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Potassium t-Butoxide Dehalogenations of Bicyclic Dihalides

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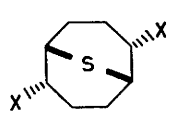
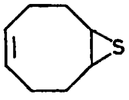
Summary Dehalogenation of bicyclic $\beta\beta'$-dihalogeno-sulphides with KOBu^t gives 7- and 8-membered cyclic diene monoepisulphides in good yields.

POTASSIUM T-BUTOXIDE debrominates and deiodinates aromatic halides[1,2] and, through carbene formation with solvent (CHCl$_3$), causes debromination of 5α,6β-dibromo steroids.[3] Dechlorination in the presence of KOBu^t has not been observed. We report a KOBu^t-promoted dehalogenation–rearrangement of sulphur-bridged bicyclic dihalides ($\beta\beta'$-dihalogeno-sulphides) which proceeds for chlorides as well as other halides.

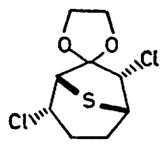
Reaction of the dichloride (**1**)[4,5] with KOBu^t (2·1 mol) in dimethyl sulphoxide (DMSO)[6] at room temperature, or better in HOBu^t [6] at 80 °C (3 h), furnished (68% yield as isolated) a halogen-free liquid alkene [δ(CDCl$_3$) 5·9 (m, 2H)], substantially pure by t.l.c. and n.m.r. spectroscopy (minor contaminant δ *ca.* 1·2). Purification was achieved, with *ca.* 50% loss, by vacuum distillation (65 °C at 1·2 mmHg) or column chromatography (Et$_2$O–light petroleum, 1 : 9) on neutral alumina.



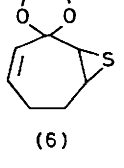
(1), X = Cl
(2), X = Br
(3), X = I



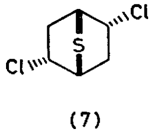
(4)



(5)



(6)

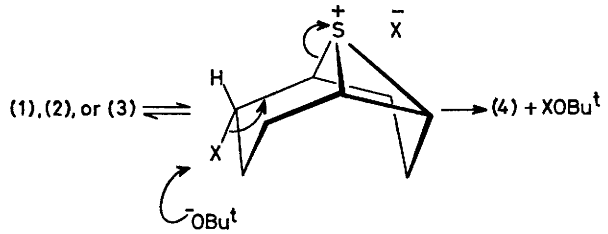


(7)

The product, C$_8$H$_{12}$S, showed HCS– (δ 2·90—3·21, m, 2H) and CH$_2$ resonances (δ 1·64—2·67, m, 8H) in the n.m.r. spectrum and was converted in high yield by treatment with Br$_2$–CCl$_4$ or I$_2$–CCl$_4$ into the bicyclic dihalides (**2**) or (**3**).[5] Its structural assignment as (**4**) was firmly established by comparison (spectra, mixed t.l.c. and g.l.c.) with an authentic sample (lit.[7] b.p. 44 °C at 0·3 mmHg) prepared by the addition of ISCN[8] to cyclo-octa-1,5-diene. It is noteworthy that KOBu^t treatment of (**1**) proceeds in higher yield than those reported for the preparation of (**4**) from cyclo-octa-1,5-diene by the S$_2$Cl$_2$[7] and ISCN[8] routes.

The dibromide (**2**) and di-iodide (**3**) react with KOBu^t in the same way as (**1**) but (**3**) gives a lower yield [51% for (**2**), 41% for (**3**)] of less pure product. This contrasts with aromatic iodides, dehalogenation of which takes place more readily.[1]

The formation of (**4**) in the KOBu^t treatment of (**1**), (**2**), and (**3**) demonstrates the suggested[9] sulphur participation in elimination reactions of 9-thiabicyclo[3.3.1]nonane derivatives, since the product in this case retains the three-membered structure of the intermediate episulphonium ion (**8**, Scheme). Elimination of positive halogen ion from (**8**) is effected by Bu^{t}O$^-$ [2] forming t-butyl hypohalite {which appears in our product mixture as the stable di-t-butyl peroxide [δ (CDCl$_3$) 1·17]} or, if DMSO is present, by MeSOCH$_2^-$,[1] the driving force being the relief of strain in the intermediate while rearrangement is facilitated by the approximate antiperiplanar alignment of the bonds which are cleaved.



(**8**)

Scheme

Support for this mechanism is derived from treatment of smaller-ring bicyclic dichlorides with KOBu^t. Compound (**5**)[10] reacts as above forming the sensitive episulphide (**6**) [m/e 184 (M^+), 152, and 151; $\delta(CDCl_3)$ 5·7 (m, 2H, vinyl), 4·0 (m, 4H, HC–O–), 2·9—3·3 (m, 2H, HCS–), and 2·3 (m, 4H, CH_2)] whereas 2,5-dichloro-7-thiabicyclo[2.2.1]heptane (**7**)[4] is inert because of the high degree of angle strain in the required intermediate.[4]

In view of the high yield with which SCl_2 adds to cyclic dienes[4,5,10,11] the above KOBu^t-promoted dehalogenation–rearrangement of the SCl_2 adducts offers a convenient method of preparing cyclic diene monoepisulphides which are difficult to obtain selectively by other routes[7,8,12] and demonstrates the principle, considered[13] less general, of converting $\beta\beta'$-dichloroalkyl sulphides into episulphides.

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