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Propellanes. 13. On the Magnitude of the Norcaradiene–Cycloheptatriene Energy Difference

Philip M. Warner* and Shih-Lai Lu

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.
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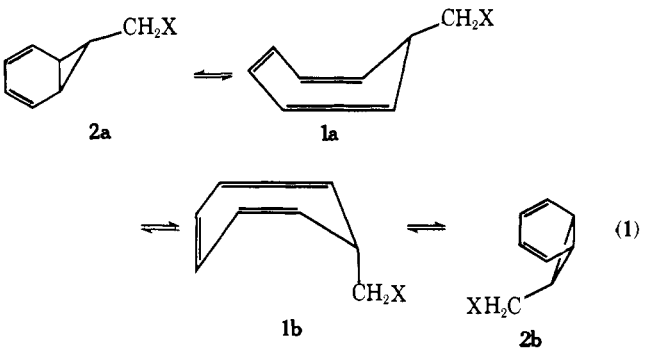
Abstract: The synthesis and solvolysis of dinitrobenzoates **15c–22c** are described. From the kinetic data, one can conclude that the *anti*-norcaradienylcarbinyl ion from **18c** is electronically stabilized relative to the syn ion derived from **22c**. More importantly, the data reveal that the norcaradiene-cycloheptatriene energy gap for a 7-alkyl substituted cycloheptatriene is only 4.0–4.5 kcal/mol, which is far below the previously estimated value (11 ± 4 kcal/mol).

Introduction

The norcaradiene-cycloheptatriene equilibrium problem was rejuvenated by Doering's demonstration[2] that Büchner's esters[3] were actually cycloheptatrienes rather than norcaradienes. Since that time, numerous substituted systems have been synthesized,[4] including some for which one could observe both norcaradiene and cycloheptatriene tautomers. The energy difference between the valence isomers for the parent system was unknown, but was estimated as 11 ± 4 kcal/mol by Doering and Willcott.[5] This widely quoted estimate, which is unfortunately still sometimes utilized,[6] came from a consideration of bond energy terms. An experimental approach[7] to the determination of the desired equilibrium constant, patterned upon Huisgen's[8] dilatometric study of the cyclooctatetraene–bicyclooctatriene valence equilibrium, was thwarted when the authors put more faith in the Doering–Wilcott estimate than in their own data. Their results in fact lead to a free energy difference of 4.0–4.5 kcal/mol, a value in full accord with our data[9] (vide infra).

Our approach to the determination of the norcaradiene–cycloheptatriene energy gap is based on Sargent's demonstration[10] that cycloheptatrienylcarbinyl systems solvolyze via preequilibrium isomerization to norcaradienylcarbinyl de-



(1)

rivatives. Conformational factors permit two distinct geometries for the monocyclic series (eq 1). Thus while Hoffmann[11] and Günther[12] have discussed the symmetry factors which stabilize the ions derived from **2a** and **2b** (and other seven-electron-withdrawing-group-substituted norcaradienes), they have not distinguished between them.

Paquette[13] has investigated the solvolysis of the conformationally fixed bicyclic systems **3** and **4**. Although not initially apparent,[13a] low temperature ^{13}C NMR indicated that **4** is closer in energy to its solvolytically reactive tricyclic tautomer

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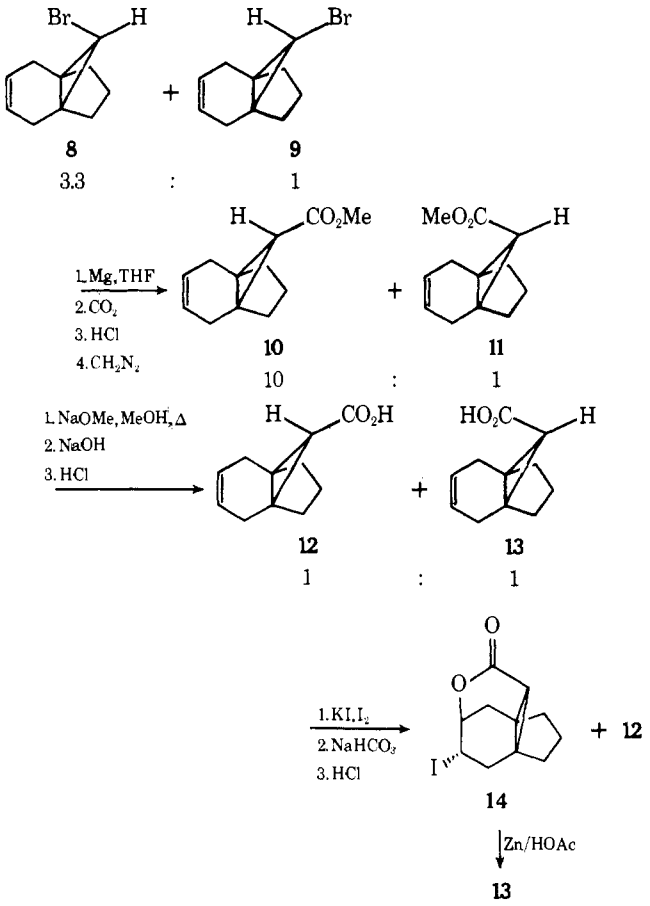
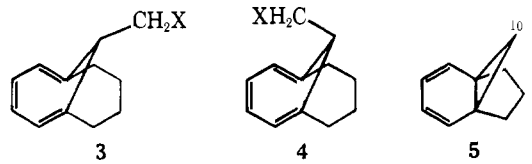
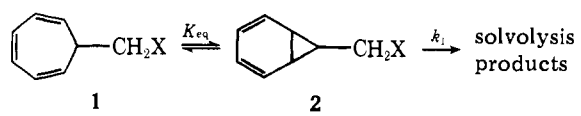
Scheme I



than is **3**. This allowed Paquette[13b] to agree with our earlier conclusion[14] that **2a** is more reactive than **2b**.



If eq 2 represents the Sargent solvolysis,[10] than our idea for obtaining K_{eq} can be readily seen. If we could solvolyze a molecule whose ground state is of structure **2**, then k_1 can be

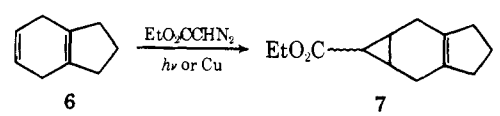


(2)

directly measured. Our choice of C_{10}-substituted derivatives of **5** was based on Vogel's[15] demonstration that **5** exists solely in the norcaradiene form. Because the extra trimethylene group of **5** may produce conformational as well as substitutional changes relative to **2**, suitable models of general structure **5**, but lacking one or both of the double bonds, also had to be studied.

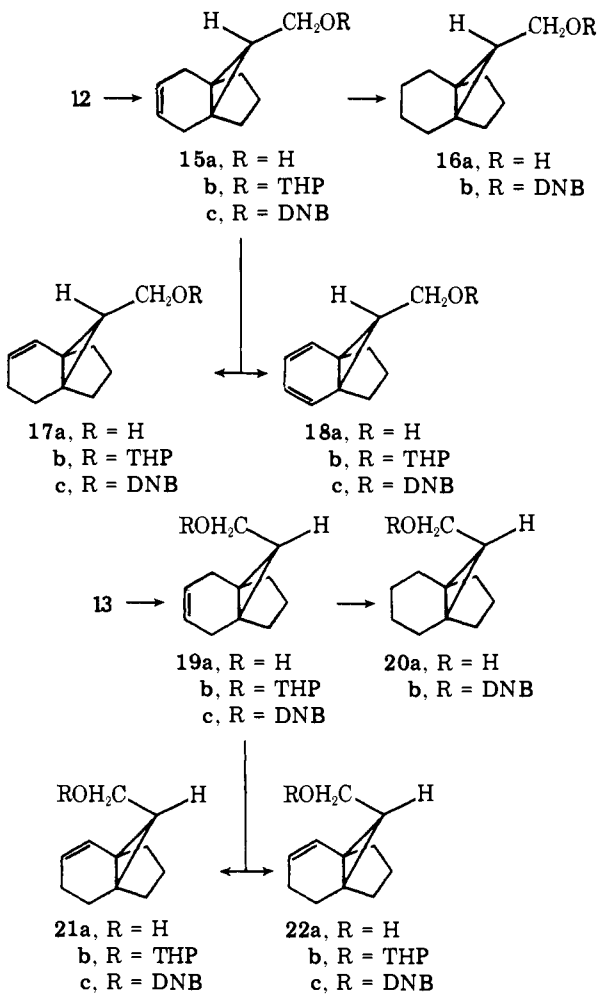
Results and Discussion

Synthesis. Not surprisingly, ethyl diazoacetate addition (photo- or copper-catalyzed) to dihydroindan (**6**) resulted solely in addition to the disubstituted double bond[16] (eq 3). We



(3)

Scheme II



thus resorted to a carboalkoxylative approach through the monobromo compounds[17] **8** and **9** (Scheme I). Thus, the Grignard reagent derived from the mixture of **8** and **9** could be carboxylated either via pouring onto dry ice or, more conveniently, by bubbling CO_2 into the solution; either way the yield was about 40% of **12** and **13**, but with **12** predominating by an order of magnitude.[18] A more equitable distribution of epimers was obtained via basic equilibration of esters **10** and **11**. Subsequently, acids **12** and **13** were separated via iodolactonization[19] of the mixture, whereby **12** remained unchanged (75% recovered). Pure **13** was retrieved in 82% overall yield after cleavage of the iodolactone (**14**).

The synthesis of the requisite cyclopropylcarbinyl compounds proceeded from **12** and **13** as outlined in Scheme II. Compounds stereochemically related to **12** are in the anti series, while those related to **13** are in the syn series. Lithium aluminum hydride reduction of **12** (**13**) routinely afforded **15a** (**19a**), which was hydrogenated to give **16a** (**20a**). The tetrahydropyranyl ether derivative **15b** (**19b**) was converted into a 1:1 mixture of **15b** (**19b**) and **17b** (**21b**) upon heating at 75 °C in KO-*t*-Bu-Me_2SO solution.[20] Separation was achieved via chromatography ($AgNO_3$-impregnated silica gel) to afford **17b** (**21b**) in 66% (51%) yield. The structure of **17** (**21**) is clearly indicated by the ^1H NMR spectra of the alcohols: **17a** shows half of an AB quartet (J = 10 Hz) at δ 6.02 (olefinic H), an approximate triplet of doublets (J = 10, J = 3 Hz) at δ 5.31 (olefinic H) and a triplet (J = 7 Hz) at δ 1.33 (cyclopropyl H); **21a** shows half of an AB quartet (J = 10 Hz) at δ 5.84 (olefinic H), a triplet of doublets (J = 10, $J \cong$ 3 Hz) at δ 5.55 (olefinic H) and a triplet (J = 7 Hz) at δ 1.10 (cyclopropyl H).

Table I. Solvolysis Data for 3,5-Dinitrobenzoates in 70:30 Acetone-Water

	compd	T (±0.1), °C	k, s^{-1}	k_{rel} (70 °C)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
anti series	**15c**	70.0	$(5.18 \pm 0.44) \times 10^{-6}$	2.1	27.6 ± 0.9	−2.6 ± 2.7
		100.0	$(1.46 \pm 0.04) \times 10^{-4}$			
	16c	70.0	$(2.17 \pm 0.09) \times 10^{-5}$	8.6	25.3 ± 0.7	−6.2 ± 2.0
		100.0	$(4.70 \pm 0.20) \times 10^{-4}$			
	17c	70.0	$(8.49 \pm 0.26) \times 10^{-6}$	3.4	26.4 ± 0.6	−4.8 ± 1.4
		100.0	$(2.10 \pm 0.06) \times 10^{-4}$			
	18c	70.0	$(2.03 \pm 0.07) \times 10^{-4}$	80	26.4 ± 0.6	1.2 ± 1.5
		100.0	$(4.96 \pm 0.15) \times 10^{-3}$			
syn series	**19c**	70.0	$(3.04 \pm 0.30) \times 10^{-6}$	1.2	25.4 ± 1.0	−9.9 ± 2.6
		100.0	$(6.64 \pm 0.06) \times 10^{-5}$			
	20c	70.0	$(1.04 \pm 0.02) \times 10^{-5}$	4.1	25.5 ± 0.3	−7.1 ± 0.6
		100.0	$(2.31 \pm 0.02) \times 10^{-4}$			
	21c	70.0	$(3.78 \pm 0.27) \times 10^{-6}$	1.5	28.7 ± 1.3	0.1 ± 3.6
		100.0	$(1.22 \pm 0.10) \times 10^{-4}$			
	22c	70.0	$(2.53 \pm 0.13) \times 10^{-6}$	1.0	25.9 ± 0.7	−8.8 ± 2.1
		100.0	$(5.86 \pm 0.22) \times 10^{-5}$			

Conversion of **15b** (**19b**) to **18b** (**22b**) was effected via bromination (CH_2Cl_2, −78 °C), followed by bisdehydrobromination (DBU in THF, 45 °C, 2 days); the isolated overall yield was 68% (65%). While uneventful for the other compounds studied herein, hydrolysis of **18b** (**22b**) had to be carefully controlled in order to avoid acid-catalyzed rearrangement to 4-vinylindan (**23**). The norcaradiene structure of **18a** was evident from the high-field cyclopropyl resonance (δ 0.35, triplet, J = 7 Hz) and the slightly deshielded methine protons (δ 3.95, doublet, J = 7 Hz). In contrast, **22a** showed a deshielded cyclopropyl proton (δ 1.18, triplet, J = 7 Hz) and a shielded methine resonance (δ 2.88, doublet, J = 7 Hz). Both compounds yielded appropriate UV spectra (see Experimental Section).

All alcohols (**15a–22a**) gave 3,5-dinitrobenzoate esters smoothly.

Kinetics. Because of solubility problems, we could not use the 60% aqueous acetone medium utilized by Sargent.[10] Our data, obtained in 70% aqueous acetone (0.1 M in RODNB), are summarized in Table I; runs were duplicate.

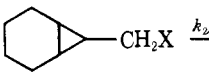
The calculated activation parameters, which are probably subject to greater error than indicated because of the fact that they are derived from measurements at only two temperatures, are generally consistent with Paquette's results[13b] (e.g., a lower $\Delta S^{\ddagger}$ for **3** than **4**). The fact that the ca. 80-fold rate difference between **18c** and **22c** is due to entropy effects is consistent with the idea that the anti transition state (from **18c**) has a spatially more diffuse charge than does that from the syn isomer, **22c**. Although one might be tempted to explain the remaining activation parameter differences, whereby one would note some discrepancies, such an attempt would be too tortuous. All of the systems studied are cyclopropylcarbinyl, and, as in another study of cyclopropylcarbinyl systems by Paquette,[21] the activation parameters follow no simple pattern. Nevertheless, the relative rate comparisons which are necessary to estimate the norcaradiene-cycloheptatriene energy gap do not change appreciably between 70 and 100 °C.

The most important lesson to be learned from Table I is that the anti configuration of the carbinyl carbon (i.e., **18c**) implicates **2a** as the reactive form of **1**. Since the steric environment of **15c–18c** is constant, and only **18c** solvolyzes appreciably faster than its epimer, steric factors cannot be a significant source of the rate difference between **18c** and **22c**. We have previously[14b] discussed the electronic origin of the observed rate difference. Via extended Hückel calculations, Stohrer and Daub[22a] have calculated that the *anti*-norcaradienylcarbinyl cation is 3.9 kcal/mol more stable than the corresponding syn ion. We may calculate the energy difference between the transition states for the formation of the epimeric norcaradienylcarbinyl cations (eq 4).

$$\Delta F = -RT \ln \frac{k_{22c}/k_{20c}}{k_{18c}/k_{16c}} = 2.5 \pm 0.1 \text{ kcal/mol (70 °C)}; \quad 2.8 \pm 0.1 \text{ kcal/mol (100 °C)} \quad (4)$$

Our calculation factors out much of the steric effects, although this point was not considered in the theoretical calculations.[22a]

In order to ascertain the norcaradiene-cycloheptatriene energy gap, we must solve eq 2. As already mentioned, since steric factors change upon going from **2a** to **18c**, we must utilize appropriate models to allow for these. For instance, with reference to eq 2 and 5, we have eq 6-8, where eq 7 is obviously the key. From our data at 100 °C, we find $K_{eq} = (2.6 \pm 0.2) \times 10^{-3}$ [23] and $\Delta F = 4.45 \pm 0.05$ kcal/mol. Alternatively, utilizing 25[10] in place of **24** (and **15c** rather than **16c**), we obtain $K_{eq} = (5.1 \pm 0.3) \times 10^{-3}$ [23] and $\Delta F = 3.93 \pm 0.05$ kcal/mol. These numbers are very similar to our previous report[14a] based on our data at 70 °C (ΔF = 4.4, 4.1 kcal/mol, respectively). Despite appreciable differences in the choice of models and experimental uncertainty in the measurements, it is seen that the derived free energy differences do not vary greatly. Even assuming larger errors in the data, the ΔF values would change by only a few tenths of a kilocalorie/mole.

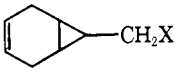


24 (5)

$$\frac{k_1^{obsd}}{k_{24}} = \frac{K_{eq}k_1}{k_{24}} \quad (6)$$

$$\frac{k_{18c}}{k_{16c}} \cong \frac{k_1}{k_{24}} \quad (7)$$

$$\therefore K_{eq} \cong \frac{k_1^{obsd}k_{16c}}{k_{24}k_{18c}} \quad (8)$$



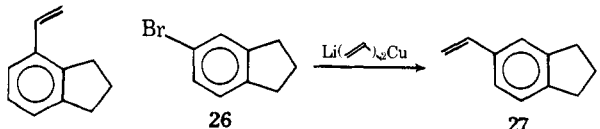
25

$$\frac{k_1}{k_{25}} = \frac{k_{18c}}{k_{15c}}$$

Products. Although the solvolysis products are not germain to the main thrust of this study, it was necessary to be sure that alkyl-oxygen cleavage was occurring. Our aforementioned experience with the acid-catalyzed rearrangement of **18b** to

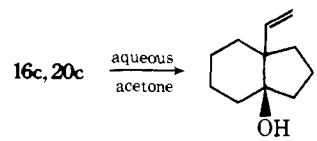
23 was worrisome, in that acyl-oxygen cleavage of **18c** to **18a** could be followed by rearrangement to the observed **23**. However, none of the alcohols (**15a–22a**) gave any of the observed solvolysis products under the unbuffered hydrolysis conditions, thereby eliminating the acyl-oxygen cleavage route.

4-Vinylindan (**23**) was identified as the only solvolysis product from **18c** (84%) and **22c** (86%) on the basis of its ^1H NMR spectrum, an IR absorption at 725 cm^{-1} (three adjacent aromatic ring protons), and its nonidentity with 5-vinylindan (**27**) which was prepared from **26** (**27** showed IR bands at 830 and 870 cm^{-1}, characteristic of a 1,2,4-trisubstituted benzene). The mechanism for formation of **23** is presumably as described by Paquette.[13b]

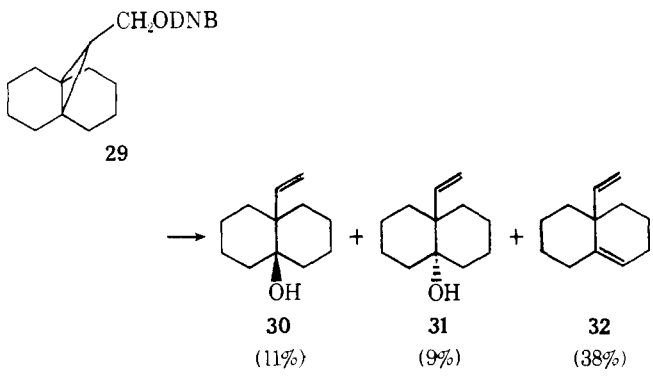


23 26 27

The products from **15c–17c** and **19c–21c** were investigated after solvolysis for 10 half-lives. All were homoallylic alcohols, but yields were not high due to product decomposition. Both **16c** and **20c** gave a ca. 40% yield of cis alcohol **28**; the stereochemistry was assigned on the basis of an additional sharp (intramolecular hydrogen bonding) hydroxyl absorption at 3570 cm^{-1} (others at 3615 and 3420 cm^{-1}). Interestingly, Paquette[13b] found the isomeric 9-vinyldecan-10-ols in almost equal amounts starting from **29**; we find no product analogous to **32**, but we cannot exclude such a product.



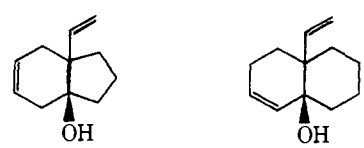
28



29

30 (11%) 31 (9%) 32 (38%)

Only small amounts of a single alcohol, presumably **33**, were isolated from unbuffered solvolysis of **15c** and **19c**. We presume the ring-fusion stereochemistry results primarily from thermodynamic considerations. However, electronic factors may be important, particularly for the one-third of the starting material (**15c, 16c, 19c, 20c**) which leads to internally returned dinitrobenzoate of general structure **28** and **33**. We have previously[14b] discussed the product (**34**) from **17c** and **21c**.



33 34

Conclusion

In summary, we have demonstrated that anti conformation **2a** is solvolytically more reactive than syn conformation **2b**, for reasons which are likely due to electronic factors, but which manifest themselves in the entropic term. Most importantly, we have shown that the energy difference between **1a** and **2a** is ca. 3.9–4.5 kcal/mol. This simply substituted cycloheptatriene provides a reasonably valid model for the parent system itself. Thus the energy gap between cycloheptatriene and norcaradiene, now studied by three independent experimental methods, appears to be well below the value originally estimated from bond energy terms.

Experimental Section

Infrared spectra were recorded on Beckman IR-12, IR-18A, and IR-4250 spectrophotometers. The ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. The proton magnetic resonance spectra were obtained on Varian A-60, and Hitachi Perkin-Elmer R-20B spectrometers, using carbon tetrachloride as the solvent and tetramethylsilane as the internal standard, unless otherwise specified. The carbon magnetic resonance spectra were recorded on a Bruker HX-90 spectrometer equipped with a Nicolet Model 1089 data package. The mass spectral studies were conducted using Atlas CH-4, High Resolution MS-9, and Perkin-Elmer 270 GLC-mass spectrometers. GLC analyses were conducted on a Varian Aerograph Model 90-P gas chromatograph. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by the Ilse Beetz Microanalytical Laboratory, Kronach, West Germany, and Spang Microanalytical Laboratory, Ann Arbor, Mich.

The following GLC columns were utilized:

A	10 ft × 0.125 in.	3% DEGS on Chromosorb P
B	6 ft × 0.25 in.	20% DEGS on Chromosorb P
C	8 ft × 0.25 in.	20% SE-30 on Chromosorb P
D	5 ft × 0.25 in.	3% SE-30 on Varaport 30
E	6 ft × 0.25 in.	20% dinonyl phthalate on Chromosorb W
F	10 ft × 0.25 in.	5% Carbowax 20M on Chromosorb W
G	6 ft × 0.25 in.	15% FFAP on Chromosorb P
H	15 ft × 0.125 in.	12% DC-550 on Chromosorb W

[4.3.1]Propell-3-enyl-*anti*- and -*syn*-10-carboxylic Acids (12 and 13). To a refluxing mixture of 6.5 g (0.27 mol) of magnesium in 26 mL of freshly distilled THF was added a solution of 6.5 mL dibromoethane in 25 mL of dry THF. After the evolution of ethylene subsided, a solution of 21.6 g (0.074 mol) of bromides **8** and **9** (3.3 to 1 ratio) in 155 mL of dry THF was added dropwise to the slurry over a period of 30 min. The resultant mixture was refluxed for 1 additional h and then cooled to room temperature. Carbon dioxide was bubbled through the mixture overnight. Dilution with 100 mL of ether was followed by acidification with 2 N HCl solution. The resulting milky suspension was extracted with ether several times, and the combined ethereal layers were than extracted with dilute NaOH solution. Reacidification of the basic solution with 2 N HCl, followed by ether extraction, drying over anhydrous Na_2SO_4 and concentration in vacuo gave 7.6 g (43%) of the white solid carboxylic acids, mp 153–156 °C (hexane). Spectral data for the separate acids are given later. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.34; H, 8.14.

Equilibration of 12 and 13 via Their Methyl Esters (10 and 11). A stirred solution of 5.0 g (28.2 mmol) of **12** and **13** in 75 mL of ether was titrated with ethereal diazomethane solution at room temperature until the yellow color persisted and no further bubbles were evolved. The solution was concentrated to give a yellow oil (5.23 g, 97%). The ratio of esters **10** to **11** was determined by ^1H NMR as 10 to 1 (δ 3.52 for OCH_3 of **10** and δ 3.47 for OCH_3 of **11**). Preparative separation of the epimers was attempted, without success, on columns E and F. A single symmetrical peak was observed in each case. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.05; H, 8.44.

To a solution of 4.33 g (22.5 mmol) of **10** and **11** in 50 mL of absolute methanol was added 12.2 g (225 mmol) of sodium methoxide. The resulting brown mixture was refluxed for 46 h. Upon cooling, the mixture was diluted with 50 mL of ether and washed with 5 × 20 mL of water. After drying over anhydrous sodium sulfate and removal of

solvent, there remained an oil which weighed 0.88 g and contained an equal amount of **10** and **11**. Acidification of the combined aqueous layers yielded the corresponding acids (3.06 g). Saponification of the remaining esters, followed by acidification, produced **12** and **13** (0.81 g). The overall yield (3.87 g) was 78%.

Separation of 12 and 13 via Iodolactonization. A solution of 10.1 g (56 mmol) of equilibrated **12** and **13** in 500 mL of 0.5 N sodium bicarbonate solution, and a solution of 28.6 g (112 mmol) of I_2 and 56.0 g (337 mmol) of KI in 150 mL of water were mixed and stirred in a 1-L flask which was wrapped with aluminum foil to avoid decomposition of the product. After 24 h, the dark brown oil was separated from the aqueous solution, which was then extracted with 3 × 200 mL of chloroform. The combined organic layers were shaken with 2 × 150 mL of 10% sodium thiosulfate solution, followed by washing with 2 × 80 mL of water and drying over anhydrous sodium sulfate. Finally, removal of solvent yielded 7.90 g of yellow solid. Two recrystallizations from 95% ethanol gave 7.75 g (90% yield based on **13** used) of **14**, mp 135–136 °C (ethanol): IR ($CHCl_3$) 1720, 1710, 1365, 1070, and 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.52 (m, 2 H), 3.40–2.30 (m, 4 H), and 2.25–1.05 (m, 7 H); mass spec, parent ion at *m/e* 304. Anal. Calcd for $C_{11}H_{13}O_2I$: C, 43.44; H, 4.31. Found: C, 43.39; H, 4.47. The aqueous solution separated from the reaction mixture was treated with 10% sodium thiosulfate solution until the red color disappeared. After acidification with 2 N hydrochloric acid, the resulting mixture was extracted with 3 × 200 mL of ether. The ethereal layers were combined, dried, and concentrated. The white solid **12** weighed 3.77 g (75%), mp 160–162 °C (ether): IR (CCl_4) 3500–2400 and 1700 cm^{-1}; ^1H NMR δ 12.7 (s, 1 H), 5.45 (m, 2 H), and 2.8–1.4 (m, 11 H); mass spec, parent ion at *m/e* 178.

Esterification of **12** with diazomethane gave a quantitative yield of **10**: IR (CCl_4) 1735 cm^{-1}; ^1H NMR δ 5.40 (m, 2 H), 3.52 (s, 3 H), and 2.7–1.5 (m, 11 H); mass spec, parent ion at *m/e* 192.

[4,3,1]Propell-3-enyl-*syn*-10-carboxylic Acid (13) from Iodolactone 14. To a solution of 7.5 g (2.46 mmol) of **14** in 12 mL of glacial acetic acid was added 2.0 g of zinc dust. The mixture was stirred at 90 °C for 6.5 h. The resulting mixture was filtered and washed with 2 × 10 mL of hot water. After cooling to room temperature, the filtrate was extracted with 3 × 30 mL of ether. Evaporation of the ether gave a white solid **13** which was redissolved in 5% potassium hydroxide and acidified with 2 N hydrochloric acid. Filtration and drying left 3.97 g (91%) of **13**, mp 145–147 °C (ether). IR (CCl_4) 3500–2400 and 1710 cm^{-1}; ^1H NMR δ 12.6 (s, D_2O exchangeable, 1 H), 5.40 (m, 2 H), and 2.7–1.3 (m, 11 H); mass spec, parent ion at *m/e* 178.

***anti*-10-Hydroxymethyl[4,3,1]propell-3-ene (15a).** To 1.95 g (51.5 mmol) of lithium aluminum hydride suspended in 30 mL of anhydrous ether in a 250-mL two-necked flask equipped with magnetic stirrer, addition funnel, and a drying tube on the top of the reflux condenser, was added 3.00 g (16.9 mmol) of **12** in 80 mL of ether at such a rate as to produce gentle reflux. The mixture was allowed to stir for 24 h. The excess hydride was decomposed by adding 25 mL of **20**% sodium potassium tartrate solution. The layers were separated, and the aqueous layer was extracted with 3 × 10 mL of ether. The combined ethereal layers were dried over anhydrous sodium sulfate and concentrated. The colorless oil solidified upon cooling, and recrystallization from hexane gave 2.18 g (79%) of **15a**. The solid was hygroscopic: IR (CCl_4) 3635, 3340, 3040, 1660, 1115, 1060, and 1020 cm^{-1}; ^1H NMR δ 5.40 (m, 2 H), 3.72 (br, OH), 3.35 (d, 2 H, J = 7 Hz), 2.20–1.20 (m, 10 H), and 1.03 (t, 1 H, J = 7 Hz). Anal. Calcd for $C_{11}H_{16}O$: *m/e* 164.1201. Found: 164.1202.

***syn*-10-Hydroxymethyl[4,3,1]propell-3-ene (19a).** Treatment of the *syn*-carboxylic acid (**13**) (3.97 g) as described for **12** gave a 92% yield (3.36 g) of the syn alcohol (**19a**), which solidified when cooled: IR (film) 3340, 3020, 1660, 1100, 1030, and 1010 cm^{-1}; ^1H NMR δ 5.47 (m, 2 H), 3.88 (br s, OH), 3.38 (d, 2 H, J = 7 Hz), 2.50–1.00 (m, 10 H), and 0.81 (t, 1 H, J = 7 Hz). Anal. Calcd for $C_{11}H_{16}O$: *m/e* 164.1201. Found: 164.1202.

***anti*-10-Tetrahydropyranyloxymethyl[4,3,1]propell-3-ene (15b).** To 2.88 g (17.6 mmol) of **15a** was added 1.50 g (17.9 mmol) of 3,4-dihydropyran, to which had been added 5 drops of concentrated hydrochloric acid. The mixture was allowed to stir at room temperature for 5 h. Dilution with 20 mL of ether was followed by extraction with 2 × 5 mL of saturated sodium bicarbonate solution and then 2 × 5 mL of water. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and evaporated. The yellow oil was chromatographed on silica gel and eluted with a hexane/ether mixture to yield 3.58 g (82%) of **15b** as a colorless oil. The sample was suitable for analysis: IR (CCl_4) 3020, 1650 (w), 1075, and 1020 (s) cm^{-1}; ^1H NMR δ 5.42 (m, 2 H), 4.48 (br s, 1 H), 3.90–3.15 (m, 4 H), 2.70–1.20 (m, 16 H), and 1.03 (t, 1 H, J = 7 Hz); mass spec, parent ion at *m/e* 248. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.36; H, 9.53.

***syn*-10-Tetrahydropyranyloxymethyl[4,3,1]propell-3-ene (19b).** Treatment of syn alcohol **19a** (3.30 g) as described for **15a** gave a brownish oil which was purified by column chromatography to yield 4.25 g (85%) of **19b**; IR (CCl_4) 3010, 1655 (w), 1075, 1050, and 1020 (s) cm^{-1}; ^1H NMR δ 5.50 (m, 2 H), 4.41 (br s, 1 H), 3.80–3.05 (m, 4 H), 2.75–1.10 (m, 16 H), and 0.87 (t, 1 H, J = 7 Hz); mass spec, parent ion at *m/e* 248. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.36; H, 9.53.

***anti*-10-Tetrahydropyranyloxymethyl[4,3,1]propella-2,4-diene (18b).** To a solution of 2.55 g (10.3 mmol) of **15b** in 10 mL of methylene chloride which was cooled to −78 °C was slowly added a solution of 1.65 g (10.3 mmol) of bromine in 1.5 mL of methylene chloride. After stirring at −78 °C for 30 min, the mixture was warmed to room temperature. Removal of solvent under vacuum at less than 35 °C resulted in a brownish oil which was used for dehydrobromination without further purification. The dibromo compound was dissolved in 10 mL of freshly distilled THF (predried over lithium aluminum hydride). Under nitrogen, 15 mL of a dry THF solution containing 5.0 g (33 mmol) of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) was slowly syringed into the solution of the dibromo compound. A brown precipitate formed as soon as the DBU was added. The resulting mixture was heated at 45 °C for 48 h. After cooling, 5 mL of water was added, followed by extraction with 4 × 15 mL of ether. The combined ethereal layers were dried, filtered, and stripped of solvent. The resulting brown oil was chromatographed on silica gel using 1% ether in hexane as the eluent. Analytically pure **18b** (1.72 g, 68%) was obtained as a slightly yellow oil: IR (film) 3040, 1080, and 1028 cm^{-1}; ^1H NMR δ 6.30–5.60 (AA′BB′, 4 H), 4.60 (br s, 1 H), 4.10–3.25 (m, 4 H), 2.40–0.90 (m, 12 H), and 0.31 (t, 1 H, J = 7 Hz); mass spec, parent ion at *m/e* 246. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.88; H, 8.76.

***syn*-10-Tetrahydropyranyloxymethyl[4,3,1]propella-2,4-diene (22b).** Treatment of **19b** (2.50 g) as described for **15b** gave a yellow oil which was chromatographed to yield 65% (1.63 g) of **22b**: IR (film) 3040, 1064, and 1035 cm^{-1}; ^1H NMR δ 5.90 (AA′BB′, 4 H), 4.36 (s, 1 H), 3.90–3.30 (m, 2 H), 3.05 (dd, 1 H, J = 12, J = 7 Hz), 2.65 (dd, 1 H, J = 12, J = 7 Hz), and 2.40–1.10 (m, 13 H); mass spec, parent ion at *m/e* 246. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.88; H, 8.76.

***syn*-10-Tetrahydropyranyloxymethyl[4,3,1]propell-2-ene (21b).** In a 100-mL three-necked flask, 3.90 g (34.8 mmol) of potassium *tert*-butoxide in 25 mL of dimethyl sulfoxide was heated to 70 °C under nitrogen. A 20-mL dimethyl sulfoxide solution containing 2.80 g (11.3 mmol) of **19b** was syringed into the mixture. The resulting mixture became dark brownish immediately. After heating at 75 °C for 14 h, the mixture was poured into 50 mL of H_2O and extracted with 4 × 50 mL of ether. The combined ethereal layers were sequentially washed with 2 × 10 mL of 10% hydrochloric acid solution, 2 × 10 mL of 0.5 N sodium bicarbonate solution, and 2 × 10 mL of water. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated to give a crude product which was chromatographed on silica gel. Elution with 2% ether in hexane gave a mixture of **19b** and **21b** (1.90 g, 68%). Separation of the mixture (0.45 g) was achieved by column chromatography, using a 12% silver nitrate-impregnated silica gel packing on a 0.5 × 20 in. column and eluting with 500 mL of hexane, then 1% Et_2O/hexane, and finally ether. Fractions (15 mL) were collected; fractions 31–59 (0.18 g) were identified as containing **19b** and fractions 65–68 (0.18 g) as containing **17b** (^1H NMR analysis): IR (film) 3020, 1660 (w), 1050, and 1020 cm^{-1}; ^1H NMR δ 5.95–5.40 (m, 2 H), 5.40 (s, 1 H), 3.90–3.00 (m, 4 H), 2.30–1.20 (m, 16 H), 1.12 (t, 1 H, J = 7 Hz); mass spec, parent ion at *m/e* 248. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.27; H, 9.61.

***anti*-Tetrahydropyranyloxymethyl[4,3,1]propell-2-ene (17b).** Treatment of **15b** (2.36 g) as described for **19b** gave a 79% (1.86 g) yield of a mixture of **15b** and **17b**. Separation was accomplished over a 12% silver nitrate impregnated silica gel 60 dry column (1 × 60 in.). Two spots (R_f 0.11 and 0.34) were found via TLC, where the TLC plate was pretreated with an acetonitrile solution containing silver nitrate (developing solvent 8% ether/hexane): IR (CCl_4) 3035, 1630 (w), 1055, and 1020 cm^{-1}; ^1H NMR δ 6.00 (d, 1 H, J = 10 Hz), 5.50–5.10 (m, 1 H), 4.50 (s, 1 H), 4.00–3.15 (m, 4 H), and 2.20–1.10 (m, 17 H); mass spec, parent ion at *m/e* 248. Anal. Calcd for

Table II. Physical Properties and Analyses for 3,5-Dinitrobenzoates **15c–22c**

compd	mp, °C	yield, %	mass spect m/e, at 70 eV		elemental anal.			
					calcd		found	
			calcd	found	% C	% H	% C	% H
15c	81–82.5	74	358	358	60.33	5.06	60.44	4.93
16c	104–105	54	360	360	59.99	5.59	59.82	5.53
17c	84–85	69	358	358	60.33	5.06	60.38	5.05
18c	113–114	36	356	356	60.67	4.53	60.64	4.69
19c	98–99	52	358.1165	358.1159				
20c	86–87	77	360	360	59.99	5.59	60.00	5.70
21c	104–105	66	358.1165	358.1144				
22c	92–94	38	356.1008	356.0983				

$C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.38; H, 9.73.

***syn*-10-Hydroxymethyl[4.3.1]propellane (20a).** A mixture of 0.59 g (3.6 mmol) of **19a** and 0.15 g of 5% Pt/C in 30 mL of ether was stirred at room temperature under a 15-psi hydrogen atmosphere for 1 h. The catalyst was then filtered off and washed with 2 × 10 mL of ether. After removal of solvent, the crude product was recrystallized from pentane (0.57 g, 97%): mp 41–42 °C; IR (CCl_4) 3620, 3350, 1085, 1060, 1045, and 1010 cm^{-1}; ^1H NMR δ 4.22 (s, OH), 3.64 (d, 2 H, J = 7 Hz), 2.10–1.00 (m, 14 H), and 0.78 (t, 1 H, J = 7 Hz); mass spec, parent ion at *m/e* 166. Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.50; H, 10.91.

***anti*-10-Hydroxymethyl[4.3.1]propellane (16a).** Hydrogenation of **15a** (0.52 g) as described for **19a** gave a 94% (0.49 g) yield of **16a** which failed to crystallize: IR (CCl_4) 3640, 3350, 1100, and 1010 cm^{-1}; ^1H NMR δ 4.00 (s, OH), 3.56 (d, 2 H, J = 7 Hz), 2.3–1.0 (m, 14 H), 0.86 (t, 1 H, J = 7 Hz); mass spec, parent ion at *m/e* 166. Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.40; H, 10.87.

***anti*-10-Hydroxymethyl[4.3.1]propella-2,4-diene (18a).** To 0.60 g (2.44 mmol) of **18b** in 2 mL of 95% ethanol was added 5 mg of *p*-toluenesulfonic acid. The mixture was stirred at 55 °C for 1 h and then poured into a mixture of 4 mL of water and 60 mL of ether. After separation of the layers, the ether layer was washed with 2 × 5 mL of 0.5 N sodium bicarbonate solution, 2 × 5 mL of water, dried, and stripped of solvent. The yellow oil thus obtained failed to crystallize. Column chromatography on silica gel (methylene chloride elution) produced 0.28 g (71%) of pure **18a**: IR (benzene) 3600, 3450, 1090, and 1010 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.40–5.60 (AA′BB′, 4 H), 4.60 (s, 1 H, OH), 3.95 (d, 2 H, J = 7 Hz), 2.70–1.30 (m, 6 H), and 0.35 (t, 1 H, J = 7 Hz); UV (cyclohexane) 272 (4170), 254 (3960), and 248 (4000) nm; mass spec, parent ion at *m/e* 162. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.22; H, 8.73.

***syn*-10-Hydroxymethyl[4.3.1]propella-2,4-diene (22a).** Treatment of 0.54 g of **22b** as described for **18b** gave 68% (0.23 g) of **22a** after column chromatography: IR (film) 3410, 3040, 1090, 1070, and 1020 cm^{-1}; ^1H NMR δ 5.95 (AA′BB′, 4 H), 4.50 (s, 1 H, OH), 2.88 (d, 2 H, J = 7 Hz), 2.70–1.20 (m, 6 H), and 1.18 (t, 1 H, J = 7 Hz); UV (cyclohexane) 257 (3230), 252 (4040), and 246 (3230); mass spec, parent ion at 162. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.22; H, 8.73.

***anti*-10-Hydroxymethyl[4.3.1]propell-2-ene (17a).** Treatment of 0.40 g of **17b** as described for **18b** gave 68% (0.18 g) of **17a** after column chromatography (elution with CH_2Cl_2): IR (CCl_4) 3630, 3330, 3030, 1640, 1100, 1065, and 1025 cm^{-1}; ^1H NMR (CCl_4) δ 6.02 (d, 1 H), 5.50–5.10 (m, 1 H), 3.57 (d, 2 H, J = 7 Hz), 2.70 (s, OH), 2.50–1.30 (m, 10 H), and 1.33 (t, 1 H, J = 7 Hz). Anal. Calcd for $C_{11}H_{16}O$: *m/e* 164.1201. Found: *m/e* 164.1194.

***syn*-10-Hydroxymethyl[4.3.1]propell-2-ene (21a).** Treatment of 0.35 g of **21b** as described for **18b** gave 65% (0.15 g) of **21a**; IR (CCl_4) 3640, 3040, 1635, 1100, 1065, and 1020 cm^{-1}; ^1H NMR δ 6.00–5.40 (m, 2 H), 3.40 (d, 2 H, J = 7 Hz), 3.00 (s, 1 H), 2.30–1.30 (m, 10 H), and 1.10 (t, 1 H, J = 7 Hz); mass spec, parent ion at *m/e* 164. Anal. Calcd for $C_{11}H_{16}O$: C, 80.49; H, 9.82. Found: C, 80.19; H, 9.87.

General Procedure for the 3,5-Dinitrobenzoates (15c–22c). To a solution of 0.20 g (1.22 mmol) of alcohol in 10 mL of dry pyridine was added 0.40 g (1.74 mmol) of 3,5-dinitrobenzoyl chloride (which was previously recrystallized twice from ether and hexane). The mixture was stirred at room temperature for 2 h and then left in the refrigerator overnight. The resulting mixture was poured onto ice–water. After ether extraction, the combined ether layers were washed with 10% HCl solution, then 0.5 N $NaHCO_3$ solution, and finally saturated NaCl solution. After drying over anhydrous sodium sulfate and removal of solvent, the remaining solid was recrystallized from CCl_4/hexane to give the pure 3,5-dinitrobenzoate. The data for the various 3,5-dinitrobenzoates (**15c–22c**) are collected in Table II.

Kinetics. A stock solution of 70:30 (by volume) acetone–water was prepared from purified acetone (distilled from $KMnO_4$) and distilled water. Solvolyses were carried out in sealed ampules, into which 3.5 mL of 0.0100 M 3,5-dinitrobenzoate solution had been transferred. A set of ampules was immersed in a constant-temperature bath at the appropriate temperature. After allowing 3 min for temperature equilibration, the zero point was taken and an accurate timer was started. After the appropriate times, the ampules were withdrawn, cooled in ice, brought to room temperature and opened. A 2.99-mL aliquot was pipetted and titrated with standardized 0.0142 M sodium hydroxide solution (bromothymol blue as indicator). In each case, good first-order kinetics were observed and average rate constants for duplicate runs were computed, utilizing calculated infinity titers.

Product Studies. Samples of the 3,5-dinitrobenzoates were solvolyzed in 70% aqueous acetone for ca. 10 half-lives. The workup consisted of removal of organic solvent under reduced pressure, extraction with ether, combination of the ether layers, and washing with 2 N sodium bicarbonate and saturated sodium chloride solution. After drying over anhydrous sodium sulfate, the solution was concentrated under reduced pressure.

Solvolysis of 18c and 22c. Only one product was isolated, identified as 4-vinylindan (**23**), in 84 and 86% yield from **18c** and **22c**, respectively. Anal. Calcd for $C_{11}H_{12}$: *m/e* 144.0939. Found: 144.0938.

Solvolysis of 16c and 20c. Only alcohol **28** was isolated in ca. 40% yield after column chromatography (silica gel, eluant): IR (CCl_4) 3615 (sharp, free OH), 3570 (sharp, intramolecularly H-bound OH), 3420 (broad, intermolecularly H-bound OH), 1632 (w, C=C), 1190 cm^{-1} (s, tertiary alcohol C—O); ^1H NMR δ 6.11 (four lines, X part of ABX, J_{AX} = 16, J_{BX} = 12 Hz), 5.21, 5.05, 4.92 (five lines, AB part of ABX, J_{AB} = 2 Hz), 2.3–1.0 (m, with a broad s centered at 1.42, 15 H). Anal. Calcd for $C_{11}H_{18}O$: *m/e* 166.1358. Found: 166.1354.

Solvolysis of 15c and 19c. The ^1H NMR and IR spectra of the crude products from either **15c** or **19c** showed one major product, identified as **33** by the following data: IR (CCl_4) 3600, 3460 (OH), 3030 (olefinic C—H), 1640 (C=C) cm^{-1}; ^1H NMR δ 5.80 (four lines, X part of ABX, J_{AX} = 17, J_{BX} = 10 Hz), 5.65 (m, 2 H), 5.12, 4.94, 4.84, and 4.78 (eight lines, AB part of ABX, J_{AB} = 2 Hz), 2.5–1.2 (m, 11 H).

Solvolysis of 17c and 21c. The ^1H NMR and IR spectra of the crude product indicated one major product, assigned structure **34** (stereochemistry tentative) on the basis of the following spectra: IR 3620, 3600, 3410 (OH), 3020 (olefinic C—H), 1630 (C=C) cm^{-1}; ^1H NMR δ 6.02 (four broad lines, X part of ABX J_{AX} = 17, J_{BX} = 11 Hz), 5.56 (m, 2 H), 4.98, 4.90, 4.81, and 4.62 (eight lines, AB part of ABX, J_{AB} = 2 Hz), 2.5–1.1 (m, 11 H).

Synthesis of 5-Vinylindan (27). 5-Bromoindan (**26**) was synthesized via bromination of indan in acetic acid according to the procedure described by Bruce:[24] bp 113–115 °C (16 Torr) (lit.[25] 110–112 °C (15 Torr)).

To 150 mL of ether and 5.8 g (30.4 mmol) of cuprous iodide was added 20 mL of 3.1 M (60.2 mmol) vinyllithium, and the mixture was allowed to react for a period of 15 min under nitrogen at −20 °C. The resultant dark brown mixture was stirred for an additional 20 min at −20 °C. After cooling to −78 °C, 2.47 g (12.5 mmol) of **26** was added dropwise. After stirring for 2 h, the flask was allowed to warm to room temperature. Addition of water (50 mL) was followed by ether ex-

traction, drying of the extract, and solvent evaporation. 5-Vinylindan (0.32 g, 18%) was obtained as a colorless oil after vacuum distillation, bp 116–121 °C (17 Torr) (lit.[26] 95–100 °C (10 Torr)).

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A Stereoselective Total Synthesis of the Prelog–Djerassi Lactone

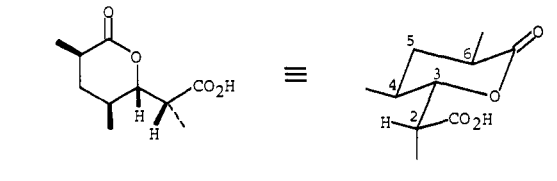
Paul A. Bartlett* and Jerry L. Adams

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received June 13, 1979*

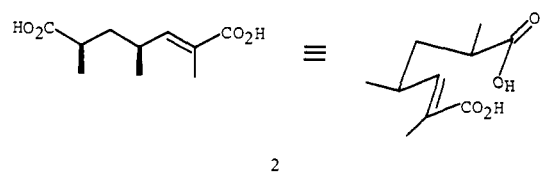
Abstract: A total synthesis of racemic Prelog–Djerassi lactone (**1**) has been achieved using the mercuric ion induced cyclization of aldehyde acid **12a** to control the stereochemistry at C-2 and C-3. Demercuration of the product (**14a**) is selectively accomplished with sodium trithiocarbonate in methanol at −60 °C, affording the Prelog–Djerassi lactone (**1**) and the 2-epi isomer **17** in a 3.5:1 ratio after hydrolysis and oxidation. Demercuration with sodium borohydride, hydrolysis, and oxidation result in the 2-epi compound **17** almost exclusively.

Introduction

The Prelog–Djerassi lactonic acid (**1**) occupies a prominent position in the chemistry of the macrolide antibiotics, having served both in their structure elucidation and in their synthesis. Isolated independently by Prelog[1] and Djerassi,[2] as a degradation product of narbomycin and methymycin, respectively, its full stereochemistry was not correctly assigned until 1970 by Rickards and Smith.[3] In 1963, Bergel'son and Batrakov reported a synthesis of this material, by a nonstereorational route involving the reduction of a keto diester precursor.[4] This synthesis has been repeated by Yamaguchi and co-workers, who noted its nonstereoselective nature.[6] In connection with the first synthesis of methymycin, Masamune prepared the Prelog–Djerassi lactone from bicyclo[4.2.1]nona-2,4,7-triene, using a carbocyclic framework to facilitate stereochemical control.[7] More recently, Masamune has reported a much shorter route employing an erythro-selective aldol condensation.[8] Three stereospecific syntheses were recently communicated by White, Stork, and Grieco, who also introduced the chiral centers on a carbocyclic framework.[9] Because of our interest in the synthesis of macrolides and in the control of stereochemistry using cyclization reactions,[10] we developed a synthesis of the Prelog–Djerassi lactone from acyclic precursors.



1



2

Synthetic Plan

Our strategy was to attempt, in effect, the isomerization of the unsaturated diacid **2** to the Prelog–Djerassi lactone (**1**),

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