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ELECTROPHILIC FRAGMENTATION-CYCLIZATION OF VARIOUS ALLENIC ESTERS

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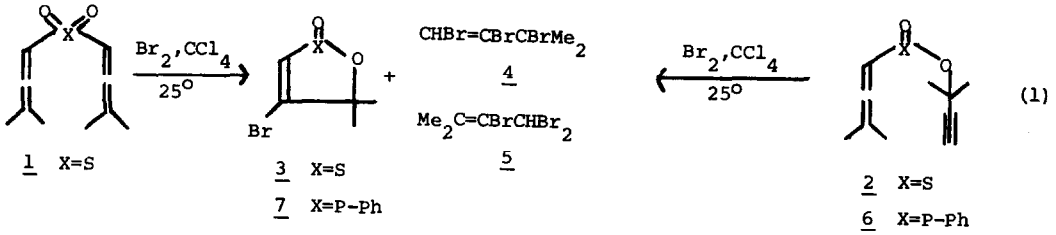
Recently, we have shown that the addition of bromine to sulfone 1 or to sulfinate 2 at room temperature, resulted in a novel spontaneous and quantitative fragmentation, with the formation of γ-sultine 3 and two isomeric tribromoproducts 4 and 5 [1]. Analogously, we have found that bromine adds to phosphinate 6 in the same manner, yielding the oxaphospholene 7 and the tribromoproducts 4 and 5 [1] (eq. 1).

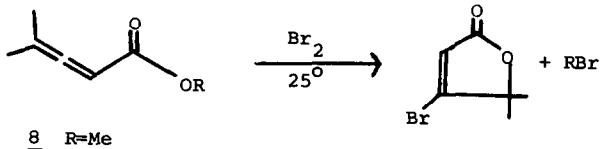


1 X=S
3 X=S
7 X=P-Ph
2 X=S
6 X=P-Ph

(1)

Based on the observation that the bromination of neither diallenyl sulfone nor γ,γ-dimethylallenyl p-tolyl sulfone resulted in the fragmentation-cyclization reported above, a tentative reaction mechanism was suggested in which a stable departing carbocation, such as α,α-dimethylpropargyl or tert-butyl, is a prerequisite to the fragmentation and subsequent cyclization[1].

In order to investigate the generality of this reaction and its synthetic potential, we examined the behaviour of various other allenic esters under conditions similar to those employed for sulfone 1. Surprisingly, despite the absence of a stable departing carbocation in methyl 4-methylpenta-2,3-dienoate (8) [2], we have found that addition of bromine (in CCl_4) to ester 8 at room temperature, resulted in a rapid and quantitative formation of lactone 9 [3] and methyl bromide [4] (eq. 2).



8 R=Me
10 R=H

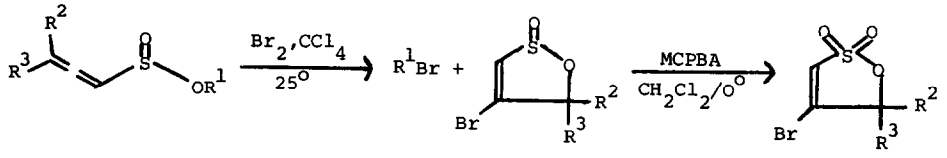
9

(2)

In addition to the standard spectral evidence, the structure of lactone 9 has also been confirmed by its ^{13}C nmr spectrum[5], as well as by the observation that addition of bromine to

4-methylpenta-2,3-dienoic acid (10)[2] gives lactone 9, under similar conditions. The cyclization of acid 10 is in accordance with the recent report of Kresze et al. on the cyclization of related allenic acids[6].

It seems therefore, that for some reason (vide infra) allenic esters, in contradistinction to allenyl sulfones[1], do not require a stable departing carbocation in order that the fragmentation-cyclization might occur. This observation is not only true for allenecarboxylic esters, but also for the corresponding sulfinic, phosphinic and phosphonic esters as well. Thus, allenesulfinates 11(a-d)[3], which also lack a stable carbocation leaving group, react with bromine at room temperature to give in high yield the γ-sultines 12(a-d)[3] and alkyl bromides (eq. 3). Besides the spectral evidence, the structures of sultines 12(a-d) has also been confirmed by their oxidation to the corresponding sultones 13(a-d)[3].

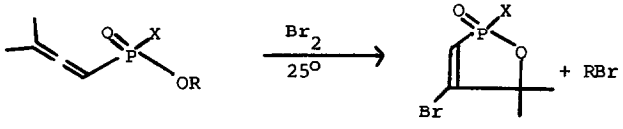


(3)

11a $R^1=R^2=R^3=Me$
b $R^1=Et$ $R^2=R^3=Me$
c $R^1=Et$ $R^2=Me$ $R^3=H$
d $R^1=Et$ $R^2=R^3=H$

12(a-d) 13(a-d)

Similarly the addition of bromine to methyl phenyl 3-methyl-1,2-butadienphosphinate (14)[3], synthesized from the corresponding acid 15[7] with diazomethane, and to diethyl 3-methyl-1,2-butadienphosphonate (16)[8], resulted in their rapid conversion to oxaphospholenes 7[1] and 19[3], respectively (eq. 4). Analogous products (7 and 20[3]) are obtained when bromine reacts with the corresponding phosphinic acid 15[7] and phosphonic acid 17[7] under the same conditions. The cyclization of these acids resemble the recently reported acid catalyzed formation of oxaphospholenes from allenephosphonic acids[9].



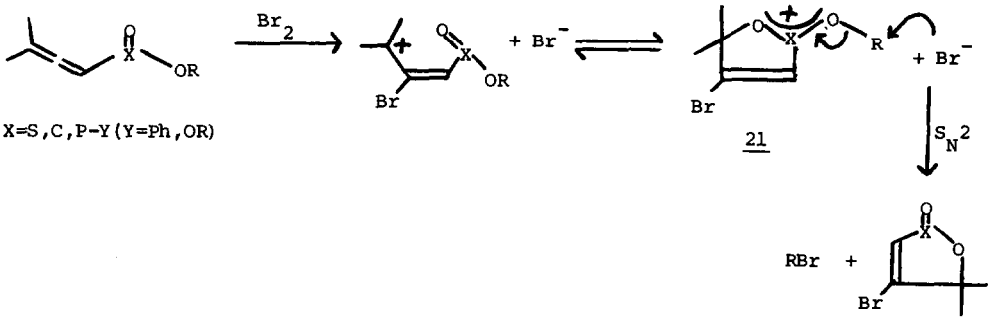
(4)

14 X=Ph R=Me
15 X=Ph R=H
16 X=OEt R=Et
17 X=OH R=H

7 X=Ph
7
19 X=OEt
20 X=OH

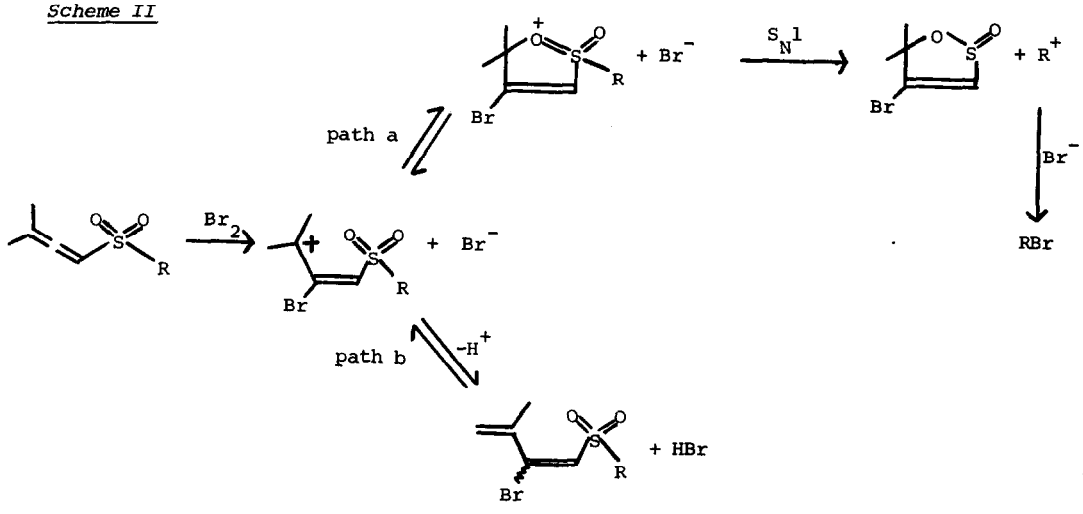
On the basis of these observations we suggest that the fragmentation and cyclization found in the bromination of the allenic esters reported above, proceeds via an S_N2 attack of bromide ion on species 21 (Scheme I):

Scheme I



On the other hand, only those mono or diallenyl sulfones which possess a stable departing carbocation undergo fragmentation[1] by an S_N1 mechanism (path a, Scheme II), while those lacking a good leaving carbonium ion prefer to eliminate a proton, yielding acyclic products (path b).

Scheme II



This S_N1 mechanism is supported by the work of Olah et al.[10] who observed that while protonated sulfones, which lack a stable carbocation group, are stable up to 65°, protonated benzyl tert-butyl sulfone cleaved to tert-butyl cation and phenylmethanesulfinic acid even at temperature as low as -78°. The absence of an S_N2 type mechanism in the bromination of primary alky allenyl sulfones such as methyl γ,γ-dimethylallenyl sulfone, may be due to the strong retarding effect exerted by the sulfonyl group on S_N2 displacements at the α-carbon atom, as a result of steric and field effects[11]. These effects do not extend to the β-position in sulfones[11], and are certainly to be absent in the case of allenic esters (vide supra).

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3. All new compounds gave satisfactory elemental analysis and/or ir, nmr and mass spectra data in accord with the assigned structures: oxaphospholene 7(mp 86-87°), lactone 9(mp 105-106°), sultine 12d(mp 64-65°), sultones 13c(mp 75-76°) and 13d(mp 84-85°).

4. This reaction bears some resemblance to the partial cyclization reported for the bromination of esters of Δ^4-cyclohexene-cis-1,2-dicarboxylic acids; M.M. Movsumzade, A.S. Kyozimov, A.L. Shabanov and Z.A. Safarova, Dokl. Akad. Nauk Az. SSR, 30 (6), 40 (1974); Chem. Abstr. 82 111649f (1975).

5. ^{13}C chemical shifts ($CDCl_3$) in ppm relative to TMS; δ 24.90 (two CH_3), 88.62 (C-O), 120.91 (=C-H), 156.60 (C-Br), 169.18 (C=O).

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