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NOVEL FORMATION OF THE 2,6-DIOXAADAMANTANE NUCLEUS

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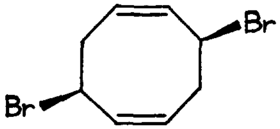
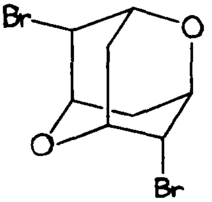
In connection with our series of reactivity studies[1] of the <u>syn</u>-dibromide (I) we sought to investigate the action of dichromate ion on (I) employing solvents known to enhance anion nucleophilicity. When a stirred solution of (I) in HMPT was treated with excess $Na_2Cr_2O_7.2H_2O$ for 3 days, and the mixture then worked up with dilute aqueous H_2SO_4, a highly crystalline compound (A), m.p. 136-137°, $C_8H_{10}Br_2O_2$ giving satisfactory microanalysis and M^+ 296, 298, 300 (approximately 1:2:1), was isolated in 65% yield.

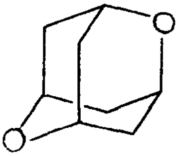


(I)

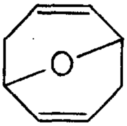


(II)

Attempts to effect dehydrobromination of product dibromide (A), even under severe conditions such as Bu^tOK in HMPT at 100° or lithium dicyclohexylamide in refluxing THF, led in each case to the recovery of (A) in high yield. The 100 Mz ^1H n.m.r. of (A) in $CDCl_3$, comprises a complex multiplet τ 5.5-5.9 (6H, C<u>H</u>-O and C<u>H</u>-Br protons) and a higher field set of resonances at τ 6.7-7.1 (2H) and τ 7.8-8.2 (2H) arising from the diastereotopic[2] protons of two equivalent methylene groups. The $Eu(DPM)_3$ shifted spectrum also implies molecular symmetry since only five distinct chemically shifted positions (2H each) were observed. On the basis, and by comparison of coupling constants with those reported[3] for 2,6-diheteroadamantanes, the syn-dibromo-2,6-dioxaadamantane structure (II), possessing C_2 symmetry, was proposed for compound (A); this was substantiated by $LiAlH_4$ reduction of (A) to 2,6-dioxaadamantane (III), m.p. 180-182°, identical to a sample independently prepared.†



(III)



(IV)

The synthetically useful double oxygen-bridging of (I) to give (II) almost certainly occurs in two distinct steps. Support for this view comes from the isolation of ca. 75% of the diene ether (IV), m.p. 32-34° (lit[4] 35-36°) when the above reaction is carried out employing neutral instead of acid work up conditions; the probable intermediacy of (IV) whose formation involves displacement of two Br^- ions may be inferred from the isolation of (II) in ca. 40% yield when pure (IV) is reacted with a solution of bromine in aqueous KBr.[5] Under the acid work up conditions normally employed, liberated Br^- is oxidised by Cr^{VI} to form Br_2 *in situ* which is then available for the second bridging step to give (II).

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† Prepared by $LiAlH_4$ reduction of the known syn-4,8-diiodo-2,6-dioxaadamantane (ref. 4).