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OXIDATION OF α-HYDROXYKETONES WITH TRIPHENYLANTIMONY DIBROMIDE AND ITS CATALYTIC CYCLE

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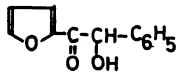
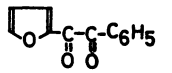
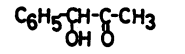
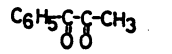
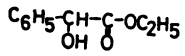
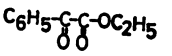
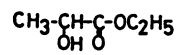
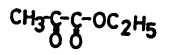
α-Hydroxyketones were oxidized into α-diketones with triphenylantimony dibromide in the presence of two equiv. of base. Antimony-catalyzed debromination and oxidation cycle was devised for the system of ethyl 2,3-dibromo-3-phenylpropionate and α-hydroxyketones.

In connection with investigations on hypervalent molecules,[1] the synthetic utilization of the expectative unique reactivity of these compounds has attracted much attention recently.[2] In a preceding communication, we described chemoselective debromination of phenacyl or benzylic bromides with tertiary stibine, where a crucial role of hypervalent antimony(V) intermediate was invoked.[3] We wish to report herein that α-hydroxyketones are smoothly oxidized into the corresponding α-dicarbonyl compounds by using triphenylantimony dibromide in the presence of two equiv. of base. The results of oxidation are summarized in Table 1. A typical procedure is as follows. To a solution of furoin (102 mg, 0.53 mmol) dissolved in dichloromethane (2.7 ml) was added triphenylantimony dibromide (272 mg, 0.53 mmol) and DBU (162 mg, 1.06 mmol), successively. The mixture was stirred at room temperature for 20 h. After removal of solvent, thin layer chromatographic separation on silica gel (hexane-ethyl acetate; 7:3) afforded 95 mg of furoil (94%) and 158 mg of triphenylstibine (84%) (Entry 5).

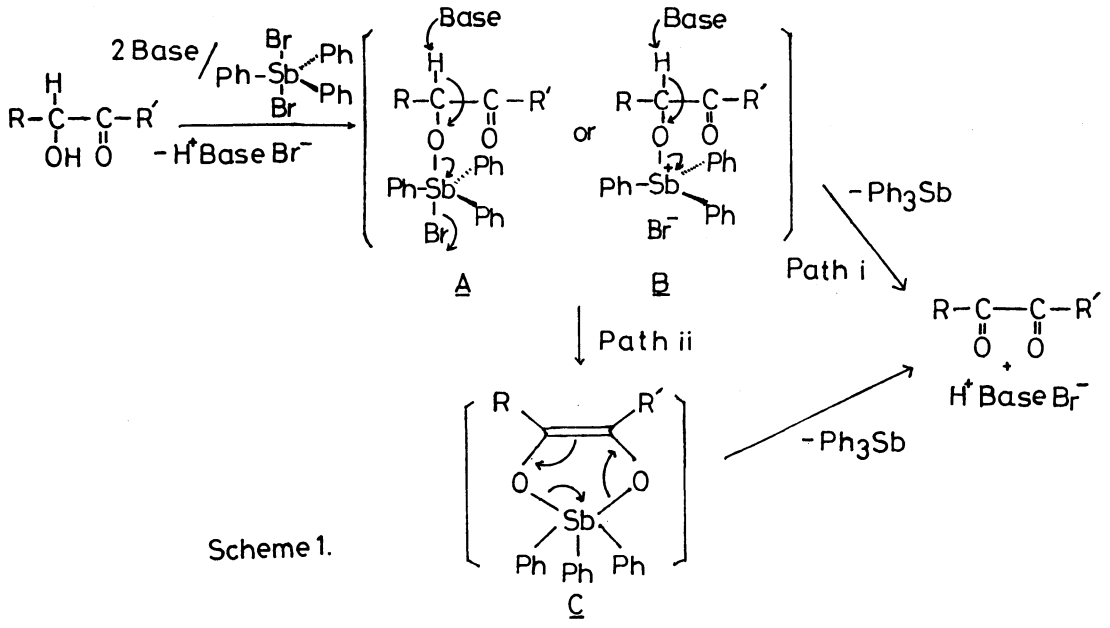
It should be noted that triphenylstibine is produced during the oxidation and two equiv. of base are necessary where the choice of base is dependent upon the acidity of carbinyl proton in α-hydroxy carbonyl compounds (Entries 3, 4, and 5). In the absence of α-hydroxyketones, triphenylantimony dibromide reacted with DBU or triethylamine to give amino-antimony complex very slowly relative to the above reaction (ca. 1/10). The structure of the complex is obscure but it could oxidize benzoin considerably slower (ca. 1/3) as compared with the present procedure.

Although detailed mechanistic investigations remain to be explored, the oxidation is rationalized at present by the sequence that the base catalyzed ligand exchange at apical position from bromine to oxygen took place to give hypervalent antimony (A) or stibonium bromide (B), which is followed by deprotonation at carbinyl position to afford α-diketone directly with loss of triphenylstibine (path i) or via hypervalent antimony (C) (path ii) as shown in Scheme 1.

Table 1. Oxidation of α-Hydroxyketones and Its Related Compounds with Tertiary Antimony Dibromide in the Presence of Base

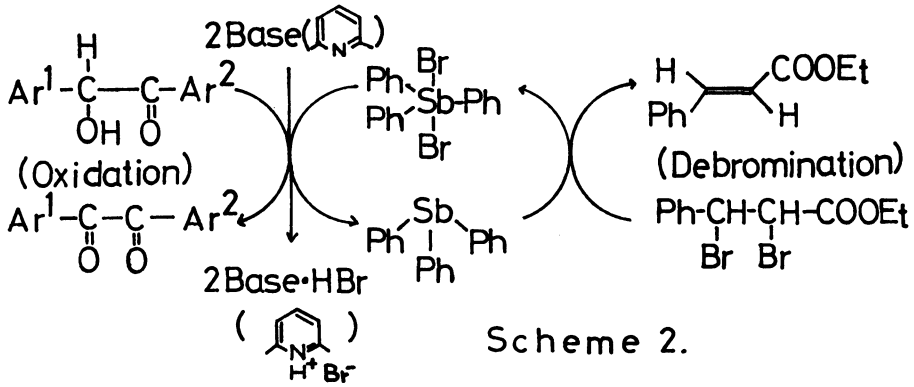
Entry	Compound	R_3SbX_2	Base	Reaction conditions (solvent, r.t., time)	Product[a),b),c)] (α-diketone/R_3Sb; yield/ %)
1	benzoin	Ph_3SbBr_2	2 x Et_3N	$CDCl_3$, 17 h	benzil; 98 /Ph_3Sb; 60
2	toluoin	Me_3SbCl_2	2 x DBU	$CDCl_3$, 19 h	tolil; 89 /(Me_3Sb)[d)]
3[e)]	furoin	Ph_3SbBr_2	2 x Et_3N	$CDCl_3$, 2 d	
4	furoin	Ph_3SbBr_2	1 x DBU	CH_2Cl_2, 2 d	furoil; 34 /Ph_3Sb; 33
5	furoin	Ph_3SbBr_2	2 x DBU	CH_2Cl_2, 20 h	fuloil; 94 /Ph_3Sb; 84
6	2,2'-thenoin	Ph_3SbBr_2	2 x DBU	CH_2Cl_2, 20 h	2,2'-thenil; 61 /Ph_3Sb; 65
7		Ph_3SbBr_2	2 x DBU	CH_2Cl_2, 18 h	 ; 94 /Ph_3Sb; 81
8		Ph_3SbBr_2	2 x DBU	CH_2Cl_2, 18 h	 ; 44 /Ph_3Sb; 74
9		Ph_3SbBr_2	2 x DBU	CH_2Cl_2, 2 h	 ; 65 /Ph_3Sb; 65
10		Ph_3SbBr_2	2 x DBU	CH_2Cl_2, 1 d	 ; 46 /Ph_3Sb; 26

a) Isolated yield by TLC on silica gel (hexane-ethyl acetate; 7-8:2-3). b) Products were all known and identified by NMR, IR, and Mass spectra as well as by direct comparison with authentic sample. c) Spectral data were fully consistent with the assigned structure. The selected data are shown in Ref. 6. d) As trimethylstibine is a very volatile material, it was not isolated. e) Furoin was recovered quantitatively and amino-antimony complex was formed.



Scheme 1.

On the other hand, the fact that the oxidation of α-hydroxyketones with Ph_3SbBr_2 led to the liberation of triphenylstibine in high yield suggested that the reaction could be carried out using a catalytic amount of Ph_3Sb or Ph_3SbBr_2 in the presence of a bromine donor (ethyl 2,3-dibromo-3-phenylpropionate)[3] and an adequate base. Actually, toluoin was oxidized to tolil in 97% yield with a catalytic amount of Ph_3SbBr_2 in the presence of a molar amount of ethyl 2,3-dibromo-3-phenylpropionate and bimolar amount of 2,6-lutidine. The oxidation rates depend upon the amount of Ph_3Sb as shown in Fig. 1. The same catalytic oxidation could be realized for both benzoin and 1-(2-furyl)-2-keto-2-phenylethanol in excellent yield.[4] The debromination and oxidation cycle did not take place at all in the absence of antimony compound (Ph_3Sb or Ph_3SbBr_2) under the same conditions. A probable reaction sequence for the antimony-catalyzed debromination-oxidation cycle is illustrated in Scheme 2.



Scheme 2.

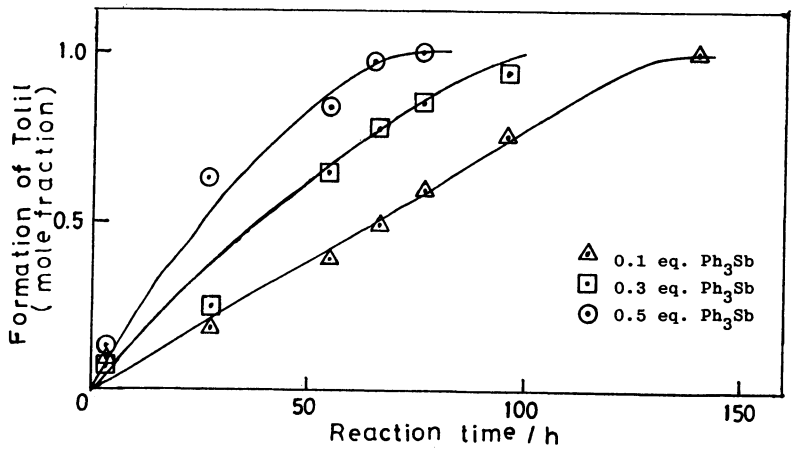


Fig. 1. Antimony-catalyzed oxidation of toluoin using various amount of Ph_3Sb.

Although there are a wide variety of methods of oxidation of α-hydroxyketones to α-diketones,[5] the present finding is an attractive one from the view point of chemistry of hypervalent molecules as well as synthetic methodology.[1,2]

References

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3) K. Akiba, A. Shimizu, H. Ohnari, and K. Ohkata, Tetrahedron Lett., 26, 3211 (1985). Triphenylantimony dibromide is easily prepared by treatment of Ph_3Sb with Br_2 and is trigonal bipyramidal containing hypervalent apical bonds; J. M. Keck and G. Klar, Z. Naturforsch, 276, 591 (1972); A. F. Well, Z. Krist., 99, 367 (1938).

4) Antimony-catalyzed debromination-oxidation cycle: To a mixture of ethyl 2,3-dibromo-3-phenylpropionate (40 mg, 0.12 mmol), toluoin (29 mg, 0.12 mmol), and 2,6-lutidine (26 mg, 0.24 mmol) in 0.4 ml of $CDCl_3$ solution was added a catalytic amount of triphenylantimony dibromide (6.1 mg, 0.012 mmol). The mixture was allowed to stand at 70 °C for 3 d. Thin layer chromatographic separation on silica gel (hexane-ethyl acetate; 8:2) gave 20 mg of ethyl cinnamate (95%) along with 28 mg of tolil (97%). By a similar method to the above, benzoin and 1-(2-furyl)-2-keto-2-phenylethanol were oxidized into benzil (83%) and 1-(2-furyl)-2-phenylethanedione (96%), respectively.

5) a) $Cu(SO_4)_2$: N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, J. Am. Chem. Soc., 71, 2997 (1949); b) Ac_2O, Me_2SO: M. VanDyke and N. D. Pritchard, J. Org. Chem., 32, 3204 (1967); c) $NaBiO_3$: N. Vinot, Bull. Soc. Chim. Fr., 1971, 2708; W. Rigby, J. Chem. Soc., 1951, 793; d) H_2CrO_4: T. -L. Ho, Chem. Ind., 1972, 807; e) Ph_3PBr_2: T. -L. Ho, Synthesis, 1972, 697; f) $Yb(NO_3)_3$: P. Girard and H. B. Kagan, Tetrahedron Lett., 1975, 4513; g) $SbCl_5$-DMSO: J. Yamamoto, Bull. Chem. Soc. Jpn., 58, 470 (1985).

6) Bis(4-methylphenyl)ethanedione; mp 99-100 °C; ^1H NMR (δ, $CDCl_3$) 2.43 (s, 6H), 7.29 (d, J=8.4 Hz, 4H), and 7.86 (d, J=8.4 Hz, 4H); lit.[5e] mp 103-104 °C. Bis(2-furyl)ethanedione; mp 163-165 °C; ^1H NMR (δ, $CDCl_3$) 6.64 (d.d, J=1.6 and 3.6 Hz, 2H), 7.64 (d.d, J=0.7 and 3.6 Hz), and 7.78 (d.d, J=0.7 and 1.6 Hz, 2H); lit. mp 165-166 °C, W. W. Hartman, J. Am. Chem. Soc., 55, 1228 (1933). 1-Phenyl-1,2-propanedione; bp 112-114 °C/20 mmHg; ^1H NMR (δ, $CDCl_3$) 2.51 (s, 3H), 7.49-7.59 (m, 3H), and 7.69-8.06 (m, 2H); lit. bp 114-116 °C/20 mmHg, W. W. Hartman and L. J. Roll, Org. Synth. Coll. Vol. 3, 20. 1-(2-Furyl)-2-phenylethanedione; mp 40-41 °C; ^1H NMR (δ, $CDCl_3$) 6.61 (d.d, J=1.8 and 3.5 Hz, 1H), 7.37 (d.d, J=0.7 and 3.5 Hz, 1H), 7.48-7.65 (m, 3H), 7.75 (d.d, J=1.8 and 0.7 Hz, 1H), and 7.98-8.07 (m,2H); lit. mp 41 C, E. Fischer, Ann., 211, 229 (1882). Bis(2-thienyl)ethanedione; mp 79-80 °C; ^1H NMR (δ, $CDCl_3$) 7.19 (d.d, J=4.0 and 4.8 Hz, 2H), 7.83 (d.d, J=1.1 and 4.8 Hz, 2H), and 8.07 (d.d, J=4.0 and 1.1 Hz); lit. 83-84 °C, S. Z. Cardon and H. P. Lankelma, J. Am. Chem. Soc., 70, 4248 (1948).

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