Table I. Carbon-13 Chemical Shifts[a] of Phenyl-Substituted Alkyl Halides

compound	alkyl	C-1	ortho, meta	para
$(C_6H_5)_2CHCl$	64.13	140.93	127.61, 128.39	127.87
$(C_6H_5)_2CHBr$	55.23	140.99	128.39	127.93
$(C_6H_5)_2CCl_2$	91.87	143.91	127.28, 128.00	128.91
$(C_6H_5)_2CBr_2$	69.20	145.15	127.80, 128.39	128.78
$(C_6H_5)_3CCl$	81.28	145.21	127.67, 129.62	*b*
$(C_6H_5)_3CBr$	78.78	145.66	127.63, 130.64	127.79
$[(C_6H_5)_2CCl]_2$	83.17	143.00	125.98, 132.74	127.48

[a] Parts per million from Me_4Si. [b] Line probably hidden under the peak at 127.67 as judged by relative peak heights.

products. Thus, it appears that the course of the reaction is shown in eq 1–4. The radicals in step 4 complete the sequence by reacting with bromine.

$$Br_2 \xrightarrow{h\nu} 2Br\cdot \quad (1)$$

$$(C_6H_5)_3C{-}CH(C_6H_5)_2 + Br\cdot \rightarrow (C_6H_5)_3C{-}\dot{C}(C_6H_5)_2 + HBr \quad (2)$$

$$(C_6H_5)_3C{-}\dot{C}(C_6H_5)_2 + Br_2 \rightarrow (C_6H_5)_3C{-}CBr(C_6H_5)_2 + Br\cdot \quad (3)$$

$$(C_6H_5)_3C{-}CBr(C_6H_5)_2 \rightleftarrows (C_6H_5)_3C\cdot + \cdot CBr(C_6H_5)_2 \quad (4)$$

The photobromination of pentaphenylethane in the presence of oxygen cleanly gives triphenylmethyl bromide and benzophenone. In related experiments it was observed that the photobromination of benzhydryl bromide with oxygen led to the ketone also. In fact, when diphenylmethyl dibromide is irradiated with oxygen in carbon tetrachloride solution, the dibromide is quantitatively converted to the ketone.

An alternative route to the scheme presented above would have the pentaphenylethyl radical dissociating to triphenylmethyl and diphenylcarbene. The reaction of the latter with bromine to form diphenylmethyl dibromide seems not to be a known reaction, though the reaction with oxygen to form benzophenone has been reported.[5] The data presented here do not allow a clear differentiation of these possibilities.

The chlorination reaction yields the chlorine analogues of the above bromination products. With 1 equiv of chlorine, about one-half of the ethane is consumed. It is clear from both the carbon and proton NMR that a small amount of nuclear chlorination occurs. With 2 equiv of chlorine the reaction product is quite complex, showing NMR bands for triphenylmethyl chloride, diphenylmethyl dichloride, and some starting materials, many extraneous peaks from nuclear chlorination, and no benzhydryl chloride.

Experimental Section

All reactions were run at room temperature using 0.410 g (1 mmol) of pentaphenylethane (kindley provided a Professor P. D. Bartlett) in 10 mL of analytical reagent grade carbon tetrachloride in a volumetric flask. The appropriate amount of halogen was added, and the flask and mixture were swept with nitrogen. Experiments conducted with oxygen were carried out in a 50-mL flask flushed with oxygen. Product analysis was carried out by evaporating off the solvent under reduced pressure and dissolving the residue in 1.5 mL of deuteriochloroform containing a small amount of tetramethylsilane. Carbon-13 NMR spectra were obtained on a JEOL FX-60 operating at 15.1 MHz. A 45° pulse width was used with 8K data points and a spectral width of 4 KHz. A 5-s pulse repetition time was used. A set of standard compounds (Table I) were run for comparison. Since each compound had two or more unique lines, identification was quite certain. Peak heights of ortho- or meta-protonated carbons were used in estimating relative yields where possible. Irradiation was carried out about 2 in. in front of a standard slide projector with a 300-W bulb.

The following reactions were carried out with results noted in the text: (a) 0.160 mg (1 mmol) of bromine under nitrogen; (b) 0.320 mg (2 mmol) of bromine under nitrogen; (c) 0.320 mg (2 mmol) of bromine under oxygen; (d) 0.071 mg (1 mmol) of chlorine under nitrogen; and (e) 0.0142 mg (2 mmol) of chlorine under nitrogen. In one experiment 1 mmol of diphenylmethyl dibromide in 10 mL of carbon tetrachloride was irradiated while dry oxygen was bubbled into the system for 2 h. The solution turned red, and presumed bromine vapor was noted at the exit tube. Benzophenone was the sole product. A similar result was obtained when 0.290 g (1.17 mmol) of benzhydryl bromide was photobrominated with 1 equiv of bromine in 10 mL of carbon tetrachloride under oxygen.

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Registry No. Pentaphenylethane, 19112-42-6; benzophenone, 119-61-9; $(C_6H_5)_2CHCl$, 90-99-3; $(C_6H_5)_2CHBr$, 776-74-9; $(C_6H_5)_2CCl_2$, 2051-90-3; $(C_6H_5)_2CBr_2$, 6425-27-0; $(C_6H_5)_3CCl$, 76-83-5; $(C_6H_5)_3CBr$, 596-43-0; $[(C_6H_5)_2CCl]_2$, 1600-30-2.

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[5] P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, 84, 3408 (1962).

On the Purported Photochemical Oxidation of Alcohols by Ag(I). A Reexamination

Roger S. Macomber,*[1a] Steven Carr,[1a] Philip Boudjouk,*[1b] and Craig Kapfer[1b]

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, and North Dakota State University, Fargo, North Dakota 58105

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It was recently reported[2] that when aqueous (or aqueous dimethyl sulfoxide) solutions of primary or secondary alcohols are irradiated at 350 nm in the presence of silver(I) ion, a nearly quantitative redox reaction takes place to give the derived aldehyde (or ketone) and metallic silver. In view of our studies on the (dark) oxidation of alkoxide ions by silver(I)[3] and our need for a mild oxidation technique for certain water-soluble polyols, these results caught our attention. Our suspicions were aroused, however, upon reading the experimental details. In a typical reaction a solution of 7.5 mmol of silver nitrate and 5 mmol of cyclohexanol in ca. 20 mL of Me_2SO–water (3/1, v/v) was degassed and irradiated (quartz vessel,[4] 350 nm) for 1.5 h. Cyclohexanone was reported to be isolated in 90% yield as its 2,4-DNP derivative; metallic silver precipitated quantitatively. In a similar experiment, irradiation of an aqueous solution of 5.6 mmol of 1,4-butanediol and 8 mmol of silver nitrate was reported to give the corresponding dialdehyde in 91% yield, together with metallic silver. It was further pointed out that these reactions did *not* proceed in the dark nor in the presence of oxygen.

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[1] (a) University of Cincinnati. (b) North Dakota State University.

[2] S. Rajan and D. Ramesh, *J. Org. Chem.*, 44, 138 (1979).

[3] R. S. Macomber, J. C. Ford, and J. H. Wenzel, *Synth. React. Inorg. Met.-Org. Chem.*, 7, 111 (1977).

[4] Why quartz was employed at this wavelength was not specified.[2]

Table I. Reaction of Silver Salts with Alcohols

expt no.	substrate	amt, mmol	salt	amt, mmol	solvent(s)	vol, mL	source[a]	time	cell	% of theor silver ppted[b]
1	1,4-butanediol	5.56	$AgNO_3$	7.50	H_2O	30	laser	30 min	quartz	<10
2	1,4-butanediol	5.56	$AgNO_3$	7.50	H_2O	30	laser	30 min	Pyrex	<10
3	1,4-butanediol	5.56	$AgNO_3$	7.50	H_2O	30	Rayonet-1	24 h	quartz	<10
4	cyclohexanol	4.99	$AgNO_3$	7.50	H_2O Me_2SO	5 15	Rayonet-1	48 h	Pyrex	18
5	cyclohexanol	4.99	$AgNO_3$	7.50	H_2O Me_2SO	5 15	Rayonet-1	48 h	quartz	11
6	cyclohexanol	4.99	$AgNO_3$	7.50	H_2O Me_2SO	5 15	none	48 h	Pyrex	0
7	cyclohexanol	99.8	$AgClO_4$	7.50	none		Rayonet-1	48 h	Pyrex	10
8	2-propanol	8.33	$AgNO_3$	7.50	H_2O Me_2SO	5 15	Rayonet-1	6 h	Pyrex	3
9	2-propanol	416	AgOTs	*c*	none		Rayonet-1	24 h	Pyrex	5
10	ethanol	326	$AgNO_3$	7.50	Me_2SO	15	Rayonet-1	48 h	Pyrex	5
11	benzaldehyde	4.72	$AgNO_3$	7.50	H_2O Me_2SO	5 15	Rayonet-1	48 h	Pyrex	13
12	none		$AgNO_3$	7.50	H_2O Me_2SO	5 15	Rayonet-1	24 h	Pyrex	12
13	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	Rayonet-1	48 h	Pyrex	<5
14	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	Rayonet-1	8 h	quartz	<5
15	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	Rayonet-2	5 h	quartz	<5
16	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	Rayonet-2	6 h	Pyrex	<5
17	1-pentanol	100	$AgNO_3$	150	H_2O Me_2SO	75 150	sun lamp	48 h	Pyrex	<5
18	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	none	3 days	Pyrex	slight silver mirror

[a] Laser: CR-18, UV line at 366.8 nm. Rayonet-1: low-pressure Hg, 350 nm. Rayonet-2: high-pressure Hg. All runs were preceeded by thorough degassing. [b] No precipitate with 2,4-DNPH was observed in any experiment except no. 11, nor was C=O absorption detected by IR; see text.[6] Yields of silver metal were determined gravimetrically. [c] Saturated solution.

Because the oxidation of an alcohol to a ketone (or aldehyde) is a two-electron process and Ag(I) is a one-electron oxidant, it was improbable that 7.5 mmol of silver ion could oxidize 5 mmol of an alcohol in 90% yield. Even more unlikely was the oxidation in 91% yield of 5.6 mmol of a *diol* (a four-electron process) by 8 mmol Ag(I). Our groups at Cincinnati and North Dakota State have attempted to reproduce these findings under a variety of conditions, and we have been unable to duplicate them. We are forced to conclude that some other adventitious oxidant must have been responsible for the reported observations.

Our experiments are summarized in Table I. As is readily apparent, there is no evidence for the photochemical oxidation of alcohols by Ag(I) for a number of substrate alcohols under a variety of irradiation conditions. Minor amounts of silver metal *do* appear after prolonged irradiation, but this is true even in the absence of alcohol substrate (experiment 12). The precipitation of silver is extremely slow in the absence of irradiation (experiments 6 and 18) and occurs more readily in aqueous Me_2SO than in pure Me_2SO or pure water (experiment 10).[5] In no case was ketone or aldehyde product detected by 2,4-DNPH[6] or IR, although test solutions containing the anticipated products easily revealed their presence. By contrast, we *were* able to reproduce the photochemical oxidation of alcohols with ferric ion.[7] Similar reactions with vanadium(III) have also been reported.[8]

Registry No. 1,4-Butanediol, 110-63-4; cyclohexanol, 108-93-0; 2-propanol, 67-63-0; ethanol, 64-17-5; benzaldehyde, 100-52-7; 1,5-pentanediol, 111-29-5; 1-pentanol, 71-41-0.

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[5] The UV spectrum of silver nitrate in water or aqueous Me_2SO shows only weak end absorption in the 350-nm region (ϵ_{max} less than 0.2).

[6] Silver ion gives a precipitate with 2,4-DNPH (mp >300 °C). Tests for carbonyl were performed after first precipitating unreacted Ag(I) as silver chloride.

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Synthesis of (1*R*,9*S*)-13-Methyl-13-azatricyclo[7.3.1.$0^{2,7}$]trideca-2,4,6-triene. Observation of a Novel Deaminative Fragmentation

Kenzo Watanabe and Toshio Wakabayashi*

Teijin Institute for Biomedical Research, 4-3-2 Asahigaoka, Hino, Tokyo 191, Japan

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A continuing effort has been devoted to the total synthesis of benzomorphans and nitrogen positional isomers of benzomorphan,[1] substances with morphine-like analgesic activity.[2] The recent development of opioid receptor binding procedures[3] has aroused renewed interest in the enantiomeric stereoselectivity of opioid receptors. We wish to report an asymmetric synthesis of a nitrogen positional isomer of benzomorphan and a novel fragmentation via cleavage of two α bonds to nitrogen atom which is encountered in the course of the synthesis.

The optically pure ester 1 ($[\alpha]^{24}{}_D$ −41.3° (*c* 1.0, EtOH)) is readily available from achiral homophthalic acid by asymmetric synthesis, which we have recently described.[4] Treatment of 1 with phosphorus pentasulfide afforded the thione 2 in 90% yield. Reaction of 2 with methyl bromoacetate afforded a crude imino thioether, to which structure 3 was assigned. Eschenmoser sulfur extrusion reaction[5] of the crude imino thioether 3 afforded the α,β-

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