the inward-pointing hydrogens on C-3 and C-7 is only 1.92 Å,[1] and thus the steric repulsion between these two hydrogens is already quite significant in the parent compound.

It can be predicted on the basis of the present data that 3,3-dimethyl-*cis*-1,4-cyclooctadiene[4] and 3,3,7,7-tetramethyl-*cis*-1,4-cyclooctadiene will both exist very predominantly in twist-boat conformations and that the barriers to ring inversion in these compounds will be considerably greater than that in 1. The boat-boat of the above tetramethyl derivative should be extremely strained, and it is likely that ring inversion in the compound will proceed via a boat-chair, which is itself of fairly high energy. However, it appears unlikely that the latter barrier will be high enough for that diene to exist in isolable enantiomeric forms at room temperature.

Experimental Section

The *cis,cis*-cycloocta-2,7-dienone ethylene ketal was prepared from cyclooctanone according to the procedure described by Garbisch.[2] The compound was purified by preparative VPC on a Carbowax 20M column. Its ^{1}H NMR spectrum (348 MHz) in $CDCl_3$ at room temperature exhibits absorption bands at δ 1.57 (5-CH_2), 2.28 (4,6-CH_2), 4.0 (9,10-CH_2), and 5.8 (CH protons). The ^{13}C NMR spectrum (63.1 MHz) in $CDCl_3$ at room temperature show bands at δ 23.9 (4,6-$^{13}CH_2$), 25.9 (5-$^{13}CH_2$), 65.2 (9,10-$^{13}CH_2$), 113.0 (3,7-^{13}CH), 106.3 (1-^{13}C), and 117.7 (2,8-^{13}CH).

^{13}C NMR spectra were measured on a superconducting solenoid NMR spectrometer operating at 59 kG.[5] The ^{1}H NMR spectra were obtained on a superconducting solenoid NMR spectrometer operating at 82 kG.[6] Tetramethylsilane was used as internal reference for both ^{13}C and ^{1}H NMR spectra.

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. 1, 72708-69-1.

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Kinetics and Mechanism of the Ene Reaction of Dimethyl Mesoxalate with Alkenes[1a]

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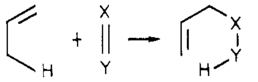
The kinetics of the ene reaction of dimethyl mesoxalate with 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, (*E*)-2-pentene, and (*Z*)-2-pentene have been studied. The reaction was found to be second order, first order with respect to each reactant. Thermodynamic parameters, viz., enthalpy ($\Delta H^* = 75$–96 kJ mol^{-1}) and entropy ($\Delta S^* = -120$ to -170 J mol^{-1} K^{-1}) of activation, as well as the lack of a significant effect of solvent polarity on the rate of the reaction, indicated a concerted mechanism. Analysis of the ΔH^* values obtained in terms of a loose transition state suggested that the transition state is product-like ("late") in character.

The reaction between an alkene containing an allylic hydrogen atom and an electron-deficient multiple bond (enophile), leading to a 1:1 adduct according to eq 1, is known as the ene synthesis.[2a-c]



(1)

In spite of the relative simplicity of the ene reaction a complete and consistent picture of its mechanism is still lacking. For different ene reactions just about all possible mechanisms have been put forward. The suggestions include a free-radical mechanism involving an intermediate diradical[3,4] or a radical pair, if a promoting transfer of a hydrogen atom is involved,[5,6] as well as an ionic mechanism,[7] and finally the often advanced concerted mechanism via a six-membered cyclic transition state.[8-10]

The concerted ene reaction is a pericyclic process and as such it can be considered in terms of orbital symmetry rules and the frontier orbital or the Dewar-Zimmermann method. As the transition state of the ene reaction has no elements of symmetry, the approaches are not rigorous. Their justification in relation to the specific ene reaction requires additional support from experimental evidence.

Kinetic methods have so far found a rather limited[11,12] application in the study of the ene reaction mechanism, and the recent prevalence of concerted mechanism proposals is based largely upon stereochemical evidence, viz., asymmetric induction,[13,14] cis configuration of the newly formed C-C and C-H bonds,[15] stereoselective migration

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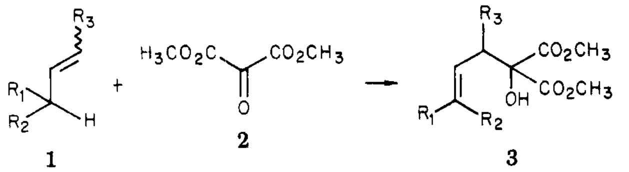
Scheme I



a, R_1 = Et; R_2 = R_3 = H
b, R_1 = Pr; R_2 = R_3 = H
c, R_1 = R_2 = Me; R_3 = H
d, R_1 = Et; R_2 = Me; R_3 = H
e, R_1 = R_2 = Et; R_3 = H
f, R_1 = Me; R_2 = H; R_3 = Me (*E* isomer)
g, R_1 = Me; R_2 = H; R_3 = Me (*Z* isomer)

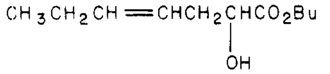
of allylic hydrogen atoms,[16] and prevalence of endo over exo addition.[13] These findings are merely suggestive of the concerted mechanism, and none has the weight of an unambiguous criterion.[17]

Moreover, on account of the wide spectrum of enophiles and the resulting diversity of mechanisms of specific reactions, further studies in cases of interest are necessary. One group of such ene reactions involves additions in which α-oxo esters are used as enophiles. These reactions have been the subject of our studies[18] for some time, and in the present paper we describe some kinetic results which throw light on their mechanism. Of the two α-oxo esters employed, namely butyl glyoxylate and dimethyl mesoxalate, the use of the latter appeared more attractive in view of the simpler stereochemistry of the products.

Results

The thermal reaction between diethyl mesoxalate and several alkenes has been carried out by us before.[18] We then demonstrated that in each case the sole product is a diethyl 2-alkenyltartronate, i.e., an ene adduct. Now we have confirmed these results in studies of the thermal reactions of dimethyl mesoxalate with 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, (*E*)-2-pentene, and (*Z*)-2-pentene (Scheme I).

VPC of the ene adducts **3a,b,d,f,g** revealed in each case the presence of two components in ratios varying from 9:1 to 8:2. Their *E*–*Z* relation was inferred from the following data. A single chromatographic peak was observed for the hydrogenation product of adduct **3a** and also adducts **3c,e** for which *Z*–*E* isomerism is not possible. In each case where a geometric isomer could arise, the *E* configuration of the double bond in the major component was proved by ^{1}H NMR. UV irradiation[19] of the adduct of *n*-butyl glyoxylate with 1-pentene (**4**) led to a change in the isomer ratio from 9:1 to 10:7. In the latter mixture, coupling constants of the vinylic protons in both isomers were obtained by ^{1}H NMR double-resonance experiments, indicating, respectively, their *E* and *Z* configurations.



$CH_3CH_2CH{=}CHCH_2\underset{OH}{\underset{|}{C}}HCO_2Bu$

4

By running a series of thermal reactions of dimethyl mesoxalate with 1-pentene in various solvents (carbon tetrachloride, bromobenzene, acetonitrile) and at various temperatures, we found that the effect of conditions on the yield and proportions of the isomers is practically nil. Likewise, in catalytic reactions ($SnCl_4$, BF_3, $AlCl_3$) conducted at room temperature the same *E*:*Z* ratio of isomers (9:1) was noted. However in the case of a reaction carried out without any solvent the ratio of isomers was 7:3. To lend mechanistic validity to the stereoselectivity of the reactions studied, we have demonstrated that the formation of geometric isomers of the ene adducts is kinetically controlled. Neither heating of the 7:3 *E*:*Z* adduct **3a** nor treatment with a catalyst affected the above proportions of the geometric isomers.

Table I. Solvent Effect on Reaction Rate

solvent	dielectric constant, D	dipole moment, μ_g	relative rate constant
CCl_4	2.23	0	1
C_6H_5Br	5.40	1.70	1.03
CH_3CN	36.2	3.92	1.0

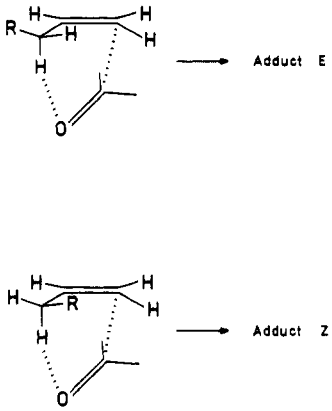


Figure 1. Conformation of alkenes with exo and endo groups R in the transition state.

From a series of kinetic experiments at various temperatures conducted under pseudo-first-order conditions with a large excess of the alkene, the order of reaction with respect to dimethyl mesoxalate was found to be unity. The overall reaction order was determined to be two (one with respect to each reactant) by carrying out experiments with equimolar quantities of dimethyl mesoxalate and alkene. Subsequently the pseudo-first-order rate constants were determined, and the corresponding second-order rate constants were calculated from the relation: $k = k'C_{al}^{-1}$, where k = second-order rate constant, k' = pseudo-first-order rate constant, and C_{al} = alkene concentration.

Analogously, the relative rate constants of reaction of 1-pentene with dimethyl mesoxalate in several solvents were determined (Table I).

From the rate constants determined at various temperatures, the energies and entropies of activation were evaluated for the ene reactions under study (Table II).

Discussion

The preponderance of the *E* over the *Z* isomer of adducts **3a,b** suggests a concerted reaction mechanism. The proportions of the geometric isomers formed are related to the ratio of the two possible conformations of an alkene in the transition state (Figure 1).

The *E* isomer corresponds to the sterically more favorable exo conformation in which, unlike the endo conformation, there is no interaction of the group R with the hydrogen atom at C-1. It would be expected that, as a consequence of the two-stage mechanism that permits rotation about the C=C bond in, for example, the diradical, the stereoselectivity would be less. This expectation is reinforced by the fact that the change in hybridization of the enophilic carbon atom from sp^2 to sp^3 would facilitate a more convenient arrangement for the alkyl group in the endo conformation, thus suppressing the preference for the exo conformation.

A firm confirmation of the concerted-mechanism hypothesis comes from the results of the kinetic study.

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Table II. Rate Constants and Thermodynamic Parameters for the Ene Reaction of Dimethyl Mesoxalate with Alkenes

alkene	temp, °C	rate constant, $10^3 k$, $m^3 mol^{-1} s^{-1}$		$k/k_{pentene}$	energy of activation, E_a, kJ mol^{-1}		entropy of activation, ΔS, J $mol^{-1} K^{-1}$
1-pentene	110	1.42 ± 0.04		1	75.6 ± 6.7		−171.4 ± 12.9
	120	2.39 ± 0.08		1			
	130	4.34 ± 0.14		1			
	140	6.56 ± 0.21		1			
1-hexene	110	1.41 ± 0.04		0.99	76.1 ± 6.7		−168.0 ± 13.3
	130	4.19 ± 0.13		0.96			
	140	6.50 ± 0.20		0.98			
3-methyl-1-butene	110	0.80 ± 0.02		0.56	82.8 ± 7.1		−157.2 ± 12.5
	130	2.48 ± 0.08		0.57			
	140	4.58 ± 0.14		0.59			
3-methyl-1-pentene	110	0.94 ± 0.03		0.66	97.8 ± 7.9		−118.7 ± 11.7
	120	1.85 ± 0.06		0.77			
	130	4.10 ± 0.13		0.94			
	140	7.32 ± 0.23		1.11			
3-ethyl-1-pentene	120	0.60 ± 0.02		0.22	85.3 ± 7.1		−135.0 ± 12.1
	130	1.03 ± 0.03		0.24			
	140	1.92 ± 0.07		0.27			
	150	2.99 ± 0.09					
		Z	*E*		*Z*	*E*	
(*E*)-2-pentene	130	1.12 ± 0.03		0.26	88.2 ± 7.5	78.6 ± 6.7	−167.6 ± 13.4
	140	0.37 ± 0.01	1.46 ± 0.04	0.28			
	150	0.69 ± 0.02	2.09 ± 0.07				
		Z	*E*		*Z*	*E*	
(*Z*)-2-pentene	130	0.12 ± 0.01	0.50 ± 0.02	0.14	98.2 ± 7.9	82.8 ± 7.1	−157.2 ± 12.5
	140	0.23 ± 0.01	0.89 ± 0.03	0.17			
	145	1.47 ± 0.04					
	150	0.47 ± 0.01	1.40 ± 0.04				

Particularly remarkable here is the low entropy of activation for the dimethyl mesoxalate ene reaction (−125 to −170 J $mol^{-1} K^{-1}$) (Table II), which is comparable with the corresponding values for [2 + 4] cycloaddition reactions. Such low values are indicative of a cyclic transition state, i.e., a concerted mechanism.

If a cyclic transition state is not involved, the ΔS^* value, which is then largely a translational term, would be smaller than that found experimentally. The translation entropy term, evaluated in an established manner,[20] for the reaction of dimethyl mesoxalate with 1-pentene at 140 °C amounted to −79 J $mol^{-1} K^{-1}$. Huntsman and Curry[21] have reported a value of $\Delta S^* = -75$ J $mol^{-1} K^{-1}$ for the intramolecular ene cyclization reaction of 3,7-dimethyl-1,6-octadiene, which is associated only with a loss of the degrees of freedom of internal rotation in the transition state. Inclusion of the translational term, calculated by us in the above value, affords $\Delta S^* = -79 + (-75) = -154$ J $mol^{-1} K^{-1}$, which is very close to that found experimentally (−167 ± 13 J $mol^{-1} K^{-1}$) for the ene reaction of dimethyl mesoxalate with unbranched alkenes.

The entropies of activation of the ene reaction obtained from

$$\Delta S^*_{ene} = \Delta S^0 + \Delta S^*_{retro} = -129 + (-36) = -165 \text{ J mol}^{-1} \text{ K}^{-1}$$

(where $\Delta S^0 = -129$ J $mol^{-1} K^{-1}$, the entropy of the reaction estimated as the difference between the standard entropies of the adduct and of the reactants with the aid of group additivity rules,[22] and $\Delta S^*_{retro} = -36$ J $mol^{-1} K^{-1}$, a typical entropy of activation of the retro-ene reaction analogous to the system concerned) coincide with experimental values. Since for the retro-ene reaction the concerted mechanism is firmly established,[23] the foregoing result suggests the same mechanism for the present ene reaction.

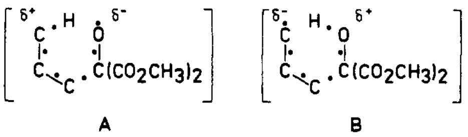

Figure 2. Loose models of the transition state of the ene reaction of dimethyl mesoxalate with alkenes.

Additional indications of the concerted mechanism of the ene reaction investigated here are the relatively low energies of activation (80 kJ mol^{-1}) (Table II) compared with bond fission energies, suggesting simultaneous rupture and formation of bonds. Finally the fact that the reactions are of the second order and the lack of a significant solvent effect on their rate (Table I) are also in accord with the concerted mechanism.

Further insight into the structure of the transition state of the ene reaction examined here was obtained by use of the model of loose four- or six-membered transition states advanced by Benson and O'Neal.[23] Its essential point is the concept of an extremely weak bond which ensures formation of the cyclic active complex, its energetic contribution being negligible. For our argument we constructed two extreme cases of loose models of the transition state (Figure 2).

In both, bond breaking and bond formation occur in a concerted manner. In model A the extremely weak bond is the O···H interaction, whereas in model B it is the C···H interaction. For the ene reaction in which migration of a

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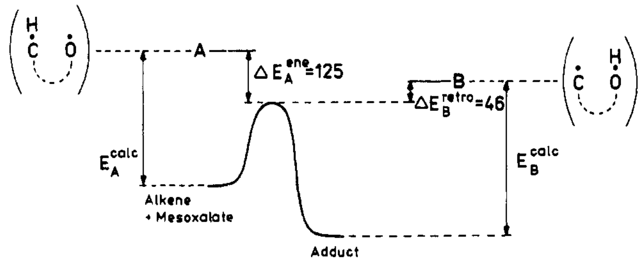

Figure 3. Diagram of the activation energies found experimentally and calculated for the loose models A and B.

hydrogen atom occurs from the carbon to the oxygen atom, model A describes an early transition state (with respect to this migration) and model B a late transition state. In the case of the reverse reaction (retro-ene), in which the hydrogen atom migrates from the oxygen to the carbon atom, the opposite applies, i.e., model A represents a late and model B an early transition state. The actual transition state lies somewhere between these two extremes. Following the approach of Benson and O'Neal,[23] we calculated activation energies of models A and B using the dissociation energies (D) of the respective bonds and assuming that the order of bonds in the transition state is $^1/_2$ or $^3/_2$.

The activation energy along the ene reaction coordinate for model A is

$$E_A(\text{calcd}) = \tfrac{1}{2}(D_{C-H} + D_{C-O\pi} + D_{C\pi-C\pi} - D_{C\pi-C\pi} - D_{C-C}) = \tfrac{1}{2}(401 + 355 - 334) = 211 \text{ kJ mol}^{-1}$$

The difference between the value calculated for model A and that obtained by us experimentally amounts to $\Delta E_A(\text{calcd}) = E_A(\text{calcd}) - E_{ene}(\text{exptl}) = 211 - 86 = 125$ kJ mol^{-1}.

Along the retro-ene reaction coordinate an analogous calculation for model B gives

$$E_B(\text{calcd}) = \tfrac{1}{2}(D_{O-H} + D_{C-C} - D_{C-O\pi} + D_{C\pi-C\pi} - D_{C\pi-C\pi}) = \tfrac{1}{2}(456 + 334 - 355) = 217 \text{ kJ mol}^{-1}$$

As the "experimental" value for our purposes for the retro-ene reaction, we have taken the energy of activation of the "parent" system, i.e., of the pyrolysis of 3-buten-1-ol, $E_{retro}(\text{exptl}) = 171$ kJ mol^{-1}.[24a,b] Here the difference between calculated and experimental value amounts to

$$\Delta E_B^{retro} = E_B(\text{calcd}) - E_{retro}(\text{exptl}) = 217 - 171 = 46 \text{ kJ mol}^{-1}$$

Differences $\Delta E_A^{ene} = 125$ kJ mol^{-1} and $\Delta E_B^{retro} = 46$ kJ mol^{-1} reflect in terms of energy the deviations of models A and B, respectively, from the actual transition state and could be regarded as a direct measure of the degree of formation of the O···H and H···C bonds in the latter. This is illustrated in Figure 3.

Since ΔE_B^{retro} is much smaller than ΔE_A^{ene}, it can be inferred that the condition of no C···H interaction (model B) is better satisfied that the condition of no O···H interaction (model A). In other words, model B is a better approximation to the real transition state than is model A, which means that in the transition state the hydrogen atom is shifted toward the oxygen atom. Advanced migration of the hydrogen atom in the transition state without charge development, as testified by the negligible solvent effect on the rate of the reaction (Table I), must be accompanied by formation of the C–C bond.

On the other hand, recent theoretical calculations concerning the ene reaction suggest that in the transition state the C–X bond is even more developed than the H–Y bond.[25]

We conclude that the ene reaction of dimethyl mesoxalate with alkenes has a concerted mechanism with a late (product-like), cyclic transition state.

Experimental Section

The ^{1}H NMR spectra were taken on a Jeol JNM-4H-100 or Varian HA-60-IL spectrometer. IR spectra were recorded for films on a Unicam SP-200 or Hilger H-800 spectrophotometer. VPC analyses were carried out on a Willy Giege G CHF 18.3 instrument.

Materials. Alkenes were purchased from Merck or Aldrich, except for 1-pentene which was obtained by pyrolysis of pentyl acetate.[26] Dimethyl mesoxalate, bp 79 °C (14 torr), was prepared according to the procedure described for diethyl mesoxalate.[27] Butyl glyoxylate was obtained by a literature method.[28] All substrates were freshly distilled before use and showed better than 99% purity by VPC. Solvents and other reagents were purified according to standard procedures.

Ene Reaction of Dimethyl Mesoxalate (2) with 1-Pentene. A solution of **2** (1.46 g, 10 mmol) and 1-pentene (0.70 g, 10 mmol) in dichloromethane was heated in a sealed glass tube at 140 °C for 16 h. Then solvent was removed and the residue distilled under reduced pressure; the fraction collected between 90 and 105 °C (0.5 torr) was diluted with ether (20 mL), washed with water (to remove unchanged **2**), and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, the crude product was distilled to give adduct **3a**: 1.55 g (62% yield), bp 89–90 °C (0.2 torr); VPC (3 m, 10% Reoplex, 180 °C) two peaks, 9:1; IR 3500 (OH), 1745 (C=O), 1240 (C—O), 980 (CH=CH) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 5.85 (d of t, 1, $J_{23} = 14.7$ Hz, $J_{12} = 6.3$ Hz, H-2), 5.50 (d of t, 1, $J_{23} = 14.7$ Hz, $J_{34} = 6.2$ Hz, H-3), 3.92 (s, 6, 2 OCH$_3$), 2.80 (d, 2, $J_{12} = 6.3$ Hz, CH$_2$-1), 2.05 (d of q, 2, $J_{34} = 6.4$ Hz, $J_{45} = 7.1$ Hz, CH$_2$-4), 1.00 (t, 3, $J_{45} = 7.0$ Hz, CH$_3$). Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.32; H, 7.42.

Adducts **3b** [bp 123–125 °C (0.6 Torr)], **3c** [bp 99–101 °C (0.5 torr)], **3d** [bp 116–117 °C (0.5 torr)], **3e** [bp 137–139 °C (0.4 torr)], and **3f** [bp 113–115 °C (0.6 torr)] were prepared in 62–74% yield according to the foregoing representative procedure. All compounds gave satisfactory elemental analyses.

Ene Reaction of Butyl Glyoxylate with 1-Pentene. A solution of butyl glyoxylate (1.03 g, 8 mmol) and 1-pentene (1.0 g, 16 mmol) was heated in a sealed glass tube at 140 °C for 20 h. The reaction mixture was diluted with ether, filtered through a silica gel column, washed with water, and dried with anhydrous magnesium sulfate. After removal of the solvent, distillation yielded adduct **4**: 0.76 g (48% yield); bp 98–99 °C (0.2 torr); VPC (3 m, 10% Reoplex, 160 °C) two peaks, 9:1;[31] IR 3400 (OH), 1740 (C=O), 970 (CH=CH) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 5.56 (m, 2, vinyl), 4.22 (t, 2, $J = 7.0$ Hz, OCH$_2$), 4.06 (s, 1, OH), 3.10 (br d, 1, $J = 6.5$ Hz, CHCO$_2$), 2.42 (m, 2, CH$_2$-3), 2.05 (d of q, 2, $J_{56} = 5.4$ Hz, $J_{67} = 7.3$ Hz, CH$_2$-6), 1.80–1.25 (m, 4, CH$_2$–CH$_2$), 1.06 (t, 3, $J_{67} = 7.2$ Hz, CH$_3$-7), 1.01 (t, 3, $J = 7.1$ Hz, CH$_3$). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.59; H, 9.81.

Dimethyl Pentyltartronate (5). Adduct **3a** (0.15 g, 0.58 mmol) in methanol solution (30 mL) was hydrogenated in the

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(24) (a) G. G. Smith and B. L. Yates, *J. Chem. Soc. C.*, 7242 (1965). (b) In a large group of retro-ene reactions the differences between activation energies are small. This is particularly true of reactions of the same type (in our case migration of a hydrogen atom from oxygen to carbon) for which the values stay within 8 kJ mol^{-1}.

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(27) C. Weygand, "Organisch Chemische Experimentierkunst", J. A. Barth, Leipzig, 1964, p 273.

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(29) In the CH$_2$-3 decoupled ^{1}H NMR spectrum of the acetyl derivative of adduct 4 (9:1) $J_{45} = 14.6$ Hz was observed, while in the case of the isomerized adduct 4 (10:7) $J_{45} = 14.7$ Hz (E) and $J_{45} = 9.1$ Hz (Z) were observed.

(30) Product of the ene reaction carried out without any solvent.

(31) "Handbook of Silylation", Pierce Chemical, 1972, method 10, p 13.

presence of platinum oxide (20 mg) to give, after workup and distillation, **5**: 0.14 g (96% yield); bp 92–94 °C (0.2 torr); VPC (3 m, 10% Reoplex, 150 °C) single peak; IR 3490 (OH), 1740 (C=O) cm^{-1}; ^{1}H NMR (CCl_4) δ 3.75 (s, 6, 2 OCH_3), 3.60 (s, 1, OH), 1.96 (br t, 2, CH_2-1), 0.92 (t, 3, J = 7.2 Hz, CH_3). Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.01; H, 8.31. Found: C, 55.38; H, 8.37.

Photochemical Isomerization of 4. A solution of **4** (0.4 g) in hexane (100 mL) under nitrogen was irradiated with ultraviolet light (Philips 250 W, max 240 nm). The reaction was monitored by VPC (3 m, 10% Reoplex, 160 °C). The initial ratio of isomers (9:1) reached the equilibrium value (10:7) after 4 h. Chromatography on a silica gel column (40 g, 200–300 mesh) and distillation gave **4**: 0.22 g (55% yield); bp 97–99 °C (0.2 torr); VPC two peaks 10:7;[29] IR 3490 (OH), 1740 (C=O), 970 (CH=CH) cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 66.21; H, 10.31.

Catalytic Isomerization of 3a and 4. 3a (VPC 7:3)[30] or **4** (VPC 10:7) was treated in dichloromethane solution at room temperature for 18 h with 1 mol equiv of Lewis acid ($SnCl_4$, BF_3, $AlCl_3$). After workup the recovered adducts **3a** and **4** showed an unchanged ratio of isomers by VPC.

Kinetic Procedure. The reactions were followed kinetically in the temperature range 110–150 °C by the ampule technique. The pseudo-first-order experiments were run with a 12–14 molar excess of alkene to at least 70–80% completion. The second-order rate constants were calculated with constant molar ratios of the reactants (1:1) over the first 50–60% of reaction.

Product Analysis. To the reaction mixture was added an appropriate amount of 2,4-dimethylnitrobenzene or *m*-dinitrobenzene as internal standard, followed by carbon tetrachloride to make the solution homogenous. Samples were withdrawn at 1–2 h intervals, quenched by cooling to −20 °C, and analyzed by VPC on a 10% Reoplex 1 m column (Chromosorb W) by using a column temperature of 100–130 °C. Peak areas were measured by weight, and the amount of adduct was calculated from the calibration against the internal standard. For each sample three VPC analyses were performed. In the case of (*E*)- and (*Z*)-2-pentene, in order to measure separately the formation of the geometrical isomers, the adducts were analyzed after silylation.[31]

Solvent Effect. Solvent effect was studied for solutions in carbon tetrachloride, bromobenzene, and methyl cyanide under the pseudo-first-order conditions (1–2% solution for dimethyl mesoxalate and 7–10% solution for the alkene). Effects were temperature independent. Table I gives results for 140 °C.

Treatment of the Data. Reaction order was determined by a graphic method. A linear plot was obtained for the pseudo-first-order data [log $(X_\infty - X)$ vs. t (where X_∞ is the concentration after termination of the reaction and X is the concentration at time t)] and for the second-order $(1/(X_\infty - X)$ vs. $t)$. Rate constants of the pseudo-first-order (k') reactions were calculated from a least-squares treatment of log $(X_\infty - X)$ against t. Second-order rate constants (k) were obtained from the relation $k = k'/A$ (where A = alkene concentration). Energies of activation were obtained by a least-squares method from the log k against T^{-1} data. Entropies of activation were obtained from the Eyring equation. The estimated precision is ca. ±7 kJ mol^{-1} in E_a and ±12.5 kJ $\mathrm{mol}^{-1}/\mathrm{K}^{-1}$ in ΔS^*.

Registry No. 1a, 109-67-1; **1b**, 592-41-6; **1c**, 563-45-1; **1d**, 760-20-3; **1e**, 816-79-5; **1f**, 646-04-8; **1g**, 627-20-3; **2**, 3298-40-6; (*E*)-**3a**, 72844-70-3; (*Z*)-**3a**, 72844-71-4; (*E*)-**3b**, 72844-72-5; (*Z*)-**3b**, 72844-73-6; **3c**, 72844-74-7; (*E*)-**3d**, 72844-75-8; (*Z*)-**3d**, 72844-76-9; **3e**, 72844-77-0; **3f**, 72844-78-1; **3g**, 72844-79-2; (*E*)-**4**, 18016-36-9; (*Z*)-**4**, 72844-80-5; **5**, 72844-81-6; butyl glyoxylate, 6295-06-3.

Mechanistic Studies of the Reaction of 4-Substituted 1,2,4-Triazoline-3,5-diones with β-Dicarbonyl Compounds

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4-Substituted 1,2,4-triazoline-3,5-diones were found to add to the α position of β-diketones and β-diketo esters, yielding both 1:1 and 2:1 adducts. The 1:1 adducts showed a dramatic stabilization of the enolic tautomer when compared to the original β-dicarbonyl compounds as evidenced by a large increase in percent enol in all solvents. Kinetic studies support reaction through the 1,4-dipolar pathway involving triazolinedione and the enolic form of the β-dicarbonyl compound. This reaction was also found to demonstrate a strong solvent dependency, hydrogen bonding solvents being rate enhancing.

Kinetic investigations[1] have shown 4-phenyl-1,2,4-triazoline-3,5-dione (PhTD) to be one of the most powerful dienophiles known. It is 10^3 times more reactive than tetracyanoethylene (TCNE) and 2×10^3 times more reactive than maleic anhydride. A significant result is the ability of PhTD to undergo reactions at room temperature, a factor which makes it an excellent dienophile for poorly reactive and unstable electrocyclic substrates. PhTD was treated with butadiene and cyclopentadiene by Cookson, Gilani, and Stevens[2] to yield the (4 + 2) cycloaddition products. This led to extensive further research with (4 + 2) cycloadditions.[3-8]

The Diels–ene pathway is also taken with PhTD. Pasto and Chen[9] first observed this reaction. They treated (4-phenylbutylidene)cyclopropane with PhTD to form the "ene" reaction product. This reaction was found to be ~30 000 times faster than that employing conventional azodicarboxylates.[10]

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