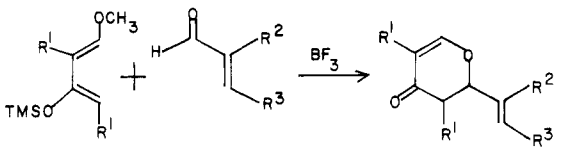
Scheme I



entry	R^1	R^2	R^3	%
a	H	H	H	50
b	H	CH_3	H	62
c	H	H	CH_3	70
d	H	H		75
e	H	H	$CH=CHCH_3$	61
f[4]	CH_3	H	CH_3	68

Experimental Section[6]

General Procedure. To a 0.1 M solution of α,β-unsaturated aldehyde in anhydrous diethyl ether under an inert atmosphere at -78 °C is added 1.1–1.2 equiv of diene followed by 1.0 equiv of boron trifluoride etherate. The reaction is continued until the aldehyde or diene has been consumed. A solution of saturated aqueous bicarbonate is added, and the ethereal layer is separated. The aqueous layer is extracted with diethyl ether. The ether solutions are combined and dried over magnesium sulfate. Filtration, evaporation of the volatiles, and chromatography[7] of the residue provides adduct **3**.

Adduct 3a: IR $\bar{\nu}$ 1685, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.37 (d, 1 H, J = 6 Hz), 5.95 (ddd, 1 H, J = 14, 10.5, 6 Hz), 5.33 (m, 2 H), 5.22 (m, 1 H), 4.9 (m, 1 H), 2.55 (m, 2 H); ^{13}C NMR δ 191.5, 162.8, 134.5, 118.2, 107.2, 79.4, 41.5; mass spectrum, m/e 124 (M^+).

Adduct 3b: IR $\bar{\nu}$ 1680, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.4 (d, 1 H, J = 6 Hz), 5.38 (d, 1 H, J = 6 Hz), 5.08 (br s, 1 H), 5.02 (br s, 1 H), 4.8 (dd, 1 H, J = 12, 5 Hz), 2.55 (m, 2 Hz), 1.8 (s, 3 H); ^{13}C NMR δ 192.2, 163.2, 141.5, 114.3, 107.1, 82.2, 40.7, 18.3; mass spectrum, m/e 138 (M^+), 123, 109, 97.

Adduct 3c: IR $\bar{\nu}$ 1690, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.37 (d, 1 H, J = 6 Hz), 5.45–6.05 (m, 2 H), 5.3 (d, 1 H, J = 6 Hz), 4.8 (m, 1 H), 2.5 (m, 2 H), 1.7 (d, 3 H, J = 6 Hz); ^{13}C NMR δ 192.3, 163.2 131.4, 127.9, 107.3, 80.1, 42.3, 18.0; mass spectrum, m/e 138 (M^+), 123, 109.

Adduct 3d: IR $\bar{\nu}$ 1680, 1600, 1500, 1450 cm^{-1}; ^1H NMR δ ($CDCl_3$, 90 MHz) 7.4 (br s, 6 H), 6.78 (d, 1 H, J = 16 Hz), 6.3 (dd, 1 H, J = 6, 16 Hz), 5.45 (d, 1 H, J = 6 Hz), 5.02 (m, 1 H), 2.55 (m, 2 H); ^{13}C NMR δ 191.9, 163.1, 135.8, 133,8, 128.9, 128.7, 127, 125.4, 107.4, 79.8, 42.1; mass spectrum, m/e 200 (M^+); mp 39–40 °C.

Adduct 3e: IR $\bar{\nu}$ 1680, 1595 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.35 (d, 1 H, J = 6 Hz), 5.4–6.8 (m, 4 H), 5.35 (d, 1 H, J = 6 Hz), 4.9 (m, 1 Hz), 2.5 (m, 2 H), 1.8 (d, 3 H, J = 6 Hz); ^{13}C NMR 192.1, 163.2, 134.5, 132.9, 130.4, 126.0, 107.4, 79.9, 42.2, 18.4; mass spectrum, m/e 164 (M^+), 149, 145, 135, 121.

Adduct 3f. Trans isomer: IR $\bar{\nu}$ 1705, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.2 (br s, 1 H), 5.35–6.10 (m, 2 H), 4.33 (dd, 1 H, J = 7, 12 Hz), 2.2–2.6 (m, 1 H), 1.8 (d, 3 H, J = 6 Hz), 1.65 (s, 3 H), 1.05 (d, 3 H, J = 7 Hz); ^{13}C NMR δ 195.2, 158.7, 132.5, 128.2, 113.0, 85.5, 43.9, 17.9, 10.9; mass spectrum, m/e 166 (M^+), 151, 137, 123.

Cis isomer: IR $\bar{\nu}$ 1705, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.20 (br s, 1 H), 5.4–6.05 (m, 2 H), 4.75 (dd, 1 H, J = 3, 6 Hz), 2.45 (dd, 1 H, J = 3, 7 Hz), 1.75 (d, 3 H, J = 6 Hz), 1.67 (s, 3 H), 1.03 (d, 3 H, J = 7 Hz); ^{13}C NMR δ 196.9, 158.5, 131.1, 125.4, 112.2, 82.7, 44.2, 17.9, 10.6, 9.9; mass spectrum, m/e 166 (M^+), 151, 137, 123.

Adduct 5: IR $\bar{\nu}$ 1640, 1580, 1490 cm^{-1}; ^1H NMR δ ($CDCl_3$, 90 MHz) 7.0–7.6 (m, 11 H), 6.57 (d, 1 H, J = 15 Hz), 6.32 (dd, 1 H, J = 5, 15 Hz), 5.3 (d, 1 H, J = 7 Hz), 4.85 (m, 1 H), 3.18 (dd, 1 H, J = 6, 15 Hz), 2.55 (dd, 1 H, J = 3, 15 Hz); ^{13}C NMR δ 190.9, 147.6, 145.0, 136.2, 132.8, 130.0, 128.4, 126.9, 125.1, 124.8, 119.1, 102.8, 60.6, 45.0; mass spectrum m/e 275 (M^+), 247, 172, 117; mp 137.5–38.5 °C.

Acknowledgment. This research was supported by PHS Grant HL48136-02. NMR spectra were obtained through the auspices of the Northeast Regional NSF/NMR Facility at Yale University which was supported by the NSF Chemistry Division Grant CHE-7916210.

Registry No. **1a**, 59414-23-2; **1f**, 82093-19-4; **2a**, 107-02-8; **2b**, 78-85-3; **2c**, 4170-30-3; **2d**, 104-55-2; **2e**, 80466-34-8; **3a**, 82093-20-7; **3b**, 82093-21-8; **3c**, 82093-22-9; **3d**, 82093-23-0; **3e**, 82093-24-1; *cis*-**3f**, 82093-25-2; *trans*-**3f**, 82093-26-3; **4**, 953-21-9; **5**, 82093-27-4; zinc chloride, 7646-85-7; boron trifluoride etherate, 109-63-7.

(6) ^1H NMR were recorded on a Varian EM-390 90-MHz spectrometer and ^{13}C NMR on a Joel FX-900 in $CDCl_3$ solution. IR spectra were measured as films on a Perkin-Elmer 710B infrared spectrometer using sodium chloride plates. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

(7) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

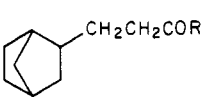
3a,6,7,7a-Tetrahydro-1*H*-indene-4-carboxylic Acid

Masateru Miyano* and Michael A. Stealey

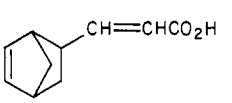
Department of Medicinal Chemistry, G. D. Searle & Co., Chicago, Illinois 60680

Received February 4, 1982

In an extention of an ω-modified prostaglandin project,[1] we required the optically active [[[2-(bicyclo[2.2.1]heptan-2-yl)ethyl]carbonyl]methylene]triphenylphosphorane (**1**). This phosphorane would be prepared readily from



1, R = $CH=PPh_3$
2, R = OH



3

2 by the imidazolide procedure.[2] The bicycloheptane-2-propionic acid **2** might be prepared by an optical resolution followed by hydrogenation of 5-norbornene-2-acrylic acid (**3**).

Commercial[3] "99% pure" **3** was treated with 1 equiv of (+)-α-methylbenzylamine in ether. The crystalline precipitates were recrystallized from acetone until the optical rotation reached a constant value. The (+)-amine salt was then treated with aqueous hydrochloric acid to liberate a crystalline (-)-acid which was presumed to be the levorotatory[4] 5-norbornene-2-acrylic acid (**3**). The ^1H NMR spectrum of this acid was, to our surprise, totally incompatible with the presumed structure (**3**). The (+)-acid, prepared in a similar manner by resolving the commercial **3** with (-)-methylbenzylamine, exhibited a ^1H NMR spectrum ($CDCl_3$) identical with that of the (-)-acid.

The elemental analysis demonstrated that these optically active acids were $C_{10}H_{12}O_2$, that is, isomeric to **3**. The UV (MeOH) absorption of 215 nm (ϵ 8600) as well as the IR ($CHCl_3$) bands at 1693 and 1645 cm^{-1} suggested the

(1) Dajani, E. Z.; Rozek, L. F.; Sanner, J. H.; Miyano, M. *J. Med. Chem.* **1976**, *19*, 1007.

(2) Miyano, M.; Stealey, M. A. *J. Org. Chem.* **1975**, *40*, 2840.

(3) Three U.S. manufacturers used to supply this substance: "Chemical Sources-U.S.A."; Directories Publishing Co., Inc.: Ormond Beach, FL, 1977; p 610; 1978; p 401. The purchase was made from two of them.

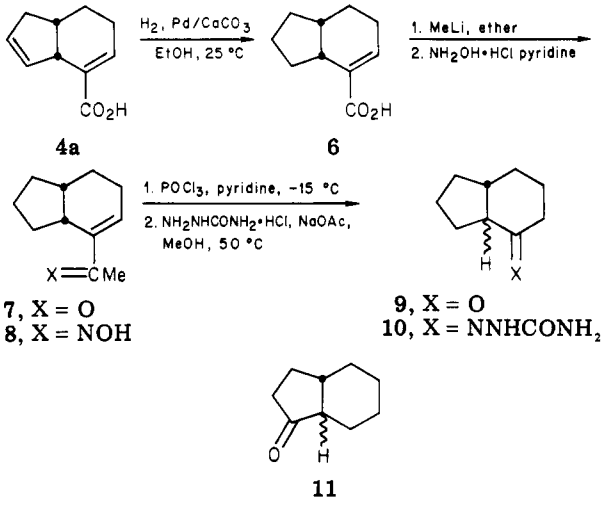
(4) The optically active 5-norbornene-2-acrylic acids were not found in the literature.

0022-3263/82/1947-3184$01.25/0

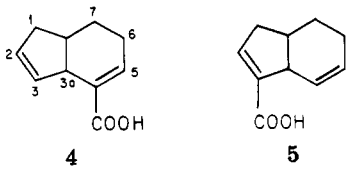
Table I. ^{13}C NMR Spectral Data of (−)-3a,6,7,7a-Tetrahydro-1*H*-indene-4-carboxylic Acid (4a) in $CDCl_3$

chemical shift, ppm (from Me_4Si)	multiplicity	assignment
172.22	s	CO_2H
142.66	d	C-5
132.86	d	C-2
130.87	s	C-4
128.69	d	C-3
44.05	d	C-3a
38.10	t	C-6
35.24	d	C-7a
24.72	t	C-7
24.33	t	C-1

Scheme I



presence of an α,β-unsaturated carboxylic acid grouping. The ^{13}C NMR spectrum (Table I) demonstrated that the (−)-acid contained four olefinic carbons, three of them carrying one hydrogen and the remaining one carrying no hydrogen. Consequently, the new acid ought to have contained two rings and two double bonds. The ^1H NMR signal of σ 3.49 suggested the presence of a methine flanked by two double bonds (C=C—CH—C=). In order to accommodate all the physical data, only two structures, **4** and **5**, both chiral, could be drawn. Compound **4** was



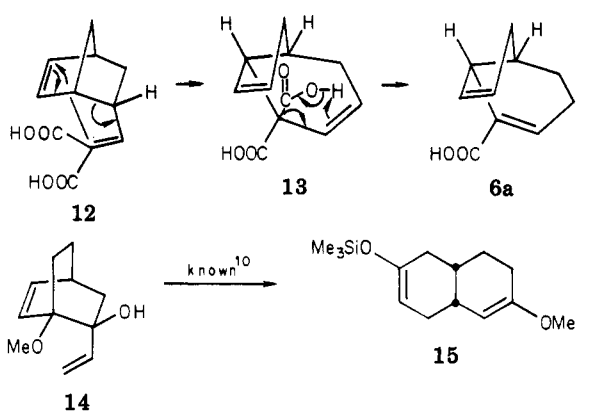
4 5

slightly favored over compound **5** due to the chemical shifts of the two olefinic carbons (132.86 and 128.69 ppm, Table I) which were in better agreement with a cyclopentene (typically 130.8 ppm) as opposed to a cyclohexene (127.4 ppm) ring. The coupling constant (6 Hz)[5] between H-3a and H-7a suggested the cis ring juncture.

Soon it was found that the new acid was not formed during the resolution but had already been present in the commercial "5-norbornene-2-acrylic acid" to an extent of 35–45%. A large quantity of the crystalline (±)-acid was obtained readily by filtration of a refrigerated commercial "5-norbornene-2-acrylic acid". The oily filtrate consisted mostly of 5-norbornene-2-acrylic acid.

(5) The double irradiation of the olefinic regions at δ 7.4 and 5.6 transformed the multiplet of H-3a (3.49 ppm) into a doublet.

Scheme II



Neither **4** nor **5** has been recorded in the literature. Perhaps the closest compound which was known was (±)-2,3,6,7,3a,7a-hexahydro-1*H*-indene-4-carboxylic acid (**6**).[6] A selective hydrogenation of the racemic acid **4a** (Scheme I) over palladium on calcium carbonate afforded a crystalline dihydro acid (mp 102–103.5 °C) which exhibited a broad triplet for H-5 at δ 7.15. The melting point and the ^1H NMR spectrum were in excellent agreement with the data given in the literature,[6] although no direct comparison was made. In order to provide additional evidence for the structure **4a**, we converted the racemic dihydro acid **6** into the methyl ketone **7** and then into the oxime **8** by routine operations. The Beckmann rearrangement of **8** produced oily perhydroindan-4-one (**9**) which had the carbonyl stretching band at 1715 cm^{-1}. The IR spectrum of **9** (a six-membered-ring ketone) was incompatible with perhydroindan-3-one (**11**, a five-membered-ring ketone). Hence, the alternate structure (**5**) for the new acid was unambiguously excluded. The oily **9** was characterized as the crystalline semicarbazone **10**, mp 194–195 °C.[7] On consideration of the reaction conditions, the semicarbazone **10** could be either cis or trans.[7]

The preparation of 5-norbornene-2-acrylic acid by Knoevenagel condensation of 5-norbornene-2-carboxaldehyde (exo/endo ratio of 1:3) and malonic acid was described in the literature.[8] It appeared very likely that the commercial "5-norbornene-2-acrylic acid" was manufactured by the known procedure.[9] We propose that an intermediate (**12**), having the strained bicyclo ring, might undergo [$2_s + 2_s + 2_s$] sigmatropic reaction as well to give a β,γ-unsaturated acid (**13**, Scheme II). The latter would be decarboxylated with concomitant migration of the double bond to give **6a**. The [3,3] sigmatropic rearrangement of **12** to **13** is somewhat similar to the oxy-Cope rearrangement[10] of bicyclooctene **14** to **15** and also somewhat similar to the transformation[11] of azabicyclooctenes to tetrahydroisoquinolines.

While this paper was in preparation, a similar rearrangement of a vinylbicycloheptene system to a tetrahydroindene ring was reported.[12]

(6) Goffic, F. L. *Bull. Soc. Chim. Fr.* **1965**, 2250.
(7) The melting point (192–193 °C) of perhydroindan-4-one semicarbazone was recorded in the literature. Brown, H. C.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1968**, 594.
(8) Kasper, F.; Kuschel, K. *J. Prakt. Chem.* **1969**, *311*, 97.
(9) One of the suppliers kindly informed us that it was indeed prepared by the Knoevenagel condensation, under a condition which was very similar to that in the literature.
(10) Evans, D. A.; Golab, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.
(11) Mariano, P. S.; Dunaway-Mariano, D.; Huesmann, P. I.; Beamer, R. L. *Tetrahedron Lett.* **1977**, 4299.
(12) Franck-Neumann, M.; Martina, D.; Brion, F. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 864.

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); ^1H NMR ($CDCl_3$) δ 7.25 (dt, 1 H, =CH), 5.78 (m, 2H, *cis*-CH=CH), 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°; ^1H 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); ^1H 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}; ^1H 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}; ^1H 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); ^1H 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); ^1H 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.

(13) The ^1H 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]

Alvaro Gonzalez[1b] and Smith L. Holt*[1c]

Department of Chemistry, University of Georgia, Athens, Georgia 30602, and Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

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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

(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.

0022-3263/82/1947-3186$01.25/0