Tetrahedron Letters No.23, pp. 2181-2183, 1967. Pergamon Press Ltd. Printed in Great Britain.

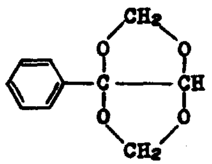
1-ARYL-2,4,6,8-TETRAOXABICYCLO[3.3.0]OCTANES FROM AROMATIC METHYL KETONES, DIMETHYL SULFOXIDE AND AN ACID CHLORIDE

RYOHEI ODA and YOSHIYUKI HAYASHI
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan

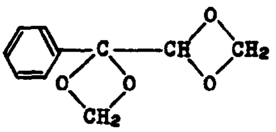
(Received 30 January 1967; in revised form 13 March 1967)

We wish to report a novel method of oxidation of methyl radicals of aromatic methyl ketones with formation of new compounds, 1-aryl-2,4,6,8-tetraoxabicyclo[3,3,0]octanes using dimethyl sulfoxide(DMSO) and certain acid chlorides.

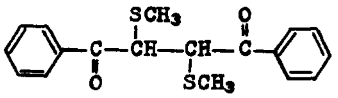
In general the reaction was carried out by adding benzoyl chloride(0.4 mole) to a solution of a aromatic methyl ketone(0.2 mole) in DMSO(1 mole) at 0-15°. The reaction mixture was kept at room temperature overnight, poured into ice, treated with cold 20% aqueous sodium hydroxide(0.84 mole) solution and finally extracted with chloroform. Thus, acetophenone undewent oxidation and acetal formation to give 45% of 1-phenyl-2,4,6,8-tetraoxabicyclo[3,3,0]octane(Ia). Traces of methyl phenacyl sulfide and phenyl glyoxal were detected in the reaction mixture. A small amount of formaldehyde dimethyl mercaptal and dimethylthio-dibenzoylethane(II)(mp 208°) were also isolated. By substituting benzoyl chloride by acetyl chloride and butyric acid chloride, 12% and 31% of Ia were obtained respectively.



Ia



Ib



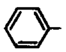
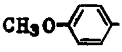
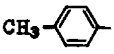
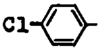
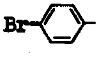
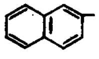
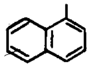
II

The structural assignment of the compound Ia was substantiated by elemental analysis, molecular weight, infrared (no C=O streching, two C-O-C bands at 1070 and 1115cm^{-1}, C-H streching at 2760cm^{-1}), nmr (the chemical schifts are reported in τ units)(aromatic protons, a multiplet at 2.36-2.83; methine proton, a singlet at 4.58; methylene protons, two singlets at 4.69 and 4.71) and acid hydrolysis to phenyl glyoxal monohydrate and formaldehyde. It seems probable that the observed singlets of the nmr of the methylene protons originate from an AX pattern and this spectrum supports dioxolane structure of Ia(1). Since all of the five aliphatic protons in structure Ib are in a different environment, the structure Ib is less possible as an alternative to the structure Ia (benzilidene formal was not isolated from the reaction mixture of benzaldehyde, benzoyl chloride and DMSO).

Similar tetraoxabicyclooctanes were obtained from other methyl ketones.

TABLE 1

1-Aryl-2,4,6,8-tetraoxabicyclo[3.3.0]octanes[a)]

Ar-	Yield(%)	Mp (°C) Bp (°C/mm)[b)]	N.m.r. in CCl_4[c)]
	45	54-5 100-2/4	2.36-2.83(m), 4.58(s), 4.69(s) 4.71(s); 5:1:2:2
	46	98-9 135-40/5	2.54-3.27(m), 4.64(s), 4.70(s), 4.72(s), 6.24(s); 4:1:2:2:3
	40	107-8 116-8/4	2.76(q), 4.62(s), 4.69(s), 4.71(s), 7.65(s); 4:1:2:2:3
	41	86-7 130-4/6	2.45-2.80(m), 4.61(s), 4.68(s), 4.72(s); 4:1:2:2
	38	91-2 139-43/5	2.39-2.77(m), 4.62(s), 4.69(s), 4.73(s); 4:1:2:2
	36	110-1	1.88-2.75(m), 4.51(s), 4.61(s), 4.65(s); 7:1:2:2
	3	165/4	1.80-2.83(m), 4.11(s), 4.70(s), 7:1:4

a) Correct elemental analyses were obtained.

b) Boiling point of the crude product.

c) m; multiplet, s; singlet, q; quartet.

On the other hand, propiophenone gave methyl 1-benzoylethyl sulfide in 45% and cyclohexanone gave 2-methylthio-2-cyclohexenone(bp 110°/5, nmr of vinyl proton, a triplet at 3.46) in 27%yield. The nmr spectra of the dioxolanes obtained are shown in Table 1. IR spectra of the dioxolanes show absorptions of dioxolane type ether linkage and a weak and sharp absorption at 2760cm^{-1}.

Some tentative conclusions about the mechanism of these reactions can be drawn. The dioxolane Ia(36%) was isolated from the reaction mixture of phenyl glyoxal, paraformaldehyde and concentrated hydrochloric acid in chloroform, although such simple dioxolane formation was not reported in literature. Carboxylic acid chlorides are known to react with sulfoxides to give α-chlorosulfides(2). Evidence that methane sulfenyl chloride would be formed from the reaction of DMSO with chloromethyl methyl sulfide, and that the oxidation of acetophenone proceeds via α-chloro-α-methylthio-acetophenone(III) was provided by following experiments. The reaction of olefins with chloromethyl methyl sulfide in DMSO gave methane sulfenyl chloride addition compounds in 40-60%. The oxidation of acetophenone was also catalysed by chloromethyl methyl sulfide or methane sulfenyl chloride. The reaction of acetophenone or methyl phenacyl sulfide with methane sulfenyl chloride in carbon tetrachloride gave III besides other compounds. Pure III(bp 141°/6, obtained from diazoacetophenone and methane sulfenyl chloride) in DMSO was oxidised within one hour to give Ia(28%), phenyl glyoxal(34%) and benzoylformic acid(30%).

Further mechanistic studies of these reactions are in progress and more complete details will be reported later.

References

1). T.A.Crabb, R.C.Cookson, Tetrahedron Letters, 679 (1964).

2). F.G.Bordwell, B.M.Pitt, J.Am.Chem.Soc., **77**, 572 (1955).