BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1502—1506 (1967)

The Photochemical Oxidation Reaction of Benzylic Alcohols in Dimethyl Sulfoxide

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(Received December 19, 1966)

A new photochemical oxidation reaction of benzylic alcohols has been developed by using DMSO as a solvent. The oxidation, which has been performed in an oxygen atmosphere, can be carried out under neutral conditions at room temperature. Detailed studies on the role of DMSO as the solvent were carried out by using benzyl alcohol; it has been established that, in the photooxidation in DMSO, the uptake of oxygen was much facilitated compared with the reactions using other solvents, and also that, the benzaldehyde formed was well protected from further oxidation by a complex formation. Three secondary benzylic alcohols gave moderate yields of the corresponding ketones. The same experiments on ten substituted benzyl alcohols have revealed that the presence of an electron-releasing group facilitates the oxidation affording benzaldehydes, whereas an electron-attracting group retards it.

Of the numerous reactions using dimethyl sulfoxide (DMSO),[1] the oxidation reaction of alcohols to aldehydes or ketones has been most extensively studied. Besides the Kornblum reaction[2] of tosylate and the related reaction of chloroformate,[3] a DMSO-dicyclohexylcarbodiimide-orthophosphoric acid[4] or a DMSO-acid anhydride mixture[5] has been successfully used to obtain carbonyl compounds, especially aldehydes from primary alcohols. It has been well established that these reactions proceed through a common intermediate, the alkoxysulfonium compound $RR'CHOS^+(CH_3)_2$, which decomposes into a carbonyl compound and dimethyl sulfide.

Recently, Traynelis and his co-worker[6] have described a different type of oxidation reaction of benzyl alcohols, in which a DMSO solution of

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[5] J. D. Albright and L. Golden, *ibid.*, **87**, 4214 (1965).

[6] V. J. Traynelis and W. L. Hergenrother, *ibid.*, **86**, 298 (1964).

the respective alcohol was heated at reflux under a stream of air. A peroxide effect clearly demonstrated the occurrence of a radical reaction in this case. The same type of oxidation reaction was also encountered when benzyl alcohols were heated with DMSO at 160—180°C.[7,8] In these thermal oxidation reactions, DMSO served as an oxidant, and dimethyl sulfide was isolated in certain cases.

This paper will report still another type of oxidation reaction of benzylic alcohols. As has been described in a preliminary paper,[9] the new method consists of the use of DMSO as a solvent for the photochemical oxidation by means of molecular oxygen under neutral conditions at room temperature. In contrast to both the above reactions, DMSO was found to be recoverable in this photooxidation reaction.

Experimental

Materials. *p*-Methoxy-, *p*-methyl-, and *p*-isopropylbenzyl alcohols and 9-hydroxyfluorene were obtained by the reduction of the corresponding carbonyl compounds with lithium aluminum hydride or sodium borohydride. *m*-Methyl, 2, 4-dimethylbenzyl alcohols and 1-hydroxymethylnaphthalene were obtained from the corresponding chloromethyl[10] or bromomethyl compounds by converting them to acetates, followed by hydrolysis.[11] Nitrobenzyl alcohols were obtained by the Cannizzaro reaction of the corresponding aldehydes. All the compounds, including those from a stock, had satisfactory physical constants. The purified materials were checked by gas chromatography. DMSO was dried over potassium hydroxide and distilled over calcium hydride under reduced pressure.

Irradiation Reaction. The irradiation was carried out using a 1000 W mercury arc lamp (Wako Denki Co., HBC-1000) mounted in a water-cooled Pyrex jacket. A solution of an alcohol and DMSO (1 : 5 mol ratio) was placed in a Pyrex vessel connected with a buret in order to measure the oxygen uptake. During the irradiation, the vessel was vigorously shaken. For the experiments in a quartz cell, a different apparatus, with the same lamp as that described above mounted in a circulated-water jacket, was used. When the irradiation was over, the DMSO solution was either subjected directly to gas chromatography or titration, or diluted with water and extracted with isopropyl ether or conventional analyses.

Gas Chromatography. A Yanagimoto GCG 220-type, apparatus equipped with Carbowax 1500 on a Celite column, was used. The column was selected following a recent report on the gas chromatography of sulfoxides.[12]

Results and Discussion

The Photochemical Oxidation of Some Benzylic Alcohols in DMSO. The irradiation reaction of secondary benzylic alcohols in DMSO in the presence of oxygen afforded a moderate yield of the corresponding ketones, as is summarized in Table 1. The ketones obtained in this way are acetophenone, benzophenone, and fluorenone. In the case of benzhydrol oxidation (Pyrex filter), where a 38.2% yield of benzophenone was secured, bis(diphenylmethyl) ether was isolated as a byproduct in a 29.2% yield. In contrast to this, irradiation in a quartz vessel resulted in the formation of benzopinacol as the sole isolable product.

The Photochemical Oxidation of Benzyl Alcohol in DMSO and Other Solvents. Since the photochemical oxidation reaction of benzylic alcohols in DMSO by means of molecular oxygen seemed to be rather general, several benzyl alcohols were subjected to a similar photo-oxidation in the hope of developing a selective oxidation method for obtaining aldehydes. The detailed studies were carried out using benzyl alcohol (Table 2).

A very rapid absorption of oxygen occurred when a DMSO solution of benzyl alcohol was irradiated, and an appreciable amount of benzaldehyde was isolated from the reaction mixture by distillation. A solution of 0.5 mol of benzyl alcohol and 2.5 mol of DMSO absorbed 0.27 mol of oxygen during 13.5 hr. The reaction mixture, as analyzed by gas chromatography, was found to consist of benzaldehyde, DMSO, benzyl alcohol, and dimethyl sulfone (7.1% from DMSO), in the order of the retention time. Benzoic acid was either isolated or titrated. In one experiment, in which a 1 : 2 solution of benzyl alcohol and DMSO was used, the reaction mixture was analyzed by the gas chromatography of aliquots removed at one-hour intervals for over 20 hr. Some of the results are shown in Table 2. The yield of benzaldehyde reached a maximum of 48% in 14 hr.

When benzyl alcohol alone was irradiated, only a very slow uptake of oxygen occurred, giving a 9.6% yield of oxidation products (Table 2). Other solvents, including dimethylformamide, acetonitrile and ligroin (bp 75—120°C) did not facilitate the oxidation reaction (Table 3). Benzene, nitrobenzene and pyridine were also not effective as the oxygenation solvent.

Air was passed through a 1 : 2 solution of benzyl alcohol in DMSO, the solution being exposed to the sun (Tokyo summer) for 12 days. On examination, 7% of benzaldehyde was detected, while

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TABLE 1. THE PHOTOCHEMICAL OXIDATION REACTION OF BENZYLIC ALCOHOLS IN DMSO

Benzylic alcohol,a)	mol	DMSO mol	Irradiation time,b) hr	Oxygen uptake Mole ratio O_2/alcohol	Yield (%) of carbonyl compound	Recovered alcohol, %
1-Phenylethanol	0.2	1.0	20	0.53	30.4f)	
	0.1	0.37	25,c) 48c)	—e)	45.7,f) 53.0f)	
Benzhydrol	0.1	0.5	12	0.55	38.2	19
	0.1	0.5	35	0.77	61.5	
	0.1	0.5	7c)	—e)	—g)	
9-Hydroxyfluorene	0.021	0.11	15	—e)	57	20.5
Benzyl alcohol						
p-Methoxy-	0.1	0.5	6.5d)	0.60	37.5h)	
m-Methyl-	0.078	0.38	14.5	0.61	35.1f)	
p-Methyl-	0.1	0.5	6.75	0.63	45.5h)	
p-Isopropyl-	0.083	0.42	10	0.53	37.7f)	
2,4-Dimethyl-	0.1	0.5	9		23.6f)	
p-Bromo-	0.03	0.15	15.5	0.61	9.1f)	37.4
	0.011	0.11	16c)	—e)	15.4	
p-Chloro-	0.2	1.0	12	0.02		88.7
m-Nitro-	0.1	1.0	12	0.02		64.6
p-Nitro-	0.1	0.48	13	0.02	1.6f)	87.3
	0.006	0.056	16c)	—e)		56
1-Hydroxymethylnaphthalene	0.1	0.5	15	0.43	23.2f)	

a) A 1 : 5 mixture of benzylic alcohol in DMSO was used except for those experiments in which either the alcohol was less soluble or a small amount of substrate was subjected.

b) Unless otherwise stated, the irradiation was performed in a Pyrex vessel.

c) A quartz vessel was used.

d) A glass plate filter was inserted.

e) Oxygen uptake was not determined.

f, h) The yield of the carbonyl compounds was determined either as 2,4-dinitrophenylhydrazonef) or as sodium bisulfite addition compound.h)

g) Only a pinacol formation was noticed.

TABLE 2. THE PHOTOCHEMICAL OXIDATION REACTION OF BENZYL ALCOHOL IN DMSO

Exp. No.	$C_6H_5CH_2OH$ mol	DMSO mol	Irradiation time, hr	Oxygen uptake Mole ratio, O_2/alc.	Result,b) %		
					$C_6H_5CH_2OH$	C_6H_5CHO	C_6H_5COOH
1	0.5	2.5	13.5	0.54	19.1	48.8	13.6
2	0.1	0.5	24.3	1.26	12.0	39.2	48.8
3a)	0.2	0.4	1.25	0.08	90.4	9.6	0
			7	0.53	52.2	32.8	15
			14	0.89	24.9	48.1	27
			20	1.34	16.7	38.2	45
4	1.0	None	14	0.11	69.8	7.8	1.8

a) Representative data from 20 hr irradiation experiments, which were checked at one-hour interval.

b) The results are expressed in yields for Exps. 1, 2 and 4, while for Exp. 3 they are expressed in a product ratio.

TABLE 3. THE PHOTOCHEMICAL OXIDATION REACTION OF BENZYL ALCOHOL IN VARIOUS SOLVENTS

$C_6H_5CH_2OH$, mol	Solvent, mol	Irradiation time, hr	Oxygen uptake Mole ratio, O_2/alc.	C_6H_5CHO	C_6H_5COOH
0.1	DMF, 0.5	5	0.039	—a)	0.02
0.1	Acetonitrile, 1.0	6	0.030	—a)	0.02
0.1	Ligroin (90 g)	12	0.14	8.0	

a) A minute quantity was detected by gas chromatography.

TABLE 4. THE PHOTOCHEMICAL OXIDATION REACTION OF BENZALDEHYDE

C_6H_5CHO, mol	Solvent, mol	Irradiation time, hr	Oxygen uptake Mole ratio, O_2/C_6H_5CHO	Recovered C_6H_5CHO, %
0.2	None	0.25[a,b]	0.12	
0.1	DMSO 0.5	11	0.37	64.0
0.1	DMSO 0.9	8[b]	0.13	83.0[c]
0.1	DMSO 1.0	9	0.14	84.7
0.1	Ligroin (75 g)	2.25	0.48	

a) Rapidly formed benzoic acid, which separated out on the wall of the vessel, inhibited further irradiation.
b) A glass plate filter was inserted.
c) By the titration, benzoic acid was found to be formed in a 9.8% yield.

no reaction occurred in the control experiments which were performed in the dark.

The fact that DMSO protects benzaldehyde from further oxidation was confirmed by carrying out irradiation studies on benzaldehyde (Table 4). It is a well-known fact that the oxygenation of benzaldehyde is much facilitated by light. Yet in DMSO more than 80% of the benzaldehyde was found to be recoverable even after irradiation for 8—9 hr in an oxygen atmosphere. The insertion of a glass plate as a light filter did not affect the reaction. In a ligroin solution benzaldehyde absorbed oxygen smoothly to give an oxidation product. From their infrared spectral studies, Ritchie *et al.*(13−15) have found that a carbonyl compound or nitrile forms a 1 : 1 complex with DMSO (or DMF). It is quite natural to assume that the formyl group is protected from further oxidation by this complex formation.

The Photochemical Oxidation Reaction of Substituted Benzyl Alcohols in DMSO. Nine substituted benzyl alcohols and 1-hydroxymethylnaphthalene were then subjected to the photo-oxidation reaction in order to explore the scope and limitation of this reaction, and also to obtain mechanistic evidence. The results are summarized in Table 1. *p*-Methoxy- and *p*-methylbenzyl alcohols absorbed oxygen much faster than benzyl alcohol, and afforded the corresponding benzaldehyde in moderate yields. Other alkyl derivatives also absorbed oxygen smoothly to give appreciable amounts of benzaldehydes. On the other hand, the presence of an electron-withdrawing group in the benzene ring retarded the oxygen uptake. *p*-Bromobenzyl alcohol gave only 9.1% of *p*-bromobenzaldehyde. *p*-Chloro-, and *m*- and *p*-nitrobenzyl alcohols did not absorb oxygen, and the starting material was recovered. The enhancement of the electron density at the benzylic position would facilitate the attack by the oxygenated radical. An electron-donating group in the benzene ring would thus be expected to stabilize the transition state and enhance the reaction rate. On the contrary, an electron-withdrawing group would retard the reaction.

The special effect of DMSO as the photo-oxidation solvent may be explained as follows. DMSO as a nucleophilic aprotic solvent may form a strong hydrogen bonding with benzylic alcohols without solvating oxygen, thus resulting in the enhancement of the electron density at the benzylic position and accelerating the oxidation reaction. Another factor which must be considered is that DMSO is known to form a charge-transfer complex with oxygen. Although DMSO has only a tail absorption at 210 mμ, dissolved oxygen is known to produce a charge-transfer complex, thus enhancing the UV absorption. Thus DMSO saturated with oxygen has optical densities of 0.53, 0.32, and 0.009 at 280, 300, and 400 mμ respectively.(16) The special effect of DMSO in this photo-oxidation may partly arise from the excitation of the DMSO-O_2 complex, the energy of which is transmitted to the substrate.

The Photochemical Stability of DMSO. Although sulfoxide is known to have a high intensity absorption band near the UV region, its photochemistry was not investigated until quite recently.(9,17,18) A preliminary paper(9) from this laboratory has already described the photochemical stability of DMSO, diphenyl sulfoxide, and dibenzyl sulfoxide. DMSO was quite stable toward irradiation. The irradiation of DMSO in an oxygen atmosphere (Pyrex) resulted in the formation of only a 1.4% yield of dimethyl sulfone. When DMSO was irradiated in a nitrogen atmosphere using a quartz cell, an odoriferous mixture resulted, from which less than 1% of dimethyl sulfide plus

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dimethyl sulfone were isolated. In the photochemical oxidation of benzyl alcohols much dimethyl sulfone was isolated, as has been described before. This may be explained in terms of the sensitized photo-oxidation with benzyl alcohols. A photosensitized oxidation of sulfoxide to sulfone was first carried out by Schenk *et al.*19)

The authors wish to express their thanks to the Ministry of Education for a grant-in-aid for fundamental scientific research.

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