Experimental Section[13]

3a,6,7,7a-Tetrahydro-1*H*-indene-4-carboxylic Acid (4a). (A) (–) Isomer. A solution of 3.28 g (20 mmol) of commercial "99% 5-norbornene-2-acrylic acid" in 15 mL of ether was treated with 2.42 (20 mmol) of (+)-α-methylbenzylamine and stored in a refrigerator. The crystals were filtered and washed with ether: 3.6 g; mp 135–136 °C; $[\alpha]^{25}{}_D$ –27.1° (1.032% in $CHCl_3$). These were recrystallized three times from acetone: mp 140–142 °C (TH); $[\alpha]^{25}{}_D$ –56.6° (0.990% in $CHCl_3$).

Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.75; H, 8.12; N, 4.91. Found: C, 75.51; H, 8.23; N, 4.91.

A suspension of the amine salt in ether was shaken vigorously with aqueous 2% hydrochloric acid. The ethereal layer was washed with 1% sodium chloride solution, dried over sodium sulfate, and concentrated to give colorless crystals. The pure (–)-**4a** was obtained by recrystallization from Skellysolve B: mp 83 °C (TH); $[\alpha]^{21}{}_D$ –151.7° (1.019% in MeOH); ^{1}H NMR ($CDCl_3$) δ 7.25 (dt, 1 H, =CH), 5.78 (m, 2H, *cis*-C**H**=C**H**), 3.49 (m, 1 H, $w_{1/2}$ 18 Hz, =C—CH<<sbsC=), 2.8–2.0 (lower envelope region, 2 H), 1.8–1.3 (higher envelope region, 2 H); UV (MeOH) 215 nm (ϵ 8600); IR ($CHCl_3$) 1693 (C=O), 1645 (C=C) cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; , 7.37. Found: C, 72.78; H, 7.13.

(B) (+) Isomer. Treatment of a commercial "5-norbornene-2-acrylic acid" with (–)-α-methylbenzylamine in ether afforded the crystalline salt of (+)-acid: mp 141 °C (TH); $[\alpha]^{25}{}_D$ +51.5° (1.00% in $CHCl_3$).

Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.75; H, 8.12; N, 4.91. Found: C, 75.65; H, 8.03; N, 4.90.

The (+)-acid was obtained in the same manner as described in part A: mp 85.5 °C (TH); $[\alpha]^{21}{}_D$ +154.3°; ^{1}H NMR, UV, and IR spectra were indistinguishable from those of the (–)-acid.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.00; H, 7.30.

(C) (±)-Acid.[14] A bottle of commercial "5-norbornene-2-acrylic acid" was stored in a refrigerator. The crystals were collected by suction and recrystallized from Skellysolve B: mp 85 °C (TH); ^{1}H NMR ($CDCl_3$) indistinguishable from that of the optically active acids. The filtrate was enriched in 5-norbornene-2-acrylic acid.

(±)-2,3,6,7,3a,7a-Hexahydro-1*H*-indene-4-carboxylic Acid (6). A solution of 3 g of (±)-**4a** in 100 mL of ethanol was agitated with 3 g of 5% $Pd/CaCO_3$ under 2 psi of hydrogen at 25 °C for 1 h. Filtration of the catalyst and evaporation of the solvent left a crystalline residue which was recrystallized from methanol to give pure **6**: 2.2 g; mp 102–103.5 °C (FJ); IR ($CHCl_3$) 1690 (C=O), 1640 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.15 (br t, 1 H, CH=, J = 4 Hz).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.37; H, 8.37.

Methyl Ketone 7. A solution of 1.86 g of **6** in 25 mL of ether was treated with 11 mL of 2.05 M methyllithium in ether at –50 to –30 °C. The mixture was stirred for 15 min without external cooling (the temperature rose to 0 °C) and poured into ice–water. The ethereal layer was dried over sodium sulfate, concentrated, and chromatographed on 10 g of SilicAR CC-7. The column was eluted with 5% ethyl acetate–benzene to give 1.5 g of **7**: IR ($CHCl_3$) 1670 (C=O), 1640 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.9 (t, 1 H, =CH, J = 4 Hz), 2.88 (m, 1 H), 2.25 (s, 3 H, CH_3CO).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.40; H, 9.87.

Oxime 8. A solution of 470 mg of **7** and 225 mg of hydroxylamine hydrochloride in 10 mL of pyridine was allowed to stand at 25 °C for 4 days. No starting ketone was found in the reaction mixture which was poured into water and extracted with methylene chloride. The organic layer was dried over sodium sulfate and concentrated to give 560 mg of crystalline **8**: mp 56 °C (FJ); ^{1}H NMR ($CDCl_3$) δ 6.14 (br t, 1 H, J = 4 Hz), 2.75 (m, 1 H), 2.01 (s, 3 H); IR ($CHCl_3$) 3625, 1670 cm^{-1}.

Anal. Calcd for $C_{11}H_{17}ON$: H, 73.70; H, 9.56; N, 7.81. Found: C, 73.56; H, 9.72; N, 7.79.

Perhydroindan-4-one (9) and Its Semicarbazone (10). To a solution of 100 mg of the oxime **8** in 0.5 mL of pyridine was added a solution of 0.2 mL of phosphorus oxychloride in 0.6 mL of pyridine at –15 °C. The mixture was stirred for 3 h, poured onto a mixture of 1.4 mL of concentrated hydrochloric acid and 10 g of ice, stirred 0.5 h, and extracted with ether. The ethereal extract was dried over sodium sulfate and concentrated to give 59 mg of oily **9**: IR ($CHCl_3$) 1715 cm^{-1} (C=O); ^{1}H NMR exhibited only envelope regions; mass spectrum, *m/e* 138 (M^+).

A solution of 59 mg of **9** in 2 mL of methanol was added to a solution of 200 mg of semicarbazide hydrochloride and 300 mg of sodium acetate in 2 mL of water. The mixture was warmed to 50 °C whereupon the crystals were filtered. Recrystallization from ethanol afforded 70 mg of **10**, mp 194–195 °C (TH).

Anal. Calcd for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.39; H, 8.79; N, 21.81.

Acknowledgment. We thank Mr. Jeffrey Kett of Aldrich Chemical Co. for helpful discussions. Gratitude is expressed to Miss Lydia Swenton for consultation on ^{13}C NMR.

Registry No. (–)-**4a**, 82135-00-0; (–)-**4a** (+)-α-methylbenzylamine, 82188-47-4; (+)-**4a**, 82135-01-1; (+)-4a (–)-α-methylbenzylamine, 82188-48-5; (±)-**4a**, 82135-02-2; **6**, 82135-03-3; **7**, 82135-04-4; **8**, 82135-05-5; **9**, 5686-83-9; **10**, 82135-06-6.

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[13] The ^{1}H NMR spectra were taken on a Varian A-60 NMR spectrometer. The decoupling experiment was carried out by using a Varian EM-390 spectrometer. The ^{13}C NMR spectrum was taken on a Varian XL-100 NMR spectrometer. The melting points were taken either on a Thomas-Hoover Unimelt (marked as TH) or on a Fisher-Johns apparatus (marked as FJ) and were uncorrected.

[14] A gas chromatographic analysis of two different commercial batches disclosed that one contained 45.06% of **3** and 44.46% of **4a** and that the other contained 55.91% of **3** and 35.78% of **4a**. A 6-ft column of 8.7% stabilized Deg plus 2.4% phosphoric acid was used at 160–200 °C. The retention times for **3** and **4a** were 5.60 and 6.25 min, respectively.

Effect of Microemulsions on the Diels–Alder Reaction: Endo/Exo Ratios in the Reaction of Cyclopentadiene and Methyl Methacrylate[1a]

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Microemulsions appear to be excellent media for facilitating chemical reactions.[2] A large number of compounds are soluble in them, they possess a large interphase volume, and they can be prepared with or without a long-chain amphiphile (surfactant). As a consequence a variety of chemical reactions can be studied and those factors, such as surfactant head group charge, media structure, interphase volume, etc., which affect the rate

Table I. Endo/Exo Ratio for the Reaction between Cyclopentadiene and Methyl Methacrylate[14]

solvent	temp, °C	endo	exo
decalin	56	33.0	67.0
DMF	30	28.4	71.6
pyridine	30	29.2	70.8
nitromethane	30	32.6	67.4
acetonitrile	30	33.0	67.0
acetone	20	29.8	70.2
ethanol	30	38.4	61.6
methanol	26	41.1	58.9

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[1] (a) Supported by NSF Grant No. CHE 7913802 and CHE 8025726. (b) University of Georgia. Present address: R.J. Reynolds Tobacco Co., New Brand R and D, Winston-Salem, NC 27102. (c) Oklahoma State University.

[2] For a review of the current literature on microemulsions, see Holt, S. L. *J. Dispersion Sci. Technol.* 1980, *1*, 423.

Table II. Product Distribution from the Reaction of Cyclopentadiene with Methyl Methacrylate

				% of 1:1 adduct					
	composition, mL			endo			exo		
region	water	2-propanol	toluene	DTGLS[a]	NaDodSO$_4$	HTAB	DTGLS[a]	NaDodSO$_4$	HTAB
B	1.90	17.83	20.26	36.8	36.5	36.1	63.2 (0.1)[b]	63.5 (0.3)	63.9 (0.2)
C	1.98	22.78	15.26	36.6	39.5	39.1	63.4 (0.2)	60.5 (0.2)	60.9 (0.2)
D	2.10	28.57	9.30	36.5	46.5	45.8	63.5 (0.1)	53.5 (0.2)	54.2 (0.3)

[a] No added surfactant. [b] Numbers in parentheses are the standard deviations for a set of three measurements. Fisher T-Prime test shows values to be significant at the 90-95% confidence level.

of reaction, can be ascertained. Reactions which have been studied include the hydrolysis of esters,[3,4] the metalation of porphyrins,[5-7] the formation of macrocyclic lactones,[8] and the Wacker reaction.[9] In addition there has been considerable interest in the possible utilization of microemulsions in photochemical processes.[10-13]

Diels–Alder reactions are sensitive to solvent polarity. Berson and co-workers[14] have investigated the reaction of cyclopentadiene with methyl methacrylate as a function of temperature and solvent polarity. This study was carried out in order to gain some insight into the factors that control the endo/exo product distribution. It was found that the percent of endo adduct increased with increasing solvent polarity (Table I). This pattern was explained on the basis of an electrostatic effect, assuming that the permanent electric dipole moment of the endo transition state is greater than that of the exo transition state.

Because the Diels–Alder reaction is so sensitive to the solvent medium it would appear that a study of the reaction of methyl methacrylate with cyclopentadiene would provide a sensitive probe of the interphase environment of detergentless microemulsions. Similar studies with added surfactant would provide information regarding changes in solvent structure and an indication of the ability of added surfactant to mediate reaction pathway. As a consequence the reaction of methyl methacrylate with cyclopentadiene was studied with solutions from three different regions of the pseudophase diagram for toluene, water, and 2-propanol both in the absence and in the presence of surfactant (sodium dodecyl sulfate and hexadecyltrimethylammonium bromide). The compositions of these solutions correspond to a water-in-oil microemulsion, B; a solution of small aggregates C; and a normal ternary solution, D.[4,15] The results are tabulated in Table II.

It will be noted that the endo/exo ratio is constant in the absence of surfactant irregardless of the structure of the medium. This is in sharp contrast to the results obtained in the ester hydrolysis[4] and porphyrin metalation studies[7] and implies that the environment experienced by the reaction in its transition state is the same in all instances. It is also evident, from Tables I and II, that the reaction occurs in a region of the medium which has a polarity only slightly less than that of ethanol (probably the interphase). When the reaction is carried out in a microemulsion to which NaDodSO$_4$ or HTAB is added, the endo/exo ratios are very similar to those obtained in the detergentless system, suggesting that the transition state has a similar environment in all three media. In the C and D regions a difference in observed however. In region C, with both NaDodSO$_4$ and HTAB, there is a slight increase of endo product, while in region D the increase is quite marked. This implies that the transition state formed during the reaction of cyclopentadiene and methyl methacrylate encounters more polar surroundings as the medium becomes less structured. This behavior appears to be characteristic of the system itself and is not notably dependent on the charge of the head group or the counterion. The most logical explanation for this behavior centers on the orientation and solubilization of the surfactant since it is only in this respect that the surfactant containing systems differ from the detergentless ones.

In region B the ionic head group is oriented toward the water-rich core of the droplet, and away from the toluene continuous phase where the nonpolar reactants are located. In this orientation the surfactant would have a limited effect on the transition state of the reaction. In region C the increase of 2-propanol breaks up the water droplets into small aggregates.

The surfactant molecules are associated with the small water-rich aggregates but the charged head groups are less shielded than in a microemulsion. Thus the effective polarity seen by the transition state is increased, generating more endo product. (This effect cannot be attributed merely to the increase in medium polarity due to the added 2-propanol as the endo/exo ratio is invariant for the detergentless systems. In addition this is the only explanation which can account for the similarity in the results in the three different microemulsions). In region D a ternary solution, the surfactant has no specific orientation as there is no driving force to orient it at a specific site. The surfactant molecules then are scattered throughout the medium with only a few water molecules associated with the head group, decreasing the shielding even further. The reactants experience a more polar environment favoring the endo adduct.

These results suggest, as did our earlier work on hydroloysis of long-chain esters[4] and formation of macrocyclic lactones,[8] that microemulsions may be used to influence pathway, yield, and rate of organic reactions.

Experimental Section

Reagents. Cyclopentadiene was obtained by cracking dicyclopentadiene (Eastman) and was collected at 40 °C. Methyl methacrylate (Aldrich), hexadecyltrimethylammonium bromide (Sigma), sodium dodecyl sulfate (Sigma), toluene (Sigma), and

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(3) Hermansky, C; Mackay, R. A. "Solution Properties of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; p 273.

(4) Borys, N. F.; Holt, S. L.; Barden, R. E. *J. Colloid Interface Sci.* **1979**, *71*, 526.

(5) Letts, K.; Mackay, R. A. *Inorg. Chem.* **1975**, *14*, 2990.

(6) Letts, K; Mackay, R. A. *Inorg. Chem.* **1975**, *14*, 2993.

(7) Keiser, B. A.; Holt, S. L.; Barden, R. E. *J. Colloid Interface Sci.* **1980**, *73*, 290.

(8) Gonzalez, A.; Holt, S. L. *J. Org. Chem.* **1981**, *46*, 2594.

(9) Gonzalez, A.; Murphy, J.; Holt, S. L. "Inorganic Reactions in Organized Media"; Holt, S. L., Ed.; American Chemical Society: Washington, DC, 1981.

(10) Jones, C. E.; Mackay, R. A. *J. Phys. Chem.* **1978**, *82*, 63.

(11) Jones, C. E.; Jones, C. A.; Mackay, R. A. *J. Phys. Chem.* **1979**, *83*, 805.

(12) Kiwi, J.; Gratzel, M. *J. Am. Chem. Soc.* **1978**, *100*, 6314.

(13) Willner, I.; Ford, W. E.; Otvos, J. W.; Calvin, M. *Nature (London)* **1979**, *280*, 823.

(14) Berson, J. A.; Hamlet, Z.; Mueller, W. A. *J. Org. Chem.* **1962**, *84*, 297.

(15) Lund, G.; Holt, S. L. *J. Am. Oil Chem. Soc.* **1980**, 264.

2-propanol (Baker) were used as received.

The surfactant-containing microemulsions had the same component compositions as the detergentless microemulsions except that the water was made 3×10^{-3} M in HTAB and 2×10^{-2} M in $NaDodSO_4$. To the above solutions was added 0.5 mL of each reactant (cyclopentadiene and methyl methacrylate), and the resulting mixtures were placed in a temperature-controlled water bath (26 °C) for 3 days in order to achieve a convenient yield of products. The product analyses were carried out by gas chromatography, using a Varian aerograph series 2700 gas chromatograph. Separations of exo/endo isomers were made on a 6 ft × 0.25 in. 8 Carbowax 1500 on Chromosorb W column. The helium flow rate was 10 mL/min and the column temperature was 105 °C. The retention times were 500 and 650 s for the endo and exo, respectively. The proportions of isomers were determined with a Perkin-Elmer computing integrator and a Perkin-Elmer Sigma 10 data system.

Registry No. Cyclopentadiene, 542-92-7; methyl methacrylate, 80-62-6.

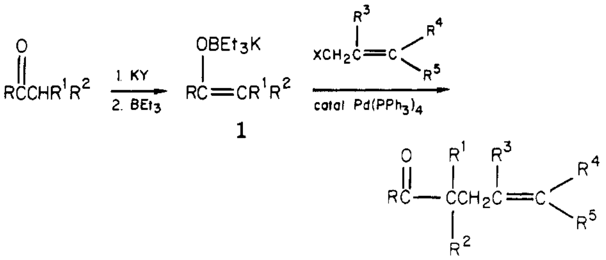
Communications

Highly Regio- and Stereospecific Palladium-Catalyzed Allylation of Enolates Derived from Ketones[1]

Summary: The reaction of potassium enoxyborates, readily obtainable by treating potassium enolates with a trialkylborane, e.g., triethylborane, with allylic electrophiles such as allylic chlorides and acetates in the presence of a catalytic amount of a palladium–phosphine complex, e.g., $Pd(PPh_3)_4$, proceeds readily at room temperature to produce the corresponding α-allylated ketones in high yields with essentially complete retention of both the enolate regiochemistry and the allyl geometry.

Sir: Allylation of enolates[2] is an important synthetic methodology, since it not only serves as an obvious route to γ,δ-unsaturated carbonyl compounds but also provides attractive routes to α-alkylated carbonyl compounds as well as 1,4- and 1,5-dicarbonyl compounds.

We report here a remarkably facile and selective procedure for allylation of enolates involving the reaction of potassium enoxyborates,[3] readily obtainable by treating potassium enolates[4] with a trialkylborane, e.g., triethylborane, with allylic electrophiles in the presence of a catalytic amount of a palladium complex, e.g., $Pd(PPh_3)_4$ (eq 1).

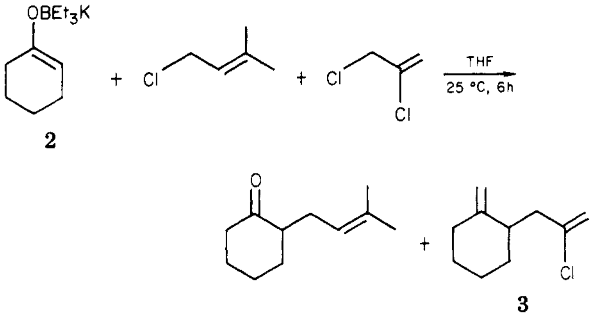


1

(1)

Y = H, N(SiMe$_3$)$_2$; X = Cl, OAc

We have recently reported that whereas lithium enolates derived from ketones do not react with trialkylboranes to form the corresponding enoxyborates,[5] the corresponding potassium enolates do[6] and that the resultant potassium enoxyborates (1) selectively react with various alkylating agents to give α-monoalkylated ketones in good yields.[3] Unfortunately, our attempts to apply this procedure to various allylic electrophiles other than allyl bromide have often led to disappointing results. Thus, for example, potassium triethyl(cyclohexenyloxy)borate (2, eq 2) does not readily react with either 2,3-dichloropropene or 1,3-dichloro-2-butene under conditions suitable for its reaction with allyl bromide.[3,7] We have found, however, that these reactions can be markedly catalyzed by a palladium–phosphine complex such as $Pd(PPh_3)_4$. Thus, whereas the uncatalyzed reactions gave only trace amounts of the allylated products in 3 h, the same reactions run in the presence of 5 mol % of $Pd(PPh_3)_4$ were essentially complete in 3 h, producing 3 or 4 in 80–95% yields.

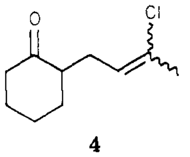


2

3

(2)

no catalyst	51%	0%
5% $Pd(PPh_3)_4$	6%	92%



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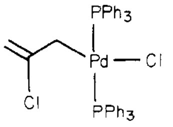

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That these reactions are genuinely catalyzed by $Pd(PPh_3)_4$ is clearly indicated by the following competitive experiments. Thus, the reaction of 2 with a 1:1 mixture of isoprenyl chloride and 2,3-dichloropropene in THF in

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[1] Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis. 29. Part 28: Negishi, E.; Jadhav, K. P.; Daotien, N. *Tetrahedron Lett.*, in press.

[2] For general reviews on alkylation of enolates, see: (a) House, H. O. "Modern Synthetic Reactions"; W. A. Benjamin: Menlo Park, CA, 1972. (b) Negishi, E. "Organometallics in Organic Synthesis"; Wiley-Interscience: New York, 1980. (c) For allylation of enolates, see: Jung, M. E. *Tetrahedron* **1976**, *32*, 3.

[3] Negishi, E.; Idacavage, M. J.; DiPasquale, F.; Silveira, A., Jr. *Tetrahedron Lett.* **1979**, 845.

[4] Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.

[5] Negishi, E.; Idacavage, M. J.; Chiu, K. W.; Yoshida, T.; Abramovitch, A.; Goettel, M. E.; Silveira, A., Jr.; Bretherick, H. D. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1225.

[6] Idacavage, M. J.; Negishi, E.; Brown, C. A. *J. Organomet. Chem.* **1980**, *186*, C55.

[7] Under comparable reaction conditions, the corresponding reaction of lithium cyclohexenolate is also very sluggish, the product yield after 19 h being ≤6%.

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