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FRAGMENTATION OF 6,6-DICHLORO-3-THIABICYCLO[3,1,0]HEXANE-3,3-DIOXIDES IN ACIDS. 2H-THIOPYRAN-1,1-DIOXIDES AND 4H-THIOPYRAN-4-ONES

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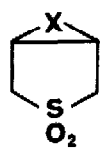
The fragmentation of bicyclic sulfolene adducts of type 1 are known to be facile concerted reactions leading usually to 1,4-dienes (2, X=CH_2, O, N-R).[1,2] When X=CCl_2 the primary fragmentation product rearranges, however, to the 1,3-diene 3.[1] Pentadienyl cations derived from dienes of type 3 have been suggested as intermediates in the formation of cyclopentenones



1

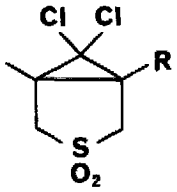
2

$CH_2=CH-CCl=CH-CH_2Cl$

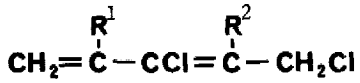
3

from dichlorocarbene adducts of allylic alcohols.[3] We therefore subjected adducts of type 1 (X=CCl_2) to decomposition in aqueous acids, hoping to expel sulfur dioxide and get the corresponding cyclopentenones by solvolysis of the intermediate dichlorides. Only in aq. acetic acid did we gather evidence that such a mechanism was operating; these results will be described elsewhere. We now report the results of fragmentation in hydrobromic[3] and hydrochloric acids, which led to thiopyran derivatives.

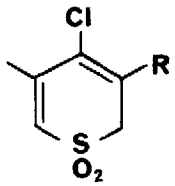
Adducts 4 and 5 are readily available from the corresponding sulfolenes by the use of phase-transfer catalysts in a biphasic chloroform-aq. NaOH system. Dry decomposition of 4 at 150-160° affords a mixture composed of the expected dichloride 6 (one geometrical isomer, bp 74°/20 mm; 60% yield) obtained by elimination of SO_2, and of the thiopyran derivative 7[4] (18%; Table 1), resulting from a concurrent elimination of HCl. Thiopyran dioxides are known to display considerable acidity, with formation of a highly stabilized 6π-electron anionic system.[5] Compound 7 was found to be readily soluble in aqueous bases, giving red solution of ion 8, from which 7 could be recovered upon acidification.



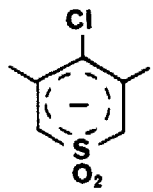
4 R=CH_3
5 R=H



6 R^1=R^2=CH_3
13 R^1=CH_3, R^2=H
14 R^1=H, R^2=CH_3

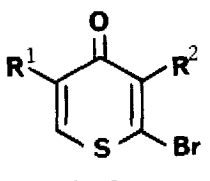


7 R=CH_3
18 R=H

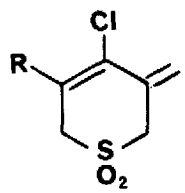


8

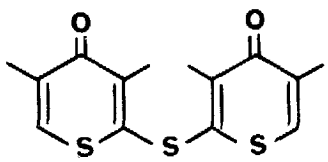
Fragmentation of 4 in 47% HBr (2 h reflux) afforded a mixture of four compounds which were, by order of elution from silica gel, the thiopyrone 9 (18-20%), 7 and 10 (12-14% altogehter) and the bis-thiopyrone 11 (15-18%).



9 R^1=R^2=CH_3
16 R^1=CH_3, R^2=H
17 R^1=H, R^2=CH_3

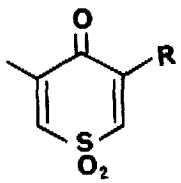


10 R=CH_3
19 R=H

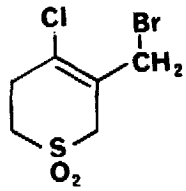


11

Thiopyrone 9 [λ max (EtOH) 244, 297, 304 nm (ε 9800, 14300, 14200);[6] ν max (KBr) 1595 cm^{-1} (very strong, broad);[7] ^{13}C nmr: C=O absorption at δ 176.5, in agreement with a polarized structure[6-9]] was hydrogenolized over Pd/C in methanol, in the presence of MgO, to the known 3,5-dimethyl-4H-thiopyran-4-one, with identical properties to those published.[10] Oxidation of the latter compound with m-chloroperbenzoic acid gave the sulfone 12. The same sulfone 12 was also obtained from 7 by oxidation with SeO_2 in ethanol. All three last-mentioned reactions were clean,



12 R=CH_3
20 R=H



15

high yield reactions. The bis-thiopyrone 11, with spectral properties similar to those of 9, could be obtained from the latter in a clean reaction with sodium sulfide in DMF.

The thiopyrans 7 and 10 are the only products formed when 4 is decomposed in boiling conc. HCl (2 hrs). They are produced in a ratio of 1:2 respectively and separated in a total 75-80% yield. The same equilibrium ratio is also attained when each is refluxed in conc. HCl for 1/2 hr. Both isomers lead to a mixture of 9 and 11 by reflux in 47% HBr. Thiopyran 10 is insoluble in aqueous

bases at room temperature, but warming in 2N NaOH converts it totally into 8, isomer 7 being recovered upon acidification.

The formation of the bromothiopyrone 9 is of interest both preparatively and mechanistically. It is obtained from readily available starting materials (three steps from dimethylbutadiene), and it carries a bromine, which is otherwise difficultly introduced into the thiopyrone ring.[8] The reduction of the sulfone in going from 7 to 9 seems to be unprecedented, but the presence of the bromine at the α-position suggests a Pummerer-type reaction, which could have occured twice, leading first to A then to B along accepted pathways.[11] At a certain stage along the line, X=Cl must have been replaced by X=OH and "B(OH)" could have then yield 9 by elimination of HBr.

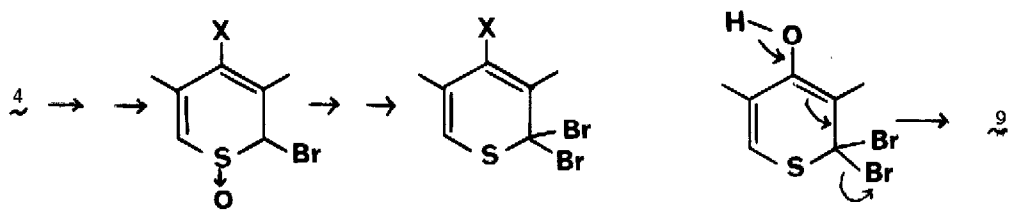


Table 1. Mp's and NMR data of thiopyran dioxides and thiopyrones.[a]

Compound	Mp, °C	2[b]	3	5	6	J[c]
7	74	3.92s,br(2)	2.16(6)		6.48s,br	
10	114	3.95s,br(2)	5.39(1), 5.90(1)[d]	2.07s,br(3)	3.85s,br(2)	
18	78	3.97s,br(2)	6.57m(1)	2.12m(3)	6.60s(1)	
19	125	3.97s,br(2)	5.47(1), 5.92(1)[d]	6.09t(1)	3.88d(2)	$J_{5,6}$=5
9	92		2.31s(3)	2.14d(3)	7.46q(1)	J_{allyl}=1
16	101		7.33s(1)	2.13d(3)	7.54q(1)	J_{allyl}=1
17	116		2.30s(3)	7.00d(1)	7.67d(1)	$J_{5,6}$=10.5
11	154		2.36s(6)	2.17d(6)	7.58q(2)	J_{allyl}=1
12	133	7.10s,br(2)[e]	2.08s(6)			
15	135	3.85s,br(2)	4.15s(2)[f]	3.20s,br(4)		

[a]Solution in $CDCl_3$; chemical shifts expressed in δ values. [b]Ring position of protons or methyls (number of protons in parenthesis). [c]Coupling constant in Hz. [d]Exocyclic methylene. [e]H-2 and H-6. [f]CH_2Br.

Fragmentation of the monomethyl derivative 5 in a series of parallel experiments led, in part, to rather dissimilar results. In the dry decomposition only a mixture of the two dichlorides 13 and 14 was obtained (80-85%) and no cyclic sulfone. (Compounds 6, 13 and 14, or their analogs, are of interest in synthesis, being reactive allylic chlorides and carrying a potential ketone function as a vinylic chloride). In 47% HBr the reaction was slower than for 4 and the major product, isolated in 13% yield, was the bromochloro compound 15, accompanied by small amounts of the thiopyrones 16 (2%) and 17 (1.1%). In conc. HCl, 5 yielded the two cyclic sulfones 18 (10%) and 19 (9%). Sulfone 20 was obtained by oxidation of 18 with SeO_2 in ethanol.

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