Piezochemical Interpretation of (C · · · H · · · X) Hydrogen Transfer in Ene Reactions

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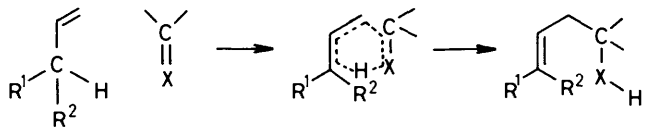
Measurement of volumes of activation has provided mechanistic information about ene reactions involving (C · · · H · · · X) hydrogen transfer (X = O, C, and N). Depending on the nature of the reactants, the mechanism can range from a rate-limiting abstraction of the allylic hydrogen, through a concerted reaction (C · · · H · · · O ene reactions) to a probable stepwise process with the rate-limiting C–N bonding at the first stage and hydrogen transfer at the second one (C · · · H · · · N transfer reactions).

The ene reaction *i.e.* addition of an enophile to an unsaturated compound bearing an allylic hydrogen, the ene component, is regarded as a pericyclic reaction involving a quasicyclic transition state. We shall designate the ene reaction as a (C · · · H · · · X) hydrogen transfer (Scheme1).



Scheme 1.

The ene reaction was regarded by Fukui [1] as an interaction of three orbital systems involving a partial electron transfer from the HOMO π-bond (ene) to the LUMO π-bond (enophile) and retrodonation from the LUMO (enophile) to the LUMO of the C–H bond in the ene component. However, several reports in later years were in conflict with this interpretation of a fully concerted pathway and numerous mechanisms, based on the two most widely accepted mechanisms, *i.e.* concerted and stepwise, have since been proposed.[2] Complex intermediates have even been detected [2,3] and presented as evidence against a concerted pathway.

Previously, we used the magnitude of the volume of activation [4] to determine the location of the transition state in (C · · · H · · · O) [5] and (O · · · H · · · O) [6] hydrogen-transfer reactions. In both cases, the reactions were consistent with completely concerted processes. A subsequent study examined the pressure dependence of the (C · · · H · · · N) hydrogen transfer which led to a quite different result: [7] the values of the volume of activation $\Delta V^{\ddagger}$ for the addition of diethyl azodicarboxylate (DEAD) to cyclopentene and cyclohexene were accounted for by a stepwise mechanism.

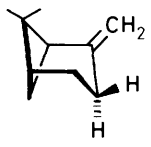
The present paper examines whether the mechanisms followed by the above ene reactions can be extended to other ene systems. The types of hydrogen transfer reported in this work encompass (C · · · H · · · X) ene reactions with X = O, C, and N.

Results

(C · · · H · · · O) *Hydrogen Transfer.*—The ene reactions involving (C · · · H · · · O) hydrogen transfer, previously studied under pressure, were carried out with simple acyclic alkenes as the ene components and dimethyl mesoxalate as the enophile.[5] The concerted nature of the reactions was supported by the fact that $|\Delta V^{\ddagger}| \geq |\overline{\Delta V}|$ ($\overline{\Delta V}$: reaction volume based on partial molar volumes). The apparent minimum in the volume profile was attributed to a compact cyclic transition state, probably originating from an angular hydrogen abstraction.[8]

It was of interest to examine the addition of mesoxalates to cyclic alkenes exhibiting the double bond either in *endo*-or *exo*-cyclic position, and hence β-pinene and cyclo-octene were studied in this work.

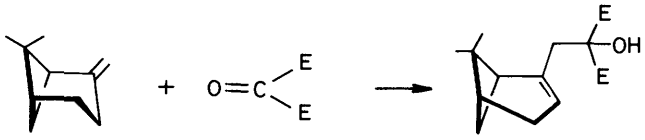
β-Pinene is known to undergo facile ene reactions under mild conditions.[9] Reaction with maleic anhydride yields predominantly an *endo* adduct.[10] The absence of skeletal rearrangement was presented as an argument against cationic or radical intermediates.[11] Subsequent stereochemical investigations were carried out on the ene addition of β-pinene to methyl pyruvate [12] and of deuteriated pinenes to methyl phenylglyoxylate and benzyne.[13] In the latter case, it was shown that the hydrogen atom involved in the transfer is that which is at C-3 and *E* to the *gem*-dimethyl bridge.



The insensitivity of the reaction rate to solvent effects, the absence of rearrangement products and the high degree of stereoselectivity argued against a sequential mechanism.

At 52.2 °C, the temperature employed in this work, β-pinene reacts readily and cleanly with diethyl mesoxalate to yield (**1**) as the only product (E = $CO_2C_2H_5$; Scheme 2).

The kinetics of the reaction were followed at different pressures which yielded the values listed in Table 1.



(**1**)

Scheme 2.

Table 1. Ene addition of diethyl mesoxalate to β-pinene.[a]

P/MPa	$k/10^{-5}$ dm^3 mol^{-1} s^{-1}	V/cm^3 mol^{-1}
0.1	3.05	$\Delta V_1^{\ddagger}$ = −35.0 (−34.5)[b]
28.5	4.39	$\Delta V_{25}^{\ddagger}$[c] = −31.3 (−30.9)[b]
39.5	4.92	$\overline{\Delta V}_{25}$[d] = −29.4
46.9	5.26	θ = 1.06 (1.05)[b]
69.3	6.67	
90.5	7.87	

[a] Solvent was CH_2Cl_2 and temperature 52.2 °C. [b] The values in parentheses refer to $\Delta V^{\ddagger}$ calculated by the least-squares method (LSM) *via* the linear relationship, equation (1). [c] $\Delta V^{\ddagger}$ Is assumed to vary linearly with temperature.[14] [d] $\overline{\Delta V}$ is the reaction volume and θ the ratio $\Delta V^{\ddagger}$:$\overline{\Delta V}$.

Table 2. Ene addition of diethyl mesoxalate to cyclo-octene. High-pressure kinetic results.

Pressure/MPa	$k/10^{-8}$ s^{-1}[a] exp	$k/10^{-8}$ s^{-1}[a] calc[b]	Volume[b]/cm^3 mol^{-1}
0.1	—	0.21	
530	5.5	6.3	$\Delta V_1^{\ddagger}$ *ca.* −33
650	11.8	11.0	$\Delta V_{25}^{\ddagger}$ *ca.* −25
705	15.8	14.1	
882	30.9	29.4	
1 060	52.5	57.6	

[a] First-order rate constants with respect to alkene. Solvent was CH_2Cl_2 and temperature 100.0 °C. [b] Calculated by LSM using equation (1).

Table 3. Ene addition of dimethyl acetylenedicarboxylate to β-pinene.[a]

P/MPa	$k/10^{-6}$ dm^3 mol^{-1} s^{-1}	V[b]/cm^3 mol^{-1}
0.1	5.05	$\Delta V_{25}^{\ddagger}$ = −52.0 (−55.7)
20.3	6.85	$\Delta V_{25}^{\ddagger}$ = −39.6 (−42.7)
28.6	8.19	$\overline{\Delta V}_{25}$ = −35.4
47.2	10.6	θ = 1.12 (1.21)
51.3	12.7	
60.6	14.2	
93.0	18.9	

[a] T (96.4 °C), solvent (CH_2Cl_2). [b] As in Table 1. The values in parentheses are LSM calculated values.

The second type of (C • • • H • • • O) hydrogen transfer was studied in the ene reaction of (*Z*)-cyclo-octene with diethyl mesoxalate. In contrast to β-pinene, the endocyclic double bond in cycloalkenes is much less reactive, since, in spite of the strong enophilic properties of the activated carbonyl bond in the mesoxalate, no detectable reaction occurs under normal pressure conditions at 100 °C (Table 2).

Under high pressure (1 000 MPa) at the same temperature, the reaction yielded the ene adduct (**2**) after 48 h in only 11% yield. The absence of reaction at 0.1 MPa precluded the determination of the volume of activation in the usual way.[14] Nevertheless, $\Delta V^{\ddagger}$ can be roughly estimated by a calculation method based on a relationship we developed some time ago.[15]

$$\log k_P = \log k_o \frac{\Delta V_o^{\ddagger}}{T} \varphi \qquad (1)$$

(T = temperature, φ = pressure parameter independent of the reaction, k_P and k_o = rate constants at pressures P and 0.1 MPa respectively). It has been shown that:

$$\varphi = [(1 + \alpha)P - (\alpha/\beta)(1 + \beta P)\ln(1 + \beta P)]/R\ln 10 \qquad (2)$$

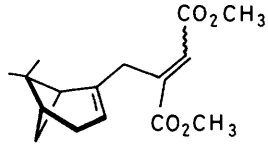
Here α = 0.170 and β is a constant for a given type of related reactions. Statistical treatment of the pressure dependence data for rate constants of ten ene-type reactions previously studied[5,6] and those of the reaction of β-pinene with diethyl mesoxalate has been carried out. Thus, it has been found for the concerted reactions of this type that β = (4.51 ± 1.12) × 10^{-2} MPa^{-1}.

The values of α and β were utilized for calculation of φ-values corresponding to pressures in the reaction of cyclo-octene with diethyl mesoxalate and then the values of k_o and $\Delta V^{\ddagger}$ were estimated by a least-squares method (LSM) according to equation (1).

Calculated and experimental values of rate constants are close to each other and the activation volume in this reaction has a reasonable value.

Comparison of the $\Delta V^{\ddagger}$ values for the addition of mesoxalate to an exo- or an endo-cyclic double bond shows that both reactions follow the same mechanistic pathway. The values are very similar to those previously obtained with ayclic alkenes[5] (−26.2 to −34.9 cm^3 mol^{-1}). Thus, in the (C • • • H • • • O) hydrogen-transfer reactions studied, the $\Delta V^{\ddagger}$ data support a picture of a classically concerted ene transformation with C–H bond breakage coupled to O–H bond formation. The θ-value is also worthy of note. The value is slightly higher than unity in harmony with earlier results[5] as well as with Fukui's model[1] and supports the hypothesis of a non-linear hydrogen transfer, as described by Kwart as a 'peusodopericyclic' process with a bent transition state.[16]

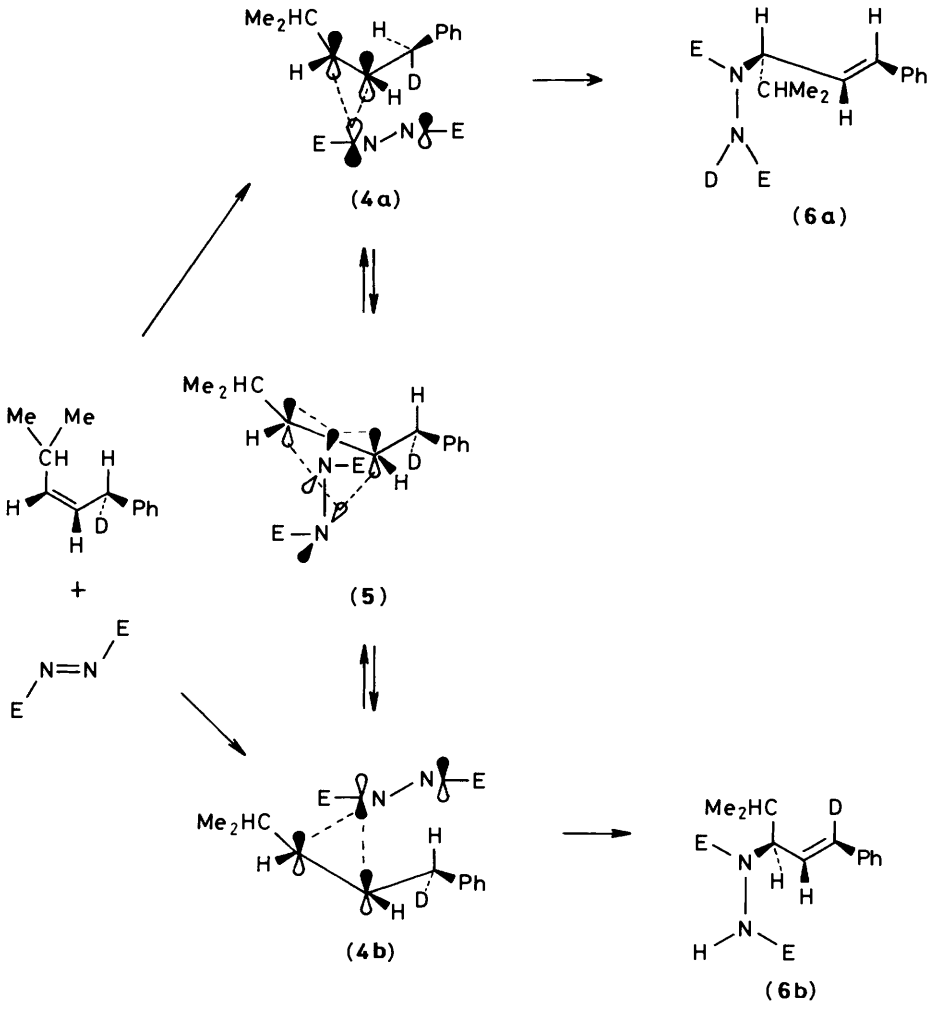
(C • • • H • • • C) *Hydrogen Transfer.*—Ene reactions involving (C • • • H • • • C) hydrogen abstraction do not readily occur,[17] since migration of hydrogen to carbon involves an unfavourable change in hybridization of the carbon atom.[18] As typical reactive compounds, we selected β-pinene as the ene component and dimethyl acetylenedicarboxylate as the enophile. Reaction was effected in xylene under reflux at atmospheric pressure with the adduct isolated in 68% yield.[10] In order to obtain kinetic measurements at several pressures, a lower temperature (96.4 °C) was required (Table 3). The ene product (**3**) was selectively produced.



(**3**)

The high negative value of $\Delta V^{\ddagger}$ obtained in the present (C • • • H • • • C) hydrogen transfer is clear evidence for a concerted reaction pathway. The reaction is more pressure sensitive than the two (C • • • H • • • O) ene reactions studied. In our opinion, the difference in the two reaction profiles lies, most probably, in the linear acetylenic structure of the enophile. This would confer a higher degree of rigidity on the transition state, and would also be expected to affect the reaction volumes. Reactions of this kind have precedence: cycloaddition of quadricyclane with the acetylenic diester.[19] Finally, it should be noted that θ > 1, is consistent with angular hydrogen abstraction.[8]

(C • • • H • • • N) *Hydrogen Transfer.*—The reactions of three ene components (allylbenzene, α-methylstyrene, and β-pinene) with the strong enophile diethyl azodicarboxylate (DEAD) were considered. In all cases, the ene reaction proceeded rapidly even



Scheme 3. Proposed mechanism of hydrogen transfer in the ene reaction of 1-deuterio- 4-methyl-1-phenylpent-2-ene and diethyl azodicarboxylate.

Table 4. Ene additions of DEAD.

Ene component	Allylbenzene	α-Methylstyrene	β-Pinene
T/°C	50.0	23.0	23.0
Solvent	Toluene	Toluene	Dichloromethane
$\Delta V^{\ddagger}_{25}$/cm^3 mol^{-1}	−27.0	−22[a]	−22[a]
$\overline{\Delta V}_{25}$/cm^3 mol^{-1}	−35.8	−32.0	−35.4
θ	0.75	0.69[b]	0.62[b]

[a] Corrected values (see text). [b] Estimated values.

at ambient temperature. Accurate rate constants were obtained only in the allylbenzene reaction. For the other ene reactions, corrections were made in order to take into account the time needed for compression and decompression, thus limiting the accuracy of the pressure measurements. Accordingly, the $\Delta V^{\ddagger}$ values for the respective reactions are given as estimated values (Table 4).

The $\Delta V^{\ddagger}$ values indicate that the three reactions are less pressure sensitive than (C···H···O) and (C···H···C) hydrogen-transfer reactions. The θ-values approach the values obtained in the addition of DEAD to cyclopentene and cyclohexene (0.68 and 0.57 respectively) for which a two-step mechanism involving a biradical intermediate was postulated.[7,20] The $\Delta V^{\ddagger}$-values obtained in this work indicate that the transition-state structure is considerably different from that of the product.

Thus, the substantially smaller values of $\Delta V^{\ddagger}$ and θ, of those obtained in the ene reactions involving (C···H···O) and C···H···C) hydrogen transfer, cannot be accounted for by a one-step concerted process. However, in a related reaction of dimethyl azodicarboxylate with (*S*)-(*Z*)-1-deuterio-4-methyl-1-phenylpent-2-ene the concerted mechanism of a new C–N bond formation and hydrogen- (or deuterium-) atom abstraction has been proved,[21] in line with an earlier study of the DEAD addition to linear alkenes.[22]

The simplest explanation for this apparent discrepancy requires the assumption that a very early transition state for a concerted process exists. However, the large magnitude of the kinetic isotope effect in the reaction involving the labelled pentene cited above (k_H/k_D *ca.* 3) is not consistent with this mechanism. Scheme 3 shows a feasible mechanism.

In Scheme 3 the intermediates (**4a**) and (**4b**) are formed in the first rate-determining step. As a driving force of reaction at this stage, a donor–acceptor interaction between the HOMO of the ene and the LUMO of the azodicarboxylate π-bonds is assumed. Due to the differing symmetries of these orbitals the bonding occurs at one of the nitrogen atoms of the azodicarboxylate (such a three-centre geometry of the bonding is evidenced by ene reactions of some alkenes with singlet oxygen, triazolinedione and C_6F_5NO).[2] An interaction of the *n* orbital of the bonding nitrogen atom of azodi-

carboxylate with the LUMO (π^*) of the ene molecule is also possible.

The formation rates of (**4a**) and (**4b**) should not notably differ but their conversion rates into (**6a**) and (**6b**) respectively will differ due to the kinetic isotope effect. It is necessary, therefore, to assume intramolecular interconversion of (**4a**) and (**4b**) without dissociation, apparently *via* structure (**5**). In accordance with this scheme, the first step is rate determining, but hydrogen abstraction in the second step regulates the kinetic isotope effect and the stereochemistry. The volume of activation characterizes the first step only. In the case of the DEAD additions to allylbenzene, α-methylstyrene, and β-pinene, this volume is small owing to the early and loose transition state.

Conclusions

The present results support the earlier conclusions reached in the pressure study of ene reactions involving (C···H···O) and (C···H···N) hydrogen transfer. In the first type of hydrogen abstraction, concerted bond-breaking (C–H) and bond-forming (H–O) processes occur as evidenced by strong negative $\Delta V^{\ddagger}$-values and θ-values higher than unity. The (C···H···N) ene reactions studied in this work provide no evidence for a one-step concerted reaction pathway. They are probably two-step processes, but the values of $\Delta V^{\ddagger}$ and θ may also be the result of a pathway located in the borderline region of competing concerted and stepwise mechanisms.

Finally, we would like to emphasize the good correlation between the mechanistic results based on the $\Delta V^{\ddagger}$ argument and those obtained by more traditional methods developed at normal pressure. Further piezochemical ene investigations are in progress.

Experimental

General.—The reactants were commercial products and distilled prior to use. Pressure kinetic measurements were made as previously described.[5] The concentrations of reactants used were generally adjusted to 0.30–0.50 mmol (ene:enophile *ca.* 1:1) in 1.2 cm^3 of solvent. The kinetics were followed by g.c. under the conditions described below. Tetramethylbenzene, tetradecane, or tetraglyme served as the internal standard. Liquid column chromatography was carried out with a 30 × 1.5 cm column filled with silica gel Merck 230–400 mesh. ^1H N.m.r. spectra were obtained at 60 MHz, with $CDCl_3$ as solvent and Me_4Si as the internal standard. I.r. spectra were recorded on a Perkin–Elmer 1310 spectrometer.

The volumes of activation were graphically determined in the usual way and checked by means of our linear relationship [equation (1)].[15] Calculation details will be given in a later publication.

Synthesis of (**1**): *the Diethyl Mesoxalate–β-Pinene adduct.*—To a solution of β-pinene (130 mg, 0.95 mmol) in CH_2Cl_2 (3 cm^3), was added diethyl mesoxalate (170 mg, 0.98 mmol). The mixture was heated in an autoclave at 100 °C for 24 h. After reaction, the residual mesoxalate was hydrolysed and the organic layer was extracted with ether and dried over $MgSO_4$. After removal of the solvent, the liquid residue was purified by column chromatography (hexane–ethyl acetate 1:1). G.c. column: Carbowax 20M 5% on Chromosorb WAW 80–100 mesh, 60–220 °C, 8 °C min^{-1}.

(**1**): viscous liquid; ν_{max} (CCl_4) 3 500, 2 980, 2 910, and 1 730 cm^{-1}; δ_H 5.30–5.40 (1 H, m), 4.24 (4 H, q), 3.67 (1 H, br s), 2.74 (2 H, br s), 2.0–2.4 (6 H, m), 1.28 (6 H, t), 1.23 (3 H, s), and 0.81 (3 H, s).

Synthesis of (**2**): (*the Diethyl Mesoxalate–Cyclo-octene Adduct*).—Cyclo-octene (127 mg, 1.15 mmol), diethyl mesoxalate (206 mg, 1.18 mmol) and CH_2Cl_2 were placed in a 1.5 cm^3 PTFE tube. The tube was introduced into the high-pressure cell and compressed at 1 000 MPa and 100 °C for 3 days. Three runs were necessary to collect enough product which was isolated as for (**1**). Purification was effected on silica gel. The eluant was hexane–ethyl acetate (2:1). G.c. conditions were the same as for (**1**).

(**2**): oil; ν_{max} (CCl_4) 3 500, 2 950, 2 905, 2 840, and 1 730 cm^{-1}; δ_H 5.28–5.80 (2 H, m), 4.22 (4 H, q), 3.77 (1 H, s), 3.40 (1 H, m), 2.11 (2 H, s), 1.35–1.70 (8 H, m), and 1.28 (6 H, t).

Synthesis of (**3**): (*the Dimethyl Acetylenedicarboxylate–β-Pinene Adduct*).—The same procedure was used as that described for the preparation of (**2**). The PTFE tube containing a CH_2Cl_2 solution of β-pinene (258 mg, 1.89 mmol) and the acetylenic diester (277 mg, 1.95 mmol) with a small amount of 4-(t-butyl)benzene-1,2-diol as a polymerization inhibitor was compressed to 300 MPa at 100 °C for 24 h. Liquid chromatography (hexane–ethyl acetate 1:1) yielded (**3**) as a pale yellow oil. G.c. conditions were Dexsil 300 1% on Chromosorb WADMCS 100–200 mesh, 60–260 °C, 8 °C min^{-1}.

(**3**): oil; ν_{max} (CCl_4) 2 950, 2 920, 1 730, and 1 650 cm^{-1}; δ_H 5.80 (1 H, s), 5.35–5.22 (1 H, m), 3.76–3.69 (3 H, two singlets), 3.00 (2 H, m), 1.9–2.5 (6 H, m), 1.25 (3 H, s), and 0.81 (3 H, s).

Synthesis of (**7**): (*the DEAD–Allylbenzene Adduct*).—A toluene mixture of allylbenzene (303 mg, 2.56 mmol) and of DEAD (448 mg, 2.57 mmol) was heated at 50 °C for 24 h. Diethyl hydrazodicarboxylate partly precipitated upon concentration and was separated from the solution by filtration. Compound (**7**) was isolated by liquid column chromatography (hexane–ether 1:2). FID g.c. conditions were OV 351 10% on Chromosorb WDMCS 80–100 mesh, 70–280 °C, 6 °C min^{-1}.

(**7**): oil; ν_{max} (CCl_4) 3 380, 2 990, 2 960, 2 910, and 1 730 cm^{-1}; δ_H 7.22 (5 H, br s), 6.40 (2 H, m), 6.22 (1 H, s), 4.20 (4 H, q), 4.10 (2 H, m), and 1.24 (6 H, t).

Synthesis of (**8**): (*the DEAD–α-Methylstyrene Adduct*).—A toluene solution of α-methylstyrene (73 mg, 0.62 mmol) and DEAD (110 mg, 0.64 mmol) was heated at 100 °C for 24 h. Work-up as for (**7**) (hexane–ethyl acetate 1:1) yielded (**8**) as a colourless, fragrant compound.

(**8**): pasty solid; ν_{max} (CCl_4) 3 450, 3 060, 3 025, 1 760, and 1 730 cm^{-1}; δ_H 7.30 (5 H, br s), 6.24 (1 H, s), 5.17 (2 H, m), 4.58 (2 H, s), 4.16 (4 H, q), and 1.24 (6 H, t).

Synthesis of (**9**) (*the DEAD–β-Pinene Adduct*).—A CH_2Cl_2 mixture of β-pinene (258 mg, 1.19 mmol) and DEAD (332 mg, 1.91 mmol) was allowed to stand at room temperature for 24 h. Liquid column chromatography (hexane–ethyl acetate 2:1)

Table 5. Partial molar volumes $\bar{V}$ at 25.1 °C.

Compound	Solvent	$\bar{V}$/cm^3 mol^{-1}
Dimethyl acetylenedicarboxylate	CH_2Cl_2	122.5
Allylbenzene	$C_6H_5CH_3$	133.5
α-Methylstyrene	$C_6H_5CH_3$	137.8
β-Pinene	CH_2Cl_2	144.5
Diethyl mesoxalate	CH_2Cl_2	148.4
Diethyl azodicarboxylate	CH_2Cl_2	152.7
Diethyl azodicarboxylate	$C_6H_5CH_3$	153.4
(**7**)	$C_6H_5CH_3$	251.1
(**8**)	$C_6H_5CH_3$	259.2
(**9**)	CH_2Cl_2	261.8
(**1**)	CH_2Cl_2	263.5
(**3**)	CH_2Cl_2	302.4

yielded (**9**) as a highly viscous liquid. G.c. conditions as for (**3**).

(**9**): ν_{max} (CCl_4) 3 450, 3 030, 2 970, 1 765, and 1 760 cm^{-1}; δ_H 6.66 (1 H, s), 5.40 (1 H, m), 4.18 (4 H, q), 3.98 (2 H, s), 1.90–2.30 (4 H, m, br), 1.23 (9 H, t + s), and 0.81 (3 H, s).

Precision Density Measurements.—Precision density measurements were performed with a digital densimeter (Model DMA 60) based on the method of Kratky *et al.*[23] The partial molar volumes were obtained at 25.1 °C as indicated in Table 5 ($\pm$0.1–0.3 cm^3 mol^{-1}). Over the examined concentration range, the apparent molar volumes were constant within experimental error.

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