A thermowell held thermocouples inside the reactor. The catalyst pellets were diluted with glass pieces of similar sizes about 1:2 weight ratio to decrease temperature changes during the reaction. All the experiments were made at atmospheric pressure. The liquid feeds were pumped into the reaction tube by a syringe-type displacement pump. The liquid products were condensed successively in ice-water and acetone–Dry Ice traps.

The gases were trapped in a liquid nitrogen condenser and at the end of each experiment collected over saturated salt-water. Hydrogen was measured in a Precision wet test meter.

At the end of each experiment the carbonaceous materials were burned off at 540° with an air–nitrogen mixture; CO_2 was absorbed in 0.1 *N* NaOH solution, and back-titrated with 0.6 *N* HCl using phenolphthalein and methyl orange indicators. The difference between the two end-points is equal to the CO_2 absorbed. Equal rate of formation of carbonaceous materials was supposed during each cut within any single experiment in the preparation of Tables I-V. Catalysts were reconditioned under hydrogen flow at 525° before each experiment for at least 2 hours.

Liquid and gaseous reaction products were analyzed by gas chromatography using two Podbielniak Chromacon vapor phase chromatographic analytical apparatus (models No. 9475 3A and 9580) with the following columns: 1. silica gel "950," 60/200 mesh, 8 ft., for C_1–C_2-compounds; 2. 35% dimethylsulfolane–dipropyl sulfone (ratio 3:7) on 30/60 mesh firebrick, 35 ft., for C_2–C_4-aliphatics; 3. 33% dimethylsulfolane on 100/120 mesh firebrick, 10 ft., for C_3–C_6-aliphatics; 4. 7% di-*n*-propyl tetrachlorophthalate on 30/60 mesh Celite, 22 ft., for C_6-diolefins and aromatics; 5. 5% 7,8-benzoquinoline on 100/120 mesh firebrick, 26 ft., for xylenes.

The hydrocarbons used were pure grade commercial products.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The Correlation of Solvent Effects on the Stereoselectivities of Diels–Alder Reactions by Means of Linear Free Energy Relationships. A New Empirical Measure of Solvent Polarity[1a]

BY JEROME A. BERSON,[1b] ZACHARIAS HAMLET AND WILLIAM A. MUELLER

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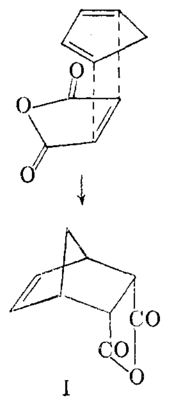
The logarithms of the ratios of stereoisomeric products in the kinetically controlled Diels–Alder additions of cyclopentadiene to methyl methacrylate and methyl *trans*-crotonate in various solvents are linearly related to a solvent parameter, Ω, defined as the logarithm of the *endo/exo* product ratio for the cyclopentadiene–methyl acrylate addition. The Alder Rule of "maximum accumulation of unsaturation" is of minor importance in determining the ratios of products; methyl acrylate obeys the rule in all solvents, methyl methacrylate violates it in all solvents, and methyl *trans*-crotonate shows borderline behavior, conforming to the rule in polar solvents but not in non-polar solvents. The solvent effects are correlated fairly well in quantitative terms by the Kirkwood–Onsager theory. The qualitative trend of the solvent effects is explicable in terms of an interaction between the permanent dipoles of the diene and dienophile. The parameter Ω is a new empirical measure of solvent polarity; it is linear in Z, in log k_{ion} for *p*-methoxyneophyl *p*-toluenesulfonate, and in log k_{rearr} for the Curtius rearrangement of benzoyl azide.

The first few experiences[2] in the study of the stereoselectivity of diene additions were deceptively simple. In the classic case,[3] cyclopentadiene and maleic anhydride reacted to give essentially exclusively the *endo* adduct I rather than the *exo* adduct II. On the basis of this (and several other examples in which the *endo* adduct was at least the heavily predominant if not exclusive product) was formulated[2] the Rule of "maximum accumulation of unsaturation." Since the Diels–Alder reaction is reversible, it was to be expected that, in those additions taking place under circumstances that permitted equilibrium to be established in favor of an *exo* adduct of greater stability, the Rule would be violated, and a number of such cases have come to light.[2,4] Nevertheless, the kinetically favored product has usually been assumed to be *endo*, in accord with the Rule, and most theories of the mechanism of the Diels–Alder reaction have postulated[4a,5,6] some kind of attractive interaction between the reacting partners that was much stronger in the *endo* transition state than in the *exo*. Recently, however, it has become increasingly clear that *exo* addition predominates in many cases in which the product-ratio is presumed[7,8] or demon-



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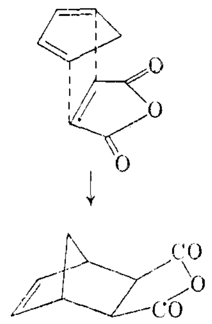

II

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[1] (a) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We are also indebted to the Alfred P. Sloan Foundation and to the Office of Scientific Research, Air Research and Development Command, U. S. Air Force (Contract No. AF 49(638)-828), for support of part of this work. (b) Alfred P. Sloan Fellow, 1957–1961. (c) For a preliminary report, see J. A. Berson and W. A. Mueller, *Tetrahedron Letters*, **No. 4**, 131 (1961).

[2] For a summary, see K. Alder and G. Stein, *Angew. Chem.*, **50**, 514 (1937).

[3] K. Alder and G. Stein, *Ann.*, **504**, 222 (1933); **514**, 1 (1934).

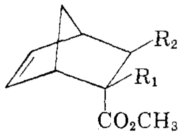
[4] *Cf. inter alia* (a) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944); (b) K. Alder, F. W. Chambers and W. Trimborn, *Ann.*, **566**, 27 (1950); (c) D. Craig, *J. Am. Chem. Soc.*, **73**, 4880 (1951); (d) J. A. Berson and R. Swidler, *ibid.*, **75**, 1721 (1953).

[5] A. Wasserman, *J. Chem. Soc.*, **828**, 1511 (1935); 432 (1936); 612 (1942); *Trans. Faraday Soc.*, **34**, 128 (1938); **35**, 841 (1939).

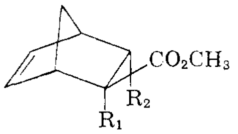
[6] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[7] (a) J. S. Meek and W. Trapp, *J. Am. Chem. Soc.*, **78**, 6049 (1956); (b) W. R. Boehme, E. Schipper, W. G. Scharpf and J. Nichols, *ibid.*, **80**, 5488 (1958); (c) M. Schwarz and M. Maienthal, *J. Org. Chem.*, **25**, 449 (1960).

strated[9] to be kinetically controlled. In order to gain some insight into the factors that control the distribution of products in Diels–Alder reactions, we examine here the behavior of three adduct systems as functions of temperature and solvent. The diene partner in each case is cyclopentadiene, and the dienophile components are methyl acrylate, methyl methacrylate, and methyl *trans*-crotonate; the adducts produced are the pairs IIIa-IVa, IIIb-IVb and IIIc-IVc, respectively.



IIIa, $R_1, R_2 = H$
b, $R_1 = CH_3, R_2 = H$
c, $R_1 = H, R_2 = CH_3$



IVa, $R_1, R_2 = H$
b, $R_1 = CH_3, R_2 = H$
c, $R_1 = H, R_2 = CH_3$

The range of solvents covers nine aprotic substances, two alcohols, and one carboxylic acid. We made some attempts to conduct experiments in aqueous systems (water–alcohols, water–dioxane, etc.) and in anhydrous formic acid, but the low solubility of cyclopentadiene in the aqueous solvents and the indications of serious side creations in formic acid led us to abandon these.

By appropriate controls, the product mixtures in all cases are shown to be kinetically determined. Consequently, if it is assumed that the formation of *endo* (N) and *exo* (X) products in a given run follow rate laws of the same form, the product ratio N/X is equal to the ratios of the specific rate coefficients k_N/k_X. Furthermore, the ground state reactants leading to a pair of *endo-exo* isomeric transition states are identical, so that log (k_N/k_X) is directly proportional to the free energy difference between the two transition states.

The temperature-dependence of the product ratio, expressed in Arrhenius form (eq. 1), gives

$$\log (k_N/k_X) = \log (A_N/A_X) + (E_X - E_N)/2.303RT \quad (1)$$

values for the ratios of the pre-exponential factors and for the differences in empirical activation energies from the intercepts and slopes of plots of log (k_N/k_X) *vs.* $1/T$. The differences in entropies of activation are given by the equation $\Delta S_N^{\ddagger} - \Delta S_X^{\ddagger} = 2.303\,R \log (A_N/A_X)$, while the differences in enthalpies of activation are identical with the differences in Arrhenius activation energies.

Since the effects of both solvent and temperature are small, it is necessary to analyze the products with high precision in order to obtain meaningful data. Purely chemical procedures, such as the iodolactone separation,[10] are not sensitive enough to deal with this problem and, furthermore, sometimes give misleading results.[11] There is the additional difficulty that conversion of those ester adducts bearing epimerizable hydrogens (IIIa, IIIc, IVa, IVc) to the free acids for analysis by iodolactonization requires a hydrolysis that cannot be conveniently carried out without changing the stereochemical composition. The esters themselves are, however, readily separable by gas chromatography, as has already been shown for the pair of adducts IIIa-IVa from methyl acrylate.[12] Each pair of epimeric esters can be analyzed gas chromatographically with a reproducibility of 0.1% in the absolute value of the % of a given component in a given sample for most of the mixture compositions encountered. The product ratio is reproducible to about this same precision in samples from replicate additions. The values for log (k_N/k_X) are therefore reliable to about 0.005 to 0.010 unit. The differences in activation enthalpies are derived from graphs which, in most cases, are drawn through only three points. This leads to a substantial uncertainty which we estimate as about 0.05 – 0.10 kcal./mole. The entropy terms are quite rough and are probably reliable to only one significant figure. The data are collected in Table I.

TABLE I

PRODUCTS FROM THE REACTIONS OF CYCLOPENTADIENE WITH VARIOUS DIENOPHILES

Solvent	Temp., °C.	% of 1:1 adduct N	% of 1:1 adduct X	log (N/X)	$\Delta H_X^{\ddagger} - \Delta H_N^{\ddagger}$, kcal./mole	$\Delta S_N^{\ddagger} - \Delta S_X^{\ddagger}$, e.u.
		With methyl acrylate				
		(IIIa)	(IVa)	(Ω)		
Triethylamine	3	76.3	23.7	0.508	+0.54	+0.37
	30	73.6	26.4	.445		
	66	72.4	27.6	.420		
Decalin	−35	80.3	19.7	.610	+ .35	+1.3
	56	76.4	23.6	.510		
	100	75.5	24.5	.489		
	139	74.8	25.2	.472		
	170	74.5	25.5	.466		
1,2-Dimethoxyethane	3	80.0	20.0	.602	+ .64	+0.43
	30	79.7	22.3	.543		
	66	77.2	22.8	.528		
Dimethylformamide	3	81.8	18.2	.652	+ .52	+1.1
	30	80.7	19.3	.620		
	66	78.9	21.1	.573		
Pyridine	3	81.4	18.6	.640	+ .76	+0.17
	30	79.7	20.3	.595		
	66	77.6	22.4	.540		
Nitromethane	3	84.6	15.4	.738	+ .64	+1.0
	30	82.7	17.3	.680		
	66	81.4	18.6	.642		
Acetonitrile	0	85.3	14.7	.764	+ .78	+0.60
	30	83.1	16.9	.692		
	66	81.1	18.9	.634		
Acetone	0	82.0	18.0	.659	+ .73	+ .37
	20	80.6	19.4	.619		
	56	78.5	21.5	.562		
1,2-Dichloroethane	3	81.4	18.6	.641	+ .60	+ .75
	30	79.8	20.2	.600		
	66	78.1	21.9	.552		
Ethanol	3	86.5	13.5	.807	+ .98	+ .14
	30	83.9	16.1	.718		
	66	82.0	18.0	.659		
Acetic acid	3	88.1	11.9	.870	+ .96	+ .50
	30	86.9	13.1	.823		
	66	83.8	16.2	.714		
Methanol	0	89.8	10.2	.944	+1.4	− .90
	26	87.5	12.5	.845		
	56	84.9	15.1	.750		

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(8) (a) K. Alder, R. Hartmann and W. Roth, *Ann.*, **613**, 6 (1958); (b) K. Alder and W. Günzl, *Chem. Ber.*, **93**, 809 (1960).

(9) J. A. Berson, A. Remanick and W. A. Mueller, *J. Am. Chem. Soc.*, **82**, 5501 (1960).

(10) C. D. ver Nooy and C. S. Rondestvedt, *ibid.*, **77**, 3583 (1955).

(11) J. A. Berson and A. Remanick, *ibid.*, **83**, 4947 (1961).

(12) A. C. Cope, E. Ciganek and N. A. Le Bel, *J. Am. Chem. Soc.*, **81**, 2799 (1959). We are indebted to Professor Cope for the communication of additional details.

		With methyl methacrylate				
		IIIb	IVb			
Triethylamine	3	22.9	77.1	−0.526	−0.40	−0.97
	30	24.2	75.8	− .496		
	66	25.4	74.6	− .469		
Decalin	56	33.0	67.0	− .308	− .74	+ .96
	100	36.4	63.6	− .243		
	139	38.2	61.8	− .208		
1,2-Dimethoxyethane	3	25.8	74.2	− .460	− .39	− .69
	30	27.4	72.6	− .422		
	66	28.7	71.7	− .404		
Dimethylformamide	3	27.6	72.4	− .420	− .52	− .11
	30	28.4	71.6	− .402		
	66	31.5	68.5	− .338		
Pyridine	3	27.7	72.3	− .417	− .35	− .64
	30	29.2	70.8	− .384		
	66	30.3	69.7	− .362		
Nitromethane	3	30.5	69.5	− .357	− .52	+ .23
	30	32.6	67.4	− .315		
	66	34.4	65.6	− .281		
Acetonitrile	0	31.6	68.4	− .336	− .39	− .12
	30	33.0	67.0	− .308		
	66	34.6	65.4	− .278		
Acetone	0	28.8	71.2	− .393	− .33	− .57
	20	29.8	70.2	− .372		
	56	31.0	69.0	− .348		
1,2-Dichloroethane	3	27.8	72.2	− .415	− .59	+ .26
	30	29.8	70.2	− .372		
	66	31.9	68.1	− .329		
Ethanol	3	33.5	66.5	− .297	− .27	− .38
	30	35.4	64.6	− .262		
	66	35.6	64.4	− .258		
Acetic acid	3	35.9	64.1	− .251	− .44	+ .46
	30	38.4	61.6	− .205		
	66	39.4	60.6	− .187		
Methanol	0	41.5	58.5	− .149	+ .10	−1.05
	26	41.1	58.9	− .156		
	56	40.7	59.3	− .163		
		With methyl *trans*-crotonate				
		IIIc	IVc			
Triethylamine	3	51.2	48.8	0.021	+0.68	−2.4
	30	47.5	52.5	− .044		
	66	45.7	54.3	− .076		
Decalin	3	52.6	47.4	.045	+ .34	−0.73
	30	52.1	47.9	.037		
	66	51.3	48.7	.022		
1,2-Dimethoxyethane	3	55.0	45.0	.088	+ .66	−2.0
	30	52.4	47.6	.042		
	66	49.3	50.7	− .013		
Dimethylformamide	3	56.9	43.1	.120	+ .23	−0.30
	30	56.0	44.0	.104		
	66	55.0	45.0	.087		
Pyridine	3	56.2	43.8	.108	+ .24	−0.36
	30	55.5	44.5	.095		
	66	54.2	45.7	.074		
Nitromethane	3	62.0	38.0	.212	+ .58	−1.1
	30	58.6	41.4	.151		
	66	57.2	42.8	.126		
Acetonitrile	3	59.8	40.2	.172	+ .44	−0.75
	30	57.4	42.6	.130		
	66	56.1	43.9	.107		
Acetone	3	57.1	42.9	.124	+ .44	−0.97
	30	55.0	45.0	.087		
	66[a]	53.6	46.4	.062		
1,2-Dichloroethane	3	56.0	44.0	.104	+ .46	−1.2
	30	54.5	45.5	.078		
	66	52.0	48.0	.035		
Ethanol	3	64.7	35.3	.264	+ .38	−0.19
	30	62.3	37.7	.217		
	66	61.7	38.3	.208		
Acetic acid	3	70.3	29.7	.373	+ .29	+ .66
	30	70.0	30.0	.367		
	66	68.4	31.6	.335		
Methanol	3	66.4	33.6	.296	+ .26	+ .53
	30	65.2	34.8	.272		
	66	65.0	35.0	.268		

[a] Extrapolated from data at 3°, 30° and 57°

Failure of the Alder Rule.—The Rule[2] of "maximum accumulation of unsaturation" is apparently of minor importance in determining the ratios of products in the present cases. While *endo* addition is the favored path with methyl acrylate under all the conditions examined, the preference is very small. Further, substitution of a methyl group for hydrogen, as in the methyl methacrylate series, reverses the preference, *exo* addition being favored under all the circumstances of Table I. This reversal is at least partially attributable to a lower activation energy for *exo* addition than for *endo* in the methyl methacrylate reactions, since $\Delta H_X^{\ddagger} - \Delta H_N^{\ddagger}$ is negative in all the solvents except methanol. The methyl *trans*-crotonate series is especially instructive in revealing the inadequacies of the Rule. The ratio of products, which is close to the statistical 1:1 distribution in all the solvents, shows Alder-type behavior in some and anti-Alder behavior in others.

Linear Free Energy Relationships.—Despite these variations in degree of adherence to the Rule, the response of the stereoselectivity to a change of solvent for all three systems is similar. In fact, log (N/X) for one dienophile is linearly related to log (N/X) for another dienophile, which implies a linear relationship between the respective differences in free energies of activation. For convenience in further correlations to be described, we choose methyl acrylate as the standard system and compare the other two dienophiles to it. The parameter Ω_t is defined as log $(N/X)_t$ for the cyclopentadiene–methyl acrylate addition at a specified temperature. Examples of the correspondences to an equation of the form (2) are given

$$\log (N/X)_t = a + b\Omega_t \qquad (2)$$

in Figs. 1 and 2, which show the data for methyl methacrylate at 3° and for methyl *trans*-crotonate at 30°. Table II summarizes the correlations at three temperatures for both methyl methacrylate and methyl *trans*-crotonate.

TABLE II

LINEAR FREE ENERGY RELATIONSHIPS

Dienophile, methyl	Temp., °C.	a[a]	b[b]	Correlation coeff. (r)[c]
Methacrylate	3	−0.969	+0.858	0.965
Methacrylate	30	− .872	+ .833	.952
Methacrylate	66	− .810	+ .857	.921
trans-Crotonate	3	− .393	+ .793	.951
trans-Crotonate	30	− .487	+ .958	.970
trans-Crotonate	66	− .671	+1.315	.928

[a] Intercept of the least squares line fitting eq. 2. [b] Slope of the least squares line fitting eq. 2. [c] *Cf.* A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 273; for a perfect correlation, $r = 1.000$.

In Fig. 1, only the decalin point is seriously off the least squares line. If this point is omitted, the correlation coefficient (r) rises from 0.965 to 0.992. Decalin shows similar behavior at the other two temperatures with methyl methacrylate also, the value of log (N/X) in this solvent being substantially higher than that required by the regression line. While it does not seem fruitful to at-

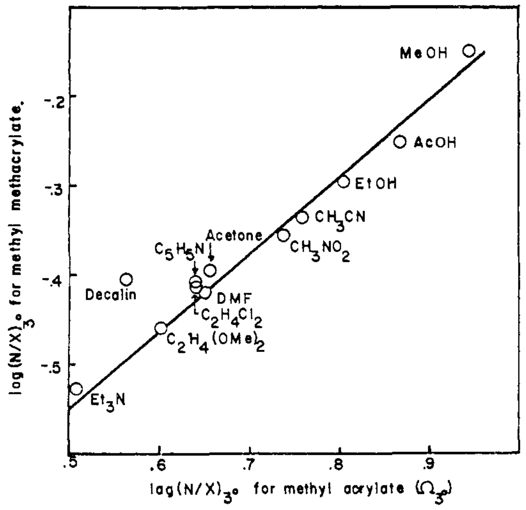


Fig. 1.—Linear free energy relationship in the stereoselectivities of the Diels–Alder additions of cyclopentadiene to methyl acrylate and methyl methacrylate. The ratio N/X is the kinetically controlled ratio of *endo* to *exo* product.

tempt a detailed analysis of occasional discrepancies of this type, it is noteworthy that the entropy difference $\Delta S_N^{\ddagger} - \Delta S_X^{\ddagger}$ in decalin is substantially more positive than those in the other solvents, and that the decalin point falls *on* the (roughly linear) graph obtained by plotting $\Delta H_X^{\ddagger} - \Delta H_N^{\ddagger}$ for methyl methacrylate *vs.* the same parameter for methyl acrylate.

The slopes (*b*) of the correlation lines are all positive and near unity; the product ratios with all three dienophiles are therefore about equally sensitive to a change of solvent.

Interpretation.—The qualitative trends are conveniently summarized in the schematic diagram, Fig. 3, which represents the situation at moderate temperatures. Any theoretical treatment of the data must deal with two presumably independent effects: (i) What factors determine the sign of the intercepts of the lines and hence the category (Alder, anti-Alder or borderline) into which the dienophile falls? (ii) What properties of liquids vary so as to product a monotonic response (with positive slope) of log (N/X) to a change of solvent? The latter effect seems easier to interpret and is considered first.

With all three dienophiles, log (N/X) becomes increasingly positive as the solvent is changed in a way that one might intuitively classify as nonpolar (decalin, triethylamine) to polar (alcohols, acetic acid). In other words, the free energy change ($F_X^{\ddagger} - F_N^{\ddagger}$) for the isomerization of the *endo* transition state into the *exo* transition state, which is identical with the activation energy difference $\Delta F_X^{\ddagger} - \Delta F_N^{\ddagger}$ and directly proportional to log (N/X), is made more positive by increasing the polarity of the solvent.

This pattern can be understood as an electrostatic effect if it is assumed that *the permanent electric dipole moment of the endo transition state is greater than that of the exo.* The assumption is reasonable if the transition state is imagined to consist of a bimolecular aggregate in which the diene and dienophile lie in roughly parallel planes.

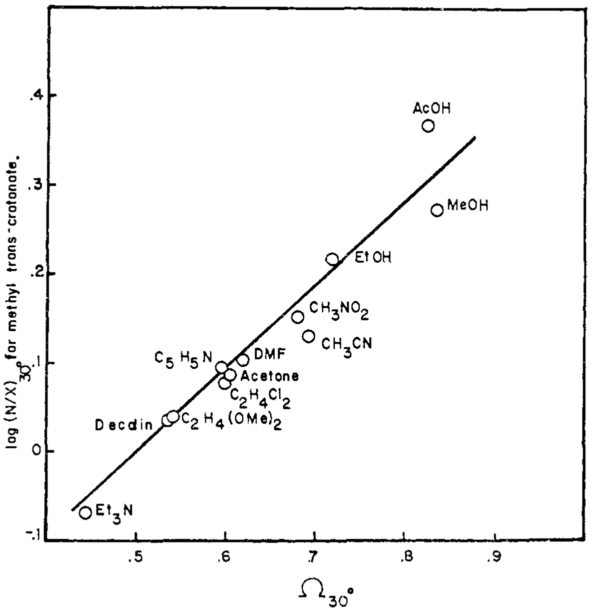
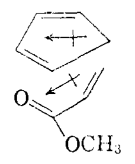
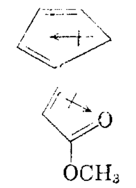


Fig. 2.—Linear free energy relationship in the stereoselectivities of the Diels–Alder additions of cylcopentadiene to methyl acrylate and methyl *trans*-crotonate. The ratio N/X is the kinetically controlled ratio of *endo* to *exo* product.

The dipole of the diene must lie with its negative end in the ring and its positive end toward the saturated methylene group, because the electronegativity of sp^2 carbon is greater than that of sp^3. The negative end of the dienophile dipole must lie toward the carboalkoxy function. Although some change in the magnitudes of the two dipole moments might be expected in passing from the reactants to the transition state, the directions are expected to remain qualitatively the same. In the *endo* transition state, the component dipoles point in roughly the same direction and, consequently, the net moment is expected to be greater than that of the *exo* transition state, where the component dipoles point in roughly opposite directions (*cf.* V, N and X).


V(N)


V(X)

The electrostatic free energy change ($\Delta F = F_{\text{soln}} - F_{\text{gas}}$) when a dipole is transferred from vacuum to a solvent is given by[13] eq. 3.

$$\Delta F = \frac{-\mu^2}{a^3}\left[\frac{D-1}{2D+1}\right] \qquad (3)$$

The difference in the free energy changes for two different dipoles ($\mu_2 > \mu_1$) is then

$$\Delta F_2 - \Delta F_1 = \frac{\mu_1^2 - \mu_2^2}{a^3}\left[\frac{D-1}{2D+1}\right] \qquad (4)$$

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[13] (a) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); (b) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

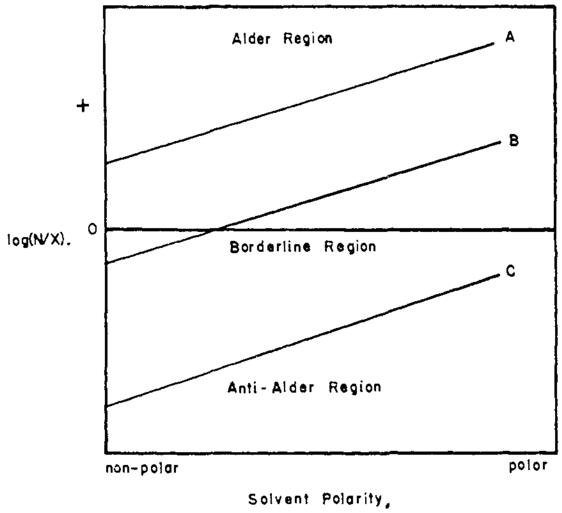

Fig. 3.—Schematic diagram illustrating behavior of the *endo-exo* product ratio as a function of dienophile and solvent at moderate temperature. Curve A represents data for methyl acrylate, B for methyl *trans*-crotonate and C for methyl methacrylate.

In eqs. 3 and 4, μ is a dipole moment, D the dielectric constant of the solvent and a the "cavity radius," the significance of which is discussed below. To the extent that an increase in the parameter $(D - 1)/(2D + 1)$ signifies an increase in polarity of the solvent, eq. 4 predicts that the free energy change favoring the solution of the solute of higher dipole moment will become more pronounced as the polarity of the solvent increases. This is just the effect observed experimentally in the transition states of the above Diels–Alder additions.

In some of the attempts to correlate solvent effects quantitatively with eq. 3, the "cavity radius" a is identified with the radius of the solute molecule.[14] Much better correlation is frequently achieved, however, when a^3 is considered to be a function of the molar volume of the *solvent*.[15a,b] The correlations[15a] are subject to the limitation that since eq. 4 embraces only electrostatic effects, such specific solute–solvent interactions as hydrogen bonding are not taken into account, and the hydroxylic and aprotic solvents fall on separate correlation lines. In Fig. 4, log (N/X) for the methyl acrylate addition at 20° ($\equiv\Omega_{20}°$) is plotted as a function of $[(D-1)/(2D+1)]\rho/M$, where ρ/M is the molar volume (density/molecular weight) of the solvent. As is expected, the points for the aprotic solvents are fitted fairly well ($r = 0.957$) by a straight line, represented by the least squares slope and intercept of eq. 5. The points for acetic

$$\Omega_{20}° = 0.0251 \left[\frac{D - 1}{2D + 1}\ \frac{10^3\rho}{M}\right] + 0.472 \qquad (5)$$

acid, methanol and ethanol are badly displaced from the line; the correlation, even for the aprotic solvents, becomes substantially worse when the solvent parameter is taken as $(D - 1)/(2D + 1)$ (which is equivalent to the assumption that a is not a function of solvent). In these respects, the correlation parallels those encountered with keto–enol equilibria,[15a] rotational isomerism[15a] and frequency shifts of infrared absorption bands.[15b,c]

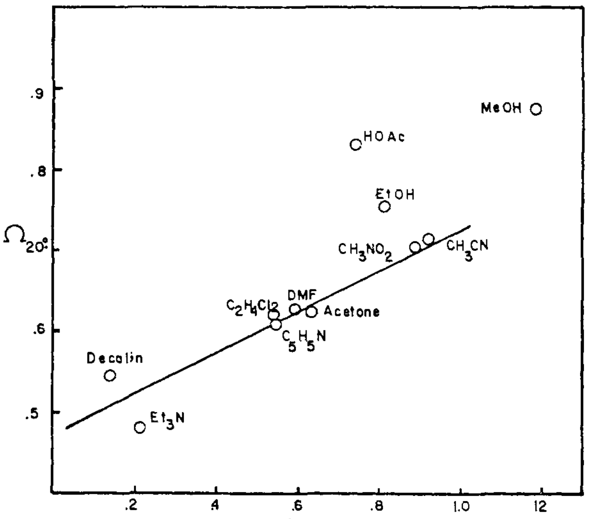

Fig. 4.—Correlation of $\Omega_{20}°$ with the Kirkwood–Onsager solvent parameter according to the method of Powling and Bernstein.[15a] The dielectric constants are taken from A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular No. 514, 1951, except for that of dimethylformamide, which is taken from G. R. Leader and J. F. Gormley, *J. Am. Chem. Soc.*, **73**, 5731 (1951). The densities are taken from the "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 28th ed., 1944.

Although the assignment of a decisive role to the permanent dipoles of the diene and dienophile thus provides an insight into the origin of the solvent effects that is qualitatively (and to some extent, quantitatively) satisfactory, it is of no help in explaining the strong preference for *endo* addition observed with maleic anhydride, nor is any connection apparent with the more subtle variations indicated in the intercepts of Fig. 3. A mutual orientation of dipoles like that of V would predict a preference for *exo* addition, and consequently cannot account for the results in systems that obey the Alder Rule. *endo* addition would, however, be favored by the attraction arising from dipole induction forces between the highly polarizable diene and the polar groups of the dienophile. Attempts[5] to estimate the strength of these forces are subject to a substantial uncertainty; the interaction energy falls off as the inverse sixth power of the distance, and it is not clear what values one should choose for this distance or for the group moments. Some appreciation of the difficulties is afforded by the variation in the calculated[5] k_N/k_X for the cyclopentadiene–benzoquinone addition, which changes from about 6 to about 1600 as the diene–dienophile distance changes from 2.33 to 1.80 Å. Nevertheless, the dipole induction effect is at least in the right direction. Similarly,

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(14) *Cf.* K. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

(15) (a) J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, **73**, 1815, 4353 (1951); (b) A. D. E. Pullin, *Spectrochim. Acta*, **13**, 125 (1958); *Proc. Roy. Soc.* (*London*), **255**, 39 (1960); (c) for other interpretations of solvent effects on infrared spectra, see *inter alia* R. J. W. Le Fèvre, *Austr. J. Chem.*, **14**, 312 (1961); L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).

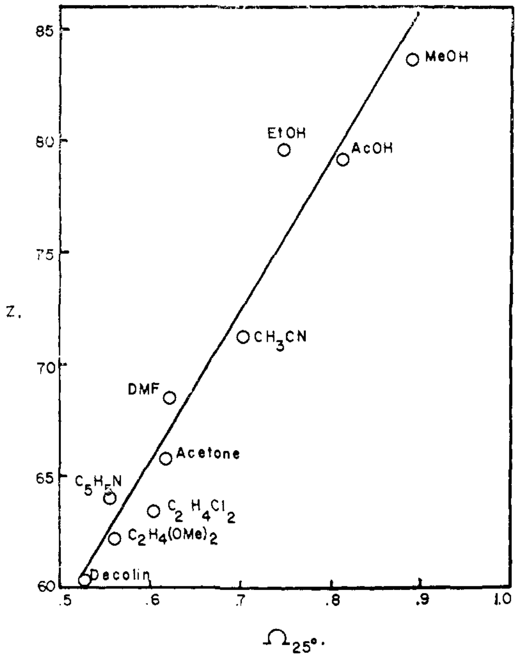

Fig. 5.—Linear relationship between Kosower's **Z**-values and Ω. The **Z**-value for decalin is assumed to be equal to that reported[16] for isoöctane.

the alternative postulate of some direct electronic interaction between the developing double bond in the diene and the unsaturated substituent of the dienophile, for example, by σ-type π-orbital overlap, would also be difficult to calculate precisely but operates in the right direction. On the basis of either model, the interaction energy would be sensitive to the conformational orientation of the dienophilic substituent. This predicts that for the interaction energy to be large, a dienophile bearing a more or less freely rotating substituent in the ground state must suffer a substantially greater loss of entropy in passing to an *endo* transition state than to an *exo* transition state. This is not borne out by the data of Table I; the entropies of activation for *endo* and *exo* addition are virtually identical. This suggests that the free energy decrease achieved by the postulated interaction in the *endo* transition state is insufficient to compensate for the loss in entropy that must be sustained. The special place occupied by such dienophiles as maleic anhydride may well be, at least in part, the result of their cyclic structure, in which the price in entropy has already been paid, and the full effect of the favorable interaction in the *endo* transition state can emerge. According to this analysis, the product composition from an acyclic dienophile is the result of a delicate balance between two opposing and relatively weak influences; it is to be expected, then, that even minor variations in structure will affect the category of Fig. 3 into which the system falls. Although it does not yet seem possible to disentangle the many small effects that such variations bring into play, it is clear that the data for the three closely related acyclic dienophiles examined here illustrate the main point.

Ω-Values as Empirical Measures of Solvent Polarity.—Among the scales that have been proposed as empirical measures of solvent polarity are **Z**, derived from the effect of solvent on the charge-transfer electronic absorption band of pyridinium iodides[16] at 25°, **Y** from the rates of solvolysis[17] of *t*-butyl chloride in hydroxylic solvents, and log k_{ion} from the rates of ionization of *p*-methoxyneophyl *p*-toluenesulfonate in aprotic media[18] at 75°. Both **Y** and log k_{ion} are linear in **Z**, and one or another of the three parameters can be used to correlate, at least roughly, a variety of other solvent-sensitive phenomena, including electronic absorption bands, rates of nucleophilic displacement, rates of rearrangement and positions of keto–enol equilibria. We now find that Ω-values, derived from the product distributions (Table I) in the cyclopentadiene–methyl acrylate addition, also serve as measures of solvent polarity.

The linear relationship between $\Omega_{25°}$ and **Z** is illustrated in Fig. 5; it has the form shown in eq. 6

$$Z = 71.7\,\Omega_{25°} + 22.1 \qquad (6)$$

where the units of **Z** are kcal./mole and Ω is a dimensionless number. The correlation coefficient (r) is 0.972. A **Z**-value for 1,2-dimethoxyethane is not included in Kosower's list,[16] but is predicted by the correlation of the other nine solvents for which both **Z** and Ω-values are known to be 61.7. In a direct spectrophotometric determination of **Z** for 1,2-dimethoxyethane, we find the value 62.1. The correlation of Fig. 5 predicts **Z**-values from Ω-values with a probable error of 1.2 kcal./mole in **Z**; it may be useful, therefore, in deriving Z-values in cases where **Z** is difficult to measure directly because of absorption by the solvent in the region of the charge-transfer band. Thus, **Z** for nitromethane is predicted by eq. 6 to have the value 71.2.

In correlating **Z**-values, $\Omega_{25°}$ is about as good as log k_{ion}. The latter parameter is linear in **Z** with $r = 0.971$.

A correlation of Ω with **Y** is prevented by the lack of Ω-values in the mixed water–organic solvents from which most of the **Y**-values are taken. As might be expected, however, $\Omega_{75°}$ does correlate log k_{ion}, at least roughly. For the eight solvents the measurements cover in common (methanol, ethanol, acetic acid, nitromethane, acetonitrile, dimethylformamide, pyridine and acetone), $r = 0.936$; the data conform to eq. 7, with the indicated least squares slope and intercept being dimensionless.

$$\log k_{\text{ion}} = 10.8\,\Omega_{75°} - 10.5 \qquad (7)$$

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[16] (a) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958); (b) E. M. Kosower, J. A. Skorcz and W. M. Schwarz, Jr., *ibid.*, **82**, 2188 (1960); (c) E. M. Kosower and J. A. Skorcz, *ibid.*, **82**, 2195 (1960).

[17] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); **79**, 1597, 1602, 1608 (1957); S. Winstein, A. H. Fainberg and E. Grunwald, *ibid.*, **79**, 4146 (1957).

[18] S. G. Smith, A. H. Fainberg and S. Winstein, *ibid.*, **83**, 618 (1961).

The logarithms of the rate constants for Curtius rearrangement of benzoyl azide in a number of solvents[19] are linear[18] in log k_{ion}. The correlation,[18] which covers the solvents, acetic acid, nitromethane, acetonitrile, pyridine, ethyl acetate and methyl ethyl ketone (the latter apparently is correlated[18] *vs.* log k_{ion} for acetone), is quite rough ($r = 0.881$). Ω is a more satisfactory parameter for these data, giving the correlation of eq. 8 with $r = 0.987$ for the solvents acetic acid, acetonitrile, nitromethane, pyridine and triethylamine. The value of log

$$\log k_{\text{rearr}} \text{ at } 65° = 2.55\,\Omega_{65°} - 2.08 \qquad (8)$$

k_{rearr} for methyl ethyl ketone is not used in the correlation, but nevertheless is well approximated by using $\Omega_{65°}$ for acetone in eq. 8; this gives a calculated log k_{rearr} of -0.67 which is to be compared with the observed[19] value of -0.64. (The units of k_{rearr} are hr.$^{-1}$.)

Each of the three scales of solvent polarity (**Z**, log k_{ion} and Ω) has practical advantages and shortcomings in application to correlations of solvent effects. The most serious drawback to the Ω scale is the difficulty of making measurements in aqueous solvents. On the other hand, the miscibility of the reagents with most other organic liquids makes it possible to extend the range of measurements further toward the non-polar region than is possible with log k_{ion} or can be achieved only by the use of secondary scales with **Z**. Further, Ω is conveniently measurable over a considerable temperature range; the data already at hand (Table I), supplemented by extrapolated or interpolated values, allow Ω to be compared with other solvent-sensitive properties at identical temperatures.

The most striking aspect of the parallelism between **Z**, log k_{ion} and Ω is the persistence of the order of polarity despite the drastic variation in the energy scale of the phenomena being observed: **Z** changes by about 24 kcal./mole in the solvent range isoöctane–methanol, $-2.3\ RT$ log k_{ion} changes by about 7 kcal./mole between ether and methanol, while $-2.3\ RT\,\Omega$ changes by about only 0.5 kcal./mole between decalin and methanol. In this respect, a set of solvents behaves like an elephant, which can lift a log or a peanut with equal dexterity.

Experimental

Solvents.—**Ethanol** was prepared by distilling commercial "100%" ethanol from magnesium ethoxide according to Fieser[20a]; it had b.p. 78.5°. **Acetic acid** was prepared from commercial reagent grade glacial acetic acid by successive distillation from potassium permanganate and triacetyl borate[20b]; it had b.p. 118°. **1,2-Dichloroethane** was prepared from Matheson, Coleman and Bell reagent grade material by distillation from phosphorus pentoxide[20c]; it had b.p. 84–85°. **1,2-Dimethoxyethane** (Matheson, Coleman and Bell reagent grade) was intermittently shaken with sodium dispersion for 2 days, decanted, and distilled from calcium hydride; it had b.p. 84–85°. **Dimethylformamide** (Eastman Kodak Co.) was stored over potassium hydroxide pellets for 3 days, decanted, passed through Linde Type 4A molecular sieve pellets,[18] and distilled at atmospheric pressure; it had b.p. 153°. **Nitromethane** was purified from commercial (Matheson, Coleman and Bell) material according to Smith, Fainberg and Winstein[18] by preliminary washing with sodium bicarbonate, sodium bisulfite, water, 5% sulfuric acid, water and sodium bicarbonate. After storage over calcium sulfate and percolation through powdered Type 4A molecular sieve, it was distilled at reduced pressure. **Pyridine**, b.p. 115°, was prepared by passing the Baker and Adamson reagent through Type 4A molecular sieve[18] and distillation. **Triethylamine**, b.p. 89.5°, was prepared by storage of Matheson, Coleman and Bell material over Type 4A molecular sieve and distillation. **Acetone**, b.p. 56.5°, was obtained by storage of Baker and Adamson reagent grade material over Type 4A molecular sieve and distillation from fresh molecular sieve.[18] **Decalin**, b.p. 68–69° (25–30 mm.), 57.6% *cis*, 42.4% *trans* by vapor chromatography, was prepared by washing Eastman practical grade "*cis*-decalin" with 7% sulfuric acid, passage through silica gel, distillation, storage over Type 4A molecular sieve pellets, and distillation. **Acetonitrile** was heated at reflux for 2 days with phosphorus pentoxide, distilled, stored over Type 4A molecular sieve pellets, and re-distilled; it had b.p. 82°. **Methanol** was the Baker and Adamson absolute A.C.S. grade used without further purification. The solvents (excluding methanol, which was used as solvent for most of the titrations) were inert to Karl Fischer reagent by the criteria of Smith, *et al.*[18] In the case of decalin, dry chloroform was used as solvent for the Karl Fischer titration.

Reactants.—Dicyclopentadiene (Matheson, Coleman and Bell technical grade) was cracked and slowly fractionated through a vacuum-jacketed 12-inch Vigreux column by distillation at atmospheric pressure. Cyclopentadiene was collected at 40–40.5°, and allowed to re-dimerize by storage over calcium sulfate. The monomer was prepared as needed by re-cracking the dimer and collected at 40.0°. **Methyl acrylate**, b.p. 78–78.5°, and **methyl methacrylate**, b.p. 98–98.5°, were distilled from commercial products through a short Vigreux column immediately before use. **Methyl** *trans*-**crotonate**, b.p. 118°, $n^{25}\text{D}$ 1.4228, was prepared by heating freshly-recrystallized *trans*-crotonic acid (from a Matheson, Coleman and Bell product), m.p. 72–73°, with methanol and sulfuric acid for 18 hours. After concentration of the mixture, dilution with water, extraction with ether, treatment with a small amount of hydroquinone, washing with bicarbonate and water, and drying over magnesium sulfate, the product was distilled through a 1-foot Widmer column. It was vapor chromatographically homogeneous on a 6-foot tri-(β-cyanoethoxy)-propane column.

Identification and Analysis of Products.—Authentic samples of the 5-norbornene-2-carboxylic acid methyl esters IIIa and IVa were prepared from the pure acids[10,21] with diazomethane; similarly, the two methyl 5-norbornene-2-methyl-2-carboxylates IIIb and IVb were prepared from the corresponding pure acids[7a,21b]; methyl 5-norbornene-3-*exo*-methyl-2-*endo*-carboxylate (IIIc) was prepared from the pure *endo*-acid[8b,22]; a sample enriched in the *exo*-ester was obtained from the acidic fraction of the iodolactone separation.[22] The identification of the vapor chromatographic peaks of the components of a reaction mixture was made by co-chromatography with an appropriate authentic sample. The analyses were carried out gas chromatographically with the Perkin–Elmer 154C instrument. Most of the determinations employed a 6 ft. × 1/4 inch tri-(β-cyanoethoxy)-propane-on-Chromosorb column, although occasionally tetrahydroxyethyl-ethylenediamine[12] or Carbowax 400 or 1500 were used. Helium at a flow rate generated by pressures of about 5–10 p.s.i. was the carrier gas in all instances; the column temperatures were maintained at a convenient level, which was usually about 100–120°. The effluent gas was monitored with a thermistor thermal conductivity cell. Clean separation of the isomers was achieved in all cases. The proportions of isomers were determined from the ratio of the planimetric areas of the peaks. In the acrylic series, a correction for the difference in the thermal conductivity of the isomers was necessary. The correction factor, determined from chromato-

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[19] M. S. Newman, S. H. Lee and A. B. Garrett, *J. Am. Chem. Soc.*, **69**, 113 (1947).

[20] (a) L. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Inc., Boston, Mass., 1955, p. 286. (b) P. 281. (c) P. 288.

[21] (a) J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4083 (1959); (b) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff and D. Willner, *ibid.*, **83**, 3986 (1961).

[22] S. Beckmann and R. Mezger, *Chem. Ber.*, **90**, 1559 (1957).

grams of mixtures of known composition, was given by true fraction of *endo* isomer = 1.03 × apparent fraction of *endo*. In the methacrylic and *trans*-crotonic series, no correction was needed. The peak areas on an individual chromatogram, and the relative areas on separate chromatograms of a given mixture, were sufficiently reproducible to allow analysis of a component with an absolute variation of about 0.1% in the absolute value of the % composition. Parallel additions of the same components under identical conditions were reproducible to about the same precision.

Diels–Alder Additions.—Temperature control at 30° and 26° was maintained to ±0.05° with a thermostat. At 3°, a refrigerated compartment and at 66° and 56°, boiling methanol and acetone vapor baths controlled temperatures to ±0.5°. At 0°(±1°) and −35°(±3°) appropriate freezing mixtures were used; at 139 ±1° xylene, and at 170 ± 1°, phenetole were used as boiling vapors. For runs at $\leqq 30°$, separate solutions of the reagents in the appropriate solvent were brought to thermal equilibrium, mixed and re-immersed in the thermostat. For runs at 56°, 66° and 100°, 2 ml. of cyclopentadiene was sealed in a thin-walled glass bulb. This was placed in a sturdy test-tube, covered with a solution of 2 ml. of the dienophile in 15–20 ml. of the solvent, and the whole inserted in the vapor-bath. After temperature equilibrium had been reached, the cyclopentadiene bulb was crushed with a clean glass rod and the reaction allowed to proceed. For the runs at 139° and 170°, where loss of dienophile by evaporation during the attainment of temperature equilibrium was excessive, the experiments were performed with a magnetically controlled break-seal device (designed by Mr. A. Remanick of this Laboratory). Into the apparatus was sealed a thin-walled bulb long enough to reach into the compartment containing the dienophile solution. A glass rod, onto which was sealed a small iron bar, rode in a track and was held away from the thin wall with a magnet. Diene solution was placed in the bulb, dienophile solution in the compartment, the whole apparatus was sealed off and brought to temperature in the vapor bath. The magnet was then removed, whereupon the heavy rod dropped, smashing the bulb wall and delivering the diene into the dienophile solution.

The time necessary to achieve convenient yields of products varied from 0.5 hour to several days, depending upon the temperature and dienophile. Initial concentrations of the reactants were in the range 0.5–1.5 *M*.

The proportions of isomers were strictly independent of the yield of products and of the proportions of reactants used initially. This demonstrates that fractionation of the adducts by preferential reaction of one of a pair of adduct isomers with excess cyclopentadiene was not a factor. The product ratio was unchanged by the incursion of any thermal isomerization at temperatures up to 139°. This was demonstrated by the recovery of pure *exo* adduct uncontaminated by even a trace of *endo* when pure *exo*-5-norbornene-2-carboxylic ester was heated at 139° in decalin; the equilibrium mixture is[13] about 1:1 *endo:exo*. Change of the product composition of the adducts with α-hydrogen (IIIa, IIIc, IVa, IVc) by epimerization in the basic solvents pyridine and triethylamine was also not a factor. Samples of adduct mixtures IIIa–IVa and IIIc–IVc were kept in these solvents for reaction periods and at temperatures corresponding to those under which the additions were carried out. A sample of the test mixture was kept without solvent under the same conditions as control. The isomer compositions as determined by vapor chromatography are given in Table III. The IIIa–IVa mixture given in Table III is *not* an equilibrium mixture.[12] Any isomerization in the IIIc–IVc mixture would have led to a mixture of four different adducts—two *cis* and two *trans*. There was no indication in the vapor chromatograms of any substance other than IIIc and IVc.

TABLE III

EPIMERIZATION EXPERIMENTS

Isomer mixture	Solvent	Temp., °C.	Recovd., % N	Recovd., % X
IIIa–IVa	None	30	74.8	25.2
IIIa–IVa	Pyridine	30	74.8	25.2
IIIa–IVa	Et_3N	30	74.8	25.2
IIIc–IVc	None	30	21.0	79.0
IIIc–IVc	Pyridine	30	21.0	79.0
IIIc–IVc	Et_3N	30	21.2	78.8
IIIc–IVc	None	66	21.1	78.9
IIIc–IVc	Pyridine	66	21.1	78.9
IIIc–IVc	Et_3N	66	21.1	78.9

The products from the additions and control runs were worked up (with the exceptions indicated below) by evaporation of the reaction mixture to a small volume *in vacuo* and bulb-to-bulb distillation of the residue *in vacuo*. In the case of solvent decalin, which interfered with the analysis when present in large quantity, the products were extracted with methanol. A control experiment showed that no fractionation of products occurred during this procedure. Acetic acid and dimethylformamide also interfered with the analyses. The reaction mixtures in these cases were diluted with water, extracted with ether, washed with water, dried over magnesium sulfate, evaporated and distilled.

Direct Determination of Z-value for 1,2-Dimethoxyethane.—The absorption spectrum of 1-ethyl-4-carbomethoxypyridinium iodide in 1,2-dimethoxyethane was determined in the region of the long wave length band by the method of Kosower.[16a] The maximum occurred at 4607 ± 4 Å. (average of four scans); Z = 62.1 kcal./mole.

COMMUNICATIONS TO THE EDITOR

CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS BY PENTACYANOCOBALTATE(II)

Sir:

The absorption of molecular hydrogen by aqueous potassium cyanocobaltate(II) was first reported by Iguchi in 1942[1]; the chemistry involved in this reaction has been elucidated recently[2] and the structure of the reduced complex has been formulated as the hydrido-ion, $[Co^{III}(CN)_5H]^{3-}$.

The possibility of utilizing this hydrogen-activating system for the reduction of organic compounds appears to have been neglected except for the early observation by Iguchi[3] that increased quantities of hydrogen were absorbed in the presence of sodium cinnamate or isatin; however, no identification of products was carried out.

We wish to report the catalytic hydrogenation of a variety of organic substrates by means of this cobalt(II) coördination compound in aqueous solution. As shown in the table, the types of compounds which have been reduced include aliphatic dienes,[4] conjugated aromatic olefins, α,β-unsatu-

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(1) M. Iguchi, *J. Chem. Soc. Japan*, **63**, 634 (1942).

(2) N. Kelso King and M. E. Winfield, *J. Am. Chem. Soc.*, **83**, 3366 (1961), and references therein.

(3) M. Iguchi, *J. Chem. Soc. Japan*, **63**, 1752 (1942).

(4) It has been brought to our attention that German Patent