

92-3; *p*-nitrobenzenethiol, 1849-36-1; tetra-*n*-butylammonium formate, 35733-58-5; tetra-*n*-butylammonium *p*-nitrobenzenethiolate, 20627-93-4; *O*-methyl oxime hydrochloride, 4229-44-1; carbobenzyloxy chloride, 501-53-1; *p*-toluenesulfonyl chloride, 98-59-9.

References and Notes

- (1) This research was supported by funds from the U. S. Public Health Service, Grants MH-18038 and CA-10,748.
- (2) Postdoctoral Fellow supported by the U. S. Public Health Service Training Grant GM-0059.
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Stereoselective Synthesis of 3-Exo-Substituted 2-endo-Acyl-5-norbornene Derivatives¹

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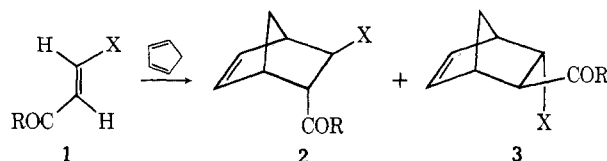
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The stereoselective addition of a variety of nucleophiles (ROH, RSH) to several 2-acylnorbornadienes provides an efficient synthesis of the title compounds. The allyl ethers derived from the addition of allyl alcohol are stable to many synthetic transformations and readily liberate the 3-exo alcohol on reductive cleavage.

During the course of model studies for the synthesis of several tetracyclic sesquiterpenes,² we required an efficient preparation of various 3-exo-substituted 2-endo-acylnorbornenes (e.g., **2**). In particular we had need of a substituent at C-3 which could be readily converted to an hydroxyl group but which would also survive further intended synthetic transformations. To this end we have investigated the reaction of cyclopentadiene with trans- β -substituted α,β -unsaturated carbonyl compounds and the addition of nucleophiles to 2-acylnorbornadienes. We have also determined that allyl ethers are effective as masked alcohols, thus satisfying our final criterion.

The results of the Diels-Alder reaction between trans- β -substituted α,β -unsaturated carbonyl compounds (**1**) and cyclopentadiene are summarized in Table I. As ex-



- a, R = H; X = OCOCH₃
 b, R = H; X = OCOC₆H₅
 c, R = CH₃; X = OCOCH₃
 d, R = *i*-C₃H₇; X = OCOCH₃
 e, R = OH; X = Cl
 f, R = CH₃; X = OCH₃

pected for an uncatalyzed reaction, the product with an endo acyl group was always predominant, the isomer ratios ranging from 2.6:1 to 5.6:1.³⁻⁶ Predictably the addi-

Table I
Reaction of Cyclopentadiene with Several Acrylic Dienophiles (1)

Dienophile	Catalyst	Yield, % ^a	[2]:[3] ^b
1a ^c		75	2.6:1
1b ^c		50	3:1
1c ^d		58	2.6:1
1d		67	3.5:1
1d	SnCl ₄ ^e	47	>15:1
1e ^f		87	5.6:1
1f		0	
1f	Cu(BF ₄) ₂ ^g	11	>15:1
1f	SnCl ₄	51	15:1

^a Isolated yields, not optimized. ^b Reference 5. ^c Reference 20. ^d Reference 21. ^e Reference 9. ^f Reference 22. ^g Reference 8.

tion of catalytic amounts of cupric⁷ and stannic⁸ salts led to significant increases in both the rate and stereoselectivity of the Diels-Alder reaction.⁹ The rather low yields (not optimized) are apparently due to extensive polymerization of the diene and resultant difficulties in the isolation procedure. However, the high specificity of the reaction makes the catalyzed procedure preferable when isomerically pure adducts are desired.

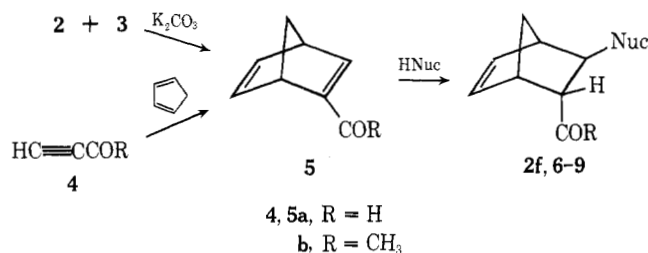
Although the acyl esters **2a-d** were thus available in quantity, they did not prove to be synthetically useful, since treatment with most basic reagents led to significant decomposition of starting material.¹⁰ A more generally useful procedure was found to be the conjugate addition of nucleophiles to 2-acylnorbornadienes (**5**). For instance,

Table II
Reaction of Several 2-Acylnorbornadienes (5) with Nucleophiles

Electrophile	Source ^a	Nucleophile	Catalyst	Product	Yield, ^b %	Isomer ^c ratio
5a	A	CH ₃ OH ^d	K ₂ CO ₃	6	35	8:1
5a	A	C ₆ H ₅ SH ^e	K ₂ CO ₃	7	75	9:1
5a	B	CH ₂ =CHCH ₂ OH ^f	K ₂ CO ₃	8	82	6:1
5b	A	CH ₃ OH	K ₂ CO ₃	2b	77	10:1
5b	B	CH ₃ OH	<i>p</i> -TsOH	2f	65	11:1
5b	A	CH ₂ =CHCH ₂ OH	K ₂ CO ₃	9	68	15:1

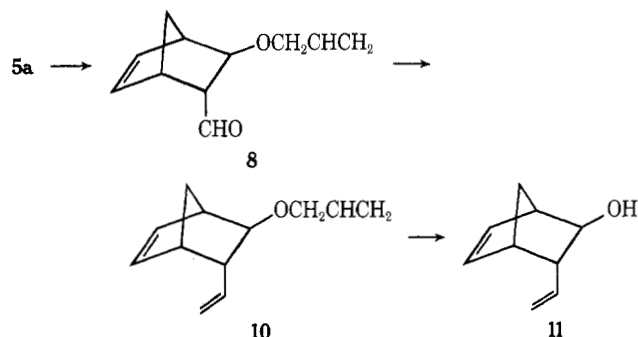
^a Method A, treatment of a solution of 2 and 3 with K₂CO₃; method B, reaction of cyclopentadiene with alkynone 4. ^b Isolated yields, not optimized. ^c The ratio of the major isomer to the sum of the minor isomers, determined by nmr spectroscopy as described in the text and ref 5. ^d Registry no., 67-56-1. ^e Registry no., 108-98-5. ^f Registry no., 107-18-6.

exposure of a mixture of acetates 2c and 3c to methanolic potassium carbonate afforded methyl ether 2f, contaminated with only trace amounts of other isomers. That un-



saturated ketone 5b was intervening in an elimination-addition process was easily demonstrated by observing its build-up from the acetate mixture in a nonnucleophilic solvent (acetone) and then noting its behavior on treatment with methanol and a trace of potassium carbonate. In fact a variety of related dienones 5 could be either generated *in situ* by elimination of acetic acid from a mixture of the Diels-Alder adducts 2-3 (method A) or by cycloaddition of the appropriate alkynone with cyclopentadiene (method B).¹¹ In each case the product smoothly added a variety of nucleophiles as summarized in Table II. It is noteworthy that in the reported examples the isomer ratio was generally significantly greater than 6:1 in a process which resulted in the simultaneous generation of two asymmetric centers.¹² Although the synthetic logic of such an addition process to generate contiguous asymmetry has been previously demonstrated,¹³ the consequences are of sufficient utility to be of interest. It is also worth noting that the related conjugate addition of diethyl malonate to 2-carbomethoxynorbornadiene has been reported to give analogous results¹⁴ and that similar chemistry is observed in the bicyclo[2.2.2]octene series.¹⁵ In each case the observed stereochemistry is presumably the consequence of initial attack of the nucleophile at the β carbon from the more accessible exo side of the norbornene ring followed by thermodynamic protonation of the resulting enolate.¹⁶

It was possible to apply this reaction to an efficient synthesis of the needed norbornene derivatives. Thus allyl alcohol added smoothly and stereoselectively to unsaturated aldehyde 5a. Unlike the corresponding acetate (2a), the resulting allyl ether group of 8 was stable to basic reaction conditions typified by Wolff-Kishner reduction, Grignard addition, and Wittig reaction (8 \rightarrow 10). Furthermore the free alcohol was readily liberated by the action of sodium in liquid ammonia,¹⁷ effectively satisfying the remaining criterion established at the outset of the study. Allyl ethers have been used only sparingly as masked alcohols, although the analogy with the chemically similar benzyl group is clear.¹⁸ The above reduction procedure for the removal of the allyl ether moiety is complementary to the recently reported hydrolytic cleavage of the same group employing rhodium(I)-catalyzed isomerization of the dou-



ble bond and subsequent hydrolysis of the enol ether.¹⁹ Taken together allyl ethers became both an effective hydroxyl masking group as well as a convenient means for effecting the addition of "protected" water to suitably activated olefins.

In conclusion we have determined that 3-exo-substituted 2-endo-acyl-5-norbornenes can be conveniently and stereoselectively prepared by the addition of a variety of nucleophiles to 2-acylnorbornadienes and further that the allyl ether moiety is a versatile hydroxyl masking group.

Experimental Section

Ir spectra were recorded on Perkin-Elmer 137 and 237 spectrophotometers; nmr spectra were determined on either a Varian A-60 spectrometer or a Jeol MH-100 spectrometer with TMS as an internal standard, and are recorded in Table III. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga., or M-H-W Laboratories, Garden City, Mich. Yields have not been optimized. The procedures detailed below are representative of the reaction in general and are not repeated for additional examples of a particular reaction type.²⁶

Dienophiles 1 and 4. *trans*-3-Acetoxypropenal (1a),²⁰ *trans*-3-benzooxypropenal (1b),²⁰ and *trans*-4-acetoxy-3-buten-2-one (1c)²¹ were prepared as described in the literature. *trans*-3-Chloroacrylic acid (1e) and *trans*-4-methoxy-3-buten-2-one (1f) were purchased from Aldrich Chemical Co. and used without further purification. The preparation of propynal²³ (4a) is described in the literature, while 1-butyne-3-one (4b) was purchased from Aldrich Chemical Co. and used as received.

***trans*-5-Acetoxy-2-methyl-4-penten-3-one (1d).** In a 2-l. flask equipped with an overhead stirrer and an N₂ inlet were placed 20.6 g (0.24 mol) of 3-methylbutanone, 5.7 g (0.25 mol) of sodium metal, 21.6 g (0.25 mol) of freshly distilled ethyl formate, 550 ml of dry ether, and 1.5 ml of ethyl alcohol and the resulting mixture was stirred at 0° under N₂ for 20 hr. The precipitated salt was collected by filtration, washed with 100 ml of dry ether, and dried *in vacuo* to afford 26 g (77%) of light yellow solid. After suspension of the above salt (26 g, 0.19 mol) in ether at 0°, 13.3 g (0.17 mol) of acetyl chloride was added dropwise and the reaction mixture was stirred at 0° under N₂ for 2 hr. Filtration and concentration of the filtrate afforded 25 g of mobile liquid which was distilled to afford 17.5 g (45% from ketone) of clear, colorless liquid, bp 53-55° (0.25 mm), that solidified on standing at -10°, ir (CCl₄) 1774 (acetate C=O), 1675 cm⁻¹ (acetyl C=O).

In some preparations, when the crude product was a mixture of *cis* and *trans* isomer by nmr analysis, it was necessary to stir a benzene solution of the crude material with a trace of *p*-toluene-

Table III
Analytical Data for Selected New Compounds^a

Compd	Bp, °C (mm)	Nmr, ^b δ
1d	53.5 (0.25)	1.08 [d, $J = 7$ Hz, 6 H, $-\text{HC}(\text{CH}_3)_2$], 2.18 (s, 3 H, $-\text{COCH}_3$), 2.72 [septet $J = 7$ Hz, 1 H $-\text{CH}(\text{CH}_3)_2$], 6.02 (d, $J = 13$ Hz 1 H, $-\text{COCH}=\text{CH}-$), 8.16 (d, $J = 13$ Hz, 1 H, $-\text{COCH}=\text{CH}-$) ^c
2a	64.5-65 (0.05)	1.48 and 1.74 (broad, 2 H, C-7 H), 2.02 (s, 3 H, $-\text{COCH}_3$), 2.70 (broad, 1 H, C-2 H), 2.98 and 3.13 (broad, 2 H, C-1 H and C-4 H), 4.73 (broad, 1 H, C-3 H), 6.19 (m, 2 H, vinyl H) 9.60 (d, $J = 1.5$ Hz, 1 H, $-\text{CHO}$) ^c
2c	89-91.5 (0.13)	1.70 (m, 2 H, C-7 H), 1.99 (s, 3 H, $-\text{COCH}_3$), 2.08 (s, 3 H, $-\text{COCH}_3$), 2.81 (t, $J = 3$ Hz, 1 H, C-2 H), 2.88 and 3.11 (broad, 2 H, C-1 H and C-4 H), 4.74 (broad, 1 H, C-3 H), 6.07 ($W_{1/2} = 4.5$ Hz, 2 H, vinyl H) ^c
2d	95 (0.08) ^d	1.05 [d, $J = 7$ Hz, 6 H, $-\text{CH}(\text{CH}_3)_2$], 1.71 ($W_{1/2} = 7$ Hz, 2 H, C-7 H), 1.99 (s, 3 H, $-\text{COCH}_3$), 2.66 [septet, $J = 7$ Hz, 1 H, $-\text{CH}(\text{CH}_3)_2$], 2.90 (m, 2 H, C-1 and C-4 H), 2.96 (t, $J = 3$ Hz, 1 H, C-2 H), 4.70 ($W_{1/2} = 5$ Hz, 1 H, C-3 H), 6.06 ($W_{1/2} = 5$ Hz, 2 H, C-5 and C-6 H) ^c
2f	70 (4) ^d	1.57 (m, 1 H, syn C-7 H), 1.76 (m, 1 H, anti C-7 H), 2.04 (s, 3 H, $-\text{COCH}_3$), 2.59 (t, $J = 3$ Hz, 1 H, C-2 H), 2.86 and 3.02 ($W_{1/2} = 8$ Hz, 2 H, C-1 and C-4 H), 3.51 ($W_{1/2} = 6$ Hz, 1 H, C-3 H), 3.26 (s, 3 H, $-\text{OCH}_3$), 5.99 ($W_{1/2} = 19$ Hz, 2 H, vinyl H) ^e
6	90 (22) ^d	1.73 ($W_{1/2} = 10$ Hz, 2 H, C-7 H), 2.58 ($W_{1/2} = 5$ Hz, 1 H, C-2 H), 3.05 ($W_{1/2} = 18$ Hz, 2 H, C-1 and C-4 H), 3.30 (s, 3 H, $-\text{OCH}_3$), 3.50 ($W_{1/2} = 5.5$ Hz, 1 H, C-3 H), 6.15 (m, $W_{1/2} = 13$ Hz, 2 H, vinyl H), 9.53 (d, $J = 1.5$ Hz, 1 H, $-\text{CHO}$) ^c
7	125-126.5 (0.06)	1.52 (m, 1 H, C-7 syn H), 1.86 (m, 1 H, C-7 anti H), 2.80 ($W_{1/2} = 12$ Hz, 1 H, C-2 H), 3.12 ($W_{1/2} = 10$ Hz, 2 H, C-1 and C-4 H), 3.38 (m, 1 H, C-3 H), 6.18 ($W_{1/2} = 20$ Hz, 2 H, vinyl H), 7.25 (m, 5 H, aromatic H), 9.42 (d, $J = 1.5$ Hz, 1 H, $-\text{CHO}$) ^c
8	77-80 (0.05)	1.65 (m, 1 H, C-7 syn H), 1.90 (, 1 H, C-7 anti H), 2.65 (m, $W_{1/2} = 5.5$ Hz, 1 H, C-2 H), 2.95 and 3.05 (broad, 2 H, C-1 and C-4 H), 3.65 ($W_{1/2} = 5$ Hz, 1 H, C-3 H), 4.00 (m, 2 H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), 5.21 (m, 2 H, $-\text{CH}=\text{CH}_2$), 5.93 (m, 1 H, $-\text{CH}=\text{CH}_2$), 6.14 (m, C-5 and C-6 H), 9.25 (d, $J = 1.5$ Hz, $-\text{CHO}$) ^c
9	90 (0.02)	1.70 (m, 2 H, C-7 H), 2.07 (s, 3 H, $-\text{COCH}_3$), 2.64 (t, 1 H, C-2 H), 2.88 and 3.05 (broad, 2 H, C-1 and C-4 H), 3.70 ($W_{1/2} = 5$ Hz, 1 H, C-3 H), 3.99 (d, $J = 5$ Hz, 2 H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), 5.17 (m, 2 H, $-\text{CH}=\text{CH}_2$), 5.71 (m, 1 H, $-\text{CH}=\text{CH}_2$), 6.04 ($W_{1/2} = 7$ Hz, 2 H, C-5 and C-6 H) ^c
10	33 (0.06)	1.59 (m, 1 H, syn C-7 H), 1.84 (m, 1 H, anti C-7 H), 2.44 (m, 1 H, C-2 H), 2.85 ($W_{1/2} = 8$ Hz, 2 H, C-1 and C-4 H), 3.18 ($W_{1/2} = 6$ Hz, 1 H, C-3 H), 3.97 (m, 2 H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), 5.00 (m, 4 H, $-\text{CH}=\text{CH}_2$), 5.45 (m, 1 H, $-\text{CHCH}=\text{CH}_2$), 5.71 (m, 1 H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), 6.09 ($W_{1/2} = 18$ Hz, 2 H, C-5 and C-6 H) ^c
11	55 (0.03)	1.58 (m, 1 H, syn C-7 H), 1.75 (m, 1 H, anti C-7 H), 2.31 ($W_{1/2} = 7$ Hz, 1 H, C-2 H), 2.70 ($W_{1/2} = 7$ Hz, 2 H, C-1 and C-4 H), 3.46 ($W_{1/2} = 5$ Hz, 1 H, C-3 H), 4.11 (1 H, $-\text{OH}$), 5.02 (m, 2 H, $-\text{CH}=\text{CH}_2$), 5.54 (m, 1 H, $-\text{CH}=\text{CH}_2$), 6.11 ($W_{1/2} = 10$ Hz, 2 H, C-5 and C-6 H) ^c

^a Reference 26. ^b Reference 25. ^c 60 MHz. ^d Kugelrohr. ^e 100 MHz.

sulfonic acid for several hours prior to distillation to obtain the pure trans isomer.

Cycloadditions of Acrylic Dienophiles (1) with Cyclopentadiene. Uncatalyzed. The uncatalyzed reactions between cyclopentadiene and dienophiles 1 were performed using the diene as solvent at 35° for 10-50 hr. The disappearance of 1 could be conveniently monitored by glc, except for acid 1e. When the reaction was judged to be complete, the volatile material was removed *in vacuo* and the ratio of products was determined by analysis of the nmr spectrum of the crude material (Table I). The product (2 and 3) was then separated from polymeric material by distillation. Isomer 2 could be separated from 3 by a combination of chromatographic techniques, although usually mixtures were employed in succeeding reactions. In general it was not possible to isolate the minor adduct (3) in a pure state.

2-endo-Acetyl-3-exo-acetoxybicyclo[2.2.1]hept-5-ene (2c). To a 500-ml round-bottom flask containing 113 g (0.89 mol) of dienophile 1c was added 168 g (210 ml, 2.54 mol) of freshly cracked cyclopentadiene and the resulting solution was allowed to stir at room temperature under an N₂ atmosphere for 43 hr, at which time the reaction was shown to be nearly complete by gas chromatography. Removal of the volatile material (0.1 mm, bath 60°) resulted in 99.1 g of oily residue which was shown to be a mixture of the two trans cycloadducts 2c and 3c (ratio 2.6:1) and a small amount of unreacted dienophile by nmr.⁵ Pure 2c (27.3 g, 15.8%) was precipitated from a cold ether-petroleum ether solution of the residue, and then distilled to afford a colorless oil, bp 89-91.5° (0.13 mm). In general it was not feasible to separate large amounts of 2 and 3 by the usual techniques. Rather the distilled mixture of isomers was carried on through succeeding steps.

Catalyzed. 2-endo-Acetyl-3-exo-methoxybicyclo[2.2.1]hept-5-ene (2f). To a stirred solution of 0.71 g (0.003 mol) of cupric tetrafluoroborate⁶ in 30 ml of acetonitrile in a 50-ml flask, cooled to 0° and under N₂ atmosphere, was added 1.00 g (0.01 mol) of dienophile 1f in 10 ml of acetonitrile. After several minutes 6.61

g (0.10 mol, 8 ml) of cyclopentadiene was added and the gradual deposit of insoluble material was observed. Within 15 min the contents of the flask could no longer be stirred, and the flask was allowed to warm to room temperature, where it remained for 15 hr. The reaction mixture was then poured into a separatory funnel containing a solution of 0.03 mol of sodium tartrate and brine. Extraction of the aqueous layer with ether (3 × 50 ml) followed by drying of the combined organics (MgSO₄) and concentration afforded a brown oil which by nmr⁵ contained the single isomer 2f and some polymeric impurities. Distillation in the Kugelrohr fashion (70°, 4 mm) yielded 0.18 g (11% yield) of pure 2f. The yields of other adducts by this procedure usually were higher (40%) but did not equal those of the uncatalyzed reactions. Other solvents tried included acetone and methanol, but in these solvents there was no apparent catalysis.

Cycloaddition of Alkynes (4) with Cyclopentadiene. 2-Formylbicyclo[2.2.1]hepta-2,5-diene (5a). In a 300-ml round-bottom flask was placed 43.3 g (54 ml, 0.66 mol) of freshly cracked cyclopentadiene and 150 ml of petroleum ether (bp 30-60°) and the resulting solution was cooled to 0° with stirring under an N₂ atmosphere. To the above was added over 30 min 32.1 g (0.60 mol) of propynal and the resulting solution was stirred at 0° for 3 hr and an additional 16 hr at room temperature. Removal of volatile material on a rotary evaporator and distillation of the residue (6-in. Vigreux column) afforded 39.5 g (55%) of pure adduct, bp 86-87.5° (27 mm) [lit.^{11a} bp 80° (20 mm)]. In other runs the yields ranged from 40 to 67%.

Addition of Nucleophiles to 5. A. 2-endo-Acetyl-3-exo-methoxybicyclo[2.2.1]hept-5-ene (2f). A solution of 0.84 g (0.043 mol) of a mixture of acetates 2c and 3c (1.8:1), 1.38 g (10 mmol) of anhydrous K₂CO₃, and 20 ml of reagent grade methanol was stirred at room temperature under a nitrogen atmosphere for 30 min. The mixture was filtered and concentrated at reduced pressure, diluted with ether and filtered, and finally concentrated to give 0.58 g of crude product composed of essentially the single iso-

mer **2f** by nmr.⁵ Distillation in the Kugelrohr fashion (70°, 4 mm) afforded 0.55 g (77%) of a clear, mobile liquid identical spectroscopically with that prepared by the cycloaddition.

B. 2-endo-Formyl-3-exo-allyloxybicyclo[2.2.1]hept-5-ene (8). In a flask containing 56.9 g (0.47 mol) of diene **5a** and cooled in an ice bath was added 200 ml of allyl alcohol and 2.3 g (0.017 mol) of anhydrous K₂CO₃. After stirring for 30 min under an N₂ atmosphere, the mixture was filtered, concentrated at reduced pressure, diluted with ether, refiltered, and concentrated to give crude allyl ether **8**. Analysis by nmr⁵ indicated the presence of three isomers (one major). Distillation of the crude product (6-in. Vigreux column) afforded 69.3 g (82%) of colorless product, bp 80–85° (0.05 mm).

2-endo-Vinyl-3-exo-allyloxybicyclo[2.2.1]hept-5-ene (10). According to the procedure of Hauser,²⁴ 16.35 g (0.05 mol) of methyltriphenylphosphonium bromide was placed in a 250-ml, three-neck flask equipped with a nitrogen inlet, addition funnel, and magnetic stirrer. The flask was alternately evacuated and filled with nitrogen (three times) and then 120 ml of dry THF was added and the resulting solution was stirred while 20.4 ml (0.045 mol) of 2.2 M butyllithium was added over 20 min. After the bright yellow slurry was stirred at room temperature for 20 min followed by cooling to –20°, 4.45 g (0.025 mol) of aldehyde **8** in 20 ml of dry THF was added over 10 min. The temperature was maintained at –20° for another 20 min and then allowed to warm to 5°, at which point 50 ml of water was added. The aqueous layer was extracted with hexane (2 × 100 ml) and the combined organic layers were dried (MgSO₄) and concentrated to give an orange oil which was distilled (short path) to afford 2.0 g (45.5%, not optimized) of clear oil, bp 33–34.5° (0.06 mm).

2-endo-Vinyl-3-exo-hydroxybicyclo[2.2.2]hept-5-ene (11). In a 100-ml, three-neck, round-bottom flask equipped with a magnetic stirrer and a Dry Ice condenser and protected from atmospheric moisture by a drying tube was placed 1.61 g (0.092 mol) of allyl ether **10** and 60 ml of NH₃. Sodium (0.425 g, 0.018 mol) was added in small pieces over 20 min, plus a small additional amount until the blue color persisted. After stirring for an additional 15 min solid NH₄Cl was added to discharge the blue color and the NH₃ was allowed to evaporate. Water (20 ml) was added and the reaction mixture was extracted with ether (3 × 75 ml), dried (MgSO₄), and concentrated to give a residual oil which was distilled in the Kugelrohr manner (55°, 0.03 mm) to give 0.92 g (73.5%) of homogeneous alcohol **11**.

Registry No.—**1a**, 51731-22-7; **1c**, 51731-15-8; **1d**, 51731-16-9; **1f**, 51731-17-0; **2a**, 51731-18-1; **2c**, 51731-19-2; **2d**, 51731-20-5; **2f**, 51731-21-6; **3c**, 51773-70-7; **4a**, 624-67-9; **4b**, 1423-60-5; **5a**, 5212-50-0; **5b**, 38739-91-2; **6**, 51731-23-8; **7**, 51731-24-9; **8**, 51731-25-0; **9**, 51731-26-1; **10**, 51731-27-2; **11**, 51731-28-3; cyclopentadiene, 542-92-7; 3-methylbutanone, 563-80-4; acetyl chloride, 75-36-5.

References and Notes

- (1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work. (b) Portions of this work were reported at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1–5, 1974.
- (2) The sesquiterpenes of particular interest are (a) cyclosativene, L. Smedman and E. Zavarin, *Tetrahedron Lett.*, 3833 (1968); (b) longicyclene, U. R. Nayak and S. Dev., *ibid.*, 243 (1963); and (c) cyclocopacamphene, F. Kido, R. Sakuma, H. Uda, and A. Yoshikoshi, *ibid.*, 3169 (1969) (each of these compounds has been previously synthesized); (d) cyclosativene, J. E. McMurry, *ibid.*, 55 (1969); (e) longicyclene, S. C. Welch and R. L. Walters, *Syn. Commun.*, 3, 15 (1973); and (f) cyclocopacamphene, E. Piers, R. W. Britton, R. J. Keziere, and R. D. Smillie, *Can. J. Chem.*, 49, 2623 (1971). A fourth tetracyclic sesquiterpene, cycloseychellene, has recently appeared: S. J. Turhune, J. W. Hogg, and B. M. Lawrence, *Tetrahedron Lett.*, 4705 (1973).
- (3) We have found that the ratio of the two products was only modestly affected by changes in solvent. Thus the ratio of **2c**:**3c** changed from 2.6:1 to 3.5:1 in going from neat cyclopentadiene to acetonitrile. The ratio in methanol was 6:1; but in general the dienophiles (e.g., **1**) reacted with hydroxylic solvents at a rate faster than they underwent cycloaddition.
- (4) K. N. Houk, *J. Amer. Chem. Soc.*, 95, 4092 (1973).
- (5) The relative amounts of the two isomers were determined by integration of the nmr absorptions for the proton at C-3 in the crude reaction mixture while the structural assignments were made by considering the chemical shift and peak shape of the C-2 and C-3 proton absorptions. In general the signal for the endo C-3 proton of isomer **2** occurs at higher field than that for the exo C-3 proton of isomer **3** (δ 5.08 for **2b**, 5.62 for **3b**) and is less well resolved. The exo C-2 proton signal for isomer **2** occurs at lower field than that for the endo C-2 proton of **3** (δ 2.90 for **2b**, 2.32 for **3b**).
- (6) Further confirmation of the assigned structures was gained by catalytic hydrogenation of the pure isomers. In compound **2d** the absorption for the C-3 proton moved from δ 4.67 to 4.70 ($\Delta\delta$ +0.03), while the same absorption for isomer **3d** changed from δ 5.15 to 4.91 ($\Delta\delta$ –0.24). The directions and magnitudes of these shifts are in accord with published values: W. C. Wong and C. C. Lee, *Can. J. Chem.*, 42, 1245 (1964).
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- (9) An appealing rationale for the enhanced specificities and rates of the Lewis acid catalyzed Diels–Alder reaction has recently appeared: K. N. Houk and R. W. Strozler, *J. Amer. Chem. Soc.*, 95, 4094 (1973).
- (10) For instance, reaction of ketone **2c** with the mildly basic methylenetriphenylphosphorane gave a substantial amount of product derived from the initial elimination of acetic acid.
- (11) The cycloadditions of cyclopentadiene with (a) propionaldehyde and (b) 3-buten-2-one have been reported: (a) A. A. Petrov, *J. Gen. Chem. USSR*, 24, 2107 (1954); (b) A. A. Petrov and N. P. Sopov, *ibid.*, 23, 1085 (1953).
- (12) The lone exception was the acid-catalyzed addition of water to aldehyde **5a**, which gave an isomer ratio of 3:1.
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- (26) All new compounds gave satisfactory ($\pm 0.25\%$) combustion analyses.