as applied to the reaction of propylene + CO + H_2O to give n- and isobutyraldehyde are given in Table I, together with comparable data using $Fe(CO)_5$. (It should be noted that the exact nature of the catalyst species present under the reaction conditions has not yet been established.)

If the polynuclear carbonyls catalyze the reaction in a manner similar to that described for $Fe(CO)_5$, then, in the absence of olefin, they could also be catalysts for the generation of hydrogen via the water gas shift reaction; i.e., $CO + H_2O \rightarrow CO_2 + H_2$. Hydrogen formation would be expected to occur via the steps given in eq 3. This catalytic generation of hydrogen is indeed observed; in the final column of Table I is given the efficiency of the generation of hydrogen under the same conditions as used in the hydroformylation reaction except for the exclusion of olefin.[18]

$$M \xrightarrow{CO} MCO \xrightarrow[-CO_2]{OH^-} MH^- \xrightarrow{H_2O} MH_2 \rightleftarrows M + H_2 \quad (3)$$
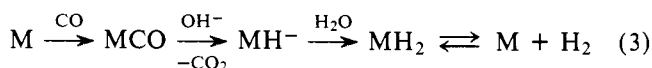
From Table I it is seen that catalysts which are efficient for the hydroformylation reaction are also efficient for the water gas shift reaction, but, not surprisingly, the converse is not always true.

Further studies directed at the development of catalysts for these and other reductions using $CO + H_2O$ in place of H_2 will be reported later.

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Regarding a Generalized Scale of Solvent Polarities[1]

Sir:

We have recently developed a scale of solvent "polarities", π, based on the solvent-induced solvatochromic shifts of seven

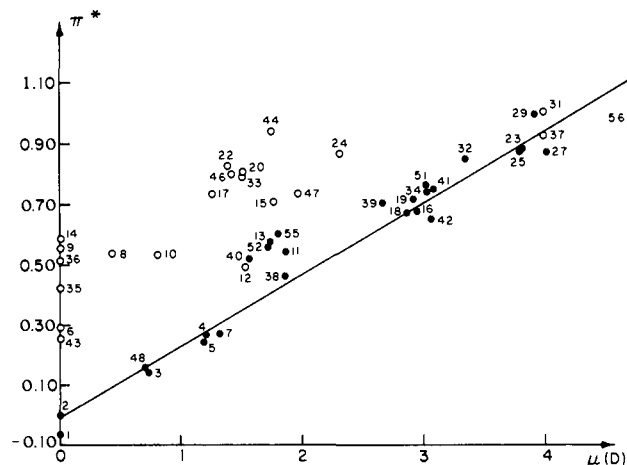**Figure 1.** π^* vs. dipole moment of the solvents. Closed circles are for select solvents, $\pi \equiv \pi_c^*$. Open circles are for other solvents; cf. footnote 24.

Table I. Select Solvents for Use in Solvent Polarity Studies with Eq 1

Solvent[a]	$\pi (\equiv \pi^*)$[b]	Solvent[a]	$\pi (\equiv \pi^*)$[b]
Hexane, heptane (1)	−0.081	Butanone (16)	0.674
Cyclohexane (2)	0.000	Acetone (18)	0.683
Triethylamine (3)	0.140	Ethyl chloroacetate (39)	0.704
Tri-n-butylamine (48)	0.162	Triethyl phosphate (19)	0.715
Di-n-butyl ether (5)	0.239	Acetic anhydride (34)	(0.747)[5]
Diisopropyl ether (4)	(0.271)[5]	Cyclohexanone (41)	0.750
Diethyl ether (7)	0.273	Cyclopentanone (51)	0.756
Butyl acetate (38)	0.460	Nitromethane (32)	0.848
Tetrahydropyran (40)	0.513	Acetonitrile (50)[c]	(0.86)[5]
Ethyl acetate (11)	0.545	γ-Butyrolactone (27)	0.873
Methyl acetate (52)	0.556	Dimethylformamide (25)	0.875
Methyl formate (55)	(0.596)[3]	Dimethylacetamide (23)	0.882
Tetrahydrofuran (13)	0.576	Sulfolane (56)	(0.988)[4]
Tri-n-butyl phosphate (42)	0.653	Dimethyl sulfoxide (29)	1.000

[a] The solvents are numbered as in ref 2 and Figure 1. [b] The π^* values are classified as in ref 2 primary values obtained from at least six different data sets, and secondary values in parenthesis, for which 3 to 5 π_i^* have been averaged (indicated by superscript). [c] The π value indicated for CH_3CN from χ_R, P, E_K, log k, and G values is 0.86 ± 0.02, and this value fits well on the correlation with μ, Figure 1. We have noted that H-bonding contributions are likely to be involved with A_N and E_T values for CH_3CN (giving apparent π^* 0.99). The smaller π^* value of 0.713 is unaccounted for at the present time.

different indicators.[2] It was shown that this scale gives a very satisfactory quantitative description of the solvent effects on more than forty $\pi \rightarrow \pi^*$ and p $\rightarrow \pi^*$ electronic transitions.

We have critically examined the π^* values in the light of other empirical solvent scales based upon a variety of spectroscopic and/or chemical reactivity data.[3] Eight of the most widely used "polarity" scales have been chosen: Dimroth's E_T,[4] Brooker's χ_R,[5] Lassau and Junger's log $k(Pr_3N + MeI)_{20 °C}$,[6] Walther's E_K,[7] Knauer and Napier's A_N,[8] Allerhand and Schleyer's G,[9] Taft's P,[10] and Brownstein's S.[11] No general correlation of useful precision exists between these scales (Figure 3 of ref 2 illustrates a typical case).

We wish to report, however, that, for a group of selected solvents (Table I), all scales give very closely equivalent re-

Table II. Correlation Results

Correlation[a]	n	R	Correlation	n	R	Correlation	n	R
μ vs. π^*	23	0.985[b]	E_K vs. log k	7	0.985	E_T vs. μ	12	0.979
E_T vs. π^*	12	0.987	A_N vs. log k	6	0.970	χ_R vs. μ	16	0.987
χ_R vs. π^*	16	0.987	G vs. log k	5	0.997	log k vs. μ	13	0.958
log k vs. π^*	13	0.985	P vs. log k	8	0.985	log k vs. μ	12[c]	0.981
E_K vs. π^*	9	0.977	S vs. log k	7	0.998	E_K vs. μ	9	0.983
$A_N{}^d$ vs. π^*	6	0.978	A_N vs. E_K	6	0.981	A_N vs. μ	6	0.997
G vs. π^*	8	0.993	G vs. E_K	e	e	G vs. μ	8	0.987
P vs. π^*	12	0.989	P vs. E_K	7	0.994	P vs. μ	12	0.957
S vs. π^*	10	0.981	S vs. E_K	5	0.969	P vs. μ	11[f]	0.972
χ_R vs. E_T	10	0.987	G vs. A_N	e	e	S vs. μ	10	0.968
log k vs. E_T	9	0.988	P vs. A_N	6	0.986	log k vs. χ_R	11	0.966
E_K vs. E_T	7	0.982	S vs. A_N	e	e	E_K vs. χ_R	7	0.969
A_N vs. E_T	e	e	P vs. G	6	0.978	A_N vs. χ_R	6	0.985
G vs. E_T	5	0.996	S vs. G	6	0.996	G vs. χ_R	6	0.997
P vs. E_T	7	0.986	P vs. S	8	0.987	P vs. χ_R	9	0.966
S vs. E_T	7	0.950				S vs. χ_R	10	0.968

[a] The number of possible different correlations are 45 (i.e., $N(N-1)/2$). [b] The inclusion of points 13, 40, 52, and 55 (solvents of particularly small steric requirements), which are clearly above the line, brings r down to 0.965 and raises σ to 0.079 (compared to 0.985 and 0.057). This result suggests that some steric contributions are included in π values; cf. also ref 9. [c] Excluding point 56. [d] We have used the values for di-*tert*-butyl nitroxide, A_N (1) of ref 8. [e] These correlations involve less than five points and are not given. [f] Excluding point 55.

sults[12] (Table II; available data gave $r = 0.97$–0.99). The elimination of highly specific effects such as hydrogen bonding and other contributions from aromatic and polyhalogenated solvents is required.[13] When these conditions are met, the following simple equation (1) prevails

$$(XYZ)_c = XYZ_0 + s\pi \tag{1}$$

where $\pi = (\pi^*)_c$, $(XYZ)_c$ is the value of the property in one of the select solvents, XYZ_0 is the corresponding value of the property in cychohexane (chosen as the reference solvent), and s measures the susceptibility to "polarity" effects. The general structural criterion for the elimination of specific contributions to the measured property solvent effect appears to be aprotic, nonpolyhalogenated, or polysubstituted molecules of the aliphatic series having a single predominant group dipole moment. Our contention is strongly supported by the excellent correlation found between π (or other "polarity") values and the molecular dipole moments[15-17] (Figure 1). This approach, of course, is necessarily an approximation since the dipole moments of the solvent molecules which interact with the solute are likely to differ somewhat from the values determined in the gas phase or in nonpolar solvents. It is of particular importance to note that the widely used dielectric function ($\epsilon - 1)/(2\epsilon + 1)$ (ϵ is the dielectric constant of the solvent) gives only a correct trend of the variation of π but fails to give a good quantitative correlation ($\sigma = 0.13$ and $r = 0.909$). The polarizability of the solvent, as measured for example by the function $f(n) = (n^2 - 1)/(2n^2 + 1)$ also plays a role (see, e.g., ref 3b, 18); the small but distinct difference between the π values for cyclohexane and n-hexane is likely a consequence thereof. However, for the entire set of select solvents, the variations of $f(n)$ are only ±0.024, around an average value of 0.196, which indicates that the contribution from polarizability is nearly constant throughout the series.

These results favor the notion that, in spite of the very different nature of the properties here considered,[19] the "aprotic polar solvent effects" are mostly determined by solvent–solute dipolar interactions rather than by a bulk effect of the solvent acting as a continuous dielectric.[20] Indeed, for the select solvents, the elusive idealized solute-independent solvent polarity parameter is indicated to be the molecular dipole moment. Theoretical justification of this result comes from application of the Block–Walker modification[21] of Onsager's reaction field theory.[22] The solvent reaction field for a solute of fixed dipole moment is found to be directly proportional (to good approximation) to the dipole moment of the solvent molecule.[23]

We recommend the use of the select solvents in Table 1 in studies of effects of aprotic polar solvents (at least eight of these covering the range of 0–1.0 in π value), since the results should prove highly beneficial for comparisons and interpretations of the susceptibilities of chemical and physical properties to solvent polarity.[24]

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$$XYX = XYZ_0 + s(\pi^* + d\delta) \tag{2}$$

where the $d\delta$ term is a measure of enhanced polarizability and other effects inherent to those solvents. $d = 0.0$ for the select solvents, $d = 0.50$ for polyhalogenated solvents, and $d = 1.00$ for aromatic solvents.[14]
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(16) (a) It can be noticed that the point for dioxane (9) in Figure 1 is too far off the line. This likely reflects the fact that, although its overall dipole moment is nil (because of the symmetry of the molecules), the bond moments are not zero (they can be estimated at $\sim$1.25 D with the bond moment for O–CH$_3$ being 1.12 D[16b] and the C–O–C bond angle, 112.45° [16c]). (b) "Structure of the Molecules and the Chemical Bond", Y. K. Syrkin and M. E. Diatkina, Ed., Dover Publications, New York, N.Y., 1964, p 206. (c) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).
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(19) Four scales are based upon solvent effects on electronic transitions, one on IR stretching vibration, one on ^{19}F NMR shifts, one on the nitrogen hyperfine splitting constant of nitroxides, one of the kinetics at 20 °C of a selected Menschutkin reaction, and one is a composite of spectroscopic, kinetic, and thermodynamic properties.

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Table I. Incorporation of [5-^{2}H]Mevalonates into **1**

Mevalonate (mmol)	**1**, mg	Incorpn, %[a]	Enrichment, %
[5-^{2}H$_2$] (8.1)	70	1.1	5.2
(5R)- (4.1)	30	0.55	3.0
(5S)- (4.6)	30	1.1	5.7

[a] Based on (3R)-mevalonate.

Scheme II

Application of Deuterium Magnetic Resonance to Biosynthetic Studies. 2. Rosenononolactone Biosynthesis and Stereochemistry of a Biological S_N2' Reaction

Sir:

The introduction of ^{2}H NMR as a biosynthetic technique[1-4] offers a powerful tool for the examination of subtle stereochemical questions heretofore accessible only with the use of tritiated substances and lengthy degradation procedures. To demonstrate the utility of this new method, potential problems of sensitivity and resolution must be overcome. In exploring the limits of ^{2}H NMR we have examined the stereochemistry of the formation of ring C in the biosynthesis of the fungal diterpene rosenononolactone (**1**).

The classic studies of Arigoni[5] and Birch[6] and the subsequent work of Hanson[7] have established many of the details of the biosynthesis of rosenononolactone. According to the accepted Scheme I, electrophilic cyclization of geranylgeranyl pyrophosphate, formed from four molecules of mevalonate, gives the bicyclic labda-8(17),13-dien-15-yl pyrophosphate (**2**). A second cyclization involving allylic displacement of the terminal pyrophosphate and concomitant hydride and methyl migrations generates ring C. The exact timing of lactone formation is as yet unknown.

The allylic displacement by which ring C is formed may formally be considered an S_N2' process. To determine the stereochemistry of this process one must answer two questions. (1) Which face of the 13,14 double bond of **2** is attacked by the terminal methylene? From the known absolute configuration of **1**,[8] it follows that cyclization occurs on the *si* face of the allyl system. (2) In which sense, syn or anti, does the pyrophosphate depart? This question may be answered by observing which
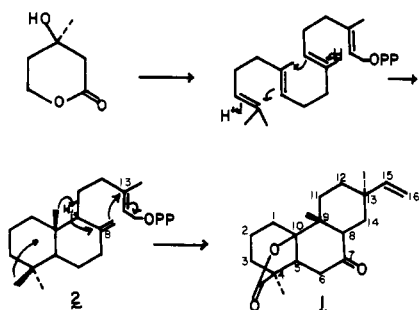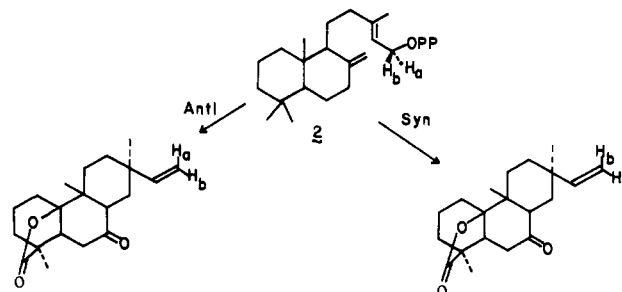
Scheme I

of the prochiral hydrogens at C-16 of **2** becomes cis (H-16Z) and which becomes trans (H-16E) to the C–C bond in the terminal vinyl group of rosenononolactone (Scheme II). We describe below the solution of this problem using ^{2}H NMR.

Analysis of the 270-MHz ^{1}H NMR of rosenononolactone (CDCl$_3$) allows, inter alia, the following proton assignments. (1) The vinyl group appears as an ABX pattern, $J_{AB} = 1.0$ Hz, $J_{AX} = 17.5$ Hz, $J_{BX} = 10.6$ Hz. The individual protons were assigned on the basis of known cis and trans coupling constants for olefinic hydrogens:[9] H-16Z = 4.97 ppm, H-16E = 4.90 ppm, H-15 = 5.80 ppm. (2) The methylene protons adjacent to the ketone may also be assigned from analysis of coupling constants: H-6β = 2.12 ppm, H-6α = 2.39 ppm ($J_{H-6\alpha-H-6\beta}$ = 13.7 Hz, $J_{H-5-H-6\beta}$ = 16.5 Hz, $J_{H-5-H-6\alpha}$ = 3.7 Hz).

A series of specifically deuterated substrates, sodium [5-^{2}H$_2$]mevalonate,[10] (5R)-[5-^{2}H]mevalonate,[11] and (5S)-[5-^{2}H]mevalonate,[11] each mixed with [2-^{14}C]mevalonate to allow calculation of enrichments, was fed to four-day-old cultures of *Trichothecium roseum* (ATCC 8685).[16] After an additional 7 days the mycelia were harvested by filtration, dried, powdered, and extracted with hexane for 24 h. The concentrate was triturated with pentane and the residue recrystallized seven–ten times from methanol to give rosenononolactone which was free of persistent traces of isorosenononolactone and small quantities of highly deuterated impurities. These experiments are summarized in Table I.

Each of the biosynthetically deuterated samples was analyzed by ^{2}H NMR.[17] Rosenononolactone (**1A**), derived from feeding of [5-^{2}H$_2$]mevalonate, shows a signal at 4.97 ppm with a shoulder at ~4.90 ppm. A sample of authentic [16-^{2}H$_2$]-rosenononolactone (**1D**)[19] gives an identical spectrum in the olefinic region as does a mixture of *cis*- and *trans*-[16-^{2}H]-rosenononolactone (**1E**).[22] The terminal methylene signals, separated by only 0.07 ppm (3 Hz), are therefore not clearly resolved. From the peak shape it was inferred that the observed signal results from the superposition of two resonances of unequal line width, the higher field signal being the broader. This conclusion was confirmed in the sequel (see below). The spectrum of **1A** also has the expected signals at 2.34 and 2.08 ppm corresponding to H-6α and H-6β, respectively. The remaining signals at 1.89, 1.71, and 1.42 ppm are presumably due to deuterium at C-2 and C-11. Rosenononolactone (**1B**), derived from (5R)-[^{2}H$_1$]mevalonate exhibits a signal at 5.01 ppm ($\nu_{1/2}$ = 3.5 Hz) while **1C** (from (5S)-[^{2}H$_1$]mevalonate) gives rise to a signal at 4.92 ppm ($\nu_{1/2}$ = 7.5 Hz). The positions of the observed signals were confirmed by doping each sample with ~$^1/_3$ part of **1E**: the signal from **1B** plus **1E** shows an up-