Tetrahedron Letters, Vol.22, No.37, pp 3679 - 3680, 1981
Printed in Great Britain

0040-4039/81/373679-02$02.00/0

OXIDATIVE CLEAVAGES OF ALIPHATIC AND CYCLIC IODIDES

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Summary. 3 Undergoes elimination on treatment with m-chloroperbenzoic acid, performic acid or SO_2Cl_2/NaOCl, while iodine is retained in the novel peracid dehydrogenation of 9.

Oxidative elimination from non-aromatic iodides has been observed[1,2] with peracid but not under other conditions known to oxidise aryl iodides.

Conversion of 1 into its sulphone with excess m-chloroperbenzoic acid (m-CPBA) resulted in partial elimination. Thus, treatment of 1 with 1.1 and 3 mol m-CPBA[3] gave respectively 2 (85%), m.p. 155-158° [ν[4] 1045/1059 cm^{-1}; δ[4] 4.4-5.0 and 5.1-5.6 (both H-CI)] and 3 (82%), m.p. 199-202° [ν 1128 and 1305 cm^{-1}; δ 5.2 (H-CI)] but, with 6 mol, 5 (62%), m.p. 130-131° [δ 4.7-5.2 (H-CI), 5.4-5.9 and 5.9-6.3 (both vinyl)] was formed along with 3 (15%). With 10 mol m-CPBA, 8[5] (70%), m.p. 165-167°, was the major product accompanied by 5 (7%). By comparison, 1-iodoheptane with 2 mol m-CPBA gave n-heptanol (27%), di-n-heptyl ether (23%) and n-heptyl m-chlorobenzoate (trace) (cf. ref. 2). Ether formation in peracid oxidation of iodides has not been previously reported.

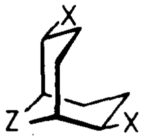
5 With m-CPBA-CH_2Cl_2 also gave 8, while with m-CPBA-MeOH, 8 and 6[6] [δ 3.3-3.4 (H-CO, H-CS), 3.3 (s, CH_3)] are formed. 5 Was inert to methanol in the absence of peracid.

Since 3 does not readily undergo elimination with bases or with silver nitrate,[7] the above results indicate involvement of intermediates with oxidised iodine atoms which can eliminate either by a syn-[2,3]-sigmatropic process or via a carbocation. The latter route is favoured by the formation of solvolysis product (6) and supported by the facile photodehydroiodination[7] of 3.

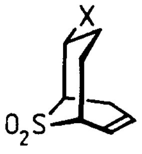
To generate a hypervalent iodine species in the absence of peracid, 3 was subjected to the conditions[8] of oxidation of iodobenzene to iodoxybenzene. Thus, 3 reacted with SO_2Cl_2 (replacing Cl_2[9]) at -78° followed by NaOCl (ca. 14%) to give 5 (30%) and 8 (61%), presumably via an iodoxy intermediate. Under similar conditions, iodocyclohexane underwent oxidative elimination and chlorination forming trans-1,2-dichlorocyclohexane.

Conversion of 1 to 8 was not achieved with peracetic acid. Here, formation of 4, m.p. 141-143° [ν 1128, 1310, 1740 cm^{-1}; δ 2.1 (s, CH_3), 3.3 (H-CS), 5.6 (H-CO)] indicates the rate of sulphur-assisted acetolysis of 1 to be faster than oxidation at iodine or sulphur. 3 Was inert to peracetic acid and to ozone but with performic acid it slowly gave 5.

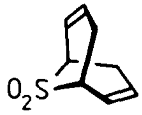
In an attempt to generate a stable hypervalent iodine compound, 9, m.p. 168-169° [ν 1107 and 1300 cm^{-1}; ^{13}C δ 23.8 (t), 29.3 (t), 44.5 (t), 54.2 (d, C-5) and 56.6 (s, C-1)], prepared (70%) by t-BuLi/I_2[10] treatment of 10, was reacted with 5 mol m-CPBA. In CH_2Cl_2 and in MeOH the major product (45% and 59% resp.) was 11, m.p. 172-175° [M^+/e 297.95257 (req. 297.95262);



1 Z = S, X = I
2 Z = SO, X = I
3 Z = SO_2, X = I
4 Z = SO_2, X = OAc



5 X = I
6 X = OMe
7 X = IO_2



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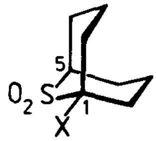
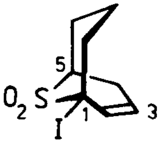


9 X = I
10 X = H



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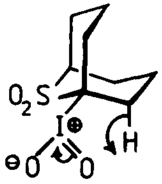

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ν 1125 and 1306 cm^{-1}; ^{13}C δ 19.7 (t), 31.0 (t), 32.4 (t), 43.2 (t), 52.4 (s, C-1), 52.4 (d, C-5), 128.6 (d) and 130.5 (d, both vinyl)]. Since substitution and direct elimination are disfavoured here, it is suggested that an initially formed hypervalent iodine compound, e.g. 12,[11] undergoes hydride transfer to a hindered carbocation which loses a proton, the bridgehead substituent being reduced in workup.[3]

Satisfactory microanalyses have been obtained for 2, 3, 4, 5 and 9.

We thank the S.R.C. for the award of a post-doctoral fellowship to C.I. de J. and A.S.

References

1. Y. Ogata and K. Aoki, *J. Org. Chem.*, 1969, 34, 3978; N.R.A. Beeley and J.K. Sutherland, *J.C.S. Chem. Comm.*, 1977, 321; R.C. Cambie, D. Chalmers, B.G. Lindsay, P.S. Rutledge and P.D. Woodgate, *J.C.S. Perkin I*, 1980, 822.
2. H.J. Reich and S.L. Peake, *J. Amer. Chem. Soc.*, 1978, 100, 4888.
3. Reactions in $CHCl_3$ or CH_2Cl_2 at 0°, filtered, washed with $Na_2S_2O_5$, NaOH, water and dried ($MgSO_4$).
4. IR data for KBr discs. NMR spectra in $CDCl_3$/TMS.
5. E. Cuthbertson and D.D. MacNicol, *J.C.S. Perkin I*, 1974, 1893.
6. Sample contaminated with 8 and the configuration at C-6 is undefined.
7. P.H. McCabe, C.I. de Jenga and A. Stewart, *Tetrahedron Letters*, subsequent paper.
8. M.W. Formo and J.R. Johnson, *Org. Syn.*, Coll. Vol. 3, 1955, 486.
9. H.J. Lucas and E.R. Kennedy, *ibid*, 482.
10. E.J. Corey and E. Block, *J. Org. Chem.*, 1969, 34, 1233.
11. Direct NMR observation, at low temperature, of the intermediates in the m-CPBA reactions of 3 and 9 was hampered by precipitation.

(Received in UK 29 June 1981)