OCH_2), 6.70 (m, 1, olefinic H).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.11; H, 8.26.

4-Acetonyl-2-cyclohexenone (15c) and 2-Acetonyl-2-cyclohexenone (16c). A combination of 1.00 g of a **8c**–**9c** mixture and 15 mL of 2 N hydrochloric acid in 15 mL of ether was stirred at 25 °C for 1 h. The ether layer was separated, the aqueous solution saturated with sodium chloride and extracted with ether, and the combined organic solutions worked up as for **15a** above. Preparative TLC of the crude product, 750 mg, and elution with 4:1 ether–hexane yielded 110 mg of diketone **16c** [IR C=O 1710 (s), 1670 cm^{-1} (s); ^{1}H NMR δ 2.17 (s, 3, Me), 3.25 (broad s, 2, $COCH_2$), 6.78 (t, 1, J = 3 Hz, H-3); mass spectrum m/e 152 (M^+), 54, 37 (base); exact mass m/e 152.0837 (calcd for $C_9H_{12}O_2$, 152.0833)] and 565 mg of diketone **15c** [IR C=O 1715 (s), 1675 (s), C=C 1616 cm^{-1} (w); ^{1}H NMR δ 2.22 (s, 3, Me), 5.95 (dd, 1, J = 10, 2 Hz, H-2), 6.81 (ddd, 1, J = 10, 3, 1 Hz, H-3); mass spectrum m/e 152 (M^+), 95, 55, 43 (base); exact mass m/e 152.0830 (calcd for $C_9H_{12}O_2$, 152.0836)].

4-Acetonyl-4-methyl-2-cyclohexenone (15d) and 2-Acetonyl-4-methyl-2-cyclohexenone (16d). A combination of 1.30 g of a **8d**–**9d** mixture and 25 mL of 2 N hydrochloric acid in 25 mL of ether was stirred at 25 °C for 1 h. Workup as for **15c**–**16c** above yielded 850 mg of oil, bp 70 °C (0.15 Torr), whose preparative GPC (180 °C) yielded 477 mg of a mixture of **16d** and its isomer, **2-acetonyl-4-methyl-3-cyclohexenone (16d′)** [10 min retention time; IR C=O 1710 (s), 1675 cm^{-1} (s); ^{1}H NMR δ 1.16 (d, <3, J = 7 Hz, Me of **16d′**), 1.72 (broad s, <3, Me of **16d**), 2.15 (s, <3, COMe of **16d′**), 2.45 (s, <3, COMe of **16d**), 5.17 (m, <1, H-3 of **16d′**), 6.51 (m, <1, H-3 of **16d**); exact mass m/e 166.0989 (calcd for $C_{10}H_{14}O_2$, 166.0993)] and 190 mg of **15d** [14 min retention time; IR C=O 1720 (s), 1675 (s), C=C 1607 cm^{-1} (w); ^{1}H NMR δ 1.25 (s, 3, Me), 2.13 (s, 3, COMe), 2.58 (s, 2, $COCH_2$), 5.78 (d, 1, J = 10 Hz, H-2), 6.80 (broad d, 1, J = 10 Hz, H-3); mass spectrum m/e 166 (M^+), 109, 108 (base), 95, 43; exact mass m/e 166.0986 (calcd for $C_{10}H_{14}O_2$, 166.0993)].

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Registry No.—**1a**, 3036-66-6; **1b**, 6651-43-0; **2a**, 61967-78-0; **2a** biscyclopropanation product, 61967-79-1; **2b**, 61967-80-4; **3a**, 2161-90-2; **3b**, 2161-94-6; **4a**, 61967-81-5; **4b**, 61967-82-6; **4c**, 61967-83-7; **4d**, 61967-84-8; **5a**, 61967-85-9; **5b**, 61967-65-5; **5c**, 61967-66-6; **5d**, 61967-67-7; **6a**, 61967-68-8; **6b**, 61967-69-9; **6c**, 61967-70-2; **6d**, 61967-71-3; **7a**, 61967-72-4; **7b**, 61967-73-5; **7c**, 61967-74-6; **7d**, 61967-75-7; **8a**, 61967-76-8; **8b**, 61967-77-9; **8c**, 61967-31-5; **8d**, 61967-29-1; **9a**, 61967-30-4; **9b**, 61967-32-6; **9c**, 61967-33-7; **9d**, 61967-34-8; **10**, 61967-35-9; **11a**, 61967-36-0; **11b**, 61967-37-1; **12a**, 61967-38-2; **12b**, 61967-39-3; **13a**, 61967-40-6; **13a** semicarbazone, 61967-41-7; **13b**, 61967-42-8; **13b** bissemicarbazone, 61967-43-9; **14a**, 61967-44-0; **14a** ethyl ether lactol isomer, 61967-45-1; **14b**, 61967-46-2; **15a**, 16831-58-6; **15a** β,γ isomer, 61967-47-3; **15b**, 16831-59-7; **15c**, 56051-94-6; **15d**, 61967-48-4; **16a**, 24124-06-9; **16b**, 61967-49-5; **16c**, 33553-25-2; **16d**, 61967-19-9; **16d′**, 61967-20-2; 1-cyclohexenecarboxaldehyde, 1192-88-7; isopropenyl acetate, 108-22-5; trimethylsilyl chloride, 75-77-4; 1-dimethoxymethylcyclohexene, 61967-21-3; trimethyl orthoformate, 149-73-5; ethyl diazoacetate, 623-73-4; diazoacetone, 2684-62-0.

References and Notes

(1) E. Wenkert, R. A. Mueller, E. J. Reardon, Jr., S. S. Sathe, D. J. Scharf, and G. Tosi, *J. Am. Chem. Soc.*, **92**, 7428 (1970).

(2) E. Wenkert, C. A. McPherson, E. L. Sanchez, and R. L. Webb, *Synth. Commun.*, **3**, 255 (1973).

(3) (a) S. S. Sathe, Ph.D. Dissertation, Indiana University, 1971; (b) B. L. Buckwalter, Ph.D. Dissertation, Indiana University, 1973; (c) M. E. Alonso, Ph.D. Dissertation, Indiana University, 1974; (d) A. A. Craveiro, Ph.D. Dissertation, Indiana University, 1974; (e) K. J. Chou, Ph.D. Dissertation, Indiana University, 1975.

(4) For other recent cyclopropanations of enol derivatives with α-diazocarbonyl reagents see (a) J. E. McMurry and T. E. Glass, *Tetrahedron Lett.*, 2575 (1971); (b) R. LeGoalter and J. L. Pierre, *C. R. Acad. Sci., Ser. C*, **273**, 193 (1973); (c) R. M. Coates, L. O. Sandefur, and R. D. Smillie, *J. Am. Chem. Soc.*, **97**, 1619 (1975).

(5) For alternate γ-alkylations (or acylations) of conjugated enones or their equivalents see inter alia S. Lüsberg, W. O. Godtfredsen, and S. Vangedal, *Tetrahedron*, **9**, 149 (1960); M. Gorodetsky and Y. Mazur, *ibid.*, **22**, 3607 (1966); M. Yoshimoto, N. Ishida, and T. Hiraoka, *Tetrahedron Lett.*, 39 (1973); G. Cainelli, G. Cardillo, M. Contento, P. Grasselli, and A. v. Ronchi, *Gazz. Chim. Ital.*, **103**, 117 (1973); J. E. Telschow and W. Reusch, *J. Org. Chem.*, **40**, 862 (1975); K. Takabe, H. Fujiwara, T. Katagiri, and J. Tanaka, *Tetrahedron Lett.*, 1237 (1975); B. M. Trost and L. S. Melvin, Jr., *J. Am. Chem. Soc.*, **98**, 1204 (1976); J. A. Katzenellenbogen and A. L. Crumrine, *ibid.*, **98**, 4925 (1976).

(6) The first observation of the cyclopropanation of the nonoxygenated double bond of a 1-oxy-1,3-butadiene system in a copper-catalyzed α-diazo ketone decomposition process (accompanying the enol ether double bond functionalization) involved the interaction of diazoacetone with the methyl dienyl ether as well as the dienyl acetate of an intermediate α,β-unsaturated aldehyde en route to β-vetivone.[3a]

(7) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

(8) V. Rautenstrauch, *Helv. Chim. Acta*, **55**, 594 (1972), and references cited therein.

(9) T.-L. Ho and C. M. Wong, *Synthesis*, 196 (1974).

(10) A. J. Birch and K. P. Dastur, *J. Chem. Soc., Perkin Trans. 1*, 1650 (1973).

(11) The methyl dienyl ether **2** (R = Me) proved difficult to obtain. The preparation of its precursor, 1-dimethoxymethylcyclohexene, is described in the Experimental Section.

(12) Acid-catalyzed ring scission of aldehyde **10** at elevated temperature produces **11a** distinctly more slowly than that of its enol ether **4a**, indicative of methoxyallyl cation participation in the transition state of the latter reaction.

(13) J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, **28**, 3356 (1963).

Addition to 2,4-Dienes. Halogenation of Ethyl Sorbate

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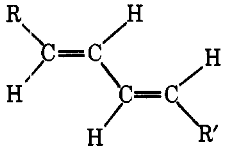
The addition of chlorine and bromine to ethyl sorbate (**1a**) gave 1,2- and 1,4-dihalo products derived from attack of the halogen across the γ,δ double bond. Chlorination of **1a** under ionic conditions proceeds through a tightly bridged chloronium ion intermediate, as indicated by the stereospecific formation of *erythro*-1,2-dichloride **3a**. Stereospecificity in **3a** is lost when chlorine is added to **1a** under radical conditions, indicating a molecule-induced homolysis for this reaction. Even under ionic conditions, bromine reacts with **1a** by a radical process unless an efficient radical scavenger is used.

The loss of stereospecificity in the ionic halogenation[2] of conjugated olefins such as β-methylstyrenes[3] and dienes[4] is ascribed to weakly bridged halonium ion intermediates. Apparently bromine bridges more tightly than chlorine, since 1,2-addition of bromine to *trans,trans*-2,4-hexadiene (**1b**) is more stereospecific (80%) than the 1,2-addition of chlorine (60%).[4] Halogenations of these dienes and olefins under radical conditions[2] involve nonbridged radical intermediates resulting in nonstereospecific products.[5]

We undertook this study to determine what effect a conjugated carbonyl group in a diene (see **1a**) would have on product formation when halogens are added to the diene. We anticipated that the carbonyl group should decrease the participation of both the α,β and γ,δ double bonds in electrophilic reactions because the inductive and resonance effects would reduce the basicity of the bonds. The effect of a conjugated carbonyl group on the addition of halogens to 2,4-dienes under radical conditions is not known.

A survey of the literature showed that the chlorinations of dienes such as **1a** and **2a,b** have not been reported. The bromination of **2a** was reported to give a γ,δ-dibromide, but no 1,2 (α,β) or 1,4 products were isolated.[6a] However, only an α,β-dibromide was isolated when either **2b** or its methyl ester were treated with bromine,[6b] presumably because stable benzyl cations were involved. There is no indication whether these products were obtained by an ionic or radical process.

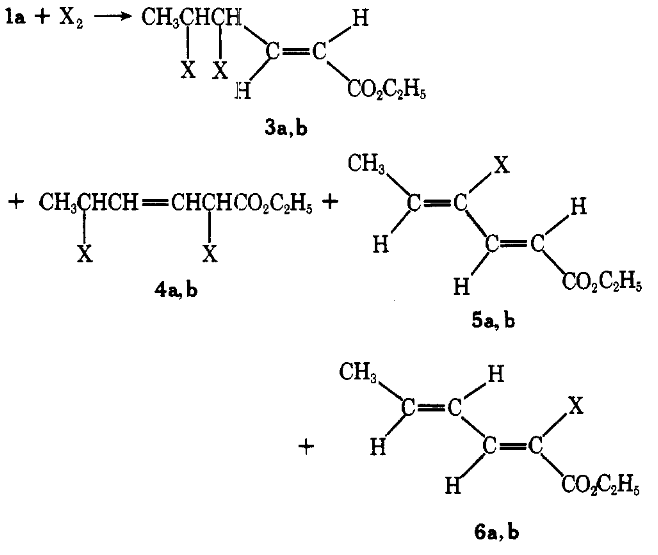


1a, R = CH_3; R′ = $CO_2C_2H_5$
b, R = R′ = CH_3
2a, R = CH_3; R′ = CO_2H
b, R = Ph; R′ = CO_2H

In this paper we report our findings on the halogenation of ethyl sorbate (**1a**) with bromine and chlorine under ionic and radical reaction conditions. Our purpose was to determine:)1) whether the reactions proceed by radical or ionic mechanisms; (2) if there are any additions to the α,β double bond; and (3) if any 1,4-dihalides are formed.

Results and Discussion

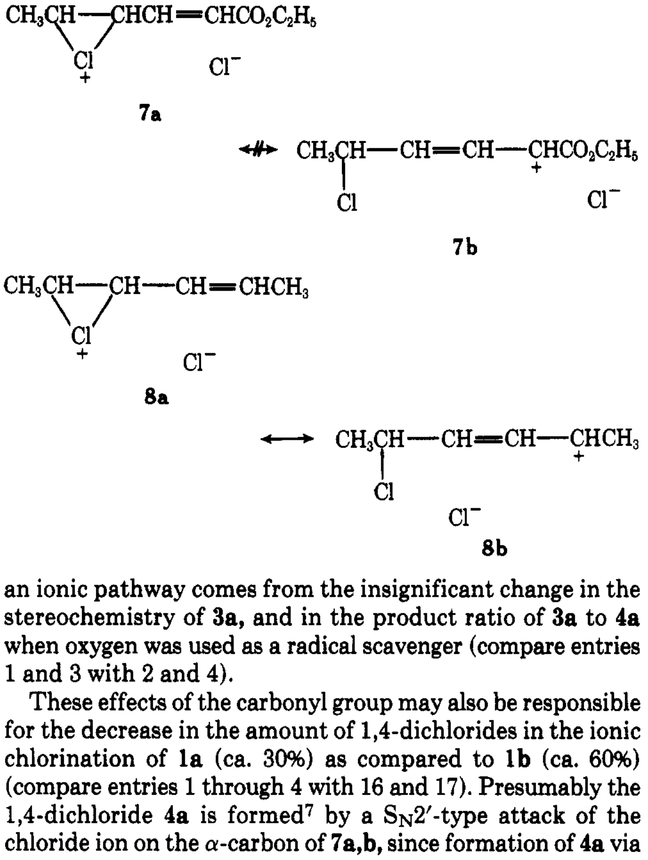
When ethyl sorbate (**1a**) was chlorinated under ionic conditions a mixture of 1,2- and 1,4-dichlorides (**3a** and **4a**, respectively) and substitution products **5a** and **6a** were obtained (Table I). Structural assignments for the dichlorides **3a** and **4a** were deduced from spectral data and by dehydrochlorinations to chlorodienes **5a** and **6a**. When a mixture of **3a** and **4a** was treated with an excess of triethylamine, **6a** was obtained in good yield from 1,4-dichloride (**4a**). Control experiments showed that the γ,δ-dichloride **3a** was stable under these reaction conditions. However, dehydrochlorination of **3a** did occur with sodium ethoxide in ethanol to give **5a**. Structures for **5a** and **6a** were assigned on the basis of their spectral data.



a, X = Cl
b, X = Br

The γ,δ-dichloride **3a** was formed by a stereospecific anti 1,2-addition, whereas ionic chlorination of *trans*-2,4-hexadiene (**1a**) was shown previously[4b] to be nonstereospecific (ca. 60% anti). Stereospecific addition to **1a** implies that a tightly bridged chloronium ion intermediate was involved. Probably delocalization of the charge does not occur in **7a,b** as happens in **8a,b** because participation of **7b** as a resonance contributor would place a positive charge next to the carbonyl group, and the resonance stabilization of the α,β-bond with the ester carbonyl would be disrupted (Scheme I). Further support for an ionic pathway comes from the insignificant change in the stereochemistry of **3a**, and in the product ratio of **3a** to **4a** when oxygen was used as a radical scavenger (compare entries 1 and 3 with 2 and 4).

Scheme I



These effects of the carbonyl group may also be responsible for the decrease in the amount of 1,4-dichlorides in the ionic chlorination of **1a** (ca. 30%) as compared to **1b** (ca. 60%) (compare entries 1 through 4 with 16 and 17). Presumably the 1,4-dichloride **4a** is formed[7] by a S_N2'-type attack of the chloride ion on the α-carbon of **7a,b**, since formation of **4a** via **9a,b** should give a significant amount of the α,β-dichloride **10** or the substitution product **6a** (Scheme II). Production of **6a** from intermediate **9a,b** should be favorable, since conjugation with the carbonyl group would be restored. We were unable to detect any **10** in the product mixture and only a trace of **6a** was obtained. Apparently there was little addition of chlorine to the α,β double bond in **1a** because of the resonance and inductive effects of the ester carbonyl.

The chlorination of **1a** under radical conditions involved nonbridged radical intermediates as indicated by the loss in stereochemistry of the 1,2 products (entry 5). Another characteristic of radical chlorination of dienes is an increase in the amount of 1,4-addition[8] (compare entries 1 through 4 with 5). Trichloramine, NCl_3, is known to react with dienes by a radical mechanism,[9] and results obtained with it and **1a** are similar to those obtained with chlorine under radical conditions[10] (compare entries 5 and 6).

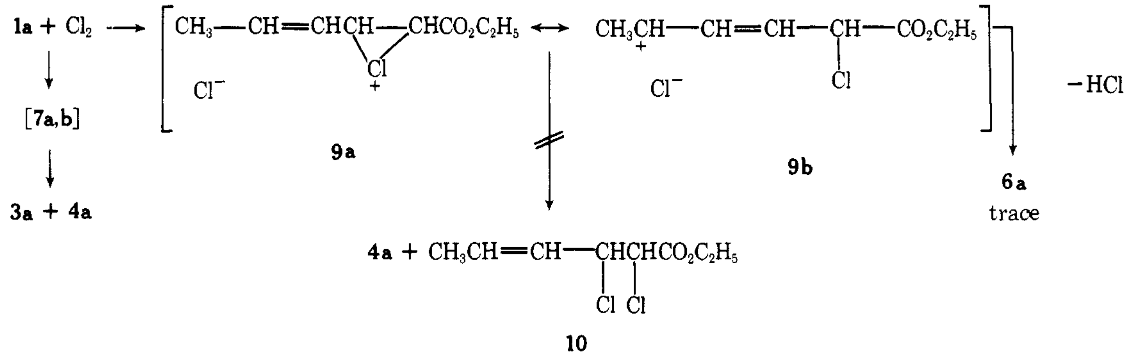
We were surprised to observe that bromine added to **1a** by a molecule-induced radical reaction as suggested by the loss of stereochemistry in **3b** (entries 8, 9, and 10). This is the first report of bromination of an olefinic system by a molecule-induced homolysis in a very dilute solution.[5a,11] Stereospecificity of the 1,2-dibromide increased significantly when luti-

Table I. Comparisons of the Chlorination and Bromination of Ethyl Sorbate and *trans,trans*-2,4-Hexadiene

Entry	Solvent	Diene[a]	Reaction conditions[b]	Halogenating reagent	Products, %[c]				Yields, %[c]	1,2-Addition, % anti[e]
					1,2-[d]	1,4-[d]	5	6		
1	CCl_4	**1a**	Dark	Cl_2	72	22	4	2	64	100
2	CCl_4	**1a**	Dark, O_2	Cl_2	77	19	3	1	50	100
3	CH_2Cl_2	**1a**	Dark	Cl_2	45	35	12	8	47	100
4	CH_2Cl_2	**1a**	Dark, O_2	Cl_2	45	35	12	8	49	100
5		**1a**[f]	$h\nu$	Cl_2 (g)	30	48	12	10	*g*	75
6	CH_2Cl_2	**1a**[h]	$h\nu$	NCl_3	44	45	9	2	42	53
7		**1a**[i]	$h\nu$	Br_2	91	5	4	0	85	70
8	CCl_4	**1a**	Dark	Br_2	91	7	2	0	85	70
9	CCl_4	**1a**	Dark, O_2	Br_2	89	4	7	0	76	75
10	CH_2Cl_2	**1a**	Dark	Br_2	83	14	3	0	72	70
11	CCl_4	**1a**	Inhibitor[j]	Br_2	*j*	*j*	*j*	*j*	*j*	90
12	CH_2Cl_2	**1a**	Dark	$Lu{\cdot}Br_2$	82	4	14	0	78	90
13	CCl_4	**1b**[k]	Dark	Br_2	29	71			90	79
14	CH_2Cl_2	**1b**[k]	Dark	Br_2	27	73			90	85
15	CH_2Cl_2	**1b**[l]	Dark	$Py{\cdot}Br_2$	95	5			72	99
16	CCl_4	**1b**[m]	Dark, O_2	Cl_2	35	65			71	63
17	CH_2Cl_2	**1b**[m]	Dark, O_2	Cl_2	48	52			71	56

[a] The diene was 0.02 mol fraction with respect to solvent. [b] The UV light was from a 275-W sunlamp. [c] Determined by VPC. [d] The 1,2- and 1,4-addition products of **1a** refer to addition across the γ,δ and α,δ carbons, respectively. [e] The percent erythro/threo for **1a** was determined by NMR analysis on the methyl and vinyl protons. [f] Chlorine gas was bubbled into neat diene. [g] The amount of chlorine gas bubbled into neat diene was not measured. [h] The diene was 0.1 mol fraction with respect to solvent. [i] Neat bromine was added to neat diene. [j] The inhibitor, 2,6-di-*tert*-butyl-4-methylphenol, has the same VPC retention time as **4b**, and it obscures **3b**, so that quantitative data could not be obtained. [k] Data from ref 4a. [l] Unpublished results. [m] Data from ref 4b.

Scheme II



dine dibromide (entry 12) was used as the brominating reagent.[12] Also the radical reaction can be decreased by using an inhibitor (2,6-di-*tert*-butyl-4-methylphenol) as indicated by an increase in the stereospecificity of **3b** (entry 11).[13] Apparently the ionic bromination of ethyl sorbate occurs so slowly that the radical process predominates unless an efficient inhibitor is used.

We were unable to isolate 1,4-dibromide **4b**, but its presence was confirmed by the same procedure that was used to establish the structure of the 1,4-dichloride (**4a**): When a mixture of **3b** and **4b** was treated with triethylamine the bromodiene (**6b**) was obtained in good yield. The 1,2-dibromide **3b** was stable under these reaction conditions.

Experimental Section

General. All of the reagents and solvents were obtained commercially except trichloramine, which was prepared as described in "Organic Syntheses." [14] Ethyl sorbate was distilled prior to use. IR and NMR were obtained on a Beckman IR-10 spectrophotometer and a Varian T-60 or EM-360-A, respectively. Vapor phase chromatographic analyses were done with a Hewlett Packard 5706A flame ionization chromatograph, and an F&M 700 chromatograph. The following columns (SS) were used: Column A, 6 ft × ⅛ in. of 2.5% SE-30 on 80/100 Chromosorb W; Column B, 10 ft × ¼ in. 2.5% SE-30 on 60/80 Chromosorb W; Column C, same as B, but 6 ft.

Halogenation Procedure. Chlorinations were done in the dark at 0 °C. The ethyl sorbate concentrations were 0.02 mol fraction with respect to the solvent. Chlorine was added as a 1.0 M solution in carbon tetrachloride. The amount of chlorine added was 20–25% of the amount of ethyl sorbate. Sunlamps (225 W) were used to generate the ultraviolet light. When oxygen was used as an inhibitor, it was bubbled into the reaction solution for ca. 3 min before the addition of the halogen, and continued during the reaction until the color of the halogen disappeared. Bromination of ethyl sorbate was carried out as above except that neat bromine was weighed into ca. 2–3 mL of carbon tetrachloride. The yields and product ratios were obtained by VPC analysis on corrected peak areas. Response factors were obtained by analysis of known mixtures prepared from pure products and the following internal standard: *p*-dibromobenzene for chlorinations, and 1,4-dichloro-2-nitrobenzene for brominations.

Reaction of Chlorine with 1a. Ionic Conditions. To 700 mg (5.0 mmol) of ethyl sorbate in 23.8 mL of carbon tetrachloride was added dropwise 1.0 mL of a 1.0 M chlorine solution in carbon tetrachloride. The reaction mixture was stirred for ca. 90 min. Analysis by VPC of this mixture on column A at 70 °C gave products **5a**, **6a**, **4a**, and **3a** with the retention times of 9, 10, 14, and 18 min, respectively. Products **3a** and **4a** were isolated by preparative VPC on column B, and the following spectral properties were recorded. **3a:** IR (CCl_4) 2980 (C–H), 1725 (C=O), 1660 (C=C),[15] 1450, 1365, and 1310 (C–H), 1260, and 1165 (C–O), 965 (C=CH), and 850 cm^{-1}; NMR (CCl_4) δ 1.30 (t, J = 6.8 Hz, 3 H), 1.66 (d, J = 6.2 Hz, 3 H), 4.16 (q, J = 6.8 Hz, 2 H), 4.0–4.6 (m, 2 H), 5.92 (dd, J = 15.2 and 0.8 Hz, 1 H), 6.8 (dd, J = 15.2 and 7.2 Hz, 1 H). **4a:** IR (CCl_4) 2990 (C–H), 1750 (C=O), 1445, 1365, and 1310 (C–H), 1260 and 1160 (C–O), 1020, 960, (C=CH), and 860 cm^{-1}; NMR (CCl_4) δ 1.31 (t, J = 6.8 Hz, 3 H), 1.60 (d, J = 6.5 Hz, 3 H), 4.16 (q, J = 6.8 Hz, 2 H), 4.0–4.8 (m, 2 H), 5.86 (m, 2 H). Compounds **5a** and **6a** had the same VPC retention time and spectra of those products obtained from the dehydrochlorination below.

Radical Conditions. Chlorine gas was bubbled into neat ethyl sorbate illuminated by UV light. Analysis by VPC on column B at 70 °C gave **3a, 4a, 5a,** and **6a** in a ratio of 1.2:1:3:4.8, respectively. Product **4a** was treated with triethylamine in pentane as described below, which gave **6a.** This mixture was distilled to obtain **3a** [bp 95–100 °C (0.02 mm)]. Analysis by NMR (vinyl hydrogens at δ −6.8 and the methyl at δ −1.66) showed the erythro/threo mixture to be 75:25, respectively. An NMR of this mixture gave the following spectra for *threo-***3a:** NMR (CCl_4) δ 1.30 (t, *J* = 6.8 Hz, 3 H), 1.60 (d, *J* = 6.2 Hz, 3 H), 4.16 (q, *J* = 6.8 Hz, 2 H), 4.0–4.6 (m, 2 H), 5.97 (dd, *J* = 15.2 and 0.8 Hz, 1 H), 6.87 (dd, *J* = 15.2 and 7.2 Hz, 1 H).

Reaction of Trichloroamine with 1a. To 0.83 g (5.93 mmol) of ethyl sorbate in 4.54 g of methylene chloride (0.10 mol fraction) was added 1 mL of NCl_3 in methylene chloride (0.79 M), Analysis by VPC on column B revealed that products **3a, 4a, 5a,** and **6a** were formed in 42% yield with a product ratio of 44:45:9:2, respectively. Product **4a** was dehydrochlorinated with triethylamine as described below. Distillation gave **3a,** which upon analysis by NMR showed the erythro/threo ratio to be 53:47, respectively.

Dehydrochlorination of 4a. To 3.40 g (0.0161 mol) of a 40:60 mixture of **3a** and **4a** and 200 mg of *p*-dibromobenzene (internal standard) in 200 mL of pentane was added 1.63 g (0.0161 mol) of triethylamine. A white precipitate formed and analysis of the solution by VPC showed that **4a** had reacted to form **6a** in 80% yield. Analysis of the reaction mixture by VPC after 1 h at 25 °C demonstrated that **3a** was stable to triethylamine under these conditions. The reaction mixture was poured into 100 mL of water, and the organic layer was washed with two 50-mL portions of 1 N HCl, 50 mL of saturated $NaHCO_3$ solution, and dried over $MgSO_4$. The solvent was removed, and **6a** was isolated by preparative VPC on column B at 70 °C. The following spectral data were obtained for **6a:** IR (CCl_4) 3010 and 2850 (C–H), 1725 and 1715 (C=O), 1640 and 1600 (C=CC=C), 1445 and 1360 (C–H), 1260 (C–O), 1230, 1160, 1085, 1035, 970 (C=CH), and 850 cm^{-1}; NMR (CCl_4) δ 1.30 (t, *J* = 6.8 Hz, 3 H), 1.93 (d, *J* = 5.6 Hz, 3 H), 4.21 (q, *J* = 6.8 Hz, 2 H), 5.9–6.6 (m, 2 H), 7.27 (d, *J* = 9.2 Hz, 1 H).

Dehydrochlorination of 3a. To 1.5 g (0.022 mol) of sodium ethoxide in 10 mL of anhydrous ethanol at 20 °C was slowly added 1.00 g (4.74 mmol) of **3a.** The reaction mixture was stirred for ca. 3 min and worked up as described for the dehydrochlorination of **4a** above. Distillation gave 0.55 g (66%) of **5a** [bp 70–71 °C (0.12 mm)] with the following spectral properties: IR (CCl_4) 3010 and 2980 (C–H), 1720 (C=O), 1635 and 1595 (C=CC=C), 1445 and 1360 (C–H), 1300, 1255 (C–O), 1155, 1080, 1040, 955 (C=CH), and 855 cm^{-1}; NMR (CCl_4) δ 1.29 (t, *J* = 6 8 Hz, 3 H), 1.94 (d, *J* = 6.5 Hz, 3 H), 4.17 (q, *J* = 6.8 Hz, 2 H), 6.13 (dd, *J* = 14.2 and 0.8 Hz, 1 H), 6.23 (dq, *J* = 0.8 and 6.5 Hz, 1 H),[16] 7.27 (d, *J* = 14.2 Hz, 1 H).

Reaction of Bromine with 1a. To 2.11 g (15.1 mmol) of ethyl sorbate and 190 mg of internal standard in 113 g of carbon tetrachloride was added 2.0 mL (3.08 mmol) of a bromine–carbon tetrachloride (247 mg/mL) solution. The reaction was stirred at 0 °C for 60 min. Analysis by VPC revealed **3b, 4b,** and **5b** to be formed in a ratio of 91:7:2, respectively (86% yield), with retention times of 16, 12, and 9 min, respectively. Product **3b** was obtained by preparative VPC on column C at 90 °C as a 70:30 erythro/threo mixture indicated by NMR spectra on vinyl and methyl hydrogens listed below. The following data were recorded: IR (CCl_4) 2970 (C–H), 1720 (C=O), 1650 (C=C),[15] 1440, 1360, and 1310 (C–H), 1250 (C–O), 1200, 1155, 1040, 975 (C=CH), and 860 cm^{-1}; NMR (CCl_4) erythro δ 1.30 (t, *J* = 6.8 Hz, 3 H), 1.87 (d, *J* = 6.2 Hz, 3 H), 4.20 (q, *J* = 6.8 Hz, 2 H), 4.2–5.0 (m, 2 H), 5.98 (d, *J* = 14.4 Hz, 1 H), 6.93 (dd, *J* = 14.4 and 0.8 Hz, 1 H); threo δ 1.30 (t, *J* = 6.8 Hz, 3 H), 1.80 (d, *J* = 6.2 Hz, 3 H), 4.20 (q, *J* = 6.8 Hz, 2 H), 4.2–5.0 (m, 2 H), 6.06 (dd, *J* = 14.4 and 0.8 Hz, 1 H), 7.00 (dd, *J* = 14.4 and 8.4 Hz, 1 H). All attempts to isolate **4b** failed, but its structure was deduced from dehydrobrominating **4b** with triethylamine to **6b** as described above for the dehydrochlorination of **4a.** The bromodiene (**6b**) was isolated by preparative VPC on column C at 95 °C and gave the following spectral properties: IR (CCl_4) 3030 and 2980 (C–H), 1730 (C=O), 1630 and 1580 (C=CC=C), 1450 and 1366 (C–H), 1250 (C–O), 1139, 1095, 1044, 998, 972 (C=CH), 923, and 825 cm^{-1}; NMR (CCl_4) δ 1.33 (t, *J* = 6.8 Hz, 3 H), 1.92 (d, *J* = 5.2 Hz, 3 H), 4.22 (q, *J* = 6.8 Hz, 2 H), 6.0–6.6 (m, 2 H), 7.57 (d, *J* = 9.2 Hz, 1 H).

Dehydrobromination of 3b. The reaction was accomplished with 0.53 g (7.3 mmol) of sodium ethoxide and 1.8 g (6.0 mmol) of **3b** in 10 mL of anhydrous ethanol as described above for the dehydrochlorination of **3a.** After the mixture was worked up as described for **3a,** distillation gave 1.0 g (77%) of **5b** [bp 60–65 °C (0.40 mm)] with the following spectral properties: IR (CCl_4) 3030 and 2990 (C–H), 1720 (C=O), 1630 and 1600 (C=CC=C), 1450 and 1365 (C–H), 1300, 1260 (C–O), 1177, 1045, 963 (C=CH), and 869 cm^{-1}; NMR (CCl_4) δ 1.30 (t, *J* = 6.8 Hz, 3 H), 1.99 (d, *J* = 7.2 Hz, 3 H), 4.21 (q, *J* = 6.8 Hz, 2 H), 6.22 (dd, *J* = 14.6 and 0.8 Hz, 1 H),[16] 6.44 (dq, *J* = 0.8 and 7.2 Hz, 1 H), 7.52 (d, *J* = 14.6 Hz, 1 H).

Bromination of 1a in the Presence of an Inhibitor. When **1a** was treated with bromine as described above, but O_2 was bubbled through the reaction mixture a product ratio of 89:4:7 was recorded by VPC analysis for **3b, 4b,** and **5b,** respectively. Distillation [bp 95–105 °C (0.05 mm)] gave **3b,** which was a 75:25 erythro/threo mixture as determined by NMR.[13] The reaction was carried out with 2.8 g (0.020 mol) of **1a** in carbon tetrachloride (0.02 mol fraction diene) and 2.2 g (0.010 mol) of 2,6-di-*tert*-butyl-4-methylphenol was added to the mixture. The product ratios and yields could not be determined, since the inhibitor interfered with the VPC analysis. Distillation gave **3b** and inhibitor. Analysis by NMR as described above showed an erythro/threo ratio for **3b** to be 90:10, respectively. Product **4b** does not survive the distillation.

Radical Reaction of Bromine with 1a. To 5.0 g (35.7 mmol) of neat **1a** with stirring at 0 °C and illumination was added dropwise 1.14 g (1.74 mmol) of neat bromine. Analysis by VPC showed **3b, 4b,** and **5b** to be obtained (85% yield) in a ratio of 91:5:4, respectively. Distillation [bp 95–105 °C (0.05 mm)] gave **3b,** which was a 70:30 erythro/threo mixture by NMR analysis.

Reaction of Lutidine Dibromide with 1a. To 4.42 g (0.0316 mol) of ethyl sorbate in 24.2 g of methylene chloride with stirring at 0 °C was added 4.0 g (0.0158 mol) of lutidine dibromide. The reaction mixture was stirred for 3 h. Analysis by VPC showed **3b, 4b, and 5b** in a ratio 82:4:14, respectively, formed in 78% yield. Distillation [bp 95–110 °C (0.05 mm)] followed by NMR analysis of the distillate displayed an erythro/threo product ratio of 90:10, respectively.

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Registry No.—**1a,** 5941-48-0; **1b,** 5194-51-4; *erythro-***3a,** 62006-40-0; *threo-***3a,** 62006-41-1; *erythro-***3b,** 62006-42-2; *threo-***3b,** 62006-43-3; **4a,** 62006-44-4; **4b,** 62006-45-5; **5a,** 62006-46-6; **5b,** 62006-47-7; **6a,** 62006-48-8; **6b,** 62006-49-9.

References and Notes

(1) (a) Point Loma College; (b) Bethany Nazarene College.

(2) Ionic conditions are defined as: low mole fraction olefin, absence of light, and presence of an inhibitor. Radical reactions are favored by neat olefin (molecule-induced homolysis), a nitrogen atmosphere, and ultraviolet illumination. See ref 5.

(3) R. C. Fahey and H. J. Schneider, *J. Am. Chem. Soc.*, **90,** 4429 (1968).

(4) (a) G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *J. Org. Chem.*, **38,** 4109 (1973); (b) G. E. Heasley, D. C. Hayse, G. R. McClung, D. K. Strickland, V. L. Heasley, P. D. Davis, D. M. Ingle, K. D. Rold, and T. S. Ungermann, *ibid.*, **41,** 334 (1976).

(5) (a) V. L. Heasley, G. E. Heasley, and S. K. Taylor, *J. Org. Chem.*, **35,** 2967 (1970); V. L. Heasley and S. K. Taylor, *ibid.*, **34,** 2779 (1969); (b) M. L. Poutsma, *ibid.*, **31,** 4167 (1966); M. L. Poutsma and J. L. Kartch, *Tetrahedron,* **22,** 2167 (1966); M. L. Poutsma, *J. Am. Chem. Soc.*, **87,** 4293 (1965).

(6) (a) K. V. Auwers and J. Heyna, *Justus Lubigs Ann. Chem.*, **434,** 140 (1923); (b) K. V. Auwers and W. Muller, *ibid.*, **434,** 165 (1923).

(7) The stereochemistry of **4a** could not be determined by spectral methods.

(8) 1,4-Products are also favored when butadiene is treated with chlorine and bromine under radical conditions. See for chlorinations M. L. Poutsma, *J. Org. Chem.*, **31,** 4167 (1966); and for brominations V. L. Heasley and S. K. Taylor, *ibid.*, **34,** 2779 (1969).

(9) V. L. Heasley, G. E. Heasley, and B. T. Gipe, *J. Org. Chem.*, submitted for publication.

(10) The difference in product ratios for the addition of chlorine and trichloramine to **1a** indicates that these radical chlorinating reagents have different steric and/or electronic requirements in the chain-transfer step (compare entries 5 and 6).

(11) This suggests that the addition of bromine to other carbonyl conjugated olefins may also react by a radical process. Bromination of diethyl malonate and diethyl fumarate were reported to react by an ionic mechanism. See R. P. Bell and M. Pring, *J. Chem. Soc. B,* 119 (1966).

(12) The stereospecificity increases significantly when other dienes are treated with amine–halogen complexes and probably represents an ionic process for these reactions: V. L. Heasley, C. N. Griffith, and G. E. Heasley, *J. Org. Chem.*, **40,** 1358 (1975), and unpublished work.

(13) Although oxygen is an effective scavanger for chlorine radicals, it is not effective with bromine radicals (compare entries 8, 10, and 11 with 9). We observed that oxygen did not inhibit radical bromination of butadiene in a previous study.

(14) P. Kovacic and S. S. Chudhary, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, N.Y., 1973, p 35.
(15) The IR stretching frequency of a double bond in conjugation with a carbonyl is very strong. See R. T. Conley, "Infrared Spectroscopy", Allyn and Bacon, Boston, Mass., 1966, p 99. The double bond stretching frequency was too weak to be observed at normal concentration in the 1,4-products where the carbonyl is not in conjugation.
(16) Bothner-By has investigated long-range coupling in a large number of butadienes and found that 1,4-vinyl protons in the trans,trans configuration show coupling constants ranging between 1.3 and 1.9 Hz, while cis,trans and cis,cis 1,4-vinyl protons show coupling between 0.5 and 0.9 Hz. Since the protons on the α,β carbons of **5** show a trans coupling (J = 14.2 Hz), the long range coupling of 0.6 Hz on the vinyl proton at δ 6.23 indicates a 1,4-cis,trans coupling in the trans,trans diene (**5**). See A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3445, 3451 (1965); A. A. Bothner-By and D. Jung, *ibid.*, **90**, 2342 (1968); A. A. Bothner-By and E. Moser, *ibid.*, **90**, 2347 (1968); A. A. Bothner-By and D. F. Koster, *ibid.*, **90**, 2351 (1968).

Liquid-Phase Photolysis of Dioxane

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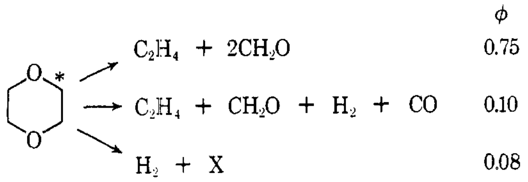
The photolysis of neat liquid-phase dioxane with a medium-pressure mercury lamp has been shown to give, in addition to gaseous products, a complicated mixture of liquid and solid products. The liquid product mixture has been partially separated, and evidence for the structures of nine previously unreported hydroxy ether and carbonyl containing components is presented. The products are postulated to result from initial CO bond scission followed by subsequent reactions of the radicals produced and from secondary photolyses. The photoproducts are not formed in any significant amount when either dioxane or dioxyldioxane is irradiated in ethanolic solution.

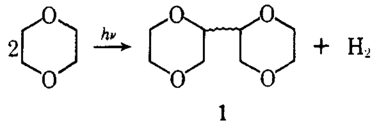
The photochemistry of simple aliphatic ethers in the gas phase has been studied by numerous workers, and a combination of radical and molecular processes reported.[1] In particular, the gas-phase photolysis of dioxane has been studied by Parrish and co-workers, both at 1470 Å[2] and with a megawatt ruby laser.[3] At 1470 Å, three processes were observed, and are given with their quantum yields in Scheme I. The laser-promoted decomposition yielded ethylene, CO, and H_2 in the ratio 1:2:2. It was postulated that these products were formed from a vibrationally excited ground state of dioxane, and that the hydrogen resulted from a molecular elimination, rather than via radical abstraction.

Scheme I



Considerably less attention has been given to the solution or neat liquid-phase photolysis of ethers, probably owing to the greater experimental difficulty of irradiating in the 200-nm region or below, where alcohols and ethers have their principal absorption band (n → σ^*). This is unfortunate because these compounds have often been used as solvents for photochemical reactions using low- and medium-pressure mercury lamps capable of emitting small to moderate amounts of radiation in this region.

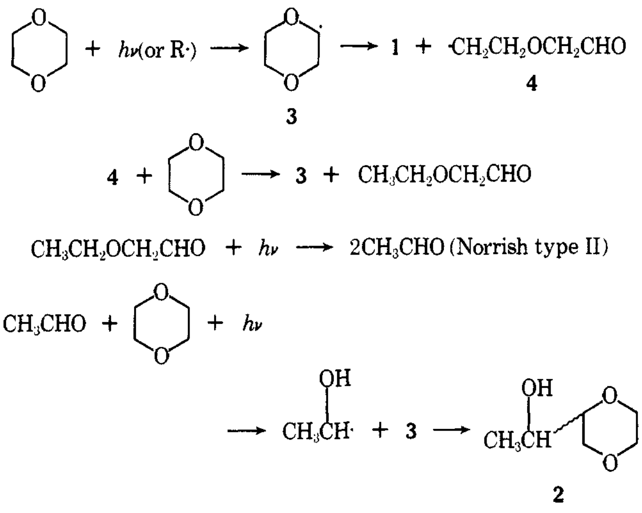
Pfordte studied the neat liquid-phase photolysis of several aliphatic ethers,[4] and reported that dioxane, after irradiation for 24 h with a medium-pressure mercury lamp, yields gaseous, liquid, and solid products. The major gaseous products were identified as H_2, CO, CH_4, C_2H_4, and C_2H_6. Minor amounts of other saturated and unsaturated hydrocarbon gases were also detected. The liquid product was not analyzed, but the solids were shown to be the racemic and meso forms of dioxyldioxane (1), for which the following mechanism of formation was advanced (eq 1).



(1)

Mazzocchi and Bowen have recently reported[5] two additional products from the 200-h photolysis of neat dioxane, the meso and racemic forms of 1-hydroxyethyldioxane (2), which they rationalize as forming via Scheme II. There is precedent for the third step in Srinivasan's photolysis of methoxyacetone[6] which efficiently yields formaldehyde and acetone. The photoreduction of acetaldehyde in dioxane was demonstrated by Mazzocchi and Bowen to occur readily.

Scheme II



Both Pfordte and these later workers used medium-pressure mercury lamps which have an approximate lower wavelength limit of 190 nm. It seemed to us unlikely that a CH bond, which normally does not absorb above 150 nm (considering the absorption spectra of simple alkanes), could be broken in the primary step of this photolysis, as claimed, particularly since rupture of a CO bond in an n → σ^* process, occurring at slightly below 200 nm, is well documented.[7] Direct photochemical CH bond scission, in contrast to H *abstraction*,