A Novel Rearrangement of 2-Adamantyl 'Hypoiodite': a One Step Synthesis of Oxa-adamantane

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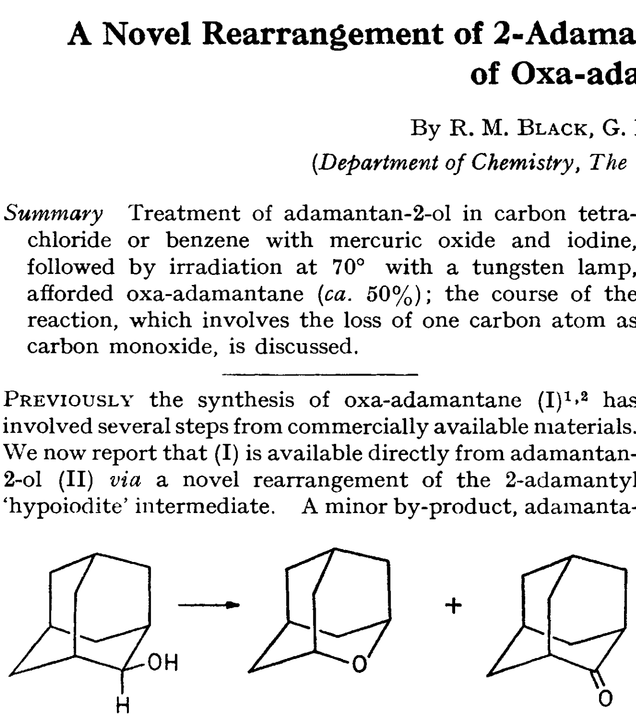
Summary Treatment of adamantan-2-ol in carbon tetrachloride or benzene with mercuric oxide and iodine, followed by irradiation at 70° with a tungsten lamp, afforded oxa-adamantane (*ca.* 50%); the course of the reaction, which involves the loss of one carbon atom as carbon monoxide, is discussed.

Previously the synthesis of oxa-adamantane (I)[1,2] has involved several steps from commercially available materials. We now report that (I) is available directly from adamantan-2-ol (II) *via* a novel rearrangement of the 2-adamantyl 'hypoiodite' intermediate. A minor by-product, adamantanone (III), is formed in a competing oxidative reaction, but is removed readily by column chromatography on alumina (eluant benzene–hexane, 2 : 1).

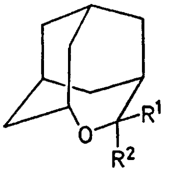


(II) (I) (III)

The thermal and/or photolytic reactions of (II) in benzene or carbon tetrachloride in the presence of excess of mercuric oxide (red or yellow) and iodine, yielded (I) and (III). The relative proportions of (I) and (III) were dependent upon the molar ratio of (II) : HgO : I_2, upon the temperature, and upon the nature of the light source (visible or near u.v.), but not upon the solvent. The conditions were optimised from a study of a large number of small scale reactions. Thus, irradiation (1 h) of a well stirred mixture of (II), mercuric oxide, and iodine (molar ratio 1 : 4 : 4) in dry carbon tetrachloride at 70° (N_2 atmosphere) with a 200 W tungsten lamp yielded (g.l.c.) (I) (54%), (III) (0·2%), and unchanged (II) (0·4%). In preparative scale reactions somewhat longer photolysis times were necessary, and (I) could be isolated in *ca.* 50% yield.

The formation of (I) from (II) appears to be limited to those cases in which the oxidant is $HgO–I_2$. Lemarchands *et al.* have reported[3] that mercuric oxide reacts with bromine or iodine to give $HgO(hal)_2$, and that silver oxide reacts with iodine or sulphur to yield Ag_2OI_2 or Ag_2OS. We have been unable to repeat the preparation of $HgOI_2$ so that a test of its efficacy in the above reactions has not proven possible. We have found that $ZnO–I_2$ and $CdO–I_2$ are ineffective in converting (II) into (I), whilst with $Ag_2O–I_2$ and $CuO–I_2$ the alcohol (II) was oxidised to the ketone (III). With $Pb(OAc)_4–I_2$, on the other hand, a 1 : 1 mixture of two as yet unidentified compounds were formed.

The unique feature of this reaction is the loss of the C-2 carbon atom of (II) as CO† with concomitant replacement by oxygen. The oxygen atom of (I) most probably originates from the hydroxy-oxygen of (II) rather than from the mercuric oxide. Thus, for example, when $Hg^{18}O$ was used,[4] analysis of (I) by g.l.c.–mass spectrometry indicated no incorporation (within experimental error) of the ^{18}O isotope. In all these reactions HgO was converted into HgI_2.

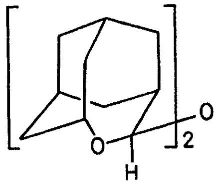


(IV)

a; $R^1 = I, R^2 = CH_2I$

b; $R^1 = R^2 = H$

c; $R^1 = H, R^2 = OH$



(IVd)

e; $R^1, R^2 = O$

f; $R^1 = H, R^2 = OHgI$

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† Detected by the deposition of metallic Pd from aqueous solutions of $PdCl_2$. A small amount of CO_2 was also detected, but is thought to arise from $HgCO_3$, which is a common contaminant of commercial HgO.

In view of our previous results on the oxidation of the methyl homologue of (II), 2-methyladamantan-2-ol, with either $Pb(OAc)_4$–I_2 or HgO–I_2 to give the di-iodo ether (IVa),[5] it seems likely that a similar ring expansion occurs in the present reaction. Compounds (III) and (IVb—e) are possible intermediates, and these reacted with HgO–I_2 under the standard (optimum) conditions to give (I) in the following respective yields: 0, 2, 36—38, 25, and 0%. Although (I) was obtained in fair yield from (IVc), its formation is complicated by direct oxidation to the lactone (IVe) and condensation to the acetal (IVd); neither product was detected in the original reactions based on (II). Although the precise nature of the species intermediate between (II) and (I) remains obscure, a structure of the type (IVf) appears to reconcile the various experimental observations.

A similar reaction of cyclohexanol with HgO–I_2 gave tetrahydropyran, albeit in very low yield (*ca.* 2%), so that conversions of the type (II) → (I) may be synthetically viable for other cyclic secondary alcohols where there is a lack of conformational flexibility, and where intramolecular H-abstraction reactions are inhibited.

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