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PHOTOCHEMICAL AND ASSISTED CLEAVAGES OF HALO-9-THIABICYCLONONANES

Peter Heggison McCabe,* Chine Isaac de Jenga and Angus Stewart
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland.

Summary. A new, high-yield photodehydroiodination of 8 is contrasted with base and silver salt treatments of thiabicyclic halides, which mainly undergo replacements by substitution or elimination-addition.

A limitation of the peracid oxidative elimination[1] of bicyclic iodides is the large excess of reagent required. Halosulphones (6, 7 and 8) proved inert to other likely elimination conditions, including amines, silver salts and ozone, while 8 with KOH-MeOH gave a mixture of 9 (major) and 12 [inseparable by column or TLC; M^+/e 330 (12), 234 (9); δ[1] 5.1 (H-CI), 4.0 (dt, H-CO), 3.4 (s, CH_3), 3.2 (H-CS)]. In this reaction, the impossibility of S_N2 and the absence of sulphur assistance to an S_N1 process suggest that 9 arises by addition of MeOH sequentially to bridgehead alkenes[2] (e.g. 14), formed through elimination of the labile α-sulphonyl H atoms. This elimination-addition process was also observed in the formation of 11, m.p. 188-190° [57%; δ 4.4 (2 H-CO), 2.9 (2 H-CS), 1.17 (6 CH_3); ν[1] 1126, 1294 cm^{-1}] from $KOBu^t$-$HOBu^t$ treatment of 10, m.p. 160-162° [δ 6.0-5.5 (2 H-CO), 3.5 (2 H-CS); ν 1645, 1132, 1310 cm^{-1}], a peracid oxidation product of 4 (vide infra).

In contrast, halosulphides (1, 2 and 3) most readily undergo sulphur-assisted substitution[3] with nucleophilic bases or elimination-rearrangements[4] with hindered bases. Silver salts also effect substitution; thus, 1 and 3 reacted (96% and 47% respectively) with $AgNO_3$ in CH_2Cl_2-water to give the unstable dinitrate (4), m.p. 76-78° (decomp.) [M^+/e 264; δ 5.3-5.8 (2 H-CO), 2.9-3.2 (2 H-CS); ν ($CHCl_3$) 1635 cm^{-1}]. Similarly, 15 formed 16 [93%, oil; δ 5.9 (2 vinyl), 5.4 (H-CO), 3.3 (2 H-CS)], while, with $AgClO_4$ in Me_2CO, 15 furnished 17,[3] a hydrolysis product (water not rigorously excluded) of the putative perchlorate (18 $\rightleftharpoons$ 21).

A facile double elimination from 8 [halogen n - σ^* (EtOH)[5] 265 nm (log ε 3.07)], was achieved by photolysis in C_6H_6 through quartz which gave 22,[6] m.p. 165-167° (73%), in a pure state. C-I Homolysis is followed by rapid electron transfer[7] and the resulting carbocation (e.g. 23), in the absence of a nucleophile, eliminates a proton. Radical derived products[7] were not detected. Conversely, photolysis in C_6H_6 of 7, m.p. 195-197° [ν 1132, 1309 cm^{-1}; λ_{max}^{EtOH} ~ 220 nm (shoulder, log ε 2.77)], in which electron transfer after C-Br homolysis is less facile,[7] furnished products of photoreduction and elimination, viz. biphenyl, a 1:1 mixture of 13 and 19 [24%; M^+/e 254, 252, 250; δ 6.3-5.5 (vinyl), 5.0 (H-CBr)] and a 1:1 mixture (35%) of 5 and 20 from which 20,[3a] m.p. 245° [17%; δ 6.3-6.0 and 5.9-5.5 (vinyl)); ν 1113, 1282 cm^{-1}] was obtained on sublimation. 6[3a] Shows no UV absorption above 205 nm and was inert to irradiation in C_6H_6. Photolyses of 1, 2 and 3 resulted in multiple product formation; here, C-S bond cleavages are likely following excitation of the sulphur n $\rightarrow$ σ^* transitions.[8]

Satisfactory microanalyses have been obtained for 7, 8, 10 and 11.

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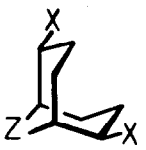
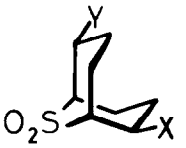
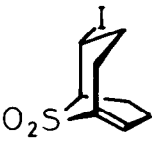


1 Z = S, X = Cl
2 Z = S, X = Br
3 Z = S, X = I
4 Z = S, X = ONO_2
5 Z = SO_2, X = H
6 Z = SO_2, X = Cl
7 Z = SO_2, X = Br
8 Z = SO_2, X = I
9 Z = SO_2, X = OMe
10 Z = SO_2, X = ONO_2
11 Z = SO_2, X = OBu^t



12 X = I, Y = OMe
13 X = Br, Y = H

15 Z = S, X = Cl
16 Z = S, X = ONO_2
17 Z = S, X = OH
18 Z = S, X = $OClO_3$
19 Z = SO_2, X = Br
20 Z = SO_2, X = H



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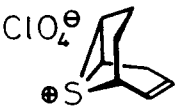

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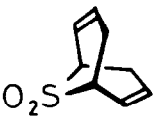

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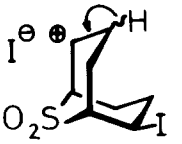

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