above for the rate constants.

Controls on Kinetic Materials. As a typical example of the method employed, 0.0428 g (1.21×10^{-4} mol) of 3-methyl-*endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate was dissolved in 5.0 mL of 80% aqueous acetone. The sample was sealed in an ampule and heated for 15 min (time for hydrolysis of ca. 25% of the ester) at 100.0 °C. The sample was cooled, poured into water, and extracted with ether. The ethereal solution was washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. All traces of solvent were removed on the vacuum pump and the sample was analyzed for 3-methyl-*exo*- and -*endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates by NMR.

Hydrolysis Products. As an example of the procedure, a sample of 0.2902 g (8.52×10^{-4} mol) of *endo*-cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate and 0.20 g (2×10^{-3} mol) of calcium carbonate were combined with 5 mL of 80% aqueous acetone and sealed in an ampule. After heating for 250 min at 100.0 °C, the mixture was cooled and poured into 50 mL of ether which contained a weighed amount of indan-1-ol internal standard. The ether solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed using a Widmer column and the products analyzed by GLC using a 5 ft × 0.25 in. 20% diethylene glycol succinate (DEGS) column on Chromosorb W and by NMR.

Controls on Hydrolysis Products. In an example of the general case, 0.0277 g (1.73×10^{-4} mol) of 3-methyl-*endo*-cycloprop[2,3]-inden-1-ol, 0.0406 g (4.06×10^{-4} mol) of calcium carbonate, and 0.0285 g (1.41×10^{-4} mol) of 3,5-dinitrobenzoic acid were combined in 5 mL of 80% aqueous acetone and sealed in an ampule. The ampule was heated at 100.0 °C for 281.0 min (ca. 5 half-lives of the corresponding ester) and then cooled to room temperature. The sample was poured into ether containing indan-1-ol (internal standard) and water was added. After ether extraction, the ethereal solution was washed with saturated sodium bicarbonate and dried over anhydrous sodium sulfate. The solution was concentrated to ca. 0.5 mL using a Widmer column and the sample was analyzed by GLC using a 5 ft × 0.125 in. SF-96/Carbowax on Chromosorb G column and by NMR.

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Registry No.—**1**, 61463-14-7; **2**, 61490-56-0; **5**, 61463-15-8; **6**, 61463-16-9; **7**, 61463-17-0; **8**, 61463-18-1; **15**, 61463-19-2; **16**, 61490-57-1; **17**, 61463-20-5; **18**, 61490-58-2; **19**, 6072-57-7; *endo*-cycloprop[2,3]inden-1-ol, 57378-75-3; methylene iodide, 75-11-6; inden-1-ol, 61463-21-6; 3,5-dinitrobenzoyl chloride, 99-33-2; cycloprop[2,3]inden-1-one, 5771-62-0; 2-phenylcyclopropanecarboxylic acid chloride, 5685-36-9; 1,2-dichloroethane, 107-06-2; *exo*-cycloprop[2,3]inden-1-ol, 57378-74-2; indan-1-ol, 6351-10-6; indan-1-one, 83-33-0; 4,4-dimethyl-1,4-dihydronaphthalen-1-one, 16020-16-9; 4,4-dimethyl-2-bromo-1-tetralone, 17426-90-3; dimethylformamide, 68-12-2; 5,5-dimethylbenzobicyclo[4.1.0]hepten-1-one, 61463-22-7; dimethyl sulfoxide, 67-68-5; 5,5-dimethylbenzobicyclo[4.1.0]hepten-1-ol, 61463-23-8; 4,4-dimethyl-1-tetralol, 53952-18-4; 4,4-dimethyl-1-tetralone, 2979-69-3; phenylcyclopropylcarbinol, 1007-03-0; phenyl cyclopropyl ketone, 3481-02-5; ethylidene iodide, 594-02-5; ethylidene chloride, 75-34-3; ethyl iodide, 75-03-6; *anti*-10-methyl-*endo*-cycloprop[2,3]inden-1-ol, 61463-24-9; *anti*-10-methyl-*exo*-cycloprop[2,3]inden-1-ol, 61490-59-3; 1-methylinden-3-yl acetate, 61463-25-0; isopropenyl acetate, 108-22-5; 3-methylinden-1-ol, 23417-85-8; 3-methyl-*endo*-cycloprop[2,3]inden-1-ol, 61463-26-1; 3-methyl-*exo*-cycloprop[2,3]inden-1-ol, 61490-60-6.

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Thermodynamics of Vinyl Ethers. 19. Alkyl-Substituted Divinyl Ethers[1]

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Chemical equilibration studies of isomeric alkyl-substituted divinyl ethers have been carried out. The thermodynamic data obtained are used for discussions concerning the spatial structure of the C=C–O–C=C system in these compounds. Divinyl ethers unsubstituted in the α position probably exist mainly in the planar (or nearly planar) s-trans,s-trans form, the planar s-cis,s-trans form being in any case excluded as the most stable structure. The latter structure is possible for an α-substituted but not for an α,α'-dialkyl-substituted divinyl ether, which assumes a nonplanar structure. The same structure applies to most α,β-dialkyl- and α,β-polyalkyl-substituted divinyl ethers. Electron distribution in the divinyloxy system is rather sensitive to the number and position of alkyl groups present, as revealed by the ^{1}H NMR shift data.

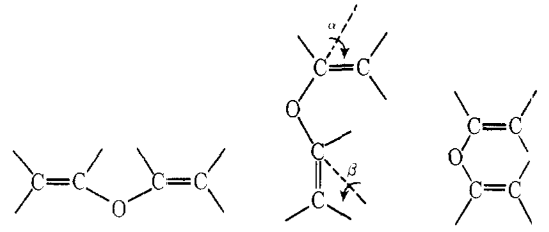
The spatial structure of divinyl ether (**1**) has been of interest ever since the finding of Dolliver et al.[2] that the conjugation energies of **1** and ethyl vinyl ether (**2**) are equal (ca. 15 kJ mol^{-1}). Since the oxygen atom of **1** is interposed between two unsaturated linkages, the stabilization due to p–π interaction in **1** might be expected to be higher than that in **2**. The similar conjugation energies of **1** and **2** thus suggest that either the O atom of **1** conjugates effectively with just one of the two vinyl groups or it conjugates with both C=C bonds but with reduced efficiency. The former alternative is reasonable if **1** is markedly nonplanar so that the p orbitals of the O atom can

$CH_2{=}CH{-}\ddot{O}{-}CH{=}CH_2$ **1**

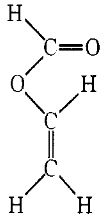
$Et{-}\ddot{O}{-}CH{=}CH_2$ **2**

effectively overlap with the π orbital of only one C=C bond. The spatial structure (conformation) of **1** has been the subject of several investigations with contradictory results. From an electron diffraction study,[3] a slightly nonplanar structure (not far from the planar s-trans,s-trans configuration shown in Scheme I) was proposed for the only stable form of **1**. The existence of at least two rotamers of 1 has been observed by other investigators. On the basis of IR and Raman spectra studies, Glague and Danti[4] suggested the planar s-cis,s-trans structure ($\alpha = \beta = 0$ in Scheme I) for the most stable rotamer, whereas the less stable rotamer was believed to have a "gauche" structure in which the two vinyl groups are not coplanar. The microwave studies of Hirose and Curle[5] gave evidence for a nonplanar s-cis,s-trans structure (α = 40–50°, β = 10–20° in Scheme I) for the most stable rotamer of 1 (the planar s-cis,s-trans structure has been proposed[6,7] for vinyl formate **3**). However, the IR and Raman spectra studies of Cadioli et al.[8] showed that the low-energy rotamer of 1 has the planar s-trans,s-trans form, whereas the high-energy rotamer assumes a nonplanar s-cis,s-trans structure with α = 45° and β = 20°. The enthalpy difference between the rotamers was obtained as ca. 2.5 kJ mol^{-1}. None of the above investigators observed the existence of the planar s-cis,s-cis rotamer, which is sterically crowded.

Scheme I



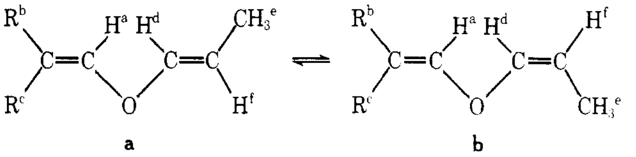
s-trans,s-trans s-cis,s-trans s-cis,s-cis



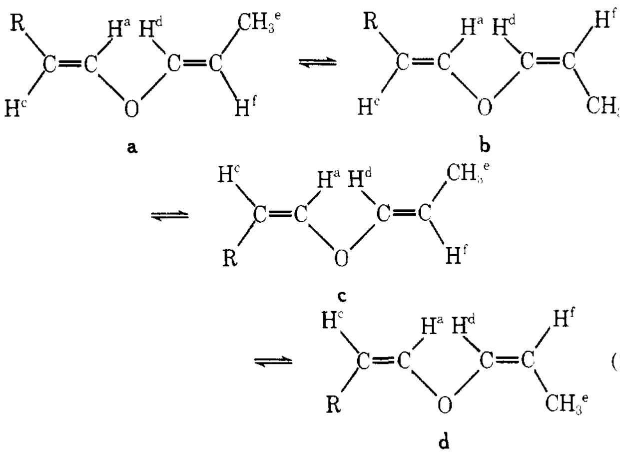
3

Besides these studies concerned with the spatial structure of the unsubstituted divinyl ether molecule, a study of the conformation of (*Z,Z*)-dipropenyl ether (**6d**, see below) has been published.[9] The planar s-trans,s-trans structure was given to the only stable form of **6d** as well as to the parent divinyl ether.

As an extension of our studies on the structure–stability relationship in compounds containing the vinyl ether moiety (-OC=C), thermodynamics of geometric and prototropic (double bond positional) isomerization reactions on alkyl-substituted divinyl ethers have now been investigated. Clarification of the spatial structures of these compounds was not our primary goal; however, it is evident that if a reaction involves a change in the conformation of the C=C–O–C=C system, the change is reflected in the values of the thermodynamic parameters of isomerization, thus providing experimental background for conclusions concerning the possible conformations of the species involved. In addition to the thermodynamic results, interesting information on the effects of alkyl substituents on electron distribution in the divinyl ether system was obtained from ^{1}H NMR shift data of protons bound to the C(sp^2) atoms. The reactions (1–4) studied in this

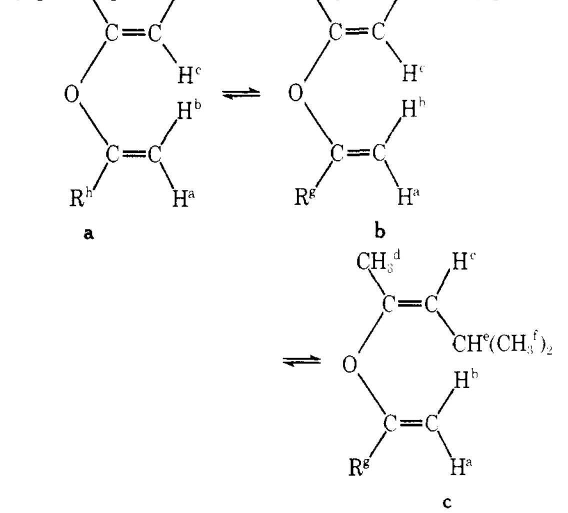


4, R = H (1)
5, R = CH$_3$



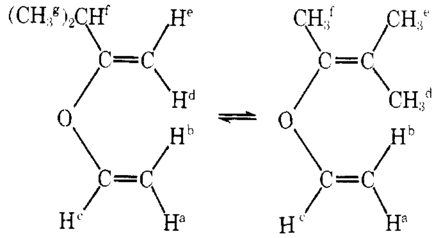
(2)

6, R = CH$_3^b$ (**6b** ≡ **6c**)
7, R = CH$_3^g$CH$_2^b$
8, R = (CH$_3^g$)$_2$CH^b

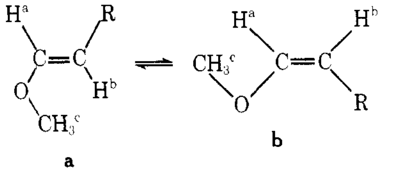


(3)

9, R = H
10, R = CH$_3$



11a **11b** (4)



(5)

12, R = CH$_3^e$CH$_2^d$
13, R = (CH$_3^e$)$_2$CH^d

Table I. Thermodynamic Data (Liquid Phase, 298.15 K) for the Reactions Studied in This Work[a]

Reaction	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
4a → **4b**	−2.33 ± 0.03	−1.5 ± 0.2	2.6 ± 0.4
5a → **5b**	−1.79 ± 0.05	−2.0 ± 0.3	−0.7 ± 0.8
6a → **6b**	−3.64 ± 0.06	−1.7 ± 0.3	6.5 ± 0.7
6b → **6d**	−0.20 ± 0.02	−2.0 ± 0.1	−6.2 ± 0.2
6a → **6d**	−3.83 ± 0.06	−3.7 ± 0.3	0.3 ± 0.8
7a → **7b**	−2.03 ± 0.11	−2.7 ± 0.6	−2.2 ± 1.6
7a → **7c**	−0.75 ± 0.10	−1.3 ± 0.5	−2.0 ± 1.5
7a → **7d**	−2.75 ± 0.07	−3.6 ± 0.4	−2.9 ± 1.0
8a → **8b**	−2.20 ± 0.01	−2.6 ± 0.1	−1.4 ± 0.1
8a → **8c**	0.18 ± 0.02	−0.5 ± 0.1	−2.1 ± 0.3
8a → **8d**	−1.73 ± 0.05	−2.6 ± 0.3	−3.0 ± 0.7
9a → **9b**	−0.35 ± 0.04	−1.0 ± 0.2	−2.0 ± 0.6
9b → **9c**	−0.08 ± 0.05	0.6 ± 0.2	2.1 ± 0.7
9a → **9c**	−0.43 ± 0.04	−0.4 ± 0.2	0.1 ± 0.5
10a → **10b**	−2.58 ± 0.06	−4.7 ± 0.3	−7.1 ± 0.9
10b → **10c**	−3.82 ± 0.05	−5.4 ± 0.2	−5.4 ± 0.6
10a → **10c**	−6.39 ± 0.09	−10.1 ± 0.5	−12.4 ± 1.1
11a → **11b**[b]	−8.25 ± 0.02	−3.3 ± 0.3	16.5 ± 1.0
12a → **12b**	1.67 ± 0.09	3.8 ± 0.5	7.1 ± 1.4
13a → **13b**	2.62 ± 0.02	4.3 ± 0.1	5.7 ± 0.3

[a] Solvents: neat for **4–8** and **12–13**, cyclohexane for **9–11**. The errors are twice the standard errors. [b] $\Delta C_p° = -44 \pm 6$ J K^{-1} mol^{-1}.

Table II. Thermodynamic Data (Gas Phase, 298.15 K) for the Reactions Studied in This Work

Reaction	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
4a → **4b**	−2.3 ± 0.4	1.5 ± 0.6
5a → **5b**	−2.7 ± 0.4	−1.5 ± 0.9
6a → **6b**	−2.3 ± 0.4	5.8 ± 0.9
6b → **6d**	−2.9 ± 0.3	−7.2 ± 0.6
6a → **6d**	−5.1 ± 0.4	−1.4 ± 0.9
7a → **7b**	−3.3 ± 0.7	−2.9 ± 1.7
7a → **7c**	−2.2 ± 0.6	−3.1 ± 1.6
7a → **7d**	−5.5 ± 0.5	−5.1 ± 1.1
8a → **8b**	−3.1 ± 0.3	−2.0 ± 0.6
8a → **8c**	−1.7 ± 0.3	−3.4 ± 0.6
8a → **8d**	−4.8 ± 0.4	−5.4 ± 0.9
9a → **9b**	−0.1 ± 0.4	−0.9 ± 0.8
9b → **9c**	−0.4 ± 0.4	1.0 ± 0.9
9a → **9c**	−0.4 ± 0.4	0.1 ± 0.7
10a → **10b**	−4.3 ± 0.4	−6.7 ± 1.0
10b → **10c**	−6.6 ± 0.4	−6.7 ± 0.8
10a → **10c**	−10.9 ± 0.6	−13.3 ± 1.2
11a → **11b**	−1.4 ± 0.4	18.9 ± 1.1
12a → **12b**	2.2 ± 0.6	4.9 ± 1.5
13a → **13b**	3.3 ± 0.3	4.4 ± 0.6

work are shown (the superscripts refer to the NMR spectra; see Experimental Section).

Many of these reactions involve *E* → *Z* transfers of alkyl groups (alkyl = Me, Et, or *i*-Pr). For comparison, reaction 5 was studied for R = Et and R = *i*-Pr (the case R = Me has been studied previously[10]).

Results and Discussion

1. Results. For most reactions ln *K* (*K* = the mean equilibrium constant at temperature *T*) proved to be a linear function of T^{-1}, justifying the use of the van't Hoff equation for determining the values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ at 298.15 K. For **11a** ⇌ **11b**, however, a plot of ln *K* vs. T^{-1} was considerably curved (i.e., $\Delta C_p° \neq 0$), and in this case the values of *K* were fitted to eq 6[11]

$$\ln K = A + BT^{-1} + C \ln T \qquad (6)$$

Table III. Thermodynamic Data (Gas Phase, 298.15 K) for Reaction 7

R (confign)	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
Me (*E*)	−2.3	0.0[a]
Me (*Z*)	−2.9	−1.4[a]
Et (*E*)	−3.3	−2.9
Et (*Z*)	−3.3	−2.0
i-Pr (*E*)	−3.1	−2.0
i-Pr (*Z*)	−3.1	−2.0

[a] Statistically corrected.

Table IV. Thermodynamic Data (Gas Phase, 298.15 K) for Reaction 8

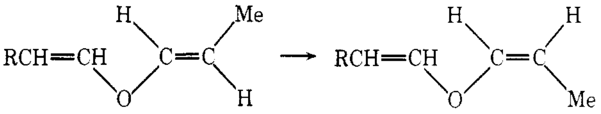
R	Configurational position of Me	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
Me	*E*	−2.3	0.0[a]
Me	*Z*	−2.9	−1.4[a]
Et	*E*	−2.2	−3.1
Et	*Z*	−2.2	−2.2
i-Pr	*E*	−1.7	−3.4
i-Pr	*Z*	−1.7	−3.4

[a] Statistically corrected.

from which the value of $\Delta C_p°$ (independent of *T*) could also be evaluated. The values of the thermodynamic functions of isomerization in the liquid phase at 298.15 K are given in Table I. The gas-phase values of $\Delta H°$ and $\Delta S°$ (Table II) were estimated from the corresponding liquid phase values and the normal boiling point data as described previously.[12]

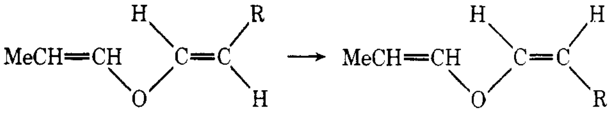
2. Thermodynamic Data. Compound **6b** (≡ **6c**) is favored at equilibrium by a statistical factor of 2. To eliminate the effects of the statistical factor on the values of $\Delta G°$ and $\Delta S°$ for **6a** → **6b**, the terms $RT \ln 2$ (= 1.72 kJ mol^{-1} at 298.15 K) and $-R \ln 2$ (= −5.8 J K^{-1} mol^{-1}) should be added to the experimental $\Delta G°$ and $\Delta S°$ values, respectively. On the other hand, the terms $-RT \ln 2$ and $R \ln 2$ should be added to the experimental $\Delta G°$ and $\Delta S°$ values for **6b** → **6d**.

The thermodynamic data of Table III (obtained from the data of Table II) reveal that the values of $\Delta H°$(g) and $\Delta S°$(g) of reaction 7 are (within experimental error) independent of



(7)

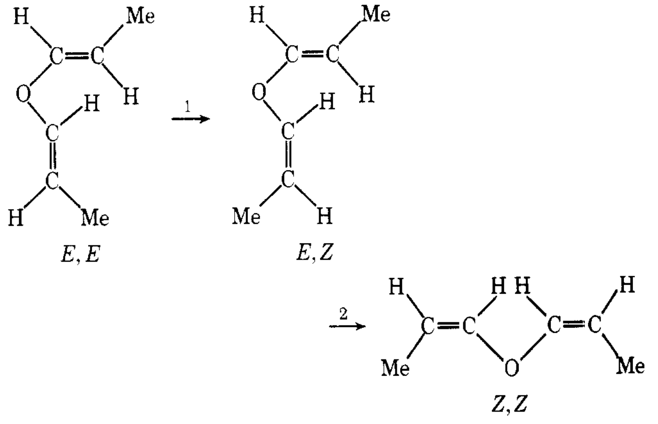
the size and configurational position (*E,Z*) of R. Similarly, the values of $\Delta H°$(g) and $\Delta S°$(g) of reaction 8 are essentially in-



(8)

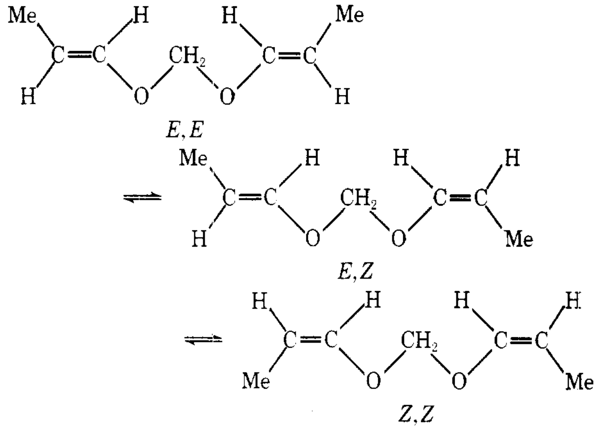
dependent of the configurational position of the Me group; however, $\Delta H°$(g) becomes less negative and $\Delta S°$(g) more negative with increasing size of R (Table IV).

The facts given above exclude the planar s-cis,s-trans structure as the most stable conformation of any of these β,β'-dialkyl-substituted divinyl ethers, as shown by the following reasoning concerning (for simplicity) the β,β'-dimethyl-substituted divinyl ether **6**. Assuming that the *E,E* (**a**) and *E,Z* (**b**) isomers exist in the planar s-cis,s-trans form, the reactions *E,E* → *Z,Z* and *E,Z* → *Z,Z* necessarily involve changes in the spatial structure of the C=C–O–C=C system, since it is evident that the *Z,Z* isomer cannot assume the planar s-cis,s-trans form because of strong repulsive Me···H interactions between the two vinyl groups (experimental evidence[9] supports the planar s-trans,s-trans structure for the *Z,Z* isomer). The stereochemical course of the reaction *E,E* → *E,Z* → *Z,Z* would thus be as follows:



The assumed course of the above reaction requires that $\Delta H_2° > \Delta H_1°$ since $\Delta H_2°$ includes the enthalpy term (>0) for the change in the conformation of the C=C–O–C=C system. This is not, however, supported by experimental facts, since $\Delta H_2°$ is slightly more negative than $\Delta H_1°$. Moreover, the statistically corrected $\Delta G°(1)$ values for steps 1 and 2 of the above reaction are equal (-1.90 kJ mol^{-1}). Hence it appears that the spatial structure of the C=C–O–C=C system remains unchanged on going from the *E,E* to the *Z,Z* isomer.

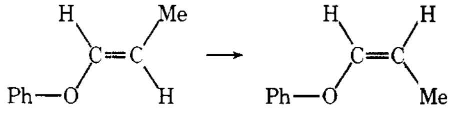
Reaction 9 was studied in a previous work.[1] The values of



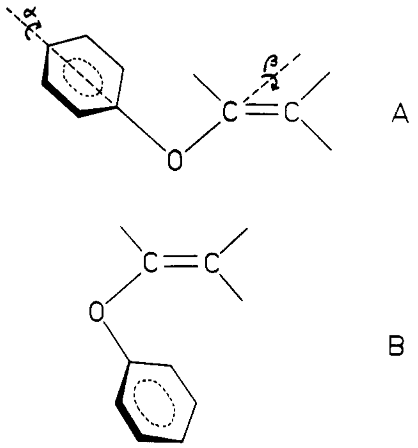
(9)

$\Delta G°$, $\Delta H°$, and $\Delta S°$ for all steps of reaction 9 are practically identical with the corresponding steps of the analogous reaction 2 with R = Me; for example, $\Delta G°(1) = -4.06 \pm 0.03$ kJ mol^{-1}, $\Delta H°(1) = -4.0 \pm 0.2$ kJ mol^{-1}, and $\Delta S°(1) = 0.3 \pm 0.4$ J K^{-1} mol^{-1} for the *E,E* → *Z,Z* isomerization (reaction 9). Since all the isomeric species of reaction 9 were found to exist mainly in the planar s-trans,s-trans form, the similarity between the thermodynamic data for reactions 9 and 2 (R = Me) suggests that the same spatial structure should also apply to the divinyl ethers in question.

The values of $\Delta H°(\mathrm{g})$ and $\Delta S°(\mathrm{g})$ for **4a** → **4b** (Table II) correspond closely to those for reaction 10, for which $\Delta H°(\mathrm{g}) = -2.3 \pm 0.3$ kJ mol^{-1} and $\Delta S°(\mathrm{g}) = 2.7 \pm 0.6$ J K^{-1} mol^{-1}.[10] Phenyl vinyl ether, the parent compound of PhOCH=CHMe, is known[13-16] to exist as a mixture of rotamers, the most stable of which has the nonplanar structure A shown in Scheme II


(10)

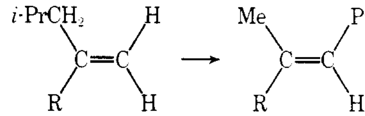
Scheme II



(according to Donnay and Garnier,[16] α = 40–50° and β = 10–20°; other values have also been suggested). Considering rotamer A alone, it is apparent that an *E* → *Z* transfer of a substituent on the β carbon of the vinyl group does not necessitate any change in the spatial structure of the phenyl vinyl ether skeleton. The practically equal values of $\Delta H°(\mathrm{g})$ and $\Delta S°(\mathrm{g})$ for the two reactions concerned thus give the idea that also the divinyl ether skeletons in **4a** and **4b** remain essentially unchanged in the reaction **4a** → **4b**. Hence the planar s-cis,s-trans structure is excluded as the most stable form of **4a** (for **4b** this structure is not likely because of steric factors).

Let us compare the thermodynamics of the *E* → *Z* transfer of R in MeOCH=CHR (reaction 5) with that in MeCH=CHOCH=CHR (reaction 2). In the former reaction the spatial orientation of the MeO group changes from the s-cis to the s-trans[10] giving rise to the more positive enthalpy changes. It would seem reasonable to expect the differences in the values of the thermodynamic parameters for the two reactions in question to be independent of R. However, this is not the case: the values of $\Delta H°(\mathrm{g})$ of reaction 5 are 3.0 (R = Me[10]), 4.4 (R = Et), and 5.0 kJ mol^{-1} (R = *i*-Pr) more positive than those of reaction 2 (the mean $\Delta H°$ values for the **a** → **c** and **b** → **d** reactions). Similarly, the $\Delta S°(\mathrm{g})$ values of reaction 5 are ca. 4 (R = Me[10]), 8 (R = Et), and 8 J K^{-1} mol^{-1} (R = *i*-Pr) more positive than those of reaction 2. The origin of these facts is not clear.

The values of $\Delta H°(\mathrm{g})$ of reaction 11 depend on R as shown


(11)

in Table V. This reaction involves an increase in the number of alkyl substituents attached to the double bond and the highest stabilization due to the increased degree of substitution is achieved in the case R = H, i.e., in ordinary olefins. The weak stabilizing ability of alkyl groups on the C=C bond of vinyl ethers is probably due to the reduced double-bond character of the olefinic linkage (see ref 18 and references cited therein). The data of Table V thus suggest that the double-bond character of the olefinic bond in the product of reaction 11 increases on going from the top (R = MeO) to the bottom (R = H). The enthalpy change for R = CH_2=C(Me)O (i.e., for **10a** → **10b**) leads to the conclusion that the C=C bond of the product (**10b**) behaves almost like an ordinary olefinic bond. This leads to the idea that conjugation between the lone electron pairs of the O atom and the C=C bond of the

Table V. Enthalpy Data (Gas Phase, 298.15 K) for Reaction 11

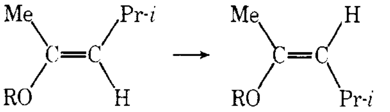
R	$\Delta H°$/kJ mol^{-1}
MeO	0.6 ± 0.4 (ref 17)
$CH_2{=}CHO$—	−0.1 ± 0.4 (this work)
$CH_2{=}\underset{Me}{C}O$—	−4.3 ± 0.4 (this work)
H	≈−6.2 (ref 17)

Table VI. Enthalpy Data (Gas Phase, 298.15 K) for Reaction 12

R	$\Delta H°$/kJ mol^{-1}
Me	11.46 ± 0.35 (ref 17)
$CH_2{=}CH$—	−0.4 ± 0.4 (this work)
$CH_2{=}\underset{Me}{C}$—	−6.6 ± 0.4 (this work)

-OC(Me)=CHPr-*i* fragment of **10b** is weak, suggesting a markedly nonplanar structure for this molecule. This result is already evident from an inspection of molecular models, since any planar structure of **10b** (or of its two isomers) would be sterically crowded. On the other hand, molecular models reveal that of the planar s-trans,s-trans and s-cis,s-trans forms, the latter is possible for **9a** and **9b**, whereas the former would lead to considerable steric strain between the α H atom of the unsubstituted vinyl group and the α substituent of the other vinyl group. The enthalpy change for reaction 11 with R = $CH_2{=}CHO$ is indeed reasonable for planar molecules. The third isomer **9c** would, however, be sterically crowded in any planar structure.

The above conclusions are substantiated by the values of $\Delta H°$(g) for reaction 12 (Table VI). The high positive enthalpy



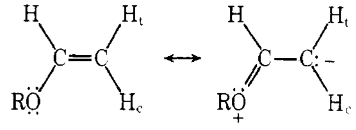
(12)

change for the case R = MeO is a result of the s-cis → gauche reorientation of the MeO group on going from the reactant to the product.[19] On the other hand, assuming no change in the spatial orientation of the R group during the reaction, the expected enthalpy change could be obtained as follows. The reactant is destabilized by the Me···*i*-Pr cis interaction (ca. 4.0 kJ mol^{-1}, ref 20) and the product stabilized by the attractive *i*-Pr···O cis interaction, which may be evaluated as ca. 1.7 kJ mol^{-1} from the values of $\Delta H°$(g) for reactions **8a** → **8c** and **8b** → **8d**. The predicted enthalpy change for reaction 12 would thus be ca. −5.7 kJ mol^{-1}, in moderate agreement with the experimental value for R = $CH_2{=}C(Me)O$, which supports the nonplanarity of the C=C–O–C=C skeleton in the two isomers concerned. However, for R = $CH_2{=}CHO$ the planar s-cis,s-trans structure is possible for the reactant (**9b**), since the enthalpy change is considerably more positive than that expected for nonplanar molecules.

The values of $\Delta S°$(g) (in J K^{-1} mol^{-1}) for reaction 11 are −6.4 ± 0.8 (R = MeO, ref 17), −0.9 ± 0.8 (R = $CH_2{=}CHO$), and −6.7 ± 1.0 [R = $CH_2{=}C(Me)O$]. Since there is no apparent reason for a change in the spatial orientation of the R group during the reaction, the entropy changes should be equal for all these reactions, as shown previously for a series of related reactions.[19] However, the entropy change for R = $CH_2{=}CHO$ is ca. 6 J K^{-1} mol^{-1} less negative than those for the other reactions. A possible explanation is that **9a** exists in the planar s-cis,s-trans form, whereas **9b** prefers a slightly nonplanar s-cis,s-trans structure, which gives rise to two enantiomers whereby the entropy of **9b** is increased by the entropy of mixing, $R \ln 2$ (= 5.8 J K^{-1} mol^{-1}). The reason for the suggested slight nonplanarity of the C=C–O–C=C system of **9b** is not clear, although it possibly originates from the increase in double-bond substitution on going from **9a** to **9b**, which leads to changes in electron distribution in the divinyloxy system (see discussion of ^{1}H NMR shift data).

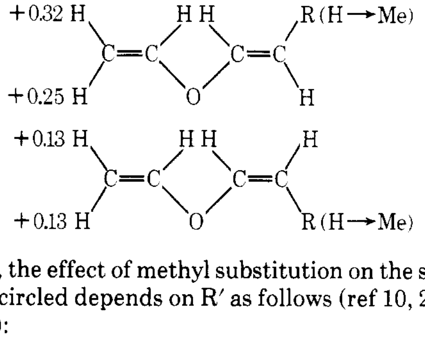
Reaction **11a** → **11b** involves a considerable change in $C_p°$. Somewhat smaller $\Delta C_p°$ values have been previously[21] recorded for related reactions with alkoxy groups substituted for the vinyloxy group of the present compounds. The **b** isomer is favored by a high entropy value. The planar s-cis,s-trans structure seems likely for **11a** and a nonplanar structure for **11b**.

3. **^{1}H NMR Shift Data.** The ^{1}H NMR signals of the β protons of the vinyl group of alkyl vinyl ethers ($ROCH{=}CH_2$) are found ca. 1 ppm upfield from the corresponding signals of 1-alkenes ($RCH{=}CH_2$). This is due to the increased electron density on the β carbon of vinyl ethers,[22,23] which arises from the p–π conjugation:

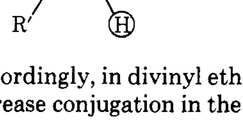


Thus it appears that the chemical shifts of the β protons of alkyl vinyl ethers could be used as an approximate measure of the extent of conjugation in the vinyloxy system. High τ values suggest enhanced conjugation and vice versa. Of the two β protons, the one trans to the RO group (H$_t$) is to be preferred for shift comparison since, owing to its longer distance from RO, H$_t$ is less susceptible to the differences in the shielding effects of varying alkyl groups than the cis proton. As an example, the H$_t$ signal of ethyl vinyl ether is found at τ 6.14 and that of divinyl ether at τ 5.79.[24] The different shift values are reasonable, since, although the conjugation energies of these compounds are equal,[2] conjugation in the latter is distributed between two vinyl groups, i.e., the conjugation energy of divinyl ether is 7.5 kJ mol^{-1} per vinyl group.

Against this background, the chemical shift data of the present compounds reveal many interesting facts. When one of the β protons of divinyl ether is replaced by a Me group, the shifts (expressed in τ values) of the β′ protons change as follows (the data are from ref 24 and this work):



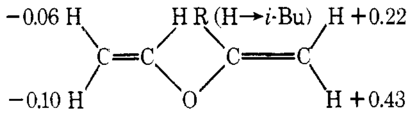
Moreover, the effect of methyl substitution on the shift of the proton encircled depends on R′ as follows (ref 10, 24, 25, and this work):

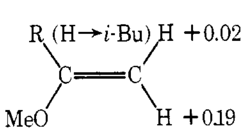


−0.29 ppm (R′ = Me)
−0.58 ppm (R′ = $CH_2{=}CHO$)
−0.64 ppm (R′ = MeO)

Accordingly, in divinyl ethers the effect of a β Me group is to increase conjugation in the unsubstituted vinyl group, and to decrease conjugation in the substituted vinyl group as shown by the high decrease in τ value for the case R′ = $CH_2{=}CHO$ relative to that for R′ = Me.

The effect of an alkyl group in the α position on the shifts of the β protons in substituted divinyl and methyl vinyl ethers is shown below (ref 17, 24, and this work):





It is seen that in divinyl ethers conjugation decreases slightly in the unsubstituted vinyl group but increases considerably in the substituted vinyl group.

In summary, electron distribution in alkyl-substituted divinyl ethers is markedly sensitive to the number and position of the substituents.

Experimental Section

Materials. (*E*)- and (*Z*)-Propenyl Vinyl Ether (4a and 4b, Respectively). A mixture of allyl alcohol (75 cm^3), ethyl vinyl ether (300 cm^3), and mercuric acetate (15 g) was allowed to stand for 7 days at room temperature, after which it was washed with water and dried ($CaSO_4$). Fractionation gave 45 g of allyl vinyl ether containing some ethyl vinyl ether, bp 60–66 °C (743 Torr). Pure allyl vinyl ether boiled at 66 °C (743 Torr). A mixture of allyl vinyl ether (17 g), Me_2SO (25 cm^3), and KOBu-*t* (4 g) was allowed to stand for 7 days at room temperature, followed by distillation. The product (13 g, **4a**:**4b** ≅ 1:20) was collected at 62 °C (760 Torr). An about 1:1 mixture of the two isomers was obtained by treating the synthetic product (10 g) with $Hg(OAc)_2$ (1.5 g) for 2 weeks at 50 °C followed by fractionation. These two mixtures of **4a** and **4b** were used for the equilibrations and for recording the NMR spectra.

(*E*)- and (*Z*)-Propenyl Isobutenyl Ether (5a and 5b, Respectively). Isobutyraldehyde diallyl acetal was prepared by heating a mixture of isobutyraldehyde (72 g), allyl alcohol (120 g), hexane (100 cm^3), and *p*-toluenesulfonic acid (1 g) in a water-removal assembly until the evolution of water ceased. After cooling, the mixture was made alkaline with NaOMe in MeOH and distilled to give 124 g of the acetal, bp 56–57 °C (8 Torr). It was isomerized to the corresponding dipropenyl acetal by KOBu-*t* in Me_2SO as described above for **4**. The yield of the product, bp 49–50 °C (7 Torr), was 85%. About 0.1 g of *p*-toluenesulfonic acid was added to 26 g of the acetal, and the mixture was heated in a distillation apparatus until the formation of propionaldehyde (rearrangement product of the unstable primary reaction product MeCH═CHOH) ceased. The residual was distilled to give 10 g of a 30:70 mixture of **5a** and **5b**, bp 117–118 °C (751 Torr).

(*E,E*)-, (*E,Z*)-, and (*Z,Z*)-Dipropenyl Ether (6a, 6b, and 6d). Diallyl ether (Fluka AG) was isomerized to dipropenyl ether (mainly **6d**) by KOBu-*t* in Me_2SO as described above (see **4**). A rapid and vigorous conversion occurred when the reactants were heated to ca. 70 °C. The product, obtained in 85% yield, was collected at 85–93 °C (774 Torr). A mixture of the synthetic product (27 g) and $Hg(OAc)_2$ (1.4 g) was refluxed for 115 h. The ratio **6a**:**6b**:**6d** was then 1:3.9:3.6. The mixture was distilled and the pure isomers separated from the distillate by preparative GLC.

(*E,E*)-, (*E,Z*)-, (*Z,E*)-, and (*Z,Z*)-1-Butenyl Propenyl Ether (7a, 7b, 7c, and 7d, Respectively). Butyraldehyde diallyl acetal [bp 181 °C (760 Torr)] was prepared from butyraldehyde and allyl alcohol in 55% yield as described above for isobutyraldehyde diallyl acetal (see **5**). The product was isomerized to the corresponding dipropenyl acetal by KOBu-*t* in Me_2SO. The reaction mixture was extracted with hexane, and the combined extracts were washed with water, dried (K_2CO_3), and distilled to give the acetal in 40% yield, bp 181 °C (760 Torr). Slow distillation of the acetal from a catalytic amount of *p*-toluenesulfonic acid gave first propionaldehyde, and then the desired products in 27% yield, bp 114–116 °C (758 Torr).

(*E,E*)-, (*E,Z*)-, (*Z,E*)-, and (*Z,Z*)-3-Methyl-1-butenyl Propenyl Ether (8a, 8b, 8c, and 8d, Respectively). See preparation of **7** (the starting aldehyde was isovaleraldehyde). Most of the product, bp 131–134 °C (760 Torr), consisted of **8d**.

2-Vinyloxy-4-methyl-1-pentene, (*E*)- and (*Z*)-2-Vinyloxy-4-methyl-2-pentene (9a, 9b, and 9c, Respectively). A mixture of methyl isobutyl ketone dimethyl acetal (30 g, 0.20 mol), 2-bromoethanol (25 g, 0.20 mol), and *p*-toluenesulfonic acid (0.1 g) was heated in a distillation apparatus until the evolution of MeOH ceased. The remainder was cooled, and 30 g (0.28 mol) of KOBu-*t* was added slowly with cooling, after which the mixture was heated. A mixture of *t*-BuOH and mainly **9a** was collected at 40 °C (15 Torr). The alcohol was removed from the mixture as an azeotrope with hexane. Fractionation of the residue gave 7 g (28%) of the desired vinyl ethers, bp 119–124 °C (752 Torr).

2-Isopropenyloxy-4-methyl-1-pentene, (*E*)- and (*Z*)-2-Isopropenyloxy-4-methyl-2-pentene (10a, 10b, and 10c, Respectively). These compounds were prepared from methyl isobutyl ketone dimethyl acetal, 1-chloro-2-propanol, and KOBu-*t* as described above for **9**, bp 132–140 °C (760 Torr).

2-Vinyloxy-3-methyl-1-butene (11a) and 2-Vinyloxy-3-methyl-2-butene (11b). See preparation of **9**. Methyl isopropyl ketone dimethyl acetal served as the starting acetal. The product, obtained in 69% yield, was collected at 99–106 °C (766 Torr).

(*E*)- and (*Z*)-1-Methoxy-1-butene (12a and 12b, Respectively). A mixture of butyraldehyde dimethyl acetal (15 g, 0.127 mol), quinoline (30 cm^3), and some *p*-toluenesulfonic acid was heated in a distillation apparatus. Cleavage of the acetal gave a mixture of MeOH and **12**, which was collected at ca. 64 °C. The alcohol was removed by extraction with water, and the organic layer was dried (K_2CO_3). Three grams (0.035 mol, 27%) of a mixture of **12a** and **12b** remained.

(*E*)- and (*Z*)-1-Methoxy-3-methyl-1-butene (13a and 13b, Respectively). See preparation of **12**. Isovaleraldehyde dimethyl acetal was used as the acetal. The yield was 44%.

In many cases the synthetic route employed gave essentially one of the several possible isomers, although at thermodynamic equilibrium the relative amounts of the other isomers were considerably higher. In those cases the synthetic product was allowed to stand in the presence of a suitable catalyst (mercuric acetate or iodine in cyclohexane) until the thermodynamic equilibrium had been achieved. The product was then distilled, and the isomers were separated from the distillate by preparative GLC if possible. The column used was a Carbowax 20M column.

^{1}H NMR spectra. The spectra were recorded at 60 MHz in CCl_4 solution with Me_3Si as internal standard. In many cases mixtures of isomers were used for recording the spectra, since pure isomers could not always be isolated. The spectra of the unsubstituted vinyl group could be analyzed as AMX spectra, since the geminal coupling constant between the β protons (i.e., the AM portion) was less than one-tenth of the difference in the chemical shifts of the β protons. The chemical shifts are given in τ values and the coupling constants in hertz. **4a:** 3.65 (a), 6.11 (b), 5.74 (c), 3.78 (d), 8.40 (e), 4.91 (f), J_{ab} = 6.4, J_{df} = 12.0, J_{bc} = 0.0, J_{ef} = 6.8. **4b:** 3.59 (a), 5.92 (b), 5.62 (c), 3.88 (d), 8.40 (e), 5.40 (f), J_{ab} = 6.9, J_{ac} = 14.1, J_{bc} = 1.7, J_{df} = 6.8, J_{ef} = 6.8, J_{de} = 1.7. **5a:** 4.13 (a), 8.40 (b, c), 3.86 (d), 8.46 (e), 5.14 (f), J_{df} = 12.4, J_{ef} = 6.9. **5b:** 4.04 (a), 8.44 (b), 8.36 (c), 4.00 (d), 8.40 (e), 5.61 (f), $J_{df} \approx J_{ef}$ = 6.8. **6a:** 3.83 (a, d), 8.46 (b, e), 5.01 (c, f), $J_{ac} = J_{df}$ = 12.3, $J_{ab} = J_{de}$ = 1.4, $J_{bc} = J_{ef}$ = 6.8. **6b:** 3.81 (a), 8.44 (b), 4.99 (c), 3.91 (d), 8.41 (e), 5.46 (f), J_{ac} = 12.9, J_{df} = 6.5, J_{bc} = 6.8, J_{ef} = 7.3. **6d:** 3.92 (a, d), 8.37 (b, e), 5.54 (c, f), $J_{ac} = J_{df}$ = 6.2, $J_{ab} = J_{de}$ = 1.5, $J_{bc} = J_{ef}$ = 7.0. **7b:** 3.79 (a), 8.03 (b), 5.01 (c), 3.97 (d), 8.41 (e), 5.50 (f), 9.00 (g), J_{ac} = 12.4, J_{bc} = 6.8, J_{bg} = 7.3, $J_{df} \approx J_{ef}$ = 6.6, J_{ab} = 1.5. **7d:** 3.99 (a), 7.88 (b), 5.60 (c), 3.99 (d), 8.41 (e), 5.66 (f), 9.03 (g), $J_{ac} \approx J_{bc}$ = 6.6, J_{bg} = 7.5, J_{de} = 1.5, $J_{df} \approx J_{ef}$ = 6.6. **8a:** 3.89 (a), 7.71 (b), 5.03 (c), 3.89 (d), 8.46 (e), 5.09 (f), 9.03 (g), $J_{ac} \approx J_{df}$ = 12.0, J_{bc} = 7.3, J_{de} = 1.5, J_{bg} = 6.9. **8b:** 3.78 (a), 7.70 (b), 5.05 (c), 3.96 (d), 8.44 (e), 5.49 (f), 9.02 (g), J_{ac} = 12.2, J_{bc} = 7.7, J_{bg} = 6.9, $J_{df} \approx J_{ef}$ = 6.8, J_{de} = 1.5. **8c:** 4.09 (a), 7.16 (b), 5.67 (c), 3.80 (d), 8.45 (e), 5.06 (f), 9.04 (g), J_{ac} = 6.2, J_{bc} = 8.7, J_{bg} = 6.9, J_{de} = 1.5, J_{df} = 12.0, J_{ef} = 6.9. **8d:** 4.04 (a), 7.12 (b), 5.71 (c), 3.93 (d), 8.39 (e), 5.54 (f), 9.02 (g), J_{ab} = 0.8, J_{ac} = 6.2, J_{bc} = 8.1, J_{bg} = 7.1, J_{de} = 1.7, $J_{df} \approx J_{ef}$ = 6.7. **9a:** 5.73 (a), 5.39 (b), 5.92 (c), 6.01 (d), 8.05 (e), 9.09 (g), 3.63 (h), J_{ab} = 1.2, J_{ah} = 6.0, J_{bh} = 13.7, J_{cd} = 1.7, J_{ef} = 2.3, J_{fg} = 6.5. **9b:** 5.82 (a), 5.50 (b), 5.50 (c), 8.22 (d), 7.6 (e), 9.02 (f), 3.70 (g), J_{ag} = 6.0, J_{bg} = 13.7, J_{ce} = 9.5, J_{ef} = 6.8. **10a:** 5.7–5.9 (a, b, c, d), 8.04 (e), 8.1 (f), 9.09 (g), 8.18 (h), J_{ef} = 1.8, J_{fg} = 6.9. **10b:** 6.09 (a, b), 5.23 (c), 8.2 (d), 9.00 (f), 8.2 (g), J_{ce} = 9.9, J_{ef} = 6.3. **10c** (only a few signals were detected): 6.1 (a, b), 5.36 (c), J_{ce} = 8.5. **11a:** 5.74 (a), 5.40 (b), 3.63 (c), 5.99 (d, e), 7.66 (f), 8.91 (g), J_{ab} = 1.1, J_{ac} = 6.2, J_{bc} = 13.6, J_{fg} = 6.7. **11b:** 6.03 (a), 5.83 (b), 3.75 (c), 8.35 (d), 8.43 (e), 8.23 (f), J_{ab} = 1.6, J_{ac} = 6.6, J_{bc} = 14.2. **12a:** 3.80 (a), 5.40 (b), 6.59 (c), 8.07 (d), 9.04 (e), J_{ab} = 12.9, J_{bd} = 6.6, J_{de} = 7.5. **12b:** 4.23 (a), 5.78 (b), 6.50 (c), 7.98 (d), 9.08 (e), J_{ab} = 6.2, J_{ad} = 1.3, J_{de} = 7.3. **13a:** 3.80 (a), 5.43 (b), 6.64 (c), ca. 7.8 (d), 9.02 (e), J_{ab} = 12.7, J_{bd} = 7.5, J_{de} = 6.9. **13b:** 4.37 (a), 5.89 (b), 6.49 (c), ca. 7.3 (d), 9.08 (e), J_{ab} = 6.4, J_{bd} = 8.8, J_{ad} = 1.3.

Configurational Assignments. The configurations of the geometric isomers of **4–8** and **12–13** were readily deduced from the magnitude of the vicinal coupling constant across the C═C bond, the cis coupling constant being 6–7 Hz and the trans coupling constant 12–14 Hz.[26] The configurations of the geometric isomers of **9** were assigned as follows. The first step in the synthesis of **9** involves a reaction between the dimethyl acetal of methyl isobutyl ketone and 2-bromoethanol under acid conditions, which leads to a formation of the isomeric species i-$BuC(OCH_2CH_2Br){=}CH_2$ and (E)- and (Z)-$MeC(OCH_2CH_2Br){=}CHPr$-i. From previous thermodynamic studies[12,17,19] it can be inferred that the more stable geometric isomer has the E configuration. In the second step, HBr is eliminated from the product of the first stage, and since this process is carried out under basic conditions, no (significant) isomerization occurs during this step. Hence the predominating geometric isomer of the final synthetic mixture must have the E configuration. The same arguments were applied for the identification of the geometric isomers of **10**.

Determination of Normal Boiling Points. The standard enthalpies and entropies of vaporization at 298.15 K were estimated from the values of the normal boiling points of the compounds studied. The boiling points were determined by the gas chromatographic method described previously.[12] The values obtained follow (in °C): **4a,** 67.0; **4b,** 62.0; **5a,** 121.3; **5b,** 117.0; **6a,** 101.9; **6b,** 98.5; **6d,** 93.5; **7a,** 125.8; **7b,** 121.8; **7c,** 120.0; **7d,** 113.8; **8a,** 138.5; **8b,** 135.3; **8c,** 131.0; **8d,** 125.0; **9a,** 114.8; **9b,** 120.4; **9c,** 114.8; **10a,** 135.8; **10b,** 138.1; **10c,** 130.8; **11a,** 95.7; **11b,** 107.9; **12a,** 72.6; **12b,** 62.6; **13a,** 86.3; **13b,** 80.0.

Equilibrations. The equilibration experiments on **4–8** and **12–13** were carried out in the neat liquid with $Hg(OAc)_2$ as catalyst, and those on **9–11** in cyclohexane solution with I_2 as catalyst. Whenever available, pure isomers were used as starting materials for the equilibrations. In all cases the position of equilibrium was approached from at least two starting mixtures with sufficiently different isomer compositions to be sure that the true thermodynamic equilibrium had been achieved. The equilibrations were carried out at at least four temperatures between 273 and 423 K. The equilibrated samples were analyzed by GLC using an 8-m Carbowax column. The gas chromatograph was equipped with a HP 3370 B electronic integrator for determining the peak areas. For more details of the equilibration procedure see ref 10 and the previous papers of this series.

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Registry No.—**4a,** 24268-10-8; **4b,** 24268-09-5; **5a,** 40716-31-2; **5b,** 40716-32-3; **6a,** 4696-28-0; **6b,** 4696-29-1; **6c,** 4696-27-9; **7a,** 61463-28-3; **7b,** 61463-29-4; **7c,** 61463-30-7; **7d,** 61463-31-8; **8a,** 61463-32-9; **8b,** 61463-33-0; **8c,** 61463-34-1; **8d,** 61463-35-2; **9a,** 61463-36-3; **9b,** 61463-37-4; **9c,** 61463-38-5; **10a,** 61463-39-6; **10b,** 61463-40-9; **10c,** 61463-41-0; **11a,** 61463-42-1; **11b,** 61463-43-2; **12a,** 10034-13-6; **12b,** 10034-12-5; **13a,** 31915-76-1; **13b,** 31915-77-2; allyl alcohol, 107-18-6; ethyl vinyl ether, 109-92-2; isobutyraldehyde diallyl acetal, 37406-14-7; isobutyraldehyde, 78-84-2; isobutyraldehyde dipropenyl acetal, 39801-12-2; diallyl ether, 557-40-4; butyraldehyde diallyl acetal, 35020-94-1; butyraldehyde, 123-72-8; isovaleraldehyde, 590-86-3; methyl isobutyl ketone dimethyl acetal, 1112-78-3; 2-bromoethanol, 540-51-2; 1-chloro-2-propanol, 127-00-4; methyl isopropyl ketone dimethyl acetal, 59554-08-4; butyraldehyde dimethyl acetal, 4461-87-4; isovaleraldehyde dimethyl acetal, 57094-35-6.

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Dark Reactions of Halobenzenes with Pinacolone Enolate Ion. Evidence for a Thermally Induced Aromatic $S_{RN}1$ Reaction[1a]

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Iodo- and bromobenzene react with potassium pinacolone enolate in dimethyl sulfoxide at 25 °C in the dark to form the substitution product, $PhCH_2COC(CH_3)_3$. The reaction behaves in fashion consistent with the $S_{RN}1$ radical chain mechanism but inconsistent with nonchain mechanisms. It is inhibited by the electron scavengers p-dinitrobenzene and benzophenone and by the radical scavenger di(*tert*-butyl) nitroxide. It is accelerated by light, and the iodobenzene/bromobenzene reactivity ratio, about 6, is the same in the dark and the photostimulated reactions. Some features of it are not understood: a strange rate law and extraordinary accelerations by O_2, nitrobenzene, and ferric nitrate. Several observations serve to rule out an aryne mechanism, but in the case of m-iodoanisole an aryne side reaction was encountered.

In recent years it has been found that halobenzenes, unsubstituted or provided even with electron-releasing substituents, will react with certain nucleophiles under stimulation by electrons or photons to form products of substitution. The behavior of these reactions is consistent with the $S_{RN}1$ mechanism,[2] a radical chain mechanism, but not with the longer known S_NAr or benzyne mechanisms. A representative aromatic $S_{RN}1$ reaction is that of phenyl halides with ketone enolate ions[3-6] of which the sort shown in eq 1 will be our present interest.

A radical chain mechanism comprises initiation, propagation, and termination steps. Of these, the steps in the propa-