Tetrahedron Letters No. 11, pp 947 - 950, 1977. Pergamon Press. Printed in Great Britain.

LITHIUM ALUMINIUM HYDRIDE PROMOTED EXTRUSION OF SO_2 FROM SULFOLENES AND SULFOLENE-ADDUCTS. 1,3-DIENES, 3-CHLORO- AND 3,3-DICHLORO-1,4-DIENES AND SKIPPED POLYENES

Yehiel Gaoni

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

(Received in UK 17 January 1977; accepted for publication 4 February 1977)

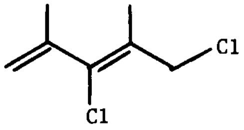
The retro-sulfolene reaction, which thermally produces 1,3-dienes from 2,5-dihydrothiophene-1,1-dioxides, is of considerable practical importance[1,2] and of high theoretical interest.[3] Its utility has been extended to bicyclo[3,1,0] sulfolene-adducts, allowing the preparation of homoconjugated dienes.[4,5] The two cycloelimination reactions are usually carried out in the range of temperatures of 80-150° and present no undue difficulty. However, some of the mono- or bicyclic sulfones may require higher temperatures and this may result in chemical modifications of the products, such as rearrangements or side-reactions,[4,6] or in massive co-sublimation of the starting sulfone.

It has now been found that sulfolenes and sulfolene-adducts of varied substitution patterns undergo elimination of SO_2 under mild conditions by reaction with lithium aluminium hydride (LAH) in ether, yielding dienes (or polyenes, when the right substitution is present) in good to very good yields (Table I). The reaction is carried out by the portionwise addition of the solid sulfone to a stirred suspension of excess LAH (1:1 by weight) in refluxing ether: there is usually an immediate evolution of hydrogen and the reflux rate increases. After an additional reflux time, or of stirring at room temperature, of 1/2-1 h, excess LAH is destroyed with ethyl acetate (unless the expected product has a low boiling point) and decomposition with saturated aq. sodium sulfate yields then a clear ethereal solution of the product.[7]

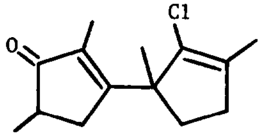
With regular sulfolenes no competitive reductions to the corresponding sulfides have been observed and the crude products were quite pure by nmr and glc analyses. With the bicyclic sulfones, especially the chlorinated ones, a certain amount of reduction did occur, but a simple separation of the fragmentation product from the reduction product could be realized by distillation.

The fragmentation of the chlorinated carbene adducts demonstrates the mildness of the present reaction. Thus, the gem-dichloride 2 (Table I), with its "unsual functionality",[4] which could not be obtained by thermal decomposition of 1 because of rearrangement into 9,[6] was obtained here as a stable distillable liquid, freezing at ∿ -6°. Dichloride 2 is converted into 9 upon treatment with acid or upon adsorption on silica-gel and, like 9, it produces cleanly ketone 10 upon hydrolysis with 80% acetic acid.[8]

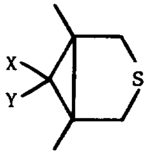
It is noteworthy that treatment of the chlorinated bicyclic sulfones 1, 3 or 7 with LAH under conditions different than those discribed (i.e., less LAH or low temperatures) results in reduction only. Thus, from 1, a whole range of reduction products, namely 11, 12, 7, 13, can be obtained.



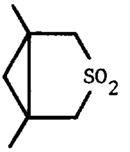
9



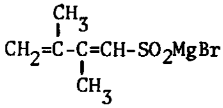
10



11 X=endo-Cl, Y=H
12 X=Y=Cl



13

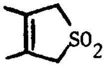
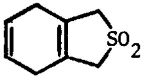
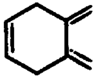
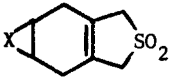
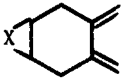
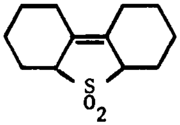
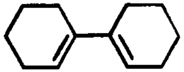
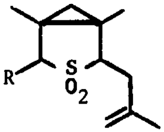
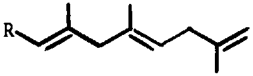
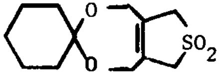
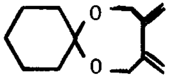
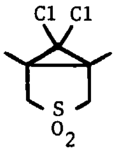
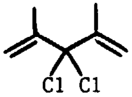
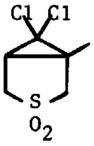
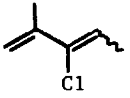
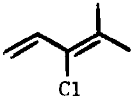
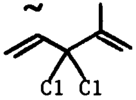
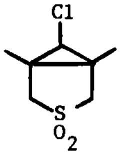
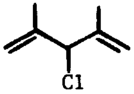


$CH_2{=}\overset{CH_3}{\overset{|}{C}}-\underset{CH_3}{\underset{|}{C}}{=}CH-SO_2MgBr$

14

In an attempt to gain some insight into the mechanism of the extrusion reaction, the sulfinate salt 14[9] was treated with LAH under the above conditions, expecting a reductive cleavage of the C-S bond. This was done with the idea that an analogous aluminium sulfinate could be formed as an intermediate in our reaction and undergo a similar cleavage. Dimethyl butadiene was indeed obtained from 14, but in rather low yields (7-10% as the maleic anhydride adduct). It is now believed that the reaction proceeds rather by thermal cleavage, through considerable lowering of the transition state for a cheletropic elimination of SO_2, the LAH serving first as a catalyst and then as a binding and reducing agent of the liberated SO_2. This assumption is based on the observations that the reaction is almost instantaneous with the solid sulfones, some of which are barely soluble in ether, and that, on the other hand,

Table I. Dienes and Polyenes from Sulfolenes and Sulfolene-Adducts[a]

Substrate	Product	%Yield[b]	Phys.data
		56[c]	
		74[d]	
		X=CH_2 74 X=CCl_2 47[e]	b 70°(bath)/1mm
		85	b 137-9°/20mm
		R=H[f] 42 R=CH_2-$\underset{CH_3}{C}$=CH_2[f] 57	b 90°(bath)/20mm b 80°(bath)/1mm
		78	b 110°(bath)/0.1mm
 1	 + 12[g] 2	65-70	b 63-65°/20mm
 3	 +  4 5 or  6[i]	92[h]	
 7	 + 11[j] 8	45	b 75°(bath)/20mm

---

a. Elemental and spectral analyses in agreement with structures were obtained for all new compounds. b. Minimum yields of isolated products. c. Isolated as the maleic anhydride adduct. d. W.J. Bailey and J. Rosenberg, J.Am.Chem.Soc., 77. 73-75 (1955). e. D. Davalian and P.J. Garratt, J.Am.Chem.Soc., 97, 6883-6884 (1975). f. Obtained from 13, with butyllithium and methallyl chloride. g. The ratio of 2 to 12 is ∿ 9:1, by nmr of the crude product. h. Crude yield. The two chlorides (ratio of ∿ 2:3 resp.) were separated for analytical purposes by preparative glc. i. Dichloride 6 is obtained impure after a short reaction time. Thermal decomposition of 3 produces only rearranged 6 (ref. 6). j. Ratio of 8 to 11 is 4:1 to 5:1. Thermal decomposition of 7 produces mainly rearranged 8.

there is no reaction at all with such sulfones that cannot undergo a cheletropic elimination of SO_2 (such as $PhSO_2R$). Further work is needed, using deuteriated sulfones and sterically labeled sulfones, in order to distinguish between the two possibilities. Whatever is the mechanism here, it must be different from that of the retro Diels-Alder reaction of the triazolinedione adducts of dienes, promoted by LAH,[10] where a reductive cleavage of the urazole ring occurs first, followed by formation of an azo compound which thermally loses nitrogen. It also must be different from that of the ring contraction of cyclic five-membered α-sulfonylcarbanions, also promoted by LAH,[11] where reduction only occurs in the absence of α-substitution.

References

1. S.D. Turk and R.L. Cobb in "1,4-Cycloaddition Reactions", J. Hamer, Ed., Academic Press, N.Y., 1967, pp 13-45.
2. H. Brachel and U. Bahr in "Methoden der Organischen Chemie" (Houben-Weyl), 4th edition, Georg Thieme Verlag, Stuttgart, 1970, Vol. 5/1c, pp 200-206.
3. W.L. Mock, J.Amer.Chem.Soc., 97, 3666-3677; 3673-3680 (1975).
4. W.L. Mock, J.Amer.Chem.Soc., 92, 6918-6926 (1970).
5. A.I. Meyers and T. Takaya, Tetrahedron Letters, 2609-2612 (1971).
6. Y. Gaoni, Tetrahedron Letters, 2167-2170 (1976).
7. A strong sulfuraceous smell sometimes present is due to trace amounts of material only.
8. Y. Gaoni, Tetrahedron Letters
9. See R.C. Krug, J.A. Rigney and G.R. Tidelaar, J.Org.Chem., 27, 1305-1309 (1962).
10. D.H.R. Barton, T. Shioiri and D.A. Widdowson, J.Chem.Soc.(C), 1968-1974 (1971).
11. J.M. Photis and L.A. Paquette, J.Amer.Chem.Soc., 96, 4715-4717 (1974).