Addition to 2,4-Dienes. Ionic and Radical Additions to Ethyl Sorbate

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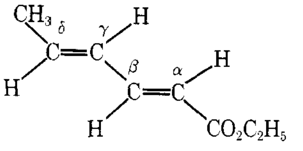
The electrophiles chlorine (Cl_2), methyl hypochlorite (CH_3OCl), bromine (Br_2), methyl hypobromite (CH_3OBr), and *N*-bromosuccinimide (NBS) were added to ethyl sorbate (1) under ionic conditions in methanol as solvent. Addition of CH_3OCl and CH_3OBr to neat 1 under ultraviolet illumination resulted in molecule-induced homolysis reactions. Under ionic conditions, addition of electrophiles to the γ,δ bond of 1 represents the major pathway, presumably because addition to the α,β bond of 1 disrupts conjugation of the π system with the carbonyl. Radical reagents attack only the β and δ carbons of 1, which gives intermediates with delocalization of radicals into the carbonyl. Attack by radical reagents at the δ carbon rather than the β carbon of 1 is preferred because the electron can delocalize over five atoms.

Recently, we reported on the addition of halogens to a diene in which the double bonds are in conjugation with the carbonyl group.[2] We found that in nonpolar solvents chlorine reacts with ethyl sorbate (1) by an ionic or radical pathway,



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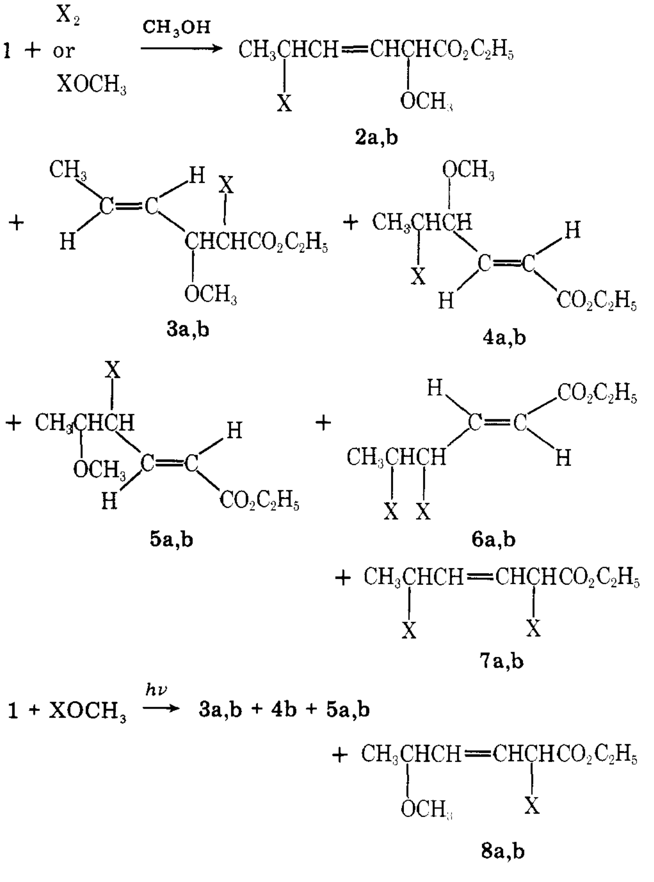
while bromine prefers to react with 1 by a radical process unless an efficient radical inhibitor is used.

In our previous study[2] only symmetrical electrophiles were used, and therefore the regiospecificity of additions could not be examined. Our goal in this investigation was to determine the regiospecificity and the relative reactivities at the α,β and γ,δ bonds of 1 with ionic and radical reagents. The following unsymmetrical electrophiles were employed under ionic conditions:[3] chlorine (Cl_2) in methanol, methyl hypochlorite (CH_3OCl) in methanol,[3] bromine (Br_2) in methanol, methyl hypobromite (CH_3OBr) in methanol,[3] and *N*-bromosuccinimide (NBS) in methanol. Unsymmetrical radical reagents were comprised of methyl hypochlorite and methyl hypobromite in neat 1 under ultraviolet illumination.[3]

Results and Discussion

Products obtained with these reagents in methanol under ionic conditions and with CH_3OCl and CH_3OBr under radical conditions are listed in Table I. Structural assignments for all of the products except **3b** and **8b** are based on spectral data.[4]

Compounds **3b** and **8b** were labile and could not be isolated by preparative VPC. Support for their structures is based on conversion to **3a** and **8a**, respectively, when a mixture of **3b**, **5b**, and **8b** was treated with excess lithium chloride in dimethyl sulfoxide. Product **8b** was converted quantitatively to **8a** in less than 5 min, and **3b** was converted in high yield to **3a** in 25 min. The reaction of **5b to 5a** was only ca. 20% complete after 24 h under these conditions. The relative reactivities of **3b**, **5b**, and **8b** with lithium chloride under S_N2 conditions lend additional support to their structure assignments. Compound **8b** is most reactive because the bromine is both allylic and adjacent to a carbonyl.[5] Apparently, **5b** is less reactive than **3b** because an allylic bromine is not as rapidly displaced as a bromine adjacent to a carbonyl.



2a,b

3a,b

4a,b

5a,b

6a,b

7a,b

8a,b

a, X = Cl; b, X = Br

Under ionic conditions, the data in Table I suggest that **10a** is an intermediate when bromine as an electrophile adds to the α,β bond of 1 (Scheme I). Products derived from **10a** will serve as a test for the relative rate of nucleophilic ring opening of a halonium ion at a carbon α to a carbonyl[5] vs. a carbon which is allylic. The data in Table I show that with bromine electrophiles only the 1,2-product **3b** is formed by attack at the α,β bond, whereas chlorine electrophiles give the 1,4-product **8a** (compare entries 3–5 with 2 in Table I).[6] The lack of any 1,4-product **8b** with bromine electrophiles indicates that an unsymmetrically bridged bromonium ion is involved at the α,β bond of **10a** since a symmetrically bridged ion should undergo some opening at the α carbon[5] and an open ion should give some **8b**. Possibly the carbon–halogen bond at the α carbon is stronger than the carbon–halogen bond at the β carbon in this bromonium ion because formation of a positive charge adjacent to a carbonyl would be unfavorable.

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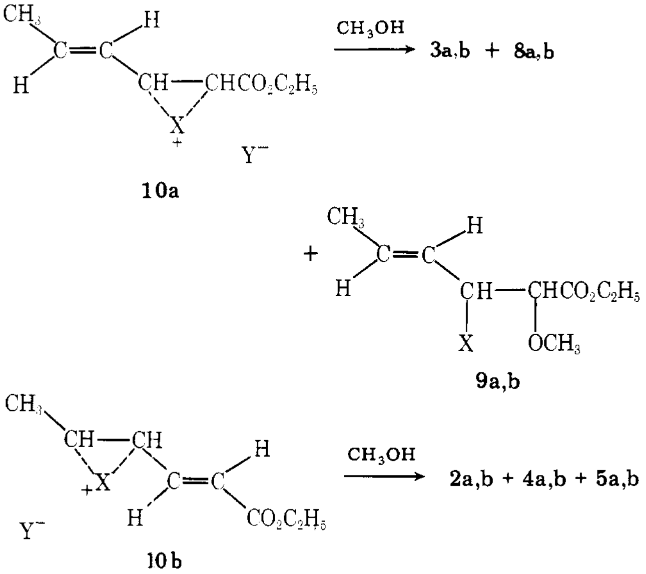
Table I. Addition of Unsymmetrical Halogenating Reagents to Ethyl Sorbate

		Products, %							
		1,4-δ-Halo	1,4-α-Halo	1,2-α-Halo	1,2-δ-Halo	1,2-γ-Halo		% addition	
Entry	Reagents[a]	**2a,b**	**8a,b**	**3a,b**	**4a,b**	**5a,b**	Yield,[b] %	α,β bond	γ,δ bond
1	Cl_2/CH_3OH[c]	*c*	*c*		83	10	56[d]	0	100
2	CH_3OCl/CH_3OH	6	5		80	9	99	5	95
3	Br_2/CH_3OH	22		24	49	5	73[e]	24	76
4	NBS/CH_3OH	36		12	41	11	61	12	88
5	CH_3OBr/CH_3OH	13		4	78	5	83	4	96
6	CH_3OCl		21	17		62[f]	72	38	62
7	CH_3OBr		6	3	4	87[f]	89	9	91

[a] Reaction was carried out at 0 °C with stirring. Ionic conditions were 0.02 mol fraction of **1** in anhydrous methanol. Radical conditions were neat **1** under nitrogen and illumination with UV light. [b] Determined by VPC to ca. ±3%. [c] Products **2a** and **8a** have the same VPC retention times, and these products can only be determined by NMR analysis. We were unable to collect this peak because it was a minor component (7%), and a substitution product identified in our previous paper[2] had a retention time close to **2a** and **8a.** [d] Yield includes 10% of a γ,δ-dichloro product (**6a**) identified previously.[2] [e] Yield includes 35% of α,β- and γ,δ-dibromo products **6b** and **7b,** which were identified previously.[2] [f] NMR and VPC analysis show a 60:40 ratio of erythro–threo isomers, respectively.

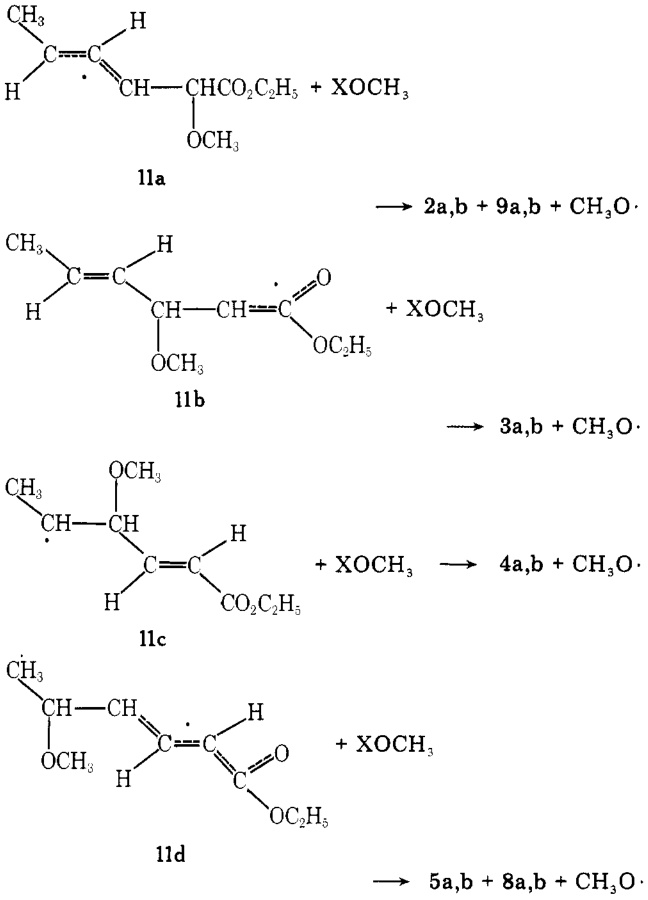
Scheme I



Addition of the electrophile under ionic conditions to the γ,δ bond of **1** (see Scheme I) represents the major pathway of these reactions, presumably because addition to the α,β bond disrupts conjugation of the π system with the carbonyl. Solvent opens the γ,δ-halonium ions of **10b** preferably at the allylic carbon to give products **4a,b** (entries 1–5). The halonium ions at the γ,δ bond must be symmetrically bridged since nucleophilic ring opening at the δ carbon to give *erythro*-**5a,b** is noted (entries 3–5). Formation of these products by a radical pathway seems unlikely since the reactions are in methanol, and a radical reaction would lead to some *threo*-**5a,b.** Products **2a,b** are the result of an S_N2'-like reaction by the solvent when the halonium ion intermediate is formed at the γ,δ bond of **1.**

Ionic reactivity of the α,β and γ,δ bonds in **1** will be governed by the relative energies of the transition states leading to intermediates **10a** and **10b.** Addition of an electrophile might be preferred at the γ,δ bond of **1** because the γ,δ bond is more basic than the α,β bond and conjugation with the ester carbonyl would not be disrupted. On the other hand, a later transition state should favor attack at the α,β bond because a more stable (delocalized) intermediate can be formed. The data in Table I show that the lower-energy (earlier) transition state leading to addition at the γ,δ bond is favored with these electrophiles. Chlorine electrophiles show a greater tendency than bromine electrophiles to attack the γ,δ bond of **1,** which suggests that the chlorine systems have an earlier transition state than bromine in these reactions.

Scheme II



X = Br or Cl

A radical may attack at the α, β, γ, or δ carbon atoms of **1** (Scheme II). Attack by a radical addend at the α carbon of **1** will form a secondary allylic radical intermediate (**11a**), while addition to the β carbon of **1** will give a secondary radical adjacent to a carbonyl, as indicated in **11b.** Similarly, intermediates **11c** and **11d** will contain a secondary radical and a secondary resonance-stabilized radical, respectively. We carried out a control experiment and found that return to the starting diene from radical intermediates **11a–d** is not a significant part of the reaction pathway (see Experimental Section). Thus, the product percentages in Table I (entries 6 and 7) very nearly represent the amount of initial attack by the radical on the α, β, γ, and δ carbons of **1.**

Under radical conditions (molecule-induced homolysis or photolysis) the major products are **5a,b,** which were shown to be a 60:40 mixture of erythro–threo isomers (entries 6 and 7). Generally, addition of radical reagents to dienes gives primarily 1,4 products.[7] In the radical reactions of CH_3OCl and CH_3OBr with **1** only small amounts of 1,4 products (**8a,b**) are formed because conjugation of the α,β bond with the ester carbonyl would be destroyed by 1,4 addition.

It is curious that there is essentially no radical attack on the α and γ carbons to give intermediates **11a** and **11c**, respectively (Scheme II).[8] Formation of **11a** disrupts resonance conjugation with the ester carbonyl, and intermediate **11c** is not stabilized by resonance. Perhaps attack at the δ carbon is the preferred pathway since the radical can be delocalized over five atoms. Apparently, delocalization of radicals into a carbonyl is energetically favorable because intermediate **11b** is produced rather than **11a** and **11c**.

Experimental Section

Materials and chemicals were obtained commercially except for methyl hypochlorite[9] and methyl hypobromite,[10] which were prepared as described in the literature. Ethyl sorbate was distilled prior to use. IR and NMR spectra were obtained on a Beckman IR-10 spectrophotometer and a Varian T-60 A or XL-100 spectrometer, respectively. Vapor phase chromatographic analysis was accomplished with a Hewlett Packard 5796A flame ionization chromatograph. Preparative vapor phase chromatography was accomplished with a Varian A–9]–P chromatograph. The following columns were used: column A (glass), 4 ft × 4 mm (i.d.), 2.5% SE-30 on 80–100 mesh Chromosorb W; column B (stainless steel), 6 ft × 0.25 in, 3% SE-30 on 80–100 mesh Chromosorb W; column C (stainless steel), 6 ft × 1/8 in, 3% SE-30 on 80–100 mesh Chromosorb W; column D, same as column C but 10 ft; column E (glass), 8 ft × 8 mm (i.d.), 5% Silicone DC-550 on 80–100 mesh Chromosorb W. The pure isolated compounds were reinjected into the VPC instrument and found to be stable under our analysis conditions. The product percentages in Table I and the yields were obtained using area/weight response factors with *p*-chloronitrobenzene as an internal standard. A 275-W sunlamp was used for ultraviolet illumination.

Reaction of Bromine with Ethyl Sorbate (1) in Methanol. To 407 mg (2.9 mmol) of **1** in 4.6 g of anhydrous methanol at 0 °C was added 158 mg (1.0 mmol) of bromine dissolved in 1.0 mL of carbon tetrachloride with stirring. The mixture was stirred for 45 min and then poured into water, extracted with methylene chloride, and dried over anhydrous $MgSO_4$. Analysis by VPC on column A at 70 °C showed products (73%) **2b, 3b, 4b, 5b, 6b,** and **7b** with retention times of 5.6, 7.7, 11, 13, 15, and 19 min, respectively. These compounds, except **3b**, were isolated by preparative VPC on column B. We were unable to isolate the labile product **3b** but assigned it the α,β structure based on its conversion to **3a**, as described below. Spectral data for the γ,δ- and α,δ-dibromo products **6b** and **7b** have been reported previously.[2] The remaining products gave the following spectral properties. **2b:** IR(CCl_4) 2990 (CH), 1750 (C=O), 1445, 1370, and 1300 (CH), 1250 and 1175 (C–O), 1140, 1085, 960 (C=CH), 850 cm^{-1}; NMR (CCl_4) δ 1.30 (t, J = 7.2 Hz, 3 H), 1.81 (d, J = 6.2 Hz, 3 H), 3.23 (s, 3 H), 3.83 (d, J = 3.2 Hz, 1 H), 3.9–4.4 (m, 1 H), 4.10 (q, J = 7.2 Hz, 2 H), 5.2–5.9 (m, 2 H).

4b: IR (CCl_4) 2990 (CH), 1720 (C=O), 1655 (C=C), 1440 and 1365 (CH), 1260 and 1160 (C–O), 1030, 970 (C=CH), 850 cm^{-1}; NMR (CCl_4) δ 1.33 (t, J = 7.5 Hz, 3 H), 1.70 (d, J = 6.4 Hz, 3 H), 3.39 (s, 3 H), 3.4–3.9 (m, 1 H), 3.95–4.4 (m, 1 H), 4.22 (q, J = 7.5 Hz, 2 H), 6.05 (d, J = 16.0 Hz, 1 H), 6.44 (dd, J = 16.0 and 6.4 Hz, 1 H).

5b: IR (CCl_4) 2990 (CH), 1725 (C=O), 1655 (C=C), 1445, 1370, and 1310 (CH), 1260 and 1150 (C–O), 1090, 1030, 970, 800 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 1.27 (d, J = 6.2 Hz, 3 H), 1.31 (t, J = 7.1 Hz, 3 H), 3.40 (s, 3 H), 3.4–3.8 (m, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 4.4–4.7 (five peak multiplet, 1 H), 6.01 (d, J = 15.5 Hz, 1 H), 6.97 (dd, J = 15.5 and 9.2 Hz, 1 H).

Reaction of *N*-Bromosuccinimide with 1 in Methanol. To 500 mg (3.57 mmol) of **1** in 5.6 of anhydrous methanol at 0 °C was added 130 mg (0.73 mmol) of NBS. The reaction mixture was stirred for 60 min, poured into water, extracted with methylene chloride, and dried over anhydrous $MgSO_4$. Analysis by VPC on column C at 120 °C gave products (61%) **2b, 3b, 4b,** and **5b** with retention times of 8.5, 11, 15, and 16 min, respectively.

Reaction of Methyl Hypobromite with 1. Ionic Conditions. To 700 mg (5.0 mmol) of **1** in 10 mL of anhydrous methanol at 0 °C was added 1.3 mL of a 0.76 M methyl hypobromite solution in carbon tetrachloride with stirring. The reaction mixture was stirred for 20 min. Analysis by VPC of this mixture on column C at 120 °C gave products **2b, 3b, 4b,** and **5b** with retention times of 7, 9, 12, and 13 min, respectively. The spectral properties of these products are given above.

Reaction of Methyl Hypobromite with 1. Radical Conditions. To 700 mg (5.0 mmol) of neat **1** at 0 °C, irradiated with UV light, was added 1.3 mL of a 0.76 M methyl hypobromite solution in carbon tetrachloride. The reaction was complete in 5 min. Analysis by VPC on column D at 120 °C gave products **8b, 3b, 4b,** and **5b** with retention times of 8, 9, 12, and 13 min, respectively. Compound **8b** was not isolated, but its structure is based on its reactivity and conversion to **8a**, as described below. Product **5b** was shown to be a 60:40 mixture of erythro–threo isomers by VPC and NMR analysis. The erythro and threo isomers of **5b** were not completely resolved but had retention times of 24 and 25 min on column D at 105 °C. The 100-MHz NMR ($CDCl_3$) spectra showed a difference in the β-vinyl hydrogens as follows: *erythro*-**5b**, δ 6.97 (dd, J = 15.5 and 9.2 Hz); *threo*-**5b**, δ 7.00 (dd, J = 15.5 and 9.2 Hz).

Reaction of the Product Mixture from Methyl Hypobromite with Lithium Chloride. To 358 mg (1.43 mmol) of **8b, 3b,** and **5b** in a ratio of 1.6:1.0:6.4, respectively, with *p*-chloronitrobenzene as an internal standard in 5 mL of dimethyl sulfoxide at 25 °C was added 304 mg (7.15 mmol) of lithium chloride. Aliquots were withdrawn, added to water, extracted with methylene chloride, and dried over anhydrous magnesium sulfate. Analysis by VPC on column D showed that **8b** was converted quantitatively to **8a** in less than 5 min, while **3b** was converted in ca. 90% yield to **3a** after 25 min. The reaction of **5b** to **5a** with lithium chloride was less than 20% complete after 24 h under these conditions.

Reaction of Chlorine with 1 in Methanol. To 560 mg (4.0 mmol) of **1** in 6.5 g of anhydrous methanol was added 1.0 mL of a 0.80 M chlorine solution in carbon tetrachloride. The reaction mixture was stirred for 45 min at 0 °C and then worked up as described above for bromine in methanol. Analysis by VPC on column D at 110 °C gave products (56%) **2a, 4a,** and **5a** with retention times of 11, 14, and 17 min, respectively. The products had the following spectra. **4a:** IR (CCl_4) 2985 (CH), 1725 (C=O), 1655 (C=C), 1445 and 1365 (CH), 1260 and 1170 (C–O), 1085, 1030, 970 (C=CH), 850 cm^{-1}; NMR (CCl_4) δ 1.30 (t, J = 7.2 Hz, 3 H), 1.47 (d, J = 6.4 Hz, 3 H), 3.36 (s, 3 H), 3.6–4.2 (m, 3 H), 4.20 (q, J = 7.2 Hz, 2 H), 6.00 (dd, J = 0.6 Hz), 6.80 (dd, J = 15.2 and 6.0 Hz, 1 H).

5a: IR (CCl_4) 2990 (CH), 1725 (C=O), 1665 (C=C), 1450, 1370, and 1310 (CH), 1260 and 1170 (C–O), 1090, 1035, 975 cm^{-1}; NMR (CCl_4) δ 1.26 (d, J = 6.2 Hz, 3 H), 1.32 (t, J = 7.2 Hz, 3 H), 3.41 (s, 3 H), 3.4–3.8 (m, 1 H), 4.22 (q, J = 7.2 Hz, 2 H), 4.3–4.7 (m, 1 H), 6.08 (dd, J = 15.2 and 0.6 Hz, 1 H), 6.90 (dd, J = 15.2 and 7.2 Hz, 1 H).

Reaction of Methyl Hypochlorite with 1. Ionic Conditions. To 1.14 g (8.13 mmol) of **1** in 13 g of anhydrous methanol at 0 °C was added 1.0 mL of a 1.62 M methyl hypochlorite solution in methylene chloride. The reaction mixture was stirred for 45 min and analyzed by VPC on column D at 100 °C (99%): **2a, 8a, 4a,** and **5a** were obtained, and the percent yields are given in Table I. The 1,4-products **2a** and **8a** have the same retention times on columns A–D, and **2a** was therefore collected as a mixture. This mixture gave an IR spectrum similar to **8a**. The NMR (CCl_4) spectrum differed from **8a** in that a doublet (J = 7.0 Hz) for the methyl substituent on the δ carbon was observed at δ 1.40 for **2a**.

Reaction of Methyl Hypochlorite with 1. Radical Conditions. To 1.14 g (8.13 mmol) of neat **1** at 0 °C, irradiated with UV light, was added 1.0 mL of a 1.62 M methyl hypochlorite solution in methylene chloride. The reaction was stirred for 45 min at 0 °C. Analysis by VPC on column D at 110 °C gave products (72% yield) **8a, 3a,** and **5a** in a ratio of 1.2:1.0:3.7, respectively. Product **5a** was shown to be a 60:40 mixture of erythro–threo **5a** isomers, respectively, by VPC and NMR analysis. Retention times were 16 and 17 min for *threo*- and *erythro*-**5a**. The NMR (CCl_4) spectrum of the erythro–threo **5a** mixture was similar to that reported for *erythro*-**5a** above except for the vinyl hydrogen of *threo*-**5a** [δ 6.95 (dd, J = 15.2 and 6.8 Hz)].

Products **3a** and **8a** were isolated pure by preparative VPC on column E and gave the following spectral data. **3a:** IR (CCl_4) 2990 (CH), 1760 (C=O), 1450 and 1370 (CH), 1265 and 1180 (C–O), 1130, 1020, 955, 850 cm^{-1}; NMR (CCl_4) δ 1.28 (t, J = 7.0 Hz, 3 H), 1.58 (d, J = 6.6 Hz, 3 H), 3.37 (s, 3 H), 4.15 (q, J = 7.0 Hz, 2 H), 4.0–4.7 (m, 2 H), 5.6–6.2 (m, 2 H).

8a: IR (CCl_4) 2980 (CH), 1750 (C=O), 1450 and 1375 (CH), 1255 (C–O), 1180, 1155, 1095, 1025, 965, 850 cm^{-1}; NMR δ 1.20 (d, J = 6.0 Hz, 3 H), 1.30 (t, J = 6.8 Hz, 3 H), 3.23 (s, 3 H), 3.3–3.8 (m, 1 H), 4.20 (q, J = 6.8 Hz, 2 H), 4.5–4.8 (m, 1 H), 5.6–6.0 (m, 2 H).

Reaction of the Product Mixture from Methyl Hypochlorite with Sodium Bromide. To 87 mg (0.42 mmol) of **8a, 3a,** and **5a** in a ratio of 1.1:1.0:3.5, respectively, with p-chloronitrobenzene as a standard in 10 mL of acetone was added 2.5 g of sodium bromide. The mixture was refluxed, and after 40 h **8a** was converted to **8b** in 74% yield. Products **3a** and **5a** did not react under these conditions.

Reaction of Methyl Hypochlorite with *cis,trans*-Ethyl Sorbate Under Molecule-Induced Homolysis Conditions. To 215 mg (1.53 mmol) of *cis,trans*-ethyl sorbate[11] at 0 °C in the dark was added 0.7 mL of 0.495 M methyl hypochlorite solution in carbon tetrachloride.[12] After 3 h at 0 °C, VPC analysis on column C at 50 °C showed that only 1.8% of **1** was formed from *cis,trans*-ethyl sorbate during this reaction. This experiment shows that return to the starting diene from intermediates **11b** and **11d** is a very minor component in this reaction pathway. Therefore, the product percentages in Table I very nearly represent the kinetic product ratio for these radical reactions. Analysis on column C at 105 °C gave products (38% yield) **8a**, **3a**, and *cis*-**5a** in a ratio of 4.5:1.0:1.6, respectively.[13] Products **8a** and *cis*-**5a** were a 60:40 ratio of erythro–threo isomers. Compound **3a** was a broad peak in the VPC analysis, but the erythro–threo isomers were not resolved under these conditions.

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Registry No.—**1**, 5941-48-0; *cis,trans*-**1**, 53282-25-0; **2a**, 66017-96-7; **2b**, 65996-25-0; **3a**, 65996-26-1; **3b**, 65996-27-2; **4a**, 65996-28-3; **4b**, 65996-29-4; *erythro*-**5a**, 65996-30-7; *threo*-**5a**, 65996-31-8; (*Z*)-*erythro*-**5a**, 65996-32-9; (*Z*)-*threo*-**5a**, 65996-33-0; *erythro*-**5b**, 65996-34-1; *threo*-**5b**, 65996-35-2; **6b**, 65996-36-3; **7b**, 62006-45-5; *erythro*-**8a**, 65996-37-4; *threo*-**8a**, 65996-38-5; **8b**, 65996-39-6.

References and Notes

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

(2) D. F. Shellhamer, V. L. Heasley, J. E. Foster, J. K. Luttrull, and G. E. Heasley, *J. Org. Chem.*, **42**, 2141 (1977).

(3) Alkyl hypochlorites and hypobromites react by an ionic process in a protic solvent or in a nonpolar aprotic solvent when an acid catalyst is used. In aprotic solvents without an acid catalyst, or in neat olefin or diene, a rapid radical reaction (molecule-induced homolysis) is observed. See (a) G. E. Heasley, V. L. Heasley, D. F. Shellhamer, W. E. Emery III, R. Hinton, and S. L. Rodgers, *J. Org. Chem.*, in press; (b) G. E. Heasley, V. M. McCully, R. T. Wiegman, V. L. Heasley, and R. A. Skidgel, *ibid.*, **41**, 644 (1976); (c) C. Walling and R. T. Clark, *ibid.*, **39**, 1962 (1974); (d) D. F. Shellhamer, D. B. McKee, and C. T. Leach, *ibid.*, **41**, 1972 (1976).

(4) (a) 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 nonconjugated double-bond frequency was too weak to be observed at normal concentration of the products. (b) NMR spectral shifts of the β-vinyl hydrogen on the α,β-unsaturated products **4a,b**, **5a,b**, and **6a,b** appear at 0.4–0.9 ppm downfield relative to the α-vinyl protons in these products. Our data show that the protons of a methyl group on the δ carbon in the NMR spectrum resonate at 1.2–1.3 ppm when a methoxy substituent is on the δ carbon, while a halogen on that carbon lowers the chemical shift to 1.4–1.8 ppm. A vinyl methyl appears at 1.28 ppm.

(5) Bimolecular substitution is greatly accelerated when a carbonyl is α to the leaving group; see E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, p 284.

(6) The absence of any 1,2 product (**3a**) from addition of chlorine electrophiles to **1** is curious. Addition of chlorine to butadiene in methanol gives only ca. 30% of 1,4 products, while addition to the 1,2 bond in *cis*- and *trans*-1,3-pentadienes gives predominately 1,4 products. See ref 3b.

(7) M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966). See ref 3a.

(8) The 4% of **4b** formed with methyl hypobromite may be due to a minor ionic component in this reaction.

(9) Methyl hypochlorite was prepared by a modification of the method used to prepare *n*-butyl hypochlorite: E. L. Jenner, *J. Org. Chem.*, **27**, 1031 (1962).

(10) V. L. Heasley, C. L. Frye, G. E. Heasley, K. A. Martin, D. A. Redfield, and P. S. Wilday, *Tetrahedron Lett.*, 1573 (1970).

(11) *cis,trans*-Sorbic acid was donated by Keith H. Hollenback, University of Oklahoma. The acid was treated with ethanol and boron trifluoride as catalyst to give *cis,trans*-ethyl sorbate.

(12) The *cis,trans*-ethyl sorbate was chosen since the intermediate **11b** destroys a cis α,β bond and would therefore be a sensitive test for a reversible intermediate. Return to the starting diene from **11b** gives back the resonance stabilization energy of a diene to a carbonyl. This molecule-induced homolysis reaction was done in the dark because UV illumination isomerized *cis,trans*-ethyl sorbate to **1**. Reaction of neat **1** with or without UV illumination did not change the product ratio.

(13) Compound **8a** rather than **5a** is the major product when methyl hypochlorite is added to *cis,trans*-ethyl sorbate. Perhaps the cis α,β bond is more reactive than the trans α,β bond of **1**.

Solid–Liquid Phase-Transfer Catalysis by a Quaternary Ammonium Salt. A Comparison with Crown Ethers and Polyalkylamines

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Aliquat 336, a quaternary ammonium salt, has been used as a phase-transfer catalyst for the solid–liquid interface. A comparison of its catalytic ability with that of 18-crown-6 ether and tetramethylethylenediamine has been made. The quaternary ammonium salt is equivalent to and in many cases markedly superior to both crown ether and tetramethylethylenediamine for catalyzing acetate, fluoride, and adeninyl anion displacement reactions. However, the cyanide anion reacts at least 100 times faster when catalyzed by crown ether relative to the quaternary salt.

Crown ethers,[1] polyamines,[2] and ammonium and phosphonium salts[3] have been established as unique and effective catalysts for anionic reactions during the last 10 years. All three of these types of catalysts derive synthetic utility from their ability to solubilize inorganic reagents (and salts) in aprotic nonpolar organic solvents. The anions of these solubilized salts possess tremendous nucleophilicity as a result of a high degree of ionic dissociation[4] and at the same time they lack any significant solute–solvent interaction. The result of this phenomenon is the ability to use inorganic reagents in organic solvents to perform a variety of synthetic reactions[1–3] which would otherwise require more drastic, less desirable conditions.

Although the principles for the catalytic ability of these classes of compounds are similar, the application of each class has until now been different. The crown ethers and polyamines function by complexing with an insoluble reagent rendering the entire entity soluble. The quaternary ammonium salts have traditionally only been used to extract the anions of salts from an aqueous solution into an organic phase for subsequent reaction with a dissolved electrophile. Herein we report our results on the ability of a quaternary ammonium salt (Aliquat 336, Q^+)[5] to function as a phase-transfer catalyst

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