

Table II. Characteristic Infrared Absorption Bands of 3-(*N*-Substituted Formidoyl)indoles

No.	Aromatic C—H Stretch, Cm. <sup>-1</sup>	N—H Stretch, Cm. <sup>-1</sup>	Indole Ring Absorptions, Cm. <sup>-1</sup>	Aromatic C=C or C=N Stretch, Cm. <sup>-1</sup>	C—H Out-of-Plane Deformations, Cm. <sup>-1</sup>	Specific Absorptions, Cm. <sup>-1</sup>	No.	Aromatic C—H Stretch, Cm. <sup>-1</sup>	N—H Stretch, Cm. <sup>-1</sup>	Indole Ring Absorptions, Cm. <sup>-1</sup>	Aromatic C=C or C=N Stretch, Cm. <sup>-1</sup>	C—H Out-of-Plane Deformations, Cm. <sup>-1</sup>	Specific Absorptions, Cm. <sup>-1</sup>
1	3020	3120 2860	1248 1125	1610 1560 1480 1440 <sup>a</sup>	780 750 697	None	6	3030	2780 2600	1230 1140	1580 1450 1410 <sup>a</sup>	900 875 845 815 780 745	C—Cl 695 —CO <sub>2</sub> <sup>-</sup> 1610 1350
2	3020	3080 2860	1240 1120	1613 1580 1493 1440 <sup>a</sup>	805 750	C—F 1190	7	3020	3080 2860	1244 1115	1610 1560 1480 1440 <sup>a</sup>	910 880 811 801 758	—CF <sub>3</sub> 1190 1163 1328
3	3025	3330 3075 2850	1238 1115	1600 1560 1480 1430 <sup>a</sup>	831 755	C—Cl 705	8	3020	3080 2870	1240 1120	1600 1560 1480 1450 <sup>a</sup>	755	C—S— 725
4	3030	3120 2860	1245 1130	1610 1480 1570 1440 <sup>a</sup>	885 860 807 755	C—Cl 694	9	3010	3380 2810	1244 1120	1613 1594 1580 1555 1460 1430 <sup>a</sup>	740	
5	3020	2793 2604	1235 1120	1580 1460 1410 <sup>a</sup>	920 840 781 741	C—Cl 683 —CO <sub>2</sub> <sup>-</sup> 1600 1350							

<sup>a</sup> Band also in region for indole ring absorption.

photometer in a potassium bromide matrix. Melting points were taken on a Hershberg melting point apparatus and are uncorrected.

#### GENERAL PROCEDURE

A toluene solution of indole-3-carboxaldehyde (0.15 mole) and amine (0.15 mole) was refluxed until the required amount of water was collected in a Dean-Stark trap. The solvent was removed using a Büchler flash evaporator and the product was recrystallized as indicated in Table I.

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#### LITERATURE CITED

(1) Walker, G.N., Moore, M.A., *J. Org. Chem.* **26**, 432 (1961).

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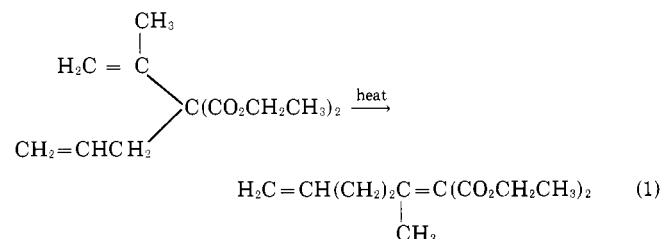
## Solvent Effects in the Cope Rearrangement

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The rate of rearrangement of diethyl allylisopropenylmalonate has been measured in several solvents at 144.4° C. Several macroscopic solvent parameters for these solvents have also been evaluated at 144.4° C.

THE influence of the solvent on the rate of the concerted nonionic Cope rearrangement (1, 5, 9) of diethyl allylisopropenylmalonate (Equation 1) has been determined as part of our investigation (2, 3) of the role of the solvent in nonionic concerted reactions.



In Table I are presented the results obtained with non-hydrogen bonding solvents for the reaction in Equation 1 along with some solvent parameters evaluated at 144.4° C. Since the rate of the reaction is the same within experimental error in the solvents *n*-decane and anisole whereas the solvent parameters differ for these solvents, it is clear that none of these macroscopic parameters alone can adequately correlate the results.

Although solvent polarity would be expected to be a less important factor than nonelectrostatic solvent interactions in a nonionic concerted reaction, the dielectric constant function  $(D - 1)/(2D + 1)$ , evaluated at 144.4° C., has been included in Table I. Regular solution theory is applicable to systems in which dispersion forces (an example of nonelectrostatic interactions) predominate (6); the solubility

parameters, evaluated at 144.4°C., for that theory are also listed in Table I.

Several empirical scales of solvent polarity have been proposed and recently reviewed (8). The  $E_T$  scale based upon the molar transition energy for the solvatochromic band of a solvatochromic dye is perhaps the most comprehensive such scale. If the  $E_T$  value for *n*-decane can be assumed to be the same as that for *n*-hexane, the  $E_T$  values for *n*-decane, anisole, and bromobenzene are 30.9, 37.2, and 37.5, respectively, at 25°C. Although extrapolation to 144.4°C. is unwarranted, there is no apparent correlation of the  $E_T$  scale with the rate constants listed in Table I.

## EXPERIMENTAL

The ultraviolet (UV) and infrared (IR) spectra were obtained with Cary Model 14 and Beckman IR-8 spectrophotometers, respectively. IR band intensity: *s*, strong; *m*, medium; *w*, weak. The nuclear magnetic resonance spectra (NMR) were obtained using carbon tetrachloride solutions of the compounds containing tetramethyl silane as an internal standard on a Varian A-60 spectrometer. The center positions of the NMR resonances are p.p.m. downfield from tetramethylsilane, parentheses indicate number of hydrogens rounded to nearest whole number, *m* = multiplet.

**Diethyl Allylisopropenylmalonate (I)** was prepared by the sodamide procedure of Cope and Hancock (4),  $n_D^{25}$  1.4503 [lit. 1.4500 (4)]; UV (ethanol solution) consists of end absorption only; IR (neat) significant absorptions 3090 *w*, 2990 *m*, 1730 *s*, 1640 *m*, 1440 *m*, 1365 *m*, 1215 *s* cm.<sup>-1</sup>, NMR, broad resonance 5.7 (1), 5.0 *m* (4), 4.1 quartet (4), 2.7 doublet (2), 1.8 singlet (3), 1.24 triplet (6).

**Diethyl 1-Methyl-4-pentenylidenemalonate (II)** was obtained by heating 0.6 ml. of I in a glass-stoppered flask flushed with dry nitrogen for 48 hours at ca. 150°C.,  $n_D^{25}$  1.4607 [lit. 1.4610, 1.4607 (1, 4)]; UV  $\lambda_{\text{max}}^{\text{EtOH}}$  222 m $\mu$ , log  $\epsilon$  = 4.0; IR (neat) significant absorptions 3090 *w*, 2990 *m*, 1725 *s*, 1640 *m*, 1440 *m*, 1365 *m*, 1245 *s* cm.<sup>-1</sup>; NMR, broad resonance 5.75 (1), 5.0 *m* (2), 4.13 quartet (4), 2.4 *m* (4), 2.0 singlet (3), 1.24 triplet (6).

**Solvents.** All solvents, previously dried, were fractionated at reduced pressures on a 55-cm. glass helices-packed column after the treatment described below, then stored over Linde 3A or 4A molecular sieves. Refractive indices are for the distilled solvents. 1,2,3-Trichloropropane (Aldrich 99+%) was washed twice with aqueous sodium hydroxide, then twice with water,  $n_D^{20}$  1.4837 [lit. 1.4834 (12)]. Bromobenzene (Matheson, Coleman and Bell, b.p. 154–56°C.) was washed once with dilute hydrochloric acid, twice with aqueous sodium hydroxide, and once with water,  $n_D^{15}$  1.5620 [lit. 1.56252 (13)]. Anisole (Fisher Certified, b.p. 153.1–53.4°C.) was washed twice with water,  $n_D^{20}$  1.5167 [lit. 1.51700 (13)]. *n*-Decane (Matheson, Coleman and Bell, b.p. 173–75°C.) was washed twice with concentrated sulfuric acid, twice with aqueous sodium hydroxide, and twice with water,  $n_D^{20}$  1.4115 [lit. 1.41189 (13)].

**Kinetic Measurements.** Glass ampoules with a capillary end and the requisite pipets and flasks for preparation of the master solution were baked in an oven (110°C.) before use. A separate master solution was prepared for each run; the solvent and compound I were pipetted into a one-necked flask and dry nitrogen was bubbled through the solution. An adapter for insertion of a syringe needle was placed in the neck, and samples (ca. 0.2 ml.) were removed from the flask and placed in the ampoules by means of a syringe. Dry nitrogen was then bubbled through the solution in the ampoule using a syringe needle, then the ampoule was sealed.

The ampoules for each run were simultaneously introduced into the temperature bath (144.4° ± 0.1°C.) and removed individually as a function of time, cooled, and an aliquot (pipet) of the contents was diluted to a standard volume in a volumetric flask with 95% ethanol, and the absorbance of the solution determined versus a blank consisting of an aliquot of the solvent, equal in volume to that of the sample, diluted with 95% ethanol to the standard volume. A Beckman model DU spectrophotometer was used for the absorbance measurements. With *n*-decane and 1,2,3-trichloropropane, the initial concentrations were 0.02 to 0.03 ml. of I per 4 ml. of solvent, 0.1 ml. from each ampoule was diluted to 25 ml., and the analytical wavelength was 222 m $\mu$ . With anisole and bromobenzene, the initial concentrations were 0.33 ml. of I per 4 ml. of solvent; 25  $\mu$ l. from each ampoule was diluted to 50 ml. Analytical wavelengths were 237.5 and 244 m $\mu$ , respectively, for anisole and bromobenzene.

The rate constants reported in Table I are the average of three individual determinations for each solvent with an average deviation from the mean of 4.9 to 5.3% for the aliphatic solvents and of 2.3 to 2.8% for the aromatic solvents. The rate data produced good first-order graphs; the rate constant values were calculated by the method of Swinbourne (11) to avoid the necessity of using an infinity value in the calculations. The requisite values were read from a graph of absorbance versus time. The reactions were followed for two half lives.

**Solvent Parameters.** Densities at 144.4°C. were determined by use of a 10-ml. volumetric flask with corrections made for the weight of air displaced. Molar refractions are independent of temperature (7) and were calculated from literature data (12, 13). The quantity  $(n^2 - 1)/(n^2 + 2)$  was calculated from the molar refractions, molecular weights, and densities at 144.4°C.

Solubility parameters,  $\delta$ , at 144.4°C. were evaluated using the definition (6)

$$\delta = \left( \frac{\Delta H^v - RT}{v^l} \right)^{1/2}$$

where  $\Delta H^v$  is the heat of vaporization and  $v^l$  the molar volume of the liquid at the requisite temperature. The heat of vaporization at the boiling point was used for  $\Delta H^v$ ; literature values (13) are available for all but 1,2,3-trichloropropane for which a value was estimated by use of Trouton's rule.

Table I. Rate Constants for Reaction of Diethyl Allylisopropenylmalonate and Solvent Parameters at 144.4°C.

Solvent <sup>a</sup>	10 <sup>5</sup> <i>k</i> , Sec. <sup>-1</sup>	Molar Refraction, Cc.	Density, G./Cc.	$\left( \frac{n^2 - 1}{n^2 + 2} \right)^{b,c}$	$\delta^{c,e}$	$\left( \frac{D - 1}{2D + 1} \right)^{a,c}$
1,2,3-Trichloropropane	5.25	30.35	1.22	0.251	8.2	
Bromobenzene	4.50	33.93	1.32	0.285	8.3	0.31
Anisole	4.10	32.91	0.869	0.264	8.0	0.29
<i>n</i> -Decane	4.10	48.51	0.628	0.215	6.1	0.18

<sup>a</sup> See experimental section for determination of solvent parameters. <sup>b</sup> *n* = refractive index. <sup>c</sup> Regular solution theory solubility parameter. <sup>d</sup> *D* = dielectric constant. <sup>e</sup> Calculated value of the parameter used.

Dielectric constants,  $D$ , for anisole and bromobenzene were obtained from the equation for total polarization (10),  $P$ ,

$$P = \frac{D-1}{D+2} \frac{M}{d} = P' + \frac{A}{T}$$

where  $d$  is density,  $M$  is molecular weight,  $A$  is a constant,  $P'$  is the distortion polarization, and  $T$  is the absolute temperature. Using the molar refraction to estimate (10)  $P'$  and literature values for  $D$  and  $d$  at a known  $T$ , values for  $A$  were calculated. Then values for  $D$  at 144.4°C. were obtained by use of the density values at 144.4°C. The  $D$  value for  $n$ -decane was obtained from the relation  $n^2 = D$  for strictly nonpolar compounds.

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#### LITERATURE CITED

- (1) Aldridge, G.R., Murphy, G.W., *J. Am. Chem. Soc.* **73**, 1158 (1951).

- (2) Berndt, D.C., Zuika, M., Clark, M.S., Jr., *Chem. Ind. (London)* 1965, p. 139.  
 (3) Berndt, D.C., *J. Org. Chem.* **32**, 482 (1967).  
 (4) Cope, A.C., Hancock, E.M., *J. Am. Chem. Soc.* **60**, 2644 (1938).  
 (5) Gibson, D.H., Pettit, R., *Ibid.*, **87**, 2620 (1965) and references therein indicate that certain hydrocarbons may react by different pathways.  
 (6) Hildebrand, J.H., Scott, R.L., "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.  
 (7) LeFevre, R.J.W., "Advances in Physical Organic Chemistry," **3**, p. 1, V. Gold, ed., Academic Press, New York, 1965.  
 (8) Reichardt, C., *Angew. Chem. Intern. Eng. Ed.* **4**, 29 (1965).  
 (9) Rhoads, S.J., "Molecular Rearrangements," **1**, Chap. 11, P. de Mayo, ed., Interscience Publishers, New York, 1963.  
 (10) Smith, J.W., "Electric Dipole Moments," Chap. 1, Butterworths Publications, London, 1955.  
 (11) Swinbourne, E.S., *J. Chem. Soc.* **1960**, p. 2371.  
 (12) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol. II, p. 204, Elsevier Publishing Co., New York, 1965.  
 (13) Weissberger, A., ed., "Techniques of Organic Chemistry," VII, 2nd ed., Interscience Publishers, New York, 1955.

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## Substituted Aziridines

### Relative Rates of Reaction and Direction of Ring Opening

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Relative reaction rates have been measured for the ring opening of various  $N$ -substituted aziridines and 2-methylaziridines by carboxylic acids. In diglyme solution, the order of decreasing reactivity for the substituent attached to the nitrogen atom is: alkyl > dialkylphosphinyl > phosphinylidene > dialkylphosphonyl > diphenylphosphinyl > diphenylphosphonyl > alkylsulfonyl > arylsulfonyl. In addition,  $N$ -substituted aziridines react more rapidly than the corresponding 2-methylaziridines. The reaction rates were much higher in chlorobenzene than in diglyme. In general, ring opening of  $N$ -substituted 2-methylaziridines occurred by rupture of the bond between nitrogen and the unsubstituted carbon atom, and by cleavage of the bond between nitrogen and the methyl-bearing ring carbon atom.

ALTHOUGH RING-OPENING REACTIONS of aziridines have been studied by several workers, the reactions of  $N$ -substituted aziridines with carboxylic acids have received little attention (2). The present study was undertaken to examine, first, the effect of aziridine substituents upon the rate of ring opening with carboxylic acids; second, the effect of the nature of the solvent upon the reaction rates; and third, the direction of ring opening of unsymmetrically substituted aziridines.

The relative rates of reaction of various  $N$ -substituted aziridines and (2-methyl)aziridines with carboxylic acids were determined by heating a solution containing the aziridine and butyric acid at 125°C. and titrating the unreacted acid with sodium hydroxide in ethanol. The results of relative rate studies in diglyme (diethylene glycol dimethyl ether) solution are shown in Table I. The choice of solvent was dictated by the fact that several of the aziridines had very low solubility in the more common solvents, and it was desirable to run as many of the reactions as possible in the same solvent. The rates are reported in terms of the quarter life and half life of butyric acid and allow

Table I. Relative Rates of Reaction of  $R-N_1R_2$  with Butyric Acid

		(Diglyme, 125°C.)	
R	R'	$T_{1/4}^a$ , Hr.	$T_{1/2}^a$ , Hr.
—C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> —	H	0.10	0.38
—C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> —	CH <sub>3</sub>	0.15	0.55
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO—	H	1.22	2.25
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO—	CH <sub>3</sub>	1.00	3.42
PO(—) <sub>3</sub>	H	1.13	2.41
PO(—) <sub>3</sub>	CH <sub>3</sub>	2.16	6.66
(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> PO—	H	9.5	26
(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> PO—	CH <sub>3</sub>	12.25	40
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PO—	CH <sub>3</sub>	27.5	78
(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> PO—	H	52	...
(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> PO—	CH <sub>3</sub>	135	...
C <sub>4</sub> H <sub>9</sub> SO <sub>2</sub> —	H	129	263
C <sub>4</sub> H <sub>9</sub> SO <sub>2</sub> —	CH <sub>3</sub>	445	1075
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> —	CH <sub>3</sub>	375	1310

<sup>a</sup>  $T_{1/4}$  represents time to 25% reaction;  $T_{1/2}$ , time to 50% reaction.