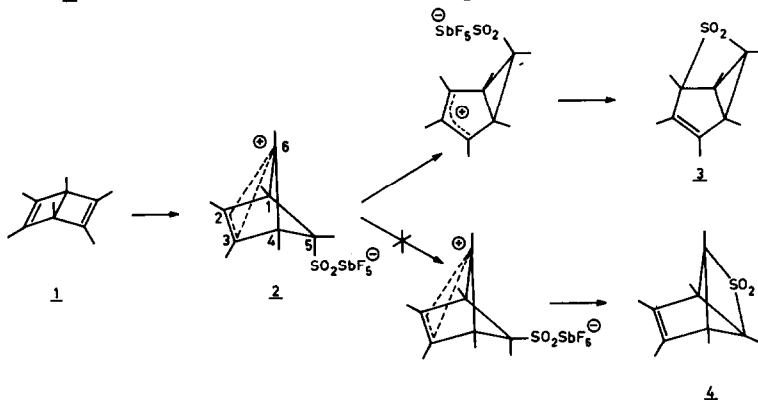


SbF₅-CATALYSED ADDITION OF SO₂ TO HEXAMETHYLDEWARBENZENE

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The electrophilic SbF₅-catalysed addition of SO₂ to cyclooctatetraene has recently been reported to occur via a homotropylium ion and to give in a ring closure step, a mixture of bicyclic and tricyclic sulfones.¹ Electrophilic additions to hexamethyldewarbenzene (**1**) provide hexamethylbicyclo[2.1.1]hexenyl cations, which in subsequent reactions yield strained compounds hardly accessible via other synthetic pathways.² In this paper it is reported that electrophilic addition of SO₂-SbF₅ to **1** gives the bicyclo[2.1.1]hexenyl cation **2** which on reaction with nucleophiles yields the strained sulfone **3**, a possible precursor of hexamethylbenzvalene.³

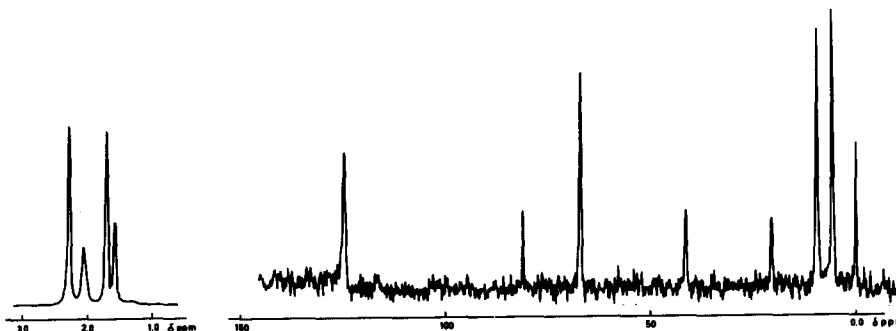


A solution of **1** in SO₂ was cooled to -95°C and SbF₅ (1.5 eq.) was added at this temperature with vigorous stirring. The pmr (left) and cmr (right) spectra of the resulting yellow solution are shown in the figure. The following assignments made in analogy to known hexamethylbicyclo[2.1.1]hexenyl cations lead to the conclusion that the endo-isomer is formed.⁴

	C-1,4	C-2,3	C-5	C-6
pmr, methyl H	1.74	2.28	2.04	1.62
cmr, methyl C	5.9	9.6	20.6	0.3
cmr, ring C	66.9	124.2	81.0	41.3

In the present solvent system ion **2** is stable up to -50°C; at higher temperatures decomposition is

observed. When the solution is allowed to react with nucleophiles (H_2O or CH_3OH/CH_3ONa) at low temperatures mixtures of sulfone 3 and some hexamethylbenzene are isolated. The former product can be



explained via the known rearrangements of hexamethylbicyclo[2.1.1]hexenyl cations⁴: rearrangement of ion 2 to a hexamethylbicyclo[3.1.0]hexenyl cation, which gives sulfone 3 in a ring closure reaction. Sulfone 4, which could be the product of ring closure of the *exo*-isomer, could not be detected. In an optimised experiment a solution of ion 2 at $-90^{\circ}C$ (10 mMol 1, 15 mMol SbF_5 in 30 ml SO_2) was poured with vigorous stirring into a large excess of a 10:1 mixture of methanol and sodium methoxide at $-80^{\circ}C$. After warming to room temperature, water and pentane were added. The organic layer was separated, washed and dried and the solvent was evaporated, yielding 1.80 g (=0,8 mMol; 80%) of a crude product which contained 94% of 3 and 6% of hexamethylbenzene. Using preparative TLC (neutral alumina, petroleum-ether 40-60⁰) pure sulfone 3 (m.p 80-81⁰) was isolated.⁵ The structure 3 is assigned on the basis of the following data: pmr spectrum: δ 0.85 (s, 1 CH_3) 1.13 (s, 1 CH_3) 1.20 (s, 1 CH_3) 1.25 (s, 1 CH_3) 1.62 (q, $J=1.5$ Hz, 1 CH_3) 1.70 (q, $J=1.5$ Hz, 1 CH_3) ; ir spectrum: absorptions at 1130 cm^{-1} and 1360 cm^{-1} (sulfone) and at 1630 cm^{-1} (alkene) ; mass spectrum: parent peak at m/e 226.

Finally, it is worth mentioning that in the absence of SbF_5 no reaction between SO_2 and hexamethyldewarbenzene is observed, even at room temperature. The described reaction represents a new example of SbF_5 catalysis in the addition of SO_2 to olefinic and aromatic hydrocarbons.^{1,6}

References

1. J. Gasteiger and R. Huisgen, *J.Amer.Chem.Soc.*, **94**, 6541 (1972).
L.A. Paquette, U. Jacobsson, and M. Oku, *J.C.S. Chem.Comm.*, **1975**, 115.
2. L.A. Paquette, R.J. Haluska, M.R. Short, L.K. Read, and J. Clardy, *J.Amer.Chem.Soc.*, **94**, 529 (1972).
H. Hogeveen, P.W. Kwant, E.P. Schudde, and P.A. Wade, *ibid.*, **96**, 7518 (1974).
3. Dr. U.E. Wiersum, AKZO Chemie, Arnhem, is presently investigating the thermal extrusion of SO_2 from 3, using flash thermolysis techniques.
4. H. Hogeveen, and P.W. Kwant, *J.Amer.Chem.Soc.*, **95**, 7315 (1973).
5. Sulfone 3 is stable in pentane solution at room temperature for several months when stored over potassium carbonate. In the absence of base decomposition to hexamethylbenzene occurs.
6. M. Brookhart, F.A.L. Anet and S. Winstein, *J.Amer.Chem.Soc.*, **88**, 5657 (1966).
G.A. Olah "Friedel-Crafts and Related Reactions", Vol. 1, Chapter 2 ; Interscience Publishers Inc., New York.