amides have been made.[18,19]

It has been pointed out that nucleofugality in 1,2-elimination reactions has been little studied.[20,21] This is because it is difficult to separate unambiguously deprotonation from departure of the leaving group.[20] In the present study, these processes have been separated in the few examples studied and we suggest that 4-substituted azetidin-2-ones could be useful probes to determine the nucleofugalities of diverse nucleofuges.

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Registry No. **1**, 28562-53-0; **4**, 31898-90-5; **5**, 31898-84-7; **6**, 31898-86-9; **7**, 31898-87-0; **8**, 93280-78-5; **9**, 93280-79-6; **10**, 93280-80-9; **11**, 93280-81-0; D_2, 7782-39-0.

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Liquid and Supercritical Carbon Dioxide as Organic Solvents

John A. Hyatt

Research Laboratories, Eastman Chemicals Division, Eastman Kodak Company, Kingsport, Tennessee 37662

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The nature of carbon dioxide in its liquid and supercritical states as a solvent for organic compounds was explored. Visible spectroscopy of solvatochromic dyes, infrared spectroscopy of ketones and pyrrole, and the exo:endo ratio of a Diels–Alder reaction in CO_2 solutions were employed as probes of solvent polarity. It was found for both liquid and supercritical CO_2 that $E_T(30) \simeq 33.8$ kcal/mol and $\Omega \simeq 0.50$; π^* is near −0.5. It is concluded that CO_2 in these states behaves very much like a hydrocarbon solvent with very low polarizability.

The central importance of solvents in chemical technology is well recognized. Indeed, scarcely a chemical process exists in which a solvent is not intimately involved in both synthesis and separation stages.[1] In most organic reactions, choice of solvents is of pivotal importance; often the solvent is the major component. The search for new solvents having wider-ranging properties continues to be a significant part of organic research.

The use of liquified gases, such as NH_3, SO_2, and HF, as reaction media is well established, and the question of whether liquified carbon dioxide has properties that make it suitable for use as a solvent in organic chemistry is a reasonable one. Carbon dioxide is readily available, inexpensive, nontoxic, nonflammable, chemically inert under many conditions, environmentally acceptable, and liquefiable at reasonable pressures.

The purpose of this paper is to present results of studies designed to assign a place for CO_2 in the series of conventional organic solvents. Literature data on the solubility of organic compounds in compressed CO_2 are augmented and summarized, and the question of the effective polarity of liquid and supercritical CO_2 is addressed. Although one might a priori expect CO_2 to be similar in CS_2 or, perhaps, to ketone solvents, it was thought that investigation of the spectroscopic properties of solvatochromic materials and of the behavior of solvent-sensitive reactions in CO_2 would give a useful picture of the nature of this unconventional solvent.

Supercritical and Subcritical Phases. The critical point of carbon dioxide is at 31 °C and 73 atm. Below this point, liquid CO_2 can be maintained under relatively modest pressure (about 950 psi at 25 °C). Above 31 °C, no amount of pressure will serve to liquify CO_2—there exists only the supercritical fluid phase that behaves as a gas, although when highly compressed, this fluid is denser than liquid CO_2 (ca. 0.47 g cm^{-1}). The subcritical liquid phase of CO_2 behaves like any other liquid; the supercritical fluid phase can also act as a solvent, but it has higher diffusivity, lower viscosity, and lower surface tension than does the liquid phase. A small but rapidly growing body of literature deals with the use of supercritical CO_2 as an extraction medium (vide infra). Current research centers upon CO_2 in the supercritical phase because it is thought to have, in general, better solvent properties than does CO_2 in the subcritical liquid phase. Indeed, the well-known solubility/pressure curve of naphthalene in CO_2 (Figure 2, ref 22b) demonstrates the type of behavior commonly encountered—solubility increases dramatically with increasing pressure above the critical point. Implicit in some current literature is the idea that the supercritical fluid phase is intrinsically different as a solvent from the subcritical liquid phase. This idea appears quite reasonable in view of the significant discontinuities in many physical properties, such as diffusivity, surface tension, viscosity, and even dielectric constant, near the critical point. But while it should be understood that supercritical CO_2 offers advantages over liquid CO_2 as a solvent (higher solubilities with increasing pressure, wider range of operating temperatures and pressures available, and density variable over a wide range), it has not been demonstrated that the solvent behavior of supercritical CO_2 is intrinsically different from that of subcritical CO_2. In fact, some recent work by Alwani has shown that the solubility of α-tocopheryl acetate in both subcritical and supercritical CO_2 increases with increasing pressure and that no significant changes in the solubility of tocopheryl acetate occur when subcritical CO_2 solutions are heated above the critical temperature at constant pressure.[2] Work is conducted in the supercritical region because useful temperatures,

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pressures, and solubility levels lie there, not because supercritical CO_2 is intrinsically a more polar solvent than subcritical CO_2.

Summary of Prior Literature. The earliest published work on CO_2 as a solvent was that of Gore in 1861;[3] he reported solubility of naphthalene and camphor and insolubility for several carboxylic acids. A number of other 19th century workers reported solubility or phase behavior of various inorganic and organic materials in liquid CO_2.[4-12] In 1906, E. H. Buchner reviewed most of the earlier work and made significant additions to the data.[13] Buchner classified CO_2-solute systems in terms of the type of two-component phase diagram obtained for the mixtures. A wide temperature range was used, and solubility determinations were qualitative—Buchner used cloud or freezing points and observations of the number of phases present to draw his conclusions.

Save for two papers by Quinn[14,15] in the 1920's, no new data on CO_2 solutions appeared until 1954, when Francis presented an extensive, quantitative study of the phase behavior of ternary systems containing liquid CO_2.[16] He reported solubility data for about 250 compounds. Several other workers reported, around 1970, results on the phase equilibria of CO_2–hydrocarbon systems over a very wide temperature and pressure range;[17-20] these studies are of interest primarily for thermodynamic and phase theory.

In the late 1970's recognition of the potential utility of compressed CO_2, both above and below the critical point, became much more widespread.[21,22] Current areas of application include the extraction or isolation of various natural products,[23] glycerides,[24] and tocopherols.[2] Related studies in which other compressed gases were used have appeared,[25] and efforts to theoretically predict the solubility properties of solutes in supercritical gas phases are under way.[26-30] The use of liquid and supercritical CO_2 as solvents for reactions, rather than for extractions, has not yet been extensively explored. Certain electrochemical reactions,[31] the polymerization of ethylene,[32] and a photoisomerization[33] have been conducted in CO_2 solution.

Table I. Selected Solubilities of Organic Compounds in Liquid CO_2

compd	solubility, wt % (22–24 °C)	ref
n-heptane	miscible	*a*
n-dodecane	miscible	*a*
n-hexadecane	8	*a*
n-tetracosane	1–2	*b*
β-carotene	0.01–0.05	*c*
p-xylene	4–25 (−46 to −16 °C)	*d*
pentamethylbenzene	17	*b*
biphenyl	2	*a*
anthracene	<0.02	*c*
benzotrichloride	2	*a*
methanol	miscible	*a*
tert-butyl alcohol	miscible	*a*
7-tridecanol	11	*b*
p-benzoquinone	7	*c*
benzophenone	4	*a*
cholestanone	1.5	*c*
methyl benzoate	miscible	*a*
diethyl phthalate	10	*a*
n-butyl hexadecanoate	3	*a*
N,N-dimethylaniline	miscible	*a*
aniline	3	*a*
diphenylamine	1	*a*
phenol	3	*a*
p-isopropylphenol	6	*a*
hydroquinone	<0.01	*c*
4-hydroxybiphenyl	0.05	*c*
α-tocopherol	1	*e*
acetic acid	miscible	*a*
phenylacetic acid	<0.1	*a*
lauric acid	1	*a*
2,4-dinitrotoluene	24	*b*
2,4-dinitrochlorobenzene	11	*b*
dicyclohexyl-18-crown-6	1	*a*
glucose	0	*b*

[a] Reference 16. [b] This work; determined by method of ref 16. [c] This work; determined by UV spectroscopy of saturated solutions. [d] Reference 19. [e] Reference 2.

Solubility of Organic Compounds in CO_2. Table I gives solubility data for a wide range of organic structural types in subcritical (liquid) CO_2. These examples were selected from a much longer series available from the literature and from work done in our laboratory; the intent is to give typical results rather than to be exhaustive. Far fewer data are available for solubilities under supercritical conditions, but the data for subcritical solutions in Table I can be used to give an idea of the supercritical solubilities. In general, for a given solute the difference in solubilities between subcritical and supercritical CO_2 are a matter of degree—often an order of magnitude or so. Seldom is a material found to be completely insoluble under subcritical conditions yet soluble in the supercritical phase.

Some generalization can be made from the large body of data from which Table I was drawn: (1) Liquid CO_2 behaves like a hydrocarbon solvent, with a few notable points of difference (e.g., methanol miscibility). (2) Liquid CO_2 does not interact strongly with typical organic weak

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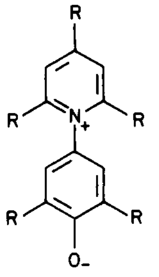
bases (e.g., anilines, pyrroles, pyridines), although it, of course, forms solid salts with aliphatic amines. (3) Liquid CO_2 has a strong homogenizing action (i.e., many pairs of immiscible or partially miscible liquids form a single phase when mixed with liquid CO_2). (4) Liquid CO_2 is a good solvent for aliphatic hydrocarbons up to at least the low C_{20}s and for most small aromatic hydrocarbons. Few polycyclic hydrocarbons show appreciable solubility. (5) Halocarbons, aldehdyes, esters, ketones, and low alcohols are freely soluble in CO_2. Higher alcohols ($>C_{10}$) are generally soluble enough for facile extraction. Glycols and glycerol have low solubility. (6) Phenols show poor solubility in CO_2, as do most anilines. Hydroquinone and other polyhydroxy aromatics are essentially insoluble. (7) Polar compounds, such as amides, ureas, urethanes, and azo dyes, exhibit poor solubility in CO_2. (8) Few materials of any structural type with molecular weights above around 500 are soluble in liquid CO_2.

Visible Spectroscopy of Organic Solutes in CO_2 Solution. The study of solubility data alone cannot give a complete picture of the nature of CO_2 as a solvent, and further characterization is desirable. The effect of a given solvent on the course of a chemical or physical change is usually rationalized in terms of the solvent's "polarity", where polarity includes the sum of all the solvent–solute interactions: coulomb, inductive, charge transfer, and hydrogen bonding. In general, the dielectric constant of a solvent does not give a good measure of solvent polarity: dielectric constant is a bulk or macroscopic property, whereas solvent–solute interactions occur at the molecular level. In practice, the effective polarity of a solvent cannot be determined by measurement of any one physical property.[34] Various empirical methods for determining solvent polarity have been developed;[34b] we have now applied several of these tests to liquid and supercritical CO_2. Kosower's scale of solvent polarity (*Z* values),[35] which is based on the position of the charge-transfer band of dissolved 4-carbomethoxy-*N*-ethylpyridinium iodide, was not applicable because of complete insolubility of the probe compound in CO_2. Similarly, direct measurement of Reichardt's molar transition energy[36] ($E_T(30)$) for CO_2 failed because of insolubility of the key negatively solvatochromic betaine dye **1**. Fortunately, the penta-*tert*-butyl betaine **2** proposed by Reichardt and Harbusch-Gornert[37] as a secondary standard for determination of $E_T'(30)$ had some solubility in CO_2, and we found the λ_{max} to be 834 nm (1000 psi, 24 °C). The absorption maximum did not shift when the sample solution in a high-pressure UV-visible cell was heated above the critical point (to 42 °C). The value λ_{max} 834 nm gives E_T' = 34.3 kcal/mol; with $E_T(30) = 1.087E_T' - 3.454$, the value = 33.8 kcal/mol is obtained for both liquid and supercritical CO_2. Examination of the $E_T(30)$ scale[37] indicates that CO_2 is in the same low polarity range as toluene, methylcyclohexane, decahydronaphthalene, and tetrachloroethylene. This result seems consistent with the solvent behavior shown in Table I.



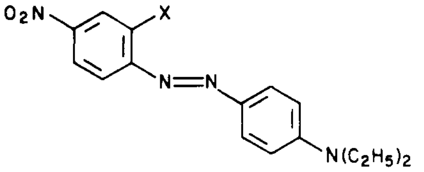
1, R = C_6H_5
2, R = *tert*-butylphenyl

Table II. Solvent Effects on Electronic Spectra of Dyes 3 and 4

solvent	$\pi\sigma^a$	dye 3 λ_{max}, nm	dye 3 ν_{max}, kK	dye 4 λ_{max}, nm	dye 4 ν_{max}, kK
CO_2 (supercritical)		429	23.31	453	22.07
CO_2 (liquid)		437	22.88	459	21.78
hexane	–0.08	451	22.17	476	21.01
cyclohexane	0.00	455	21.98	480	20.83
diethyl ether	0.27	462	21.65	493	20.28
toluene	0.54	475	21.05	500	20.00
acetone	0.71	485	20.62	513	19.49
dimethylformamide	0.88	501	19.96	525	19.04
dimethyl sulfoxide	1.00	510	19.60	530	18.86

^{a} Data of ref 39.

A second examination of the behavior of solvatochromic dyes in CO_2 solution utilized compounds **3** and **4**. Like most azo dyes, **3** and **4** exhibit a bathochromic shift of the visible charge-transfer band with increasing solvent polarity.[38] Table II gives the λ_{max} of **3** and **4** in various solvents. The λ_{max} values for **3** and **4** are linear with the Taft–Kamlet π^* scale of solvent dipolarity and polarizability.[39] From the data of Table II and ref 39, we obtain



3, X = H
4, X = CF_3

$$\nu(\mathbf{3})_{max} = 22.10 - 2.31\pi^* \text{ (kK)}$$

$$\nu(\mathbf{4})_{max} = 20.87 - 1.97\pi^* \text{ (kK)}$$

with correlation coefficients of ν = 0.985 (sd = 0.19 kK) and 0.994 (sd = 0.10 kK), respectively. By using these correlation equations one can calculate π^* values for supercritical CO_2 of –0.52 (dye **3**) to –0.60 (dye **4**); for liquid CO_2 the corresponding range is –0.34 to –0.46. These are probably the lowest π^* values seen to date; fluorocarbon π^* values are in the –0.33 to –0.41 range[40] and most hydrocarbons have π^* = 0.00 to –0.08.[39]

Refractive indices correlate with π^*; the η value of liquid CO_2 at 24 °C is 1.173,[41] which is consistent with typical fluorocarbon and hydrocarbon values of 1.27 and 1.35, respectively.[39] These data, taken with the $E_T(30)$ and Ω results (vide infra), suggest that liquid and supercritical CO_2 have dipolarities close to those of hydrocarbons, but have polarizabilities which are even lower than those of

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Table III. Solvent Effects on $\nu_{C=O}$ of Acetone[a]

solvent	$\nu_{C=O}$, cm^{-1}	$\Delta\nu$	$10^3(\Delta\nu/\nu_0)$
none (gas phase)	1736	0	0
n-hexane	1722	14	8.1
CO_2 (liquid, 23 °C)	1720	16	9.2
benzene	1716	20	11.5
chloroform	1712	24	13.8
methanol	1709	27	15.6

[a] Determined at ambient temperature on a Perkin-Elmer Model 283B Instrument. 1% concentration.

Table IV. Solvent Effects on $\nu_{C=O}$ of Cyclohexanone[a]

solvent	$\nu_{C=O}$, cm^{-1}	$\Delta\nu$	$10^3(\Delta\nu/\nu_0)$
none (gas phase)	1740	0	0
hexane	1722	18	10.3
CO_2 (liquid, 22 °C)	1718	22	12.6
CO_2 (supercritical, 41 °C)	1719	21	12.1
toluene	1712	28	16.1
chloroform	1702	38	21.8
methanol	1700	40	23.0

[a] Determined at ambient temperature on a Perkin-Elmer Model 283B Instrument. 1% concentration.

Table V. Solvent Effects on ν_{N-H} of Pyrrole[a]

solvent	ν_{N-H}, cm^{-1}	$\Delta\nu$	$10^3(\Delta\nu/\nu_0)$
none (gase phase)	3530	0	0
hexane	3506	24	6.8
CO_2 (liquid, 23 °C)	3400	130	36.8
toluene	3454	76	21.5
ethyl acetate	3400	118	33.4
diethyl ether	3356	174	49.3

[a] Determined at ambient temperature on a Perkin-Elmer Model 283B Instrument. 1% concentration.

fluorocarbon solvents. Thus CO_2 can be considered a solvent which bridges the gap in polarizability between fluorocarbons and the gas phase.

IR Spectroscopy of Solutions in CO_2. Although less well-known than the published work on UV–visible solvent shifts, solvent effects on IR spectra can be significant and informative. Bellamy et al.[42] studied solvent-induced frequency shifts of the N–H stretch in pyrrole and correlated the shifts with H bonding; Reisse and Chiurdoglu[43] studied solvent effects on C–X vibrational frequences in halocyclohexanes and correlated the shifts with axial–equatorial equilibria, and hence with solvent polarity; and Josien[44] reported similar studies on solvent effects on aldehyde and ketone C═O stretching frequencies. In view of these published studies, we thought that IR spectrophotometry of selected probe compounds in CO_2 could provide further information on the effective polarity acting on compounds dissolved in CO_2.

In order to build on the data already available, we examined the IR spectra of acetone (C═O stretch), cyclohexanone (C═O stretch), and pyrrole (N—H stretch) in CO_2 solution. The examination of the iodocyclohexane C—I vibration was precluded because of interference from the high-pressure cell IRTRAN-2 window material.

Table VI. Determination of Berson's Ω

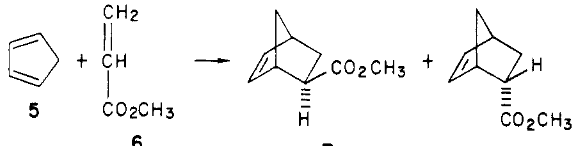
solvent	temp, °C	Ω = log (endo/exo)
heptane	23	0.43[a]
cyclohexane	24	0.47[a]
toluene	22	0.45[a]
CO_2 (liquid, 885 psi)	21	0.50[a]
CO_2 (supercritical, 1235 psi)	41	0.47[a]
pyridine	21	0.56[a]
pyridine	30	0.59[b]
acetonitrile	30	0.69[b]
dimethylformamide	24	0.68[a]
methanol	21	0.78[a]
methanol	26	0.84[b]

[a] This work. [b] Reference 42.

Results are tabulated in Tables III–V. The term, $(\Delta\nu/\nu_0) \times 10^3$, where ν_0 = gas-phase vibrational frequency in cm^{-1} and $\Delta\nu = (\nu_{\text{solvent}} - \nu_0)$, gives a convenient measure of solvent effect.[43] From the IR studies of acetone and cyclohexanone, two conclusions are warranted: (1) From the point of view of the carbonyl group of a dissolved ketone, CO_2 is similar to nonpolar hydrocarbon and halocarbon solvents. (2) Cyclohexanone dissolved in subcritical CO_2 does not experience any significant change in environment when heated above the critical temperature.

For pyrrole in solution, CO_2 behaves like a solvent in the ether to ethyl acetate range. This behavior is inconsistent with both the ketone IR and the dye UV–visible data and may be due to a small but significant degree of N–H hydrogen bonding to CO_2. Thus CO_2 may be in the ether–ethyl acetate hydrogen bond basicity range.

Determination of Berson's Ω Value for CO_2. Study of the behavior of a well-known, solvent-sensitive reaction conducted in liquid and supercritical CO_2 solution should provide a useful complement to the spectroscopic evaluations described. A model reaction well suited to the CO_2 system appeared to be the Diels–Alder reaction of cyclopentadiene, **5**, and methyl acrylate, **6**. This reaction produces a mixture of methyl *exo*- and *endo*-norbornenecarboxylates (**7** and **8**, respectively) in high yield at a convenient rate at ambient temperature.



5 **6** **7** **8**

In 1962 Berson, Hamlet, and Mueller[45] reported that the 8:7 product ratio for this reaction is kinetically determined and varies with solvent polarity. These workers studied this reaction in 12 different solvents and defined a dimensionless parameter Ω for each solvent, where Ω = log (endo/exo).

It was demonstrated that Ω is linear in *Z* (Kosower's spectral-based solvent parameter[35]), in log k_{ion} (Winstein's parameter based on rates of ionization of *p*-methoxyneophyl tosylate in aprotic media),[46] and in logs of rate constants of the Curtius rearrangement of benzoyl azide.[47] Results, in general, were consistent with the Kirkwood–Onsager theory.[48,49] Thus it appeared that determination of Ω would give a good, operational (i.e., reaction-based) measure of the behavior of liquid and supercritical CO_2 as reaction solvents.

Data on 8:7 ratios from the reaction of **5** with **6** in liquid CO_2 (21–22 °C), in supercritical CO_2 (40 ± 2 °C), and in a variety of other solvents are given in Table VI. Our values for Ω were about 0.05 unit higher for solvents pre-

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viously examined by Berson. The reason for this discrepancy is unknown. It probably reflects a systematic difference in the analytical methods. At any rate, a variation of $\pm 0.05\Omega$ is acceptable for our purpose, which is to place CO_2 in the series of conventional solvents.

Our results of $\Omega = 0.50$ for liquid CO_2 and 0.47 for supercritical CO_2 place CO_2 close to hydrocarbon solvents in polarity. This is, of course, consistent with our spectroscopic studies. The small decrease in Ω under supercritical conditions is an expected temperature effect.[45]

Conclusions

Carbon dioxide exhibits properties typical of hydrocarbon solvents, such as toluene; however, for basic molecules, such as pyrrole, CO_2 provides more H bonding basicity than do hydrocarbon solvents. No significant difference in polarity can be detected between the liquid and supercritical phases. It is hoped that this view of CO_2 as a "hydrocarbon" solvent with unusual properties (infinite compressibility in the supercritical state, low surface tension and visosity, low polarizability, and ease of solute recovery) will lead to additional exploration of its utility in chemistry.

Experimental Section

Visible Spectroscopy. A high-pressure, 1-cm quartz-windowed flow cell was charged with ca. 5 mg of dye (**2**,[37] **3**,[38] or **4**[38]), purged with gaseous CO_2, cooled to 10 °C, and filled with liquid CO_2 by distillation from a lecture bottle. Then the temperature in the sealed cell was allowed to rise to 22 °C; the cell containing the resulting saturated solution of dye in liquid CO_2 was placed in a Cary 17 UV–visible spectrophotometer, and the λ_{max} was determined. The temperature in the sealed cell was then maintained at 40 °C, and the resulting solution in supercritical CO_2 was analyzed in the Cary 17.

Infrared Spectroscopy. Solutions of 0.1–10% of acetone, cyclohexanone, or pyrrole in CO_2 were prepared by distilling the requisite amount (ca. 100 g) of CO_2 into a cooled, 150-mL autoclave containing a weighed amount (ca. 1.0 g) of the organic solute. The autoclave was connected via a pump to an IRTRAN-2 windowed IR flow cell of 0.1-mm path length placed in a Perkin-Elmer Model 283B IR spectrophotometer. The entire system was controlled at 22 °C and at 40 °C (for liquid and supercritical solutions, respectively), and the spectra were obtained from the CO_2 solution passing through the flow cell. Pressure was monitored at the autoclave head and was 1000 and 2000 psi.

Determination of Berson's Ω: Starting Materials and Products. Authentic *exo*- and *endo*-norbornene-4-carboxylate methyl esters **7** and **8** were prepared by literature methods.[45,50,51] Cyclopentadiene was prepared from dicyclopentadiene, distilled through a 12-in. vigreaux column, and stored at −78 °C under nitrogen. Methyl acrylate was freshly distilled and kept at −5 °C under N_2 until used. Solvents were purified by standard methods immediately before use.[52]

Analytical Methods. Gas chromatographic analysis of mixtures of **7** and **8** was conducted with a 10 ft × $^{1}/_{8}$ in. column of 20% 20 NHPA Carbowax liquid phase on 100–120 mesh Chromosorb W chromomatographic support. Column temperature initially was 120 °C, programmed to 170 °C at 4 °C/min, and held at 170 °C for 20 min. The injection port temperature was 220 °C, and the thermal conductivity detector oven temperature was 330 °C. Under these conditions, baseline separation of **3** and **4** was achieved. Retention times were 17.06 min for exo (**7**) and 18.75 min for endo (**8**). Electronic integration of product peaks with an HP 5200 integrating reporter gave area percent of **7** and **8**. Injection of a known composition mixture of **7** and **8** proved that area percents obtained this way were equivalent to mole percents **7** and **8** (within 0.2%). This result was confirmed by injection of a known mixture of **7** and of **8** with *p*-dichlorobenzene internal standard.

Reactions in Liquid CO_2. An autoclave of about 300-mL capacity was charged with 2.60 g (0.0302 mol) of methyl acrylate, a sealed evacuated ampul containing 2.0 g (0.0302 mol) of cyclopentadiene, and three steel ball bearings (approximately 10 g each) to break the ampul when the autoclave was rocked. The autoclave was sealed and charged with 122 g of CO_2 by distillation from a lecture bottle. After equilibration to ambient temperature (21–22 °C), the autoclave was rocked for 8 h, vented slowly, and the residual mixture of products **3** and **4** was analyzed as described above.

Reactions in Supercritical CO_2. The technique used was identical with that described for runs in liquid CO_2, except that the autoclave was heated to 40 °C (±2 °C) before the autoclave was rocked to break the ampul and mix the reactants. After 8 h reaction time, the autoclave was cooled and vented, and the product was collected for analysis.

Controls. Samples of pure **7** and **8** were subjected to reaction conditions. Subsequent analyses proved that the samples were unchanged; therefore, **7** and **8** were not equilibrated under the reaction conditions. Furthermore, mixtures of 90:10 **7**:**8** and 10:90 **7**:**8** were prepared and analyzed by VPC. Results proved that isomerization of **7** to **8** (and of **8** to **7**) did not occur during analysis.

Reactions in Other Solvents. Reactions of **5** and **6** in solvents other than CO_2 were conducted by dissolving 2.6 g (0.0303 mol) of methyl acrylate in 120 g of purified solvent. The solution was placed in a constant temperature bath, stirred under N_2, and treated with 2.0 g (0.0302 mol) of cyclopentadiene that had just been warmed from −78 °C (storage temperature) to the temperature of the bath. Aliquots were analyzed directly by VPC as described above.

Solubilities. It was determined by use of the high-pressure UV–visible cell previously described that both cyclopentadiene and methyl acrylate are soluble in liquid and in supercritical CO_2 at the concentration used in the reactions (1.7–2.0 wt %). The organic compound was placed in the cell which was then sealed and filled with CO_2 by distillation from a lecture bottle. Visual examination at ~20 °C and at 40–45 °C disclosed clear solutions for both **5** and **6**.

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Registry No. **3**, 3025-52-3; **4**, 32044-93-2; CO_2, 124-38-9; acetone, 67-64-1; cyclohexanone, 108-94-1; pyrrole, 109-97-7.

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