tralized with dilute H_2SO_4. The ether layer was washed with water, dried ($MgSO_4$), and evaporated to give 1.0 g (65%) of the hydroxymethyl derivative **11**, mp 175–176°.

Anal. Calcd for $C_{17}H_{26}O_3$: C, 74.9; H, 7.4. Found: C, 75.2; H, 7.2.

Registry No.—**1**, 18133-84-1; **7**, 25517-40-2; **9**, 18133-83-0; **10**, 25517-93-5; **11**, 25517-94-6; 2,4′-dibromo-4-hydroxy-3,5,2′,6′-tetramethyldiphenyl ether, 18133-82-9.

Double-Bond Isomerizations in Unsaturated Esters and Enol Ethers. I. Equilibrium Studies in Cyclic and Acyclic Systems[1,2]

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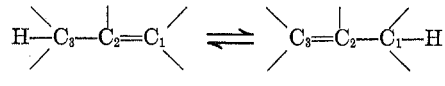
Equilibrium data are presented for tautomeric equilibria in three carbon olefinic systems incorporating methyl, methoxy, and methoxycarbonyl substituents on five- and six-membered rings and acyclic chains. Geometric equilbria have been studied for combinations of these same groups as substituents on a double bond. Equilibrations were achieved thermally, with base catalysis in protic and aprotic solvents, with iron pentacarbonyl in hydrocarbon solvent, and, in those cases in which an enol ether structure is maintained in the isomerization, by trace amounts of iodine in an inert solvent. The iodine-catalyzed isomerization has been demonstrated to be intermolecular by a deuterium exchange experiment.

Since the pioneering studies of Kon, Linstead, and coworkers, the effect of structure on the position of olefin equilibrium in three-carbon systems has continued to receive attention.[3] In general, the relative stabilities of the 1,2 and 2,3 isomers of acyclic systems have been successfully correlated with the conjugative and induc-



tive contributions of substituents located on the three-carbon allylic chain.[4] Notable failures of the predictive power of this approach can be expected when unfavorable steric[5] or polar[6] interactions are superimposed on normal conjugative and inductive effects. Such departures from predicted behavior appear to be especially prevalent in cyclic systems in which conversion to a more favorably disposed geometric arrangement is precluded.[6,7] For example, the fact that equilibration of 2-alkoxy-1-alkoxycarbonylcyclohexenes strongly favors the 2,3 isomer[8] would not have been expected on the basis of earlier analyses.[4] In an effort to sort out and evaluate the contributions of these various factors in cyclic systems of particular interest to us, we have studied positional and configurational equilibria in unsaturated cyclic and acyclic systems incorporating methyl, methoxy, and carbomethoxy groups in various combinations. This paper reports the results of the equilibrium studies. A quantitative assessment of the electronic, steric, and polar contributions of these substituents is made in the accompanying paper.[9]

(1) Taken in part from the Ph.D. dissertations of J. K. Chattopadhyay, University of Wyoming, 1967, and E. E. Waali, University of Wyoming, 1970.

(2) This research was supported by National Science Foundation Grants GP-1517 and GP-6375. E. E. W. expresses his gratitude for a National Science Foundation Summer Traineeship in 1967.

(3) See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 200, for a summary and leading references to recent work.

(4) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 562; (b) P. B. de la Mare, *J. Chem. Soc.*, 1602 (1952).

(5) K. L. Rinehart, Jr., and L. J. Dolby, *J. Org. Chem.*, **22**, 13 (1957)

(6) R. C. Fuson and J. A. Haefner, *ibid.*, **27**, 1957 (1962).

(7) N. Heap and G. H. Whitman, *J. Chem. Soc. B*, 164 (1966).

(8) S. J. Rhoads and R. W. Hasbrouck, *Tetrahedron*, **22**, 3557 (1966), and this paper.

(9) S. J. Rhoads and E. E. Waali, *J. Org. Chem.*, **35**, 3358 (1970).

Results

The systems examined are displayed in Tables I and II. The cyclic compounds in Table I are subject to tautomeric equilibration but not to geometric; the acyclic systems in Table I are subject to both. The olefinic systems in Table II were included in the study in order to assess the magnitude of steric and polar interactions of the three variable groups when any two of them are held in a *cis* relationship.

The required compounds were prepared in a variety of standard ways, detailed in the Experimental Section. In each system, the individual isomeric species involved were isolated and characterized by their spectral properties and, when possible, by comparison with authentic samples prepared by independent routes. In this connection, the synthetic utility of photochemical *trans* to *cis* isomerizations of the unsaturated esters **9a**, **10a**, **11**, and **14** and of the photoconversion of α,β, to β,γ isomerides in the ester systems **9** and **10** deserves notice. Others[10] have called attention to the fact that irradiation of α,β-unsaturated esters provides a general synthetic method for the preparation of the often less accessible β,γ isomer. In the case of the ester system **10**, the photoisomerization may be exploited to permit the preparation of the two geometric isomers of each positional isomer. As may be seen in Figure 1, the photochemical behavior of *E*-**10a**[11] is characterized by a rapid buildup of *Z*-**10a**,[11] the geometric species required for the α,β–β,γ isomerization.[10] A decay in the concentration of *Z*-**10a** is accompanied by the formation of *Z*- and *E*-**10b**. The desired isomer(s) may be isolated from the photoreaction mixture after the appropriate irradiation time by glpc trapping.

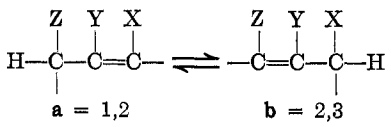
The method required for equilibration depends strongly on the structural features of the isomeric system. In the unsaturated ester systems **1**, **2**, **5**, **6**, **9**, **10**, and **11**, equilibrium is achieved only after rather extended heating at temperatures of 100–120° in the presence of strong base or iron pentacarbonyl.[12] Purely

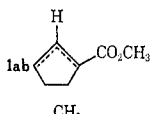
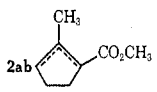
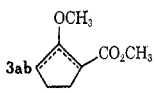
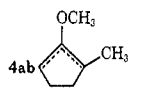
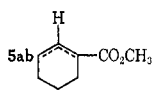
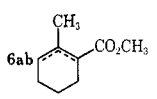
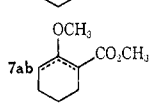
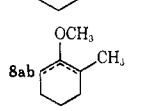
(10) P. J. Kropp and H. J. Krauss, *ibid.*, **32**, 3222 (1967); R. R. Rando and W. von E. Doering, *ibid.*, **33**, 1671 (1968).

(11) See J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968), for the designation of geometric isomers as *E* and *Z*.

(12) R. Damico, *J. Org. Chem.*, **33**, 1550 (1968).

TABLE I
TAUTOMERIC EQUILIBRIA IN
CYCLIC AND ACYCLIC ALLYLIC SYSTEMS



System	K_{eq} (2,3/1,2)	$\Delta G°$[a] (kcal/mol)	Equilibration method[b] and temp, °C
 1ab	0.06	+2.1 ± 0.2	A, 100
 2ab	0.06	+2.1 ± 0.2	A, 100
 3ab	0.47 0.53	+0.64 ± 0.04 +0.37 ± 0.03	B, 150 C, 25
 4ab	2.0	−0.41 ± 0.03	C, 25
 5ab	0.05	+2.2 ± 0.2	A, 100
 6ab	0.32	+0.85 ± 0.04	A, 100
 7ab	5.0 7.5	−1.35 ± 0.05 −1.2 ± 0.05	B, 150 C, 25
 8ab	1.5	−0.26 ± 0.02	C, 25
$CH_3CH{=}CH{=}$	0.45	+0.63 ± 0.04	A, 117
$CHCO_2CH_3$	0.51	+0.53 ± 0.04	D, 117
9ab (*Z* and *E*)	0.36	+0.79 ± 0.05	E, 117
$CH_3OCH{=}CH{=}$	12.7	−2.9 ± 0.3	B, 300
$CHCO_2CH_3$	31.3	−2.5 ± 0.3	E, 92
10ab (*Z* and *E*)			

[a] Uncertainties are based on reproducibility of equilibrium composition of ±1% on duplicate runs. [b] Methods: A, sodium methoxide–methanol; B, thermal, neat; C, iodine–cyclohexane; D, sodium methoxide–HMPT; E, iron pentacarbonyl–octane.

thermal isomerizations[13] of these systems require prolonged heating at 250–300° and show extensive material losses. On the other hand, those systems in which an enol ether function is maintained in the isomerization, *i.e.*, **3**, **4**, **7**, **8**, **12**, **13**, and **14**, are quite labile. Trace amounts of acidic impurities often suffice to bring about rapid equilibration at ordinary temperatures. Although various protic acids have been employed as catalysts to isomerize enol ethers of this type,[14,15] we have found iodine, used in low concentration in an inert solvent, to be much superior for equilibrium studies. In most cases, equilibrium is established within minutes at room temperature without detectable diversion of material by side reactions.

Analyses of the equilibrated systems were made by glpc methods, standardized against synthetic mixtures of known composition. Whenever possible, the achievement of equilibrium was accomplished from both directions. Results of such experiments generally agreed with ±1%. The conditions used for the equilibrations, the equilibrium constants, and the corresponding free energy changes are shown in the tabulations.[16]

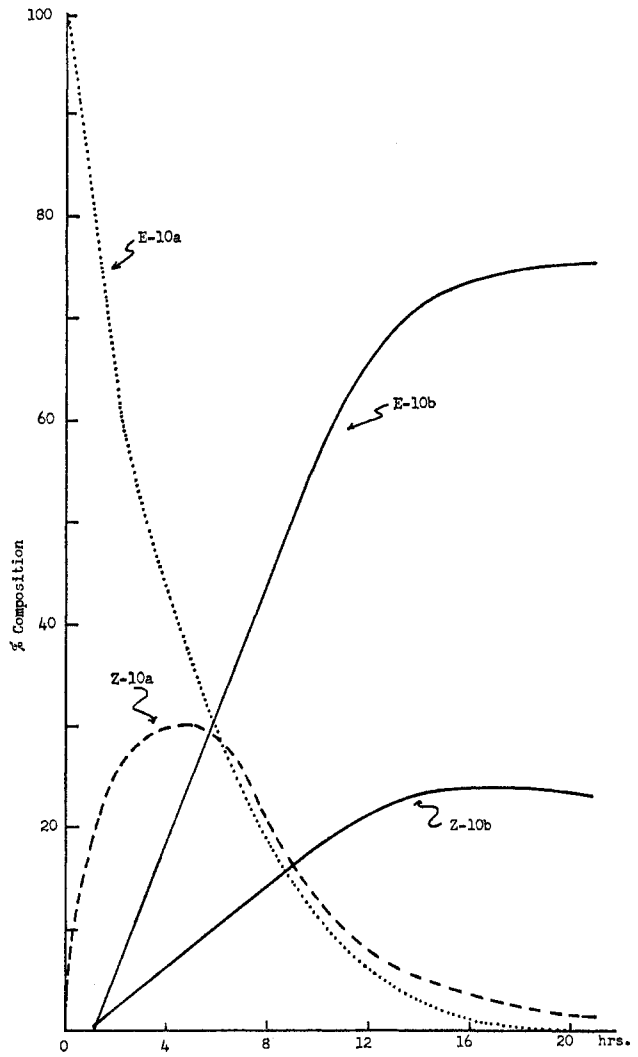


Figure 1.—Photoisomerization of methyl 4-methoxy-2-butenoate, *E*-**10a**, and *Z*-**10a**.

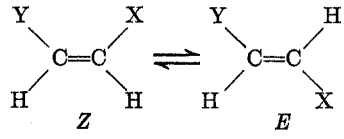
Discussion

Several of the systems, or close relatives of them, have been studied by other workers. Linstead's early work included the carboxylate anions of the pentenoic[17] and cyclohexene carboxylic acids,[18] corresponding to the ester systems **9** and **5**. Equilibrium values of K = 0.47 ($\Delta G°$ = +0.6 kcal/mol) and K = 0.05 ($\Delta G°$ = +2.2 kcal/mol) for the acyclic and cyclic systems, respectively, were found when the equilibrations were carried out in aqueous sodium hydroxide at 100°. The

(13) D. E. McGreer and N. W. K. Chiu, *Can. J. Chem.*, **46**, 2225 (1968), and earlier papers quoted therein.
(14) H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963).
(15) P. Salomaa and P. Nissi, *Acta Chem. Scand.*, **21**, 1386 (1967).
(16) It is noteworthy that the differences in solvent and temperature which were utilized for equilibration of the various isomeric systems appear to have only small effects on the equilibrium composition and/or the corresponding free energy change for a given system. See, for example, the data for systems **3ab**, **7ab**, **9ab**, and **10b**. In the free energy terms, these changes reflect, at most, a difference of only a few tenths of a kilocalorie.
(17) Quoted in ref 4b.
(18) E. Boorman and R. P. Linstead, *J. Chem. Soc.*, 258 (1935).

TABLE II

GEOMETRIC EQUILIBRIA IN OLEFINIC SYSTEMS



Z E

No.	System Y	System X	K_{eq} (E/Z)	$\Delta G°$, kcal/mol	Equilibration method[a] and temp, °C
11	CH_3	CO_2CH_3	6.25	-1.4 ± 0.05	D, 117
12	CH_3	OCH_3	1.21	-0.12 ± 0.03	C, 25
13	C_2H_5	OCH_3	1.82	-0.36 ± 0.03	C, 25
14	CH_3O	CO_2CH_3	124	-3.6 ± 0.5	C, 100
9a	C_2H_5	CO_2CH_3	~11–23[b]	~−2	A, D, E, 117
10a	CH_3OCH_2	CO_2CH_3	~4–5[b]	~−1	E, 92
10b	CH_3O	$CH_2CO_2CH_3$	~1[b]	~0	E, 92
			1.15	-0.08 ± 0.02	C, 25

[a] See footnote b, Table I. [b] Estimates based on analyses of tautomeric equilibria under conditions cited in Table I.

agreement with the results for the corresponding methyl esters recorded in Table I is remarkably good, and confirms the idea that the stabilizing effects of $-CO_2^-$ and $-CO_2R$ are approximately equal.[4] Owen and Sultanbawa[19] examined the base catalyzed isomerization of the anion of γ-methoxycrotonic acid (corresponding to the ester system **10**) in aqueous and alcoholic media, and concluded that the equilibrium favored the β,γ isomer with $K = 2.3$ ($\Delta G° = -0.6$ kcal/mol). This result contrasts with our findings for the methyl esters, wherein we find a much stronger preference for the β,γ isomer, **10b**. Hine and coworkers[20] also examined this system as the methyl ester equilibrated with potassium methoxide in *t*-butyl alcohol at 35° and could detect none of the α,β isomer, **10a**, after 60 half-lives. As Hine has pointed out, it seems highly unlikely that such a difference could be accounted for by the mere replacement of carboxylate by carbomethoxy. One may speculate that the experiments of Owen and Sultanbawa were complicated by a concurrent addition of solvent to the olefinic bond; that such addition occurs readily has been demonstrated by Hine[20] and also has been observed in our investigation.

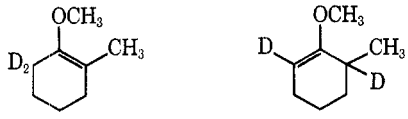
The methyl crotonate–methyl isocrotonate system, **11**, has been studied by three other groups. Thermal equilibrations at 195° in the liquid phase[21] and at 200–500° in the gas phase[22] provided values of $K = 7$ and $K = 4.5$, whereas an N-bromosuccinimide (NBS) catalyzed equilibration in carbon tetrachloride at 77°[23] led to a value of $K = 10$. Our value for this system, measured in hexamethylphosphortriamide (HMPT) at 117° ($K = 6.25$), is in fair agreement with these reports.

House and Kramer[14] have reported equilibrium values for the ethyl ether analogs of the methyl enol ethers, **4** and **8**. Their method of equilibration consisted of heating the ethers at 100° with *p*-toluenesulfonic acid for 60–100 hr. Under these conditions, they found equal amounts of the 1,2 and 2,3 isomers in both ring systems, *i.e.*, $K = 1$. These results differ somewhat from our findings for the methyl ethers; using the iodine catalysis method, we observe a preponderance of the 2,3 isomer in both cases ($K = 1.2$ and 2.0).

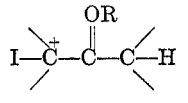
Finally, attention is called to the *E*/*Z* equilibrium values for methyl propenyl ether, **12**, and methyl 1-butenyl ether, **13**. In both cases, the equilibrium values reflect a slight bias in favor of the *E* isomer. These results are at variance with other reports on acyclic enol ethers which claim that the *Z* isomer is the more stable. Thus, Price and Snyder[24] report that in the phenyl propenyl ether system, the *Z* isomer is the more stable, accounting for 65% of the equilibrium mixture. Salomaa and Nissi[15] have reported $K_{E/Z} = 0.5$ for the methyl propenyl ether system, **12**, and $K_{E/Z} = 0.24$ for the methyl butenyl ether system, **13**. The equilibration method used by Price and Snyder was not reported, but Salomaa and Nissi stated that they followed the isomerizations in dilute dioxane solution at 25° in the presence of benzoic acid (ether–catalyst ~3:1). We have been unable to duplicate these experiments. Our experience with protic acid catalysts such as benzoic and *p*-toluenesulfonic acid is that consumption of the catalyst occurs before equilibration is complete. If larger amounts of acid are used, polymerization ensues. Quite recently, Okuyama, Fueno, and Furukawa[25] have presented a careful study of *cis–trans* equilibria in a series of enol ethers, including the system **12**. Equilibrations were carried out in the liquid phase with mercuric acetate as a catalyst. For methyl propenyl ether, **12**, they report $K_{E/Z} = 1.03$ at 25°, *i.e.*, a slight preponderance of the *trans* isomer, in qualitative agreement with our results in a hydrocarbon solvent. Attention is also directed to the relative stabilities of the *cis*/*trans* pair, *Z*-**10b** and *E*-**10b**. As in the case of the simple enol ether, **12**, the geometric isomers show almost equal stabilities at 25°. From such examples, one may conclude either that the steric requirement of the methoxy group is very small or that there are other, unappreciated, factors which stabilize enol ethers in the *cis* geometry.[25] It also follows, from a comparison of the systems **12** and **10b**, that, sterically, the groups $-CH_3$ and $-CH_2CO_2CH_3$ are about equivalent. In the same way, comparison of the geometric equilibria of the systems **11** and **10a** reveals similar steric requirements for $-CH_3$ and $-CH_2OCH_3$.

(19) L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3098 (1949).
(20) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Org. Chem.*, **32**, 2600 (1967).
(21) D. E. McGreer, W. Wai, and G. Carmichael, *Can. J. Chem.*, **38**, 2410 (1960).
(22) J. N. Butler and G. J. Small, *ibid.*, **41**, 2492 (1963).
(23) R. N. Gedye and A. Nechvatel, *J. Chem. Soc.*, 5925 (1964).
(24) C. C. Price and W. H. Snyder, *J. Amer. Chem. Soc.*, **83**, 1773 (1961).
(25) T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, **25**, 5409 (1969).

The facility and cleanness of the iodine-induced 1,3-hydrogen migrations in the enol ether systems **3**, **4**, **7**, and **8** prompted an investigation of the inter- *vs.* intramolecular nature of the rearrangement. Conceivably, the hydrogen transfer could occur intramolecularly within an iodine–enol ether complex. Accordingly, an exchange experiment using a mixture of the deuterated ethers, **8a**-d_2 and **8b**-d_2, and nondeuterated ethers was carried out under the isomerization conditions. Mass spectral analysis of the d_2, d_1, and d_0 composition before and after equilibration showed that a distribution of the deuterium labels close to statistical had been achieved during the equilibration. We conclude that the isomerization is intermolecular and visualize an ionic process initiated by the electrophilic species[26]



8a-d_2 **8b**-d_2



Experimental Section

Infrared spectra were recorded as thin films with a Perkin-Elmer Model 621 or Beckman IR-10 instrument. Ultraviolet spectra were measured in methanol in matched 1-cm silica cells at 25° with a Beckman DB spectrophotometer. Nmr spectra were obtained on solutions in carbon tetrachloride with TMS internal standard with either a Varian A-60 or HA-100 instrument. Mass spectral analyses were performed with a Consolidated Engineering Corporation 21-103-C mass spectrometer. Photoisomerizations were carried out at ambient temperature in dilute solutions in quartz tubes placed within a circular bank of 16 General Electric G8T5 Germicidal Lamps (rich in 2537 Å). Carefully purified solvents were employed in all the equilibration experiments and spectral measurements.

Methyl 1-Cyclopentene-1-carboxylate (1a) and Methyl 2-Cyclopentene-1-carboxylate (1b).—Cyclopentene-1-carboxylic acid, mp 120–121° (lit.[27] 121°), prepared by the method of Wheeler and Lerner,[27] was esterified with diazomethane to give the corresponding methyl ester, **1a**: bp 63–65° (10 mm); ir 1724, 1636 cm^{-1}; uv max 222 nm (ϵ 8300); nmr δ 6.70 (m, 1, HC=C) (lit.[28] δ 6.9), 3.67 (s, 3, OCH_3), ~2.5 (m, 4, allylic CH_2), 1.92 (m, 2, CH_2); purity by glpc, >99%. Reduction of 2-carbomethoxycyclopentanone with $NaBH_4$ in methanol and dehydration of the resulting hydroxy ester with P_2O_5 in benzene, according to the procedure of Bokil and Nargund,[29] produced a 1:3 mixture of **1a** and **1b**, bp 60–65° (15 mm). **1b** was isolated by glpc trapping: ir 1741, 1620 cm^{-1}; uv no max >210 nm; nmr δ 5.7 (m, 2, HC=CH) (lit.[28] δ 5.8), 3.65 (s, 3, OCH_3), ~3.3 (m, 1, allylic H α to ester), 2.8–2.0 (br m, 4, CH_2CH_2).

Methyl 2-Methyl-1-cyclopentene-1-carboxylate (2a) and Methyl 2-Methyl-2-cyclopentene-1-carboxylate (2b).—Dehydration of the cyanohydrin of 2-methylcyclopentanone according to the procedure of King and Robinson[30] gave a mixture of unsaturated nitriles, bp 70–75° (16 mm). Hydrolysis and esterification of the crude acids with diazomethane yielded a mixture of methyl esters, bp 73–75° (15 mm). Glpc analysis showed the presence of three components which were isolated by glpc trapping and purified by recycling. The major component was identified as **2a** by its spectral properties; ir 1720, 1650 cm^{-1}; uv max 231 (ϵ 10,900); nmr δ 3.67 (s, 3, OCH_3), ~2.5 (m, 4, allylic CH_2), 2.08 (m, 3, allylic CH_3), 1.75 (m, 2, CH_2). The component with the shortest retention time was identified as **2b**: ir 1742, 1660 cm^{-1}; uv no max >210 nm; nmr δ 5.47 (m, 1, HC=C), 3.65 (s, 3, OCH_3), ~3.25 (br m, 1, allylic H α to ester), ~2.5–1.9 (br m, 4, CH_2CH_2), 1.72 (m, 3, allylic CH_3). The minor component with intermediate retention time was identified as methyl 5-methyl-1-cyclopentene-1-carboxylate: ir 1728, 1630 cm^{-1}; uv max 222 nm (ϵ 9300); nmr δ 6.60 (m, 1, HC=C), 3.50 (s, 3, OCH_3), ~2.9 (m, 1, tertiary allylic H), ~2.3 (br m, 4, CH_2CH_2), 1.13 (d, 3, CH_3).

Methyl 2-Methoxy-1-cyclopentene-1-carboxylate (3a) and Methyl 2-Methoxy-2-cyclopentene-1-carboxylate (3b).—Treatment of 2-carbomethoxycyclopentanone with an ethereal solution of diazomethane according to the procedure of Lacasa, *et al.*,[31] yielded **3a**, white platelets from pentane, mp 39.5–40.0° (cor) in 85% yield; S. E. 159 (calcd for $C_8H_{12}O_5$ 156); ir 1717, 1695, 1636 cm^{-1}, str bands characteristic of β-alkoxy-α,β-unsaturated esters[32]; uv max 254 nm (ϵ 13,600); nmr δ 3.78 (s, 3, OCH_3 of ether), 3.57 (s, 3, OCH_3 of ester), 2.5 (m, 4, allylic CH_2), 1.83 (m, 2, CH_2). Distillation of **3a** through a Podbielniak column at 40 mm pressure at a rate which allowed equilibration produced the β,γ isomer, **3b**: bp 120–125° (40 mm); ir 1743, 1655 cm^{-1} (C=O and C=CO of unconjugated ester and enol ether[32]); uv no max >210 nm; nmr δ 4.57 (m, 1, HC=C), 3.60 (s, 3, OCH_3), 3.52 (s, 3, OCH_3), ~3.4 (m, 1, tertiary allylic H α to ester), ~2.5–1.8 (br m, 4, CH_2CH_2).

1-Methoxy-2-methyl-1-cyclopentene (4a) and 2-Methoxy-3-methyl-1-cyclopentene (4b).—The dimethyl ketal of 2-methylcyclopentanone was prepared with methyl orthoformate in methanol with *p*-toluenesulfonic acid catalyst according to the general procedure of House and Kramer,[14] bp 80–84° (40 mm), in 65% yield. Dealcoholation with $NH_4H_2PO_4$[14] produced a mixture of **4a** and **4b**, bp 120° (590 mm), in 86% yield. The enol ethers were separated and purified by glpc trapping (15% Carbowax 20M on Gas-Chrom P, 115°). **4a**: ir 1692 cm^{-1}, str (C=CO); uv no max >210 nm; nmr δ 3.51 (s, 3, OCH_3), 2.5–2.0 (br, m, 4, allylic CH_2), 1.8 (m, 2, CH_2), 1.50 (m, 3, CH_3). **4b**: ir 3072, w (HC=C), 1643 cm^{-1}, str (C=CO); uv no max >210 nm; nmr δ 4.29 (m, 1, HC=C), 3.51 (s, 3, OCH_3), 2.7–1.2 (br complex, 5, CH_2CH_2CH), 1.03 (d, 3, CH_3).

Methyl 1-Cyclohexene-1-carboxylate (5a) and Methyl 2-Cyclohexene-1-carboxylate (5b).—Diazomethane esterification of 1-carboxycyclohexene, mp 37–38°,[27] produced **5a**, bp 100° (30 mm): ir 1719, 1657 cm^{-1}; uv max 217 nm (ϵ 10,300); nmr[12] δ 6.90 (m, 1, HC=C), 3.66 (s, 3, OCH_3), 2.2 (m, 4, allylic CH_2), 1.6 (m, 4, CH_2CH_2). The β,γ isomer, **5b**, was isolated from equilibrated mixtures of **5a** and **5b** by glpc trapping: ir 1734, 1645 cm^{-1}; nmr[12] δ 5.68 (m, 2, H-C=C-H), 3.56 (s, 3, OCH_3), 2.94 (m, 1, tertiary), 2.5–2.1 (br, complex, 6, $CH_2CH_2CH_2$).

Methyl 2-Methyl-1-cyclohexene-1-carboxylate (6a) and Methyl 2-Methyl-2-cyclohexene-1-carboxylate (6b).—The method of Jones, *et al.*,[33] was followed for the preparation of 2-methyl-1-cyclohexane-1-carboxylic acid, mp 86–87° (lit.[33] 87°). Diazomethane esterification afforded **6a**, isolated and purified by glpc: ir 1722, 1654 cm^{-1}; uv max 225 nm (ϵ 9600); nmr δ 3.61 (s, 3, OCH_3), ~2.2 (m, 4, allylic CH_2), 1.96 (m, 3, CH_3), ~1.6 (m, 4, CH_2CH_2). The unconjugated isomer, **6b**, was isolated from equilibrated mixtures by glpc trapping: ir 1735, 1666 cm^{-1}; nmr δ 5.45 (m, 1, HC=C), 3.54 (s, 3, OCH_3), 2.84 (m, 1, tertiary), 2.1–1.2 (br complex, 6, $CH_2CH_2CH_2$), 1.59 (narrow m, 3, allylic CH_3).

Methyl 2-Methoxy-1-cyclohexene-1-carboxylate (7a) and Methyl 2-Methoxy-2-cyclohexene-1-carboxylate (7b).—Treatment of 2-carbomethoxycyclohexanone with methyl orthoformate and sulfuric acid according to the procedure of Michael[34] furnished the dimethyl ketal. Slow distillation of the latter through a Podbielniak column at 40 mm promoted dealcoholation and the more volatile isomer, **7b**, was collected as a colorless liquid. Recrystallization of the solid pot residue from pentane yielded **7a**, colorless plates; mp 45.5–46.0° (cor); S.E. 172 (calcd for $C_9H_{14}O_3$, 170); ir 1716, 1690, 1628 cm^{-1};[32] uv max

(26) This species is implicated by the kinetic studies of Eley and coworkers on the iodine-promoted polymerization of vinyl ethers: D. D. Eley and A. W. Richards, *Trans. Faraday Soc.*, **45**, 425, 436 (1949); D. D. Eley and J. Saunders, *J. Chem. Soc.*, 4167 (1952).

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(32) See ref 8 and S. J. Rhoads and R. W. Holder, *Tetrahedron*, **25**, 5443 (1969), for characteristic spectral properties of enol ethers of β-keto esters.

(33) E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 4073 (1956).

(34) A. Michael, *J. Amer. Chem. Soc.*, **57**, 161 (1935).

254 (ε 10,300); nmr δ 3.60 (s, 6, OCH_3), ~2.2 (m, 4, allylic CH_2), ~1.6 (m, 4, CH_2CH_2). The β,γ isomer, **7b**, showed bp 123–128° (40 mm); ir 1746, 1671 cm^{-1}; uv no max >210 nm; nmr δ 4.68 (t, 1, HC=C), 3.60 (s, 3, OCH_3), 3.45 (s, 3, OCH_3), ~3.1 (m, 1, allylic H α to ester); 2.3–1.4 (br complex, 6, CH_2-CH_2CH_2).

1-Methoxy-2-methyl-1-cyclohexene (8a) and 2-Methoxy-3-methyl-1-cyclohexene (8b).—The dimethyl ketal of 2-methylcyclohexanone, prepared in the manner described for the corresponding cyclopentanone derivative, underwent dealcoholation when heated with anhydrous ferric chloride[34] to yield a mixture of **8a** and **8b**, bp 58–60° (22 mm), which was separated by preparative glpc. The component with the shorter retention time proved to be **8b**: ir 1671 cm^{-1} (str, C=CO); nmr δ 4.45 (t, 1, HC=C), 3.41 (s, 3, OCH_3), ~2.4–1.2 (br complex, 7, $CH_2CH_2CH_2$ and tertiary allylic H), 1.03 (d, 3, CH_3). The second component, **8a**, showed the spectral properties: ir 1685 cm^{-1} (str, C=CO); nmr δ 3.38 (s, 3, OCH_3), ~2.2–1.4 [br complex, 8, $(CH_2)_4$], 1.54 (m, 3, CH_3).

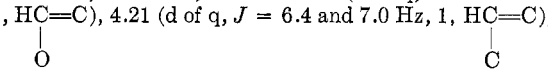
Methyl 2-Pentenoate (9a) and Methyl 3-Pentenoate (9b).—Esterification of a mixture of 2- and 3-pentenoic acids produced by dehydrobromination[35] of 2-bromopentanoic acid yielded a mixture consisting of 85% **9a** and 15% **9b**, bp 58–60° (35 mm). Pure samples of *E*-**9a**, *Z*-**9a**, and *E*-**9b** were trapped by preparative glpc (15% Carbowax 20M on Gas-Chrom P at 110°) for spectral analysis. *E*-**9a**: ir 1725, 1657, 970 cm^{-1}; nmr δ 6.87 (d of t, 1, J = 15 and 6 Hz, HC_3=C), 5.67 (d of t, 1, J = 15 and 1.7 Hz, HC_2=C), 3.55 (s, 3, OCH_3), 2.16 (m, 2, CH_2), 1.02 (t, 3, CH_3). *Z*-**9a**: ir 1721, 1629 cm^{-1}; nmr δ 6.10 (d of t, J = 11.2 and 7.2 Hz, 1, HC_3=C), 5.62 (d of t, J = 11.2 and 1.6 Hz, 1, HC_2=C), 3.60 (s, 3, OCH_3), 2.62 (m, 2, CH_2), 1.04 (t, 3, CH_3). *E*-**9b**: ir 1740, 1657, 961 cm^{-1}; nmr δ 5.47 (m, 2, HC=CH), 3.57 (s, 3, OCH_3), 2.89 (m, 2, CH_2), 1.68 (m, 3, CH_3).

Samples of **9b** were also prepared by irradiation of the mixture of *E*-**9a** and *Z*-**9a** as a dilute solution in pentane (5%) containing 6% benzene.[10] The presence of a small amount of *Z*-**9b** in the photoproduct was indicated by the appearance of two methoxy signals in the nmr spectrum of the β,γ isomer but the geometric isomers were not separable by the glpc conditions employed.

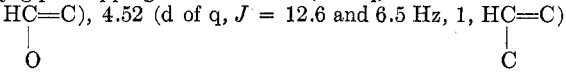
Methyl 4-Methoxy-2-butenoate (10a) and Methyl 4-Methoxy-3-butenoate (10b).—The conjugated isomer, **10a**, prepared by the method of Sultanbawa, *et al.*,[36] was largely *E*-**10a**, accompanied by a small amount of *Z*-**10a**. Preparative glpc (15% Carbowax 20M on Gas-Chrom-P at 130°) furnished a pure sample of *E*-**10a**: ir 1724, 1664, 965 cm^{-1}; nmr[20] δ 6.86 (d of t, J = 15.6 and 4.0 Hz, 1, HC_3=C), 5.97 (d of t, J = 15.6 and 2.0 Hz, 1, HC_2=C), 3.66 (s, 3, OCH_3), 3.32 (s, 3, OCH_3), 4.02 (d of d, J = 2.0 and 4.0 Hz, 2, CH_2). Irradiation of a 5% solution of *E*-**10a** in pentane containing 2% benzene was continued 4 hr at which time *Z*-**10a** had reached its maximum concentration (Figure 1). Glpc trapping afforded pure *Z*-**10a**: ir 1711, 1651 cm^{-1}; nmr δ 6.28 (d of t, J = 11.7 and 4.9 Hz, 1, HC_3=C), 5.71 (d of t, J = 11.7 and 3.2 Hz, 1, HC_2=C), 4.40 (d of d, J = 4.9 and 3.2 Hz, 2, CH_2), 3.64 (s, 3, OCH_3), 3.32 (s, 3, OCH_3). Samples of *E*-**10b** and *Z*-**10b** could be isolated from the photoreaction mixture allowed to proceed to completion (rich in *E*-**10b**), or from the thermal (~1:1 in *trans* and *cis* isomers) or base-catalyzed (almost exclusively *Z*-**10b**) equilibration mixtures. Glpc trapping afforded pure samples. *E*-**10b**: ir 1739, 1659 cm^{-1}; nmr[20] δ 6.32 (d of t, J = 12.8 and 1.4 Hz, 1, HC_4=C), 4.72 (d of t, J = 12.8 and 7.5 Hz, 1, HC_3=C), 3.56 (s, 3, OCH_3), 3.46 (s, 3, OCH_3), 2.84 (d of d, 2, CH_2). *Z*-**10b**: ir 1737, 1668 cm^{-1}; nmr[20] δ 5.91 (d of t, J = 6.1 and 1.7 Hz, 1, HC_4=C), 4.48 (d of t, J = 6.1 and 7.0 Hz, 1, HC_3=C), 3.68 (s, 3, OCH_3), 3.62 (s, 3, OCH_3), 2.99 (d of d, 2, CH_2).

Methyl 2-Butenoate (11).—Fischer esterification of crotonic acid produced **11**, bp 110–112° (590 mm). Preparative glpc (15% Reoplex-400 on Gas-Chrom P at 110°) permitted isolation of pure *E*-**11**: ir 1722, 1658, 965 cm^{-1}; nmr[37] δ 6.89 (d of q, J = 15.4 and 6.9 Hz, 1, HC_3=C), 5.76 (d of q, J = 15.4 and 1.65 Hz, 1, HC_2=C), 3.62 (s, 3, OCH_3), 1.86 (d of d, J = 6.9 and 1.65 Hz, 3, CH_3). The *cis* isomer, *Z*-**11**, was prepared by photoisomerization of *E*-**11** in a pentane–benzene solution by the method described earlier. After 25 hr of irradiation the concentration of *Z*-**11** had reached a maximum and only minor amounts of the β,γ isomer, methyl 3-butenoate, had formed. Preparative glpc gave pure *Z*-**11**: ir 1720, 1648 cm^{-1}; nmr[37] δ 6.28 (d of q, J = 11.4 and 7.0 Hz, 1, HC_3=C), 5.72 (d of q, J = 11.4 and 1.6 Hz, 1, HC_2=C), 3.64 (s, 3, OCH_3), 2.14 (d of d, J = 7.0 and 1.6 Hz, 3, CH_3).

Methyl Propenyl Ether (12).—Base-catalyzed isomerization of methyl allyl ether (bp 35–39° at 590 mm, ir 1646 cm^{-1}) was accomplished by a 17-hr reflux period in 0.15 *M* sodium methoxide solution in DMSO. The major component of the reaction mixture (96%) was the *cis* isomer, *Z*-**12**, which was purified by glpc trapping: ir 1667, 720 cm^{-1}; nmr[38] δ 5.72 (d of q, J = 6.4 and 1.8 Hz, 1, HC=C), 4.21 (d of q, J = 6.4 and 7.0 Hz, 1, HC=C),

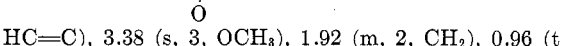


3.42 (s, 3, OCH_3), 1.47 (d of d, J = 7.0 and 1.8 Hz, 3, CH_3). Isomerization of *Z*-**12** with iodine in *n*-decane produced a *cis*–*trans* mixture from which the pure *trans* isomer, *E*-**12**, was isolated by glpc trapping: nmr[38] δ 6.15 (d of q, J = 12.6 and 1.5 Hz, 1, HC=C), 4.52 (d of q, J = 12.6 and 6.5 Hz, 1, HC=C),

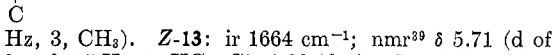


3.34 (s, 3, OCH_3), 1.49 (d of d, J = 6.5 and 1.5 Hz, 3, CH_3).

Methyl 1-Butenyl Ether (13).—The mixture of *E*-**13** and *Z*-**13** obtained by dealcoholation of *n*-butyraldehyde dimethyl acetal with $NH_4H_2PO_4$, by the procedure of House and Kramer,[14] was separated by preparative glpc (25% Reoplex-400 on Chromosorb W at 65°). *E*-**13**: ir 1674, 1657 cm^{-1}; nmr[39] δ 6.21 (d of t, J = 12.5 and 1.3 Hz, 1, HC=C), 4.62 (d of t, J = 12.5 and 5.6



Hz, 1, HC=C), 3.38 (s, 3, OCH_3), 1.92 (m, 2, CH_2), 0.96 (t,

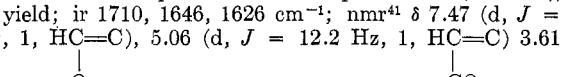


J = 7.6 Hz, 3, CH_3). *Z*-**13**: ir 1664 cm^{-1}; nmr[39] δ 5.71 (d of t, J = 6.3 and 1.5 Hz, 1, HC=C), 4.23 (d of t, J = 6.3 and 7.0

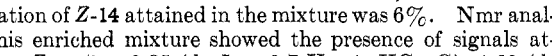
Hz, 1, HC=C), 3.47 (s, 3, OCH_3) 2.02 (m, 2, CH_2), 0.92 (t,

J = 7.7 Hz, 3, CH_3).

Methyl 3-Methoxy-2-propenoate (14).—The dimethyl acetal of methyl α-formylacetate, prepared by the general method described by Deno[40] from methyl α-bromoacetate and methyl orthoformate, was examined without purification by nmr: δ 4.67 [t, J = 6 Hz, 1, $HC(OCH_3)_2$], 3.56 (s, 3, CO_2CH_3), 3.19 [s, 6, $(CH_3O)_2C$], 2.26 (d, J = 6 Hz, 2, CH_2). Dealcoholation of the acetal was accomplished in the following way: 5.2 g of the acetal and 0.1 g *p*-toluenesulfonic acid were placed in a flask equipped with a short path distillation head and heated to 120°. Methanol was slowly removed as the pot temperature rose to 150°. Additional quantities of catalyst were added; the procedure was repeated until the formation of methanol ceased. Distillation of the residue produced *E*-**14**: bp 159–164° (594 mm), in 61% yield; ir 1710, 1646, 1626 cm^{-1}; nmr[41] δ 7.47 (d, J = 12.2 Hz, 1, HC=C), 5.06 (d, J = 12.2 Hz, 1, HC=C) 3.61



(s, 3, OCH_3), 3.55 (s, 3, OCH_3). The *cis* isomer, *Z*-**14**, could be prepared by short term photoisomerization of *E*-**14** in carbon tetrachloride solution. Under these conditions, the maximum concentration of *Z*-**14** attained in the mixture was 6%. Nmr analysis of this enriched mixture showed the presence of signals attributed to *Z*-**14**:[41] δ 6.35 (d, J = 6.7 Hz, 1, HC=C), 4.69 (d,



J = 6.7 Hz, 1, HC=C), 3.80 (s, 3, OCH_3), 3.57 (s, 3, OCH_3).

Equilibration Methods.—In all the equilibrations except the iron pentacarbonyl catalyzed cases, samples of the substrate, neat or in solution, with the appropriate catalyst and internal standard, were degassed and sealed under nitrogen in thoroughly

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(40) N. C. Deno, *J. Amer. Chem. Soc.*, **69**, 2233 (1947).

(41) E. Winterfeldt and H. Preuss, *Chem. Ber.*, **99**, 450 (1966).

cleaned Pyrex tubes. The progress of the isomerizations was monitored by glpc analysis. Whenever possible, equilibrium was achieved starting with each isomer. In the iron pentacarbonyl catalyzed systems, the substrate and catalyst were dissolved in octane or "isooctane" and the mixture held at reflux temperature under a nitrogen atmosphere. Isomerizations induced by iron pentacarbonyl were followed by ir analysis. After equilibrium had been established, heating was continued to destroy the remaining iron catalyst before glpc analysis of the equilibrated sample was carried out. The methods and results are summarized in Tables III and IV. In the cases of catalysis by iodine

TABLE III

TAUTOMERIC EQUILIBRATIONS

Starting material	Equilibrium composition[a] % 1,2 isomer	% 2,3 isomer	Equilibration conditions[b]
1a	94.3	5.7	A: 0.5 *M* in substrate
1b	95.2	4.8	and catalyst; 4–10 hr, 100 ± 5°
2a	94.3	5.7	A: 0.5 *M* in substrate
2b	94.2	5.8	and catalyst; 4–10 hr, 100 ± 5°
3a	69.6	30.4	B: neat, 240 hr, 150
3b	67.0	33.0	± 5°
3a	64.5	35.5	C: 2.0 *M* in substrate,
3b	65.4	34.6	0.05 *M* in catalyst, 0.5–1 hr, 25 ± 1°
4a	34.5	65.5	C: 0.15 *M* in sub-
4b	33.2	66.8	strate, 0.003 *M* in catalyst, 10–20 min, 25 ± 1°
5a	95.5	4.5	A: 0.5 *M* in substrate
			and catalyst, 4–10 hr, 100 ± 5°
6a	75.6	24.4	A: 0.5 *M* in substrate
			and catalyst, 4–10 hr, 100 ± 5°
7a	11.7	88.3	C: 2.0 *M* in substrate,
7b	11.8	88.2	0.05 *M* in catalyst, 0.5–1 hr, 25 ± 1°
8a	39.4	60.6	C: 2.0 *M* in substrate,
8b	39.6	60.4	0.05 *M* in catalyst, 0.5–1 hr, 25 ± 1°
9a	73.5	26.5	E: 0.2 *M* in substrate, 0.04 *M* in catalyst, 46 hr, 117 ± 5°
9a	66.3	33.7	D: 1.4 *M* in substrate, 0.02 *M* in catalyst, 4 hr, 117 ± 5°
80% **9a** + 20% **9b**	69.1	30.9	A: 0.5 *M* in substrate and catalyst, 9 hr, 117 ± 5°
E-**10a**	8.6	91.4	B: neat, 500 hr, 220 ± 5°
Z-**10a**	7.2	92.8	B: neat, 15 hr,
22% **10a** + 78% **10b**	7.5	92.5	300 ± 5°
22% **10a** + 78% **10b**	3.1	96.9	E: 0.2 *M* in substrate, 0.04 *M* in catalyst, 50 hr, 92 ± 5°

[a] Values are averages of at least three determinations on a given equilibrium mixture. [b] See footnote *a*, Table I.

(method C) and by iron pentacarbonyl (method E) the material balance was excellent as judged by internal standards or by comparison of glpc analyses of an equilibrated mixture against a synthetic mixture which had not been subjected to equilibration conditions. Thermal isomerizations (method B) often were accompanied by appreciable material loss and were extremely slow; only the more labile systems **3**, **7**, and **10** could be brought to near equilibrium by this method. Method A showed good reproducibility and material balance for the cyclic esters **1**, **2**, **5**, and **6** but extensive material loss was observed for the acyclic

TABLE IV

GEOMETRIC EQUILIBRATIONS

Starting material	Equilibrium composition[a] % *Z* isomer	% *E* isomer	Equilibration conditions[a]
Z-**11**	13.8	86.2	D: 1.4 *M* in substrate, 0.02 *M* in catalyst, 3 hr, 117 ± 5°
Z-**12**	44.8	55.2	C: 0.15 *M* in substrate, 0.003 *M* in catalyst, 2–5 hr, 25 ± 1°
Z-**13**	36.0	64.0	C: 0.15 *M* in sub-
21% *Z*-**13** + 79% *E*-**13**	34.5	65.5	strate, 0.003 *M* in catalyst, 2.5 hr, 25 ± 1°
E-**14**	0.8	99.2	C: CCl_4 solution,
6% *Z*-**14** + 94% *E*-**14**	0.8	99.2	0.15 *M* in substrate, 0.003 *M* in catalyst, 8 hr, 100 ± 5°
19% *Z*-**10b** + 81% *E*-**10b**	46.5	53.5	C: 0.12 *M* in substrate, 0.003 *M* in catalyst, 10 hr, 25 ± 1°

[a] See footnotes, Table III.

systems **9** and **10**, presumably by addition of solvent to the olefinic bond. Substitution of the aprotic solvent, HMPT, and a lower catalyst concentration corrected this problem and also shortened the time required for the achievement of equilibrium (method D).

Glpc Analysis.—The equilibrated samples were analyzed by glpc methods standardized against synthetic mixtures of known composition. In all cases, the integrated areas of the peaks corresponded to the composition of the mixture within the reproducibility of duplicate runs (±1%). Analysis conditions were carefully checked for each isomeric system to assure that isomerization did not occur during analysis. Analyses were performed with either a Perkin-Elmer 154-C vapor fractometer or a Varian Aerograph A-90-P instrument. Helium was the carrier gas in all cases. The columns and conditions for each system are shown in Table V.

TABLE V

GLPC ANALYSIS CONDITIONS

System	Column[a]	Temp, °C	Elution order
1ab	I	140	**1b**, **1a**
2ab	I	150	**2b**, **2a**
3ab	II	124	**3b**, **3a**
4ab	III	72	**4b**, **4a**
5ab	I	150	**5b**, **5a**
6ab	I	150	**6b**, **6a**
7ab	II	124	**7b**, **7a**
8ab	III	114	**8b**, **8a**
9ab	IV	75	*Z*-**9a**, *Z*- + *E*-**9b**, *E*-**9a**
10ab	V	82	*Z*-**10a**, *Z*-**10b**, *E*-**10b**, *E*-**10a**
11	IV	72	*Z*-**11**, *E*-**11**
12	IV	20	*Z*-**12**, *E*-**12**
13	IV	50	*Z*-**13**, *E*-**13**
14	VI	117	*E*-**14**, *Z*-**14**

[a] I: Perkin-Elmer "K" packing, 2.6 m. II: 2.5% Reoplex-400 on Gas-Chrom P, 3 m. III: 10% UCON Polar, on Gas-Chrom P, 3 m. IV: 15% diisodecyl phthalate on Gas-Chrom P, 3 m. V: 15% diphenyl phthalate on Gas-Chrom P, 3 m. VI: 15% Reoplex 400 on Chromosorb W, 4 m.

2,6,6-d_3-2-Methylcyclohexanone.—The trideuterated ketone was prepared by the general procedure described by Seibl and

Gauman[42] by three successive treatments of 2-methylcyclohexanone with a 10% solution of DCl–D_3PO_4 in D_2O. Nmr analysis of the exchanged ketone indicated the deuterium content to be about 95% of that calculated for the d_3 compound.

6,6-d_2-1-Methoxy-2-methylcyclohexene (8a-d_2) and 1,3-d_2-2-Methoxy-3-methylcyclohexene (8b-d_2).—The enol ethers of the deuterated 2-methylcyclohexanone, prepared in the presence of methanol-d_1 by the method described earlier, were isolated by glpc trapping and identified by their spectral properties. Mass spectral analysis of **8b**-d_2 at low ionization voltage showed the deuterium distribution to be 78.8% d_2 species, 18.4% d_1 species, and 2.8% d_0 species after correction for natural isotopic contributions.[43] Moreover, analysis of a sample of **8b**-d_2 before and after glpc trapping showed that negligible amounts of exchange or fractionation occurred on the column.

Deuterium Exchange Experiment.—An equilibrium mixture of **8a**-d_2 and **8b**-d_2 was diluted with nonlabeled equilibrated ethers to give a sample with the deuterium distribution: d_2, 41.1%, d_1, 20.3%, and d_0, 38.6%. The mixture was then subjected to the conditions of the iodine catalyzed equilibrations. After 24 hr the mixture of isomers was isolated by glpc trapping and the deuterium distribution redetermined. The final distribution was d_2, 23.5%, d_1, 49.1%, and d_0, 27.4%, in close agreement with the statistical distribution of d_2, 26.8%, d_1, 48.8%, and d_0, 24.4%.

Registry No.—**1a**, 25662-28-6; **1b**, 2258-56-2; **2a**, 25662-30-0; **2b**, 25662-31-1; **3a**, 25662-32-2; **3b**, 25662-33-3; **4a**, 25662-34-4; **4b**, 25662-35-5; **5a**, 18448-47-0; **5b**, 25662-37-7; **6a**, 25662-38-8; **6b**, 25662-39-9; **7a**, 25662-40-2; **7b**, 25662-41-3; **8a**, 1728-38-7; **8b**, 1728-37-6; **9a** (*E*), 15790-88-2; **9a** (*Z*), 15790-87-1; **9b** (*E*), 20515-19-9; **10a** (*E*), 13168-99-5; **10a** (*Z*), 25665-54-7; **10b** (*E*), 13168-97-3; **10b** (*Z*), 13214-13-6; **11** (*E*), 623-43-8; **11** (*Z*), 4358-59-2; **12**(*E*), 4188-69-6; **12** (*Z*), 4188-68-5; **13** (*E*), 10034-13-6; **13** (*Z*), 10034-12-5; **14** (*E*), 5788-17-0; **14** (*Z*), 5739-81-1; methyl 5-methyl-1-cyclopentene-1-carboxylate, 25662-44-6.

(42) J. Seibl and T. Gauman, *Helv. Chim. Acta*, **46**, 2857 (1963).

(43) K. Biemann, "Mass Spectrometry, Organic Chemical Application," McGraw-Hill, New York, N. Y., 1962, Chapter 5.

Double-Bond Isomerizations in Unsaturated Esters and Enol Ethers. II. Evaluation of Conjugative, Steric, and Polar Effects of Alkyl, Alkoxy, and Alkoxycarbonyl Substituents on Positional and Configurational Equilibria[1]

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Three carbon tautomeric equilibrium data for five- and six-membered cyclic olefinic systems bearing methyl, methoxy, and methoxycarbonyl substituents are analyzed in terms of stabilizing and destabilizing contributions to the observed free-energy changes. Stabilizing energies of 2.3, 6.8, and 2.6 kcal/mol are assigned to alkyl, OCH_3, and CO_2CH_3, respectively. Destabilizing *cis* interactions found for the six-membered ring and acyclic systems are CH_3 *vs.* CO_2CH_3, 1.4 kcal/mol; OCH_3 *vs.* CO_2CH_3, 3.5 kcal/mol; CH_3 *vs.* OCH_3, 0.1 kcal/mol. In the five-membered ring, the destabilizing *cis* interaction of OCH_3 *vs.* CO_2CH_3 amounts to 1.8 kcal/mol. A destabilizing interaction resulting from opposed alkyl–methoxy conjugation is assigned a value of 1.7 kcal/mol.

In 1952, in an analysis of the factors affecting the position of prototropic equilibrium in a number of open-chain unsaturated systems, de la Mare presented an empirical method for correlation of experimentally observed free-energy changes with the individual free-energy contributions of various substituent groups.[3] The group contributions were assessed from available heat of hydrogenation and equilibrium data. Pertinent to the present discussion are the values assigned to alkyl and ester groups, alone and in combination. Thus, a stabilizing value of 2.3 kcal/mol was assigned to each alkyl or substituted alkyl group in an ethylenic system and a stabilizing value of only 1.0 kcal/mol for each α- or β-alkyl substituent in an α,β-unsaturated acid derivative. It was further postulated that the effectiveness of any alkyl group is reduced by 0.5 kcal/mol for each cross- or opposed-hyperconjugation involving another alkyl group. A stabilizing, conjugative interaction of 3.8 kcal/mol was assigned to a carboxylate, ester, or nitrile function. de la Mare's calculated values for the free energy differences in a series of α,β–β,γ-unsaturated acid, ester, and nitrile systems were in reasonably good agreement with the experimental values. It may be noted, however, that the systems tested involved only open chain acid derivatives, most of them capable of configurational as well as positional isomerization, and that the substituent variation in these systems was limited to alkyl groups.

In the present paper, a similar analysis of five- and six-membered cyclic systems bearing methyl, methoxy, and methoxycarbonyl substituents is offered. In these cases, however, the introduction of a geometry-constraining ring and an additional polar group invalidates the simple treatment derived for alkylated acyclic acid derivatives. In order to restore the predictive power of the analysis, it has been necessary to evaluate the magnitude of such steric and polar effects and to include their contributions to the net free energy changes.

Results

The equilibrium data employed in this analysis are presented in the accompanying paper.[4] The free energy changes involved in the equilibrations of these systems will be interpreted according to the following postulates. (1) That the conjugative (or hyperconjugative) interaction of a double bond with an alkyl or substituted alkyl, methoxy, or methoxycarbonyl group stabilizes an ethylenic system. (2) That *cis* interactions

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(2) National Science Foundation Summer Research Fellow, 1967.

(3) P. B. D. de la Mare, *J. Chem. Soc.*, 1602 (1952).

(4) S. J. Rhoads, J. K. Chattopadhyay, and E. E. Waali, *J. Org. Chem.*, **35**, 3352 (1970).