Concertedness in Thermal Intermolecular Ene Reactions of Dimethyl Mesoxalate and Substituted Alkenes

Gérard Jenner* and Mihalis Papadopoulos

Laboratoire de Chimie Organique Appliquée, ERA No. 826, Université Louis Pasteur, Ecole Nationale Supérieure de Chimie, 67008 Strasbourg, France

The activation volumes and pressure dependence of rate constants for thermal ene reactions of dimethyl mesoxalate with substituted alkenes have been determined. The data support a concerted mechanism in which the transition state is highly product-like and in which transfer of the hydrogen atom occurs in a nonlinear fashion.

There has been considerable recent interest in the ene synthesis,[1,2] which provides a route to the formation of carbon–carbon bonds through use of C=C or C≡C bonds as activating groups. However, the addition of an alkene bearing an allylic hydrogen to the double or triple bond of an enophile requires rather drastic conditions, and usually the yields are low unless Lewis acids[2,3] or high-pressure conditions[4] are employed to promote the reaction at milder temperatures. The reaction involves a multicentric addition with migration of the ene double bond and a 1,5 hydrogen shift. Like Diels–Alder reactions, thermal ene reactions are particularly facile with electron-donor (ene) and electron-deficient (enophile) components that maximize the HOMO (ene)–LUMO (enophile) interaction.[5]
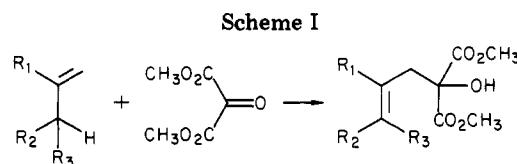
It has been proposed[6] that the mechanism of the ene reaction can range from a rate-limiting abstraction of the allylic hydrogen, through a spectrum of concerted reactions, to rate-limiting biradical formation. Among pericyclic reactions, however, a comparison of [4 + 2] cycloadditions with ene additions reveals differences.

(1) The flexibility of the ene system is larger, allowing the hydrogen atom to swing down toward the π bond in the transition state. In a sigmatropic 1,5 shift, the preferred approach geometry involves a planar carbon framework with a suprafacial placement of the hydrogen atom,[7] while a concerted reaction maximizes allylic resonance with suprafacial addition to the termini of the π bonds.

(2) Unlike Diels–Alder additions, the transition state in the ene reaction cannot have elements of symmetry, rendering impossible the use of elaborate calculation methods developed in the last decade.[8] However, according to orbital symmetry rules the ene reaction is symmetry allowed.

(3) The ene synthesis usually has higher energy requirements (activation energy of the order of 105–150 kJ/mol), while activation entropies are about the same order of magnitude[9] (−125 to −170 J/mol K).

Achmatowicz has recently shown, on the basis of thermodynamic parameters and solvent polarity[10] as well as

Scheme I

alkene	product	R_1	R_2	R_3
n-C$_4$H$_9$CH=CH$_2$	1	H	H	n-C$_3$H$_7$
C$_2$H$_5$CH(CH$_3$)CH=CH$_2$	2	H	CH$_3$	C$_2$H$_5$
t-C$_4$H$_9$CH$_2$C(CH$_3$)=CH$_2$	3	t-C$_4$H$_9$CH$_2$	H	H
(C$_2$H$_5$)$_2$C=CH$_2$	4	C$_2$H$_5$	H	CH$_3$
i-C$_3$H$_7$C(CH$_3$)=CH$_2$	5a	CH$_3$	CH$_3$	CH$_3$
	5b	i-C$_3$H$_7$	H	H

deuterium kinetic isotope effects,[11] that the transition state in the ene reaction appears to be product-like. We here show that the activation volume ($\Delta V^{\ddagger}$), determined by study of the pressure dependence of reaction kinetics, can also provide insight into the mechanism of thermal ene reactions.[12]

Results and Discussion

According to the results of Achmatowicz,[10] it is unlikely that zwitterions are involved in thermal ene reactions. Accordingly, we did not explore the dependence of the activation volume on solvent polarity but focused our study on the distinction between one-step and multistep (discrete biradical intermediate) processes. We have investigated reactions of unbranched and branched alkenes with dimethyl mesoxalate (Scheme I), which reacts at temperatures appropriate for our high-pressure experimental conditions. These reactions afforded Z and E isomers, or other ene adducts, according to the particular hydrogen atom abstracted. The products were the tertiary alcohols 1–5.

The kinetics of the ene reactions in the pressure range 1–1330 bar showed clean second-order rate constants (Table I). Activation volumes were deduced from the initial slope of the curve smoothed by calculation (Table II). Several observations can be made from the data in Tables I and II.

(1) GC analysis of the ene adducts revealed the formation of Z and E isomers where they could normally be expected. However, GC separation of the products of some reactions (Table II, entries 1 and 2) was inadequate because of the chromatographic column employed (Reoplex). Excellent separation was achieved in the other reactions

(1) (a) Conia, J. M.; Le Perchec, P. *Synthesis* 1975, 1. (b) Jacobson, B. M.; Feldstein, A. C.; Smallwood, J. I. *J. Org. Chem.* 1977, *42*, 2849. (c) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 476. (d) Snider, B. B.; Killinger, T. A. *J. Org. Chem.* 1978, *43*, 2161.
(2) Snider, B. B. *Acc. Chem. Res.* 1980, *13*, 426 and references therein.
(3) Stephenson, L.; Orfanopoulos, M. *J. Org. Chem.* 1981, *46*, 2200.
(4) Gladysz, J. A.; Yu, Y. S. *J. Chem. Soc., Chem. Commun.* 1978, 599.
(5) Epiotis, N. D. In "Theory of Organic Reactions"; Springer-Verlag: New York, 1978; pp 150–152.
(6) (a) Ahlgren, G.; Akermark, B. *Tetrahedron Lett.* 1970, 1885. (b) Kato, M.; Okamoto, Y.; Chikamoto, T.; Miwa, T. *Bull. Chem. Soc. Jpn.* 1978, *51*, 1163.
(7) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* 1965, *87*, 2511.
(8) Dewar, M. J.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* 1978, *100*, 5650.
(9) Franzus, B. *J. Org. Chem.* 1963, *28*, 2954.
(10) Achmatowicz, O.; Szymoniak, J. *J. Org. Chem.* 1980, *45*, 1228.

(11) Achmatowicz, O.; Szymoniak, J. *J. Org. Chem.* 1980, *45*, 4774 and references therein.
(12) Jenner, G.; Rimmelin, J. *Tetrahedron Lett.* 1980, 3039.
(13) Papadopoulos, M.; Jenner, G. *Tetrahedron Lett.* 1981, 2773.
(14) Elyanov, B. S.; Vasylvitskaya, E. M. *Rev. Phys. Chem. Jpn.* 1980, *50*, 169.

Table I. Pressure Dependence of the Rate Constants [a,b]

pressure (±5 bar)	1[c] [1 (Z + E)]	2, [2 (Z + E)]	3, 3	entry 4		entry 5	
				(E)-4	(Z)-4	5a	5b
1	1.43	0.93	1.92	6.90	5.05	1.02	1.32
135						1.26	1.63
155			2.44				
185				9.28	6.15		
235				10.23	7.41		
335	2.19	1.36	3.13				
400						1.98	2.60
450		1.40	3.59	15.29	9.98		
470	2.57	1.67					
615			4.36	18.20	12.63		
740	3.61	1.96	5.07			2.69	3.80
820		2.35					
940		2.79					
1020		2.71	7.11				
1030	5.01			30.6	19.55	3.62	4.84
1050	5.20						
1315				35.5	22.1		
1330	6.71	3.91				4.54	6.01

[a] Reaction conditions: solvent, CCl_4; temperature, 110.0 ± 0.1 °C. [b] $10^6 k$ L mol^{-1} s^{-1}; precision of about 3%. [c] The former kinetic results[13] for this reaction were slightly underestimated due to a systematic error in the weight calculation of the adduct. This table restores the corrected values. Accordingly, albeit the conclusions drawn in the former work remain a fortiori quite valid, the $\Delta V^{\ddagger}$ value is a little more negative (see Table II) than that previously given.

Table II. Activation Volume Data (mL/mol)

entry (corresponding alkene)	type of H abstraction	$-\Delta V^{\ddagger}_T$ [a]	$-\Delta V^{\ddagger}_{25}$ [b]	$-\overline{\Delta V}_{25}$ [c]	$(\Delta V^{\ddagger}/\overline{\Delta V})_{25}$ [c]
1 (hex-1-ene)	secondary (1)	39	28.4	27.0	1.05
2 (3-methylpent-1-ene)	tertiary (2)	36	26.2	26.5	0.99
3 (2,4,4-trimethylpent-1-ene)	primary (3)	44	32.0	30.9	1.04
4 (2-ethylbut-1-ene)	secondary (Z)-4	45	32.8	31.3	1.05
	(E)-4	48	34.9	31.3	1.12
5 (2,3-dimethylbut-1-ene)	tertiary (5a)	45	32.8	31 .9	1.03
	primary (5b)	46	33.5	31.9	1.05

[a] Activation volume at temperature T (±3-5 mL/mol). [b] Activation volume calculated for T = 25 °C according to ref 14. [c] Reaction volume calculated from partial molar volumes of reactants and adduct (±0.5 mL/mol) determined with a digital densimeter. $\Delta V^{\ddagger}/\overline{\Delta V}$ is given within ±0.10 (at 25 °C).

(entries 4 and 5) with OV-351 or FFAP columns. Only one isomer was formed from 2,4,4-trimethyl-1-butene (entry 3). Apparently steric interference by the *tert*-butyl group prevents abstraction of the hydrogen atom from the neighboring methylene group, despite the activating effect of the methyl group in a favorable position on the C–C double bond. The situation is different with 2,3-dimethyl-1-butene (entry 5), where both types of hydrogen abstraction take place. In the tertiary abstraction mode, the isopropyl group is less bulky (steric value z = 2.7[15]) than the t-$C_4H_9CH_2$ group (z = 6).

With the other three alkenes, the E/Z isomer ratio has the following values: 7:3 (entry 1), 9:1 (entry 2), and 3:2 (entry 4). Achmatowicz[10] rationalized the results in the first two cases by proposing that the E isomer corresponds to the sterically more favorable exo conformation. However, in entry 4 both isomers are formed in almost the same amount, suggesting the possibility of C–C rotation in the transition state, i.e., a biradicaloid process that would decrease the stereoselectivity.

(2) The rate constants at atmospheric pressure differ by a factor of 7, which is not large considering the effects that may be involved. It is known[16] that in the ene reaction a primary hydrogen migrates the most rapidly and that abstraction of a tertiary hydrogen leads to the lowest rate. Obviously this result indicates the relative accessibility of

Table III. Pressure Effect on the Isomer Distribution (Entry 4)

pressure, bar	% E	% Z
1	57.0 ± 0.5	43.0 ± 0.5
615	59.0	41.0
1315	61.0	39.0
3700	63.5	36.5

the protons. However, the rate constants in our reactions may depend on at least three factors: (a) the type of hydrogen abstraction, (b) the activating influence of the substituent on C_2, and (c) the bulk of the substituent adjacent to the hydrogen that is abstracted.

The fastest of our reactions was that involving 2-ethyl-1-butene (entry 4), reflecting the relatively unbulky methyl group and the strong activating effect of the ethyl group on C_2. The lowest rate was for 3-methyl-1-pentene (entry 2), which involves transfer of a tertiary hydrogen with no activating influence of an alkyl group on C_2.

(3) The rate constants are very sensitive to pressure, yielding high negative values for the activation volume (–36 to –48 mL/mol). Such values are rather unexpected and consistent only with a quasi-cyclic transition state like that in the Diels–Alder reaction.[17] The $\Delta V^{\ddagger}$ for a biradical

(15) Jenner, G.; Kellou, M. S. *Tetrahedron* 1981, *37*, 1153.
(16) Hoffmann, H. M. *Angew. Chem., Int. Ed. Engl.* 1969, *8*, 566.

(17) (a) McCabe, J. R.; Eckert, C. A. *Acc. Chem. Res.* 1974, *7*, 251; *Ind. Eng. Chem. Fundam.* 1974, *13*, 168. (b) Brun, C.; Jenner, G. *Tetrahedron* 1972, *28*, 3113. (c) Rimmelin, J.; Jenner, G. *Ibid.* 1974, *30*, 3081. (d) Jenner, G.; Rimmelin, J. *Ibid.* 1976, *32*, 1107.

Table IV. Partial Molar Volumes (±0.1–0.3 mL/mol)

partial molar vol, mL/mol	compd					
	dimethyl mesoxalate	hex-1-ene	3-methyl-pent-1-ene	2,4,4-trimethyl-pen t-1-ene	2-ethyl but-1-ene	2,3-dimethyl-but-1-ene
$\overline{V}$	120.0	125.4	126.6	156.9	122.3	126.1
$\overline{V}$ (adduct)		218.4	220.1	246.0	211.0	213.2

process in [4 + 2] cycloadditions is about 10 mL/mol lower than the pericyclic process, as reported for the cyclo-dimerization of chloroprene.[18] In our ene reactions, a concerted process is corroborated by the similarity of the values for ΔV^{*} and the reaction volume $\overline{\Delta V}$, which suggests that the transition state is highly product-like (i.e., a late transition state). Even for entry 4, the value of ΔV^{*} argues against the biradicaloid process formerly suggested by the essentially equivalent amounts of Z and E isomers formed.

The activation volumes for the formation of the two isomers differ by about 3–4 mL/mol. Although this value is about the same as the estimated error in ΔV^{*}, it indicates that pressure favors slightly the formation of the E isomer over the Z isomer. We therefore measured the effect of pressure on the isomer distribution in the reaction with 2-ethyl-1-butene (Table III). As expected from the ΔV^{*} values, pressure increases the proportion of the E isomer, which has the sterically more favorable conformation.

Our data on activation volume thus support the conclusions deduced by other authors on the basis of regioselectivity[19] and stereochemical evidence (transfer of chirality[20] and predominance of endoid addition[21]), high negative activation entropies,[10] secondary isotope effects,[3,11] and the kinetics of retro-ene reactions.[22]

Our ene reactions can be influenced by steric crowding about the carbon atom that bears the hydrogen to be shifted. It has been shown that the transition states of hindered reactions become later with increasing hindrance, as a consequence of the Hammond postulate.[15,23] However, if the process is concerted, steric hindrance should not shift the transition state along the reaction coordinate because the atoms in the transition state will have reached essentially their positions in the product. Accordingly, the steric activation volume[15] is zero or very low, and the value of ΔV^{*} will not reflect steric interactions in the transition state. Our values for ΔV^{*} show that the transition states for reactions that involve abstraction of a tertiary hydrogen are not smaller than those that involve abstraction of primary or secondary hydrogens.

Although the ene reaction was originally considered to involve linear hydrogen transfer,[16] Achmatowicz[10] showed that nonlinear transfer is more plausible. In a nonlinear process, the transition state should be slightly more compressed than the product. Our results support the nonlinear hypothesis because the ratios of $(\Delta V^{*}/\overline{\Delta V})_{25}$ are close to unity, indicating a tight transition state.

On the basis of the activation volume and the ratios of $\Delta V^{*}/\overline{\Delta V}$, we conclude that the mechanism of the thermal ene reaction of alkenes and dimethyl mesoxalate is essentially concerted. In such a process, C–C bond formation

and allylic hydrogen transfer occur simultaneously. However, we think that in the transition state the formation of the O–H bond is determining with respect to C–H bond breaking. As in the simultaneous establishment of the two bonds in Diels–Alder reactions,[24] the relationship between these two events is unknown and probably varies with the system involved. Finally, our values for $\Delta V^{*}/\overline{\Delta V}$ support the calculations of Fukui[25] and the results of Achmatowicz[11] in favoring a mechanism for these ene reactions that involves nonlinear hydrogen transfer. However, it is premature and very probably false to make a conclusion as to the ubiquity of the concerted scheme. In other ene reactions for which optimum geometry for the transition state is not accessible, stepwise or mixed concerted–stepwise routes may be followed.

From a synthetic point of view, high pressure should greatly facilitate some ene reactions because activation volumes as negative as −40 mL/mol would increase the reaction rate by a factor of nearly 5000 at 10 kbar, allowing a substantial lowering of the reaction temperature.[26] The ene reaction thus takes a place on the list of potential high-pressure synthetic applications like other addition reactions.[27]

Experimental Section

^{1}H NMR spectra were obtained at 60 MHz with a Perkin-Elmer R-32 spectrometer. Me$_4$Si served as an internal standard. Infrared spectra were recorded as films on a Perkin-Elmer 457 spectrometer. GC was performed on a Hewlett-Packard 5700 gas chromatograph with a thermal-conductivity detector, (helium carrier gas, 20 mL/min) or on an FID Girdel 3000 gas chromatograph with a flame ionization detection (nitrogen carrier gas, 15 mL/min). Three columns were used: Reoplex (for entries 1 and 2), 1 m × $^1/_8$ in. i.d., WAW chromosorb, 80–100 mesh, injection and detection at 200 °C, temperature program 60–220 °C at 8 °C/min; FFAP (for entries 3 and 5), 2.5 m × $^1/_8$ in. o.d., Carbowax (other conditions as for Reoplex column); OV-351 (entry 4), 5 m × $^1/_8$ in. o.d., 10%, Gas Chrom Q, 100–120 mesh, isothermal at 180 °C, injection 220 °C, detection 200 °C (the latter was used on the FID Girdel apparatus).

Materials. Alkenes were purchased from Fluka. Dimethyl mesoxalate was prepared by SeO$_2$ oxidation of dimethyl malonate.[28]

Ene Reactions of Dimethyl Mesoxalate. The high-pressure device and the sample tube of Teflon (which must be filled completely) are essentially the same as described previously.[17b–d] A solution of mesoxalate (1.4 mmol) and alkene (1.9 mmol) in carbon tetrachloride (2 mL) and 0.11 mL of toluene was prepared in a Teflon tube of appropriate volume and submitted to pressure at 110 °C for the desired reaction time. Then the pressure was quickly relieved, and the content of the sample tube was analyzed by GC. Peak areas were converted to milligrams with experi-

(18) Stewart, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 635.

(19) Gassman, P. G.; Richmond, S. D. *J. Chem. Soc., Chem. Commun.* **1968**, 1630.

(20) (a) Hill, R. K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1964**, *86*, 965. (b) Stephenson, L. M.; Mattern, D. L. *J. Org. Chem.* **1976**, *41*, 3614.

(21) (a) Berson, J. A.; Wahl, R. G.; Perlmutter, H. D. *J. Am. Chem. Soc.* **1966**, *88*, 187. (b) Hill, R. K.; Morgan, J. W.; Shetty, R. V.; Synerholm, M. E. *Ibid.* **1974**, *96*, 4201.

(22) (a) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1967**, *71*, 2903. (b) Houminer, Y. *J. Org. Chem.* **1980**, *45*, 999.

(23) Le Noble, W.; Asano, T. *J. Am. Chem. Soc.* **1975**, *97*, 1778.

(24) Lambert, J. B.; Mc Laughlin, C. D.; Mark, V. *Tetrahedron* **1976**, *32*, 2075.

(25) Fukui, K.; Inagaki, S.; Fujimoto, H. *J. Am. Chem. Soc.* **1976**, *98*, 4693.

(26) Jenner, G. *Nouv. J. Chim.* **1979**, *3*, 329.

(27) (a) Von der Brück, P.; Bühler, R.; Heuck, C. C.; Plieninger, H.; Weale, K. E.; Westphal, J.; Wild, D. *Chem.-Ztg.* **1970**, *94*, 183. (b) Bieniek, D.; Korte, F. *Naturwissenschaften* **1972**, *59*, 529. (c) Jurczak, J.; Chmielewski, M.; Filipek, S. *Synthesis* **1979**, 41. (d) Jenner, G. "High-Pressure Science and Technology"; Vodar, B., Ed.; Pergamon Press: New York, 1980; p 787. (e) Dauben, W. G.; Kessel, C. R.; Takemura, K. H. *J. Am. Chem. Soc.* **1980**, *102*, 6893.

(28) Müller, R. *Chem. Ber.* **1933**, *66*, 1668.

mental calibration curves and toluene as an internal standard.

For preparative purposes, higher concentrations of mesoxalate (8.5 mmol) and alkene (10.5 mmol) in 3 mL of CCl$_4$ were used. The reactions were conducted at 1 bar in stainless-steel tubes (temperatures and yields given below). After the reaction, the solution was diluted, unreacted dimethyl mesoxalate was hydrolyzed with water, and the organic phase was dried over MgSO$_4$ overnight. After removal of the solvent, the liquid residue was placed onto silica gel (Merck, 70–230 mesh) in a 30 × 15 cm column and eluted with petroleum ether–ethyl acetate (95:5).

All adducts were colorless liquids. Adducts 1 and 2 were analyzed previously;[10] however, spectral results were missing. The structures of the new adducts (3–5) were based on spectral data and established by comparison with the structures of 1 and 2.

Adduct 1 (Z + E): obtained at 130 °C, 24 h; 95% yield; GC, 2 peaks in a 7:3 ratio; IR 3500 (OH), 1745 (C=O), 1620 (C=C); ^{1}H NMR (CCl$_4$) δ 5.85 (dt, 1, CH=CHCH$_2$), 5.50 (dt, 1, CH$_2$CH$_2$CH=C), 3.79 (s, 6, OCH$_3$), 2.70 (d, 2, C=CHCH$_2$), 2.01 (dq, 2, CH$_2$CH$_2$), 1.40 (m, 2, CH$_3$CH$_2$), 0.90 (t, 3, CH$_3$).

Adduct 2 (Z + E): obtained at 140 °C, 18 h; 95% yield; GC, 2 peaks in a 9:1 ratio; IR 3500 (OH), 1735 (C=O), 1625 (C=C); ^{1}H NMR (CCl$_4$) δ 5.10 (t, 1, CH$_3$C=CHCH$_2$), 3.78 (s, 6, OCH$_3$), 2.78 (d, 2, C=CHCH$_2$), 2.00 (m, 2, CH$_3$CH$_2$), 1.60 (s, 3, CH$_3$C=C), 0.90 (t, 3, CH$_3$).

Adduct 3: obtained at 140 °C, 15 h; 70% yield; GC, 1 peak, t_R = 18.8 min; IR 3500 (OH), 1730 (C=O), 1625 (C=C); ^{1}H NMR (CCl$_4$) δ 4.95 (d, 2, CH$_2$=C), 3.75 (s, 6, OCH$_3$), 2.82 (s, 2, C=CCH$_2$), 2.01 (s, 2, (CH$_3$)$_3$CCH$_2$), 0.90 (s, 9, CH$_3$). Anal. Calcd for C$_{13}$H$_{22}$O$_5$: C, 60.44; H, 8.58; O, 30.97. Found: C, 60.24; H, 8.68; O, 31.03.

Adduct 4: obtained at 120 °C, 22 h; 90% yield; GC, 2 peaks in a 3:2 ratio, t_R = 19.5 [(E)-4], 20.6 min [(Z)-4]; IR 3500 (OH), 1730 (C=O), 1660 (C=C) [(Z)-4], 1625 (C=C) [(E)-4]; ^{1}H NMR (CCl$_4$) δ 5.50 and 5.35 (m, 1, J = 7 Hz [(Z)-4], 18 Hz [(E)-4], CH=C), 3.80 (s, 6, OCH$_3$), 2.88 and 2.72 (s, 2, C=CCH$_2$), 2.02 (q, 2, CH$_3$CH$_2$C=C), 1.62 (d, 2, CH$_3$C=C), 0.97 (t, 3, CH$_3$). Anal. Calcd for C$_{11}$H$_{18}$O$_5$ (4, Z + E): C, 57.38; H, 7.88; O, 34.74. Found: C, 57.31; H, 7.76; O, 34.68.

Adducts 5a + 5b: obtained at 140 °C, 18 h; 100% yield (2:3 5a/5b). Anal. Calcd for C$_{11}$H$_{18}$O$_5$: C, 57.38; H, 7.88; O, 34.74. Found: C, 57.28; H, 7.57; O, 35.03.

Adduct 5a. GC, 1 peak, t_R = 15.4 min; IR 3500 (OH), 1740 (C=O), 1620 (C=C); ^{1}H NMR (CCl$_4$) δ 3.78 (s, 6, OCH$_3$), 2.90 (s, 2, C=CCH$_2$), 1.65 (s, 9, CH$_3$C=C).

Adduct 5b. GC, 1 peak, t_R = 16.4 min; IR 3500 (OH), 1740 (C=O), 1620 (C=C); ^{1}H NMR (CCl$_4$) δ 4.88 (d, 2, CH$_2$C=C), 3.78 (s, 6, OCH$_3$), 2.81 (s, 2, C=CCH$_2$), 2.30 (m, 1, CH—C=C), 1.00 (d, 6, CH$_3$).

Partial Molar Volumes. Precision density measurements permit the apparent molar volume Φ_V to be determined according to the known equation

$$\Phi_V = \frac{M_w}{d_0} - \frac{d - d_0}{d_0}\frac{1000}{C}$$

in which M_w is the molecular weight of the solute and C its molar concentration and where d and d_0 are the densities of the solution and the solvent, respectively. Over the examined concentration range, the Φ_V values were constant within experimental error.

Density measurements were performed with a digital densimeter (Sodev Model 02D) based on the model of Kratky and al.[29] The partial molar volumes were found as in Table IV (at 25.11 °C in CCl$_4$ as solvent) (±0.1–0.3 mL/mol).

Registry No. (E)-1, 72844-72-5; (Z)-1, 72844-73-6; (E)-2, 72844-75-8; (Z)-2, 72844-76-9; 3, 82865-22-3; (E)-4, 82865-23-4; (Z)-4, 82865-26-7; 5a, 82865-24-5; 5b, 82865-25-6; CH$_3$O$_2$CCOCO$_2$CH$_3$, 3298-40-6; n-C$_4$H$_9$CH = CH$_2$, 592-41-6; C$_2$H$_5$CH(CH$_3$)CH = CH$_2$, 760-20-3; t-C$_4$H$_9$CH$_2$C(CH$_3$) = CH$_2$, 107-39-1; (C$_2$H$_5$)$_2$C = CH$_2$, 760-21-4; i-C$_3$H$_7$C(CH$_3$) = CH$_2$, 563-78-0.

(29) Kratky, O.; Leopold, H.; Stabingen, H. *Angew. Phys.* 1969, *27*, 273.

Nafion-Catalyzed Photoreaction. Photoisomerization of 3-Methylene-1,2,4,5,6,6-hexamethylcyclohexa-1,3-diene[1]

Ronald F. Childs* and Alicja Mika-Gibala[2]

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

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The heptamethylbenzenonium cation 2 was shown to be produced when a CH$_2$Cl$_2$ solution of 3-methylene-1,2,4,5,6,6-hexamethylcyclohexa-1,3-diene (1) is brought into contact with "anhydrous" Nafion in its acid form. Treatment of the Nafion with methanolic sodium hydroxide regenerates 1. Under the conditions used here, the number of active sites on the Nafion was found to be 0.347 mmol/g. Irradiation of the Nafion with light of wavelength greater than 380 nm caused 2 to be converted mostly to vinylcyclopentadiene 5, with minor amounts of pentamethylcyclopentadiene and hexamethylbenzene also being produced. No photoisomerization of 1 took place when it was irradiated under the same conditions in the absence of Nafion. The quantum efficiency for the conversion of 2 adsorbed onto the Nafion was found to be 0.48 ● 0.05; the same value as is found for the isomerization of 2 in homogeneous solutions. The product 5 could be displaced from the Nafion by more 1. This permitted the reaction to be carried out in a continuous mode with the Nafion functioning as a photocatalyst for the process.

Over the past few years, many photoreactions of carbenium ions and protonated carbonyl compounds have been reported.[3,4] In strongly acidic media, where the reactants and photoproducts are stable as carbocations, the most commonly observed type of reaction are photoisomerizations. Frequently these photoisomerizations are very clean reactions, give rise to different products than those obtained from the neutral precursors of the carbocations, and are relatively efficient. As such, the photoreactions of carbocations are attractive from a preparative

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(2) On leave from the Technical University of Wroclaw, Poland.

(3) Cabell-Whiting, P. W.; Hogeveen, H. *Adv. Phys. Org. Chem.* 1979, *9*, 1.

(4) Childs, R. F. *Rev. Chem. Intermed.* 1980, *3*, 285.