7**, 307, cite a coupling constant of 52·6 c./sec. for the CHF$_2$ group.

Printed by W Heffer & Sons Ltd Cambridge England