Detection of nitrite ion from the photooxidations of **1a** and **1c** was accomplished by testing with acidic ferrous sulfate;[10] a dark green-brown color indicated the presence of nitrite, even in the presence of the dye. A blank solution including all components of the reaction before irradiation gave no color change. Nitrate ion gave no color change.

Benzophenone was isolated after 7 h of photooxidation of **1c** by evaporating the solvent, washing with water to remove the dye, and recrystallizing the residue, yield 60%, mp 48–49.5 °C. It was identified by GC and mixture melting point comparison with an authentic sample.

Relative reactivities were obtained by inclusion of 0.1 M 2-methyl-2-butene (competitive singlet oxygen acceptor) and 0.1 M cyclohexane (internal standard) in the reaction solution. The appearance rate of the benzophenone and the disappearance rate of the 2-methyl-2-butene were monitored up to 50% conversion, during which time both were linear (zero order). The ratio of the slopes was taken to be the ratio of their absolute rate constants with singlet oxygen. Appropriate blank reactions were run: with oxygen bubbling and no irradiation, with irradiation and nitrogen bubbling, and with irradiation and oxygen bubbling but no dye. These blanks amounted to less than 10% of the photooxidation reaction and were simply subtracted from the reaction rates.

Quenching by Dabco was demonstrated by running two parallel photooxidations, containing 0.1 M **1c**, 0.1 M 2-methyl-2-butene, and 1×10^{-4} M rose bengal in methanol. One solution contained 1×10^{-3} M Dabco. After 3 h of irradiation, the solution with Dabco showed no detectable reaction, while in the other solution both **1c** and 2-methyl-2-butene showed substantial reaction.

Acknowledgments. We are pleased to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for generous financial support of this work.

Registry No.—**1a**, 574-66-3; **1b**, 3376-34-9; **1c**, 58074-11-6; 2-methyl-2-butene, 513-35-9; acetone oxime, 127-06-0.

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(1) Visiting Associate Professor, University of Southern California, 1975–1976; address correspondence to this author at California State University, Fullerton.
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A Chromium(II)-Promoted Heterolytic Fragmentation Reaction. Application to the Synthesis of 1,5-Dienes[1]

James H. Babler* and Alan E. Moormann

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

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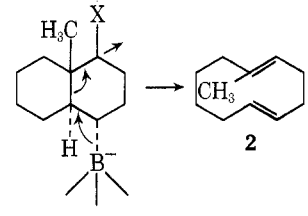
Interest in the stereoselective synthesis of 1,5-dienes has increased markedly in the last decade, as attested by the variety of methods[2] that have been developed for obtaining this class of compounds. Among the important natural products that possess two (or more) double bonds in a 1,5 relationship are a number of medium-ring sesquiterpenes[3] possessing the 1,5-cyclodecadiene skeleton as well as several important acyclic compounds such as squalene, farnesol, and the juvenile hormone of *Hyalophora cecropia*.[4]

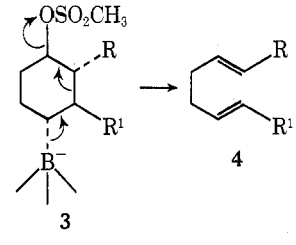
One of the more promising approaches to such systems involves the base-promoted heterolytic fragmentation[5] of appropriately substituted decalinboronate derivatives (e.g., **1** in eq 1) for the stereospecific synthesis[3] of 1,5-cyclodecadienes (**2**). Fragmentation of the corresponding cyclohexaneboronate (**3**) has been shown[6] likewise to yield in a stereospecific manner an acyclic 1,5-diene (**4**) (eq 2).



(1)

1

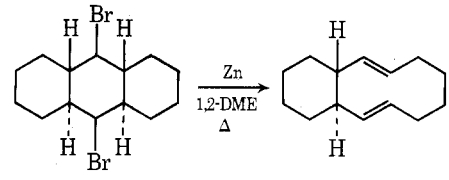
X = OSO_2CH_3, Br, etc.



(2)

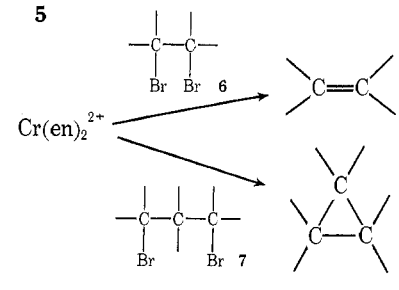
3 **4**

The report[7] of a zinc-initiated fragmentation reaction of a cyclic 1,4-dibromide (**5**) (eq 3), together with studies of Kochi and Singleton[8] involving the reaction of ethylenediaminechromium(II)[9] with 1,2- and 1,3-dibromides (**6** and **7**, respectively) (eq 4), suggests that chromium(II) should also initiate fragmentation of an alicyclic bromide possessing a suitable nucleofugal group at the γ carbon.



(3)

5

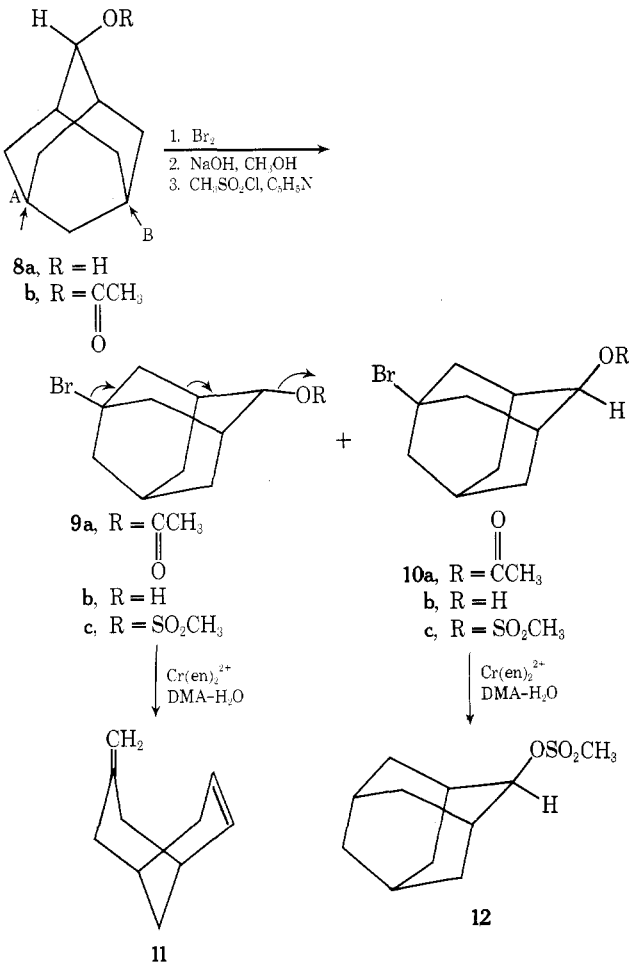


(4)

If successful, the use of chromium(II) may be advantageous over that of zinc since fragmentation reactions involving the latter are generally run at elevated temperature, conditions under which a Cope rearrangement of the 1,5-diene products can occur.[10]

The system selected for testing the feasibility of a Cr(II)-promoted fragmentation reaction directed toward the synthesis of 1,5-dienes was bromomesylate **9c**. The preparation of this substrate from the commercially available[11] 2-adamantanol (**8a**) is outlined in Scheme I. Acetylation of alcohol **8a** using acetic anhydride–pyridine afforded the corresponding acetate (**8b**)[12] in 94% yield. Ionic bromination of the latter (**8b**) afforded an undetermined mixture[13]

Scheme I



of bromoacetate epimers (**9a** and **10a**) in modest yield. Subsequent saponification followed by conversion of the alcohol product (**9b** and **10b**) to the corresponding mesylates (**9c** and **10c**) proceeded smoothly.

Treatment of this mixture of bromomesylates (**9c** and **10c**) with ethylenediaminechromium(II) in aqueous dimethylacetamide at room temperature for 1.5 h afforded the anticipated fragmentation product, 7-methylenebicyclo[3.3.1]non-2-ene (**11**), in 40% yield. The structure of the latter was verified by both elemental analysis as well as comparison of its ir and NMR spectral data with those previously reported[14] for this same diene. The other product on the basis of elemental analysis and its ir and NMR spectra was assigned structure **12**, and is presumed to have been formed by simple reduction of cis bromomesylate **10c**, which lacks the antiperiplanar relationship of the participant bonds required for a concerted fragmentation. Only in the trans isomer (**9c**) can the stereoelectronic requirement for concerted reaction be met.

Experimental Section[15]

2-Adamantanol Acetate (8b). A solution of 25.0 g of 2-adamantanol[11] (**8a**) in 250 ml of 1:1 acetic anhydride–pyridine was stirred overnight at room temperature. The mixture was subsequently poured onto 250 g of ice and acidified with concentrated hydrochloric acid. Extraction with ether afforded 30 g (94%) of acetate **8b**[12] as an oil: λ_{max} (film) 1735 (C=O), 1451, 1370, 1362, 1252, 1211, 1100 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 4.93 (m, CHOAc), 2.06 ppm [s, $OC(=O)CH_3$].

1-Bromo-4-adamantanol Acetate (9a and 10a). A solution of 25.0 g (129 mmol) of 2-adamantanol acetate (**8b**) in 100 ml of bromine was stirred at room temperature for 16 h, after which the reaction was quenched by pouring this mixture onto 500 g of ice and adding solid sodium bisulfite (and ice, to maintain the temperature below 25 °C) to destroy the excess bromine. Extraction of the product with ether followed by dissolution of the oily residue in 25 ml of pentane and chilling this mixture afforded 7.0 g (20%) of crystalline acetate mixture **9a** and **10a**: mp 75–79 °C; λ_{max} (KBr) 1741, 1378, 1364, 1350, 1041 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 4.88 (multiplet, CHOAc), 2.10 ppm [s, $OC(=O)CH_3$]. Anal. Calcd for $C_{12}H_{17}O_2Br$: C, 52.76; H, 6.27; Br, 29.25. Found: C, 52.40; H, 6.33; Br, 29.25.

1-Bromo-4-adamantanol (9b and 10b). A solution of 7.0 g of acetate mixture **9a** and **10a** in 75 ml of methanol containing 1 ml of 50% aqueous sodium hydroxide was stirred for 2 h at room temperature. The product was isolated by pouring this mixture onto 200 g of ice, followed by acidification with concentrated aqueous HCl and dilution to 500 ml by addition of water. The yield of crystalline alcohol mixture **9b** and **10b** was 5.6 g (95%): mp 130–140 °C; λ_{max} (KBr) 3270 (OH), 1051, 1011 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 3.85 (m, CHOH), 2.83 (m, 1 H), 2.63 ppm (m, 1 H). Anal. Calcd for $C_{10}H_{15}OBr$: C, 51.96; H, 6.54; Br, 34.57. Found: C, 52.34; H, 6.50; Br, 34.81.

1-Bromo-4-adamantanyl Methanesulfonate (9c and 10c). Methanesulfonyl chloride (10 ml) was added dropwise to a stirred solution of 5.6 g (24.2 mmol) of alcohol mixture **9b** and **10b** in 40 ml of dry pyridine. After this mixture was stirred at room temperature for 18 h, it was poured onto 200 g of ice and acidified with concentrated hydrochloric acid. Extraction with dichloromethane, followed by recrystallization from pentane, afforded 5.7 g (76%) of mesylate (**9c** and **10c**): mp 116–120 °C; λ_{max} (KBr) 1332, 1172, 915 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 4.82 (m, $CHOSO_2CH_3$), 3.05 ppm (s, CH_3SO_3). Anal. Calcd for $C_{11}H_{17}O_3BrS$: C, 42.72; H, 5.54; Br, 25.84; S, 10.37. Found: C, 42.79; H, 5.44; Br, 25.85; S, 10.75.

7-Methylenebicyclo[3.3.1]non-2-ene (11). Chromous chloride was prepared under a nitrogen atmosphere by mixing 10 g of granular zinc with a solution of 26.6 g of chromic chloride hexahydrate in 25 ml of deoxygenated water. After addition of 15 ml of concentrated hydrochloric acid to this system, as soon as the solution became light blue it was rapidly transferred to an addition funnel, into which was subsequently added 26 ml of deoxygenated ethylenediamine. This mixture was then added rapidly to a stirred solution of 5.5 g (17.8 mmol) of bromomesylate (**9c** and **10c**) in 200 ml of dimethylacetamide. The solution was stirred for 1.5 h at room temperature after which it was poured into 1600 ml of cold water. Extraction with ether, followed by removal of the solvent via distillation through a Vigreux column at atmospheric pressure, dissolution of the oily residue in hot pentane, and chilling of the latter solution, afforded 21% yield of mesylate **12**: mp 63–65 °C; λ_{max} (KBr) 1342, 1179, 990, 966, 930, 909 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 4.90 (m, CHOMs), 3.00 ppm (s, CH_3SO_3). Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88. Found: C, 57.08; H, 7.73. Diene **11** was recovered from the filtrate by placing it on a column of silica gel (100 ml) and elution with pentane. Removal of the pentane by distillation afforded 0.95 g (40%) of **11**: λ_{max} (film) 1649, 1431, 880, 730 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.67 (s, 2 H, CH=CH), 4.75 (s, 1 vinyl H), 4.57 ppm (s, 1 vinyl H). Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.25; H, 10.60.

Acknowledgment. The authors wish to thank Searle Laboratories, a division of G. D. Searle & Co., for their support of this work. In particular, the service rendered by their Analytical Resources and Methods Department is gratefully acknowledged.

Registry No.—**8a**, 700-57-2; **8b**, 19066-22-9; **9a**, 58241-07-9; **9b**, 58241-08-0; **9c**, 58241-09-1; **10a**, 58267-56-4; **10b**, 58267-57-5; **10c**, 58267-58-6; **11**, 37439-70-6; **12**, 31616-68-9; bromine, 7726-95-6; methanesulfonyl chloride, 124-63-0.

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(4) B. M. Trost, *Acc. Chem. Res.*, **3**, 120 (1970).

(5) For recent reviews, see C. A. Grob and P. W. Schiess, *Angew. Chem., Int. Ed. Engl.*, **6**, 1 (1967); C. A. Grob, *ibid.*, **8**, 535 (1969).
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(9) For a review of the applications of chromium(II) salts in preparative organic chemistry, see J. R. Hanson, *Synthesis*, 1 (1974).
(10) C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, **46**, 483 (1963).
(11) Aldrich Chemical Co., Inc., Milwaukee, Wis.
(12) A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1345 (1968).
(13) Bromination of acetate **8b** is anticipated to be most favorable at the two bridgehead positions labeled A and B in structure **8** shown in Scheme I. Ionic attack of bromine at site A yields the trans isomer **9a**, whereas attack at site B affords the corresponding cis bromoacetate (**10a**). Since the two stereoisomers failed to separate on silica gel TLC and attempts to separate the mixture via fractional crystallization were unsuccessful at this stage as well as after subsequent reactions, no further attempt was made to determine the stereochemistry of the reaction products.
(14) J. H. Liu, G. A. Gauger, and P. Kovacic, *J. Org. Chem.*, **38**, 543 (1973).
(15) Reactions were carried out under a nitrogen atmosphere. The isolation of reaction products was accomplished by extracting the aqueous layer thoroughly with the specified solvent. Anhydrous sodium sulfate was used to dry the combined extracts, and the solvent was removed on a rotary evaporator under reduced pressure. Melting points were determined on a Fisher-Johns block and are corrected. The NMR spectra were recorded with a Varian A-60 NMR spectrometer and infrared spectra were obtained using a Beckman IR-12 spectrophotometer. Elemental analyses were performed by the Analytical Resources and Methods Department, Searle Laboratories, G. D. Searle & Co.

Oxidation of Trimethylsilyl Ethers via Hydride Abstraction. A New Method for Alcohol Oxidation

Michael E. Jung

Contribution No. 3557 from the Department of Chemistry, University of California, Los Angeles, California 90024

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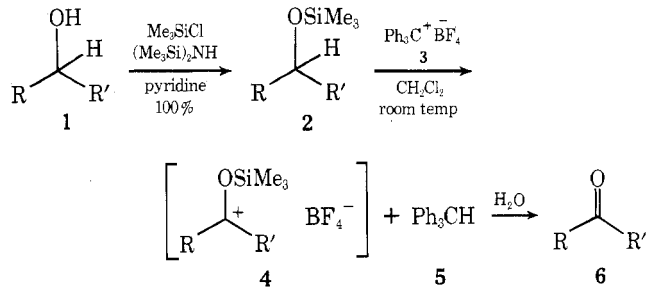
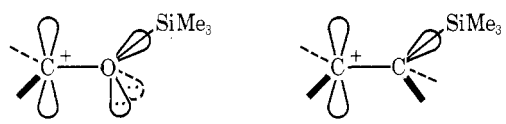
I wish to report a new method for the oxidation of alcohols to ketones and aldehydes under extremely mild conditions in nearly quantitative yields. The key step of this two-step procedure involves the treatment of the trimethylsilyl ethers **2** of the alcohols **1** with a triphenylcarbenium (trityl) salt **3** in methylene chloride at room temperature. The carbonyl compounds **6** are produced cleanly and can be easily isolated from the by-product, triphenylmethane (**5**), by simple distillation or chromatography. A variety of alcohols have been subjected to this new oxidation technique, the products and yields of which are listed in Table I.

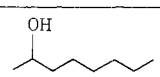
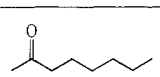
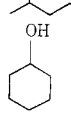
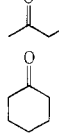
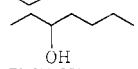
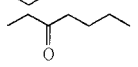
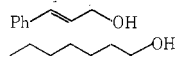
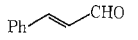
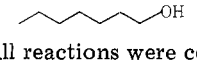
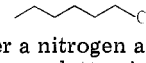


The oxidation of alkyl ethers to carbonyl compounds by trityl salts has been observed previously[1] but only recently has this become a useful synthetic method. Barton has used this technique in the oxidation of ketone acetals and in the deprotection of steroidal benzyl ethers and carbonates.[2] Doyle has also employed this oxidation in the disproportionation of trityl alkyl ethers by a cationic chain reaction process.[3] The trimethylsilyl ethers were chosen for the present study for several reasons. First, they could be quickly and easily prepared in quantitative yields. Secondly, the amount of simple complexation of the trityl salt and the ether oxygen could be lessened because of steric hindrance between the very bulky trimethylsilyl group and the trityl cation. Finally, it was anticipated that the trimethylsilyl group could provide additional stabilization to the carbonium ion β to it by a mechanism of vertical stabilization such as in **7**. This is completely analogous to the all-carbon case, **8**, which has been shown to offer a great deal



of stabilization.[4] For example, the Hammett electrophilic para-substitution constant, σ_p^+, for the trimethylsilylmethyl group (Me_3SiCH_2) is -0.66.[4] This very closely approximates the value for the methoxyl group (MeO), $\sigma_p^+ = -0.74$,[4] implying in a general sense that a trimethylsilyl group β to a carbonium ion stabilizes that ion to about the same extent as a methoxyl group α to it. Therefore it was anticipated that the stability of the carbonium ion, e.g., **4**, could be enhanced by changing the group attached to oxygen from alkyl to trimethylsilyl. In agreement with this expectation the silyl ether **9** is oxidized somewhat faster than the *tert*-butyl ether **10** under identical conditions, although **10** also gives cyclohexanone in reasonable yield. However, this result is not conclusive because the difference in rates may be due to other effects, e.g., steric effects, since the

Table I. Oxidation of Trimethylsilyl Ethers with $Ph_3C^+BF_4^-$[a]

Starting alcohol	Registry no.	Product[b]	Registry no.	% yield[c]
	123-96-6		111-13-7	95
	108-93-0		108-94-1	99 (92)
	589-82-2		106-35-4	98
PhCH2OH	100-51-6	PhCHO	100-52-7	100
	104-54-1		104-55-2	100
	111-70-6		111-71-7	38

[a] All reactions were conducted in CH_2Cl_2 at 25 °C under a nitrogen atmosphere. [b] The products were identified by comparison (GC, NMR, ir) with authentic samples. [c] The yields were determined by gas chromatographic analysis through reference to an internal standard, normally mesitylene. The numbers in parentheses are isolated yields. The yields of triphenylmethane are all 100%.