

(C_{8,10}); Z-4, 36.90 (C_{4,9}), 37.70 (C_{8,10}). The analysis was done by ¹³C NMR integration of an oxygen-saturated CDCl₃ solution by means of the 1PDNA pulse sequence with delay time of 36 s; 1500 transients were taken.³⁴ The E/Z peak ratios were 43:57 based on C₂, 44:56 based on C₆, 42:58 with C_{4,9}, and 43.5:56.5 with C_{8,10}.

2-Bromo-2-(2,2,2-trichloroethyl)adamantane. Treatment of methyleneadamantane (1 equiv), dissolved in bromotrichloromethane (10 equiv), with di-*tert*-butyl peroxide (0.3 equiv) at 105 °C for 4 h gave a product the ¹H NMR spectrum of which showed that no starting olefin was left (δ 4.50) and that the product (CH₂CCl₃, δ 3.72) had virtually completely decomposed by elimination: the three single peaks observed at δ 6.20–6.25 suggest that the allylic halide products are capable of allylic rearrangement and/or halide exchange. If benzoyl peroxide was substituted (0.06 equiv) and the reaction done at 80 °C for 3–4 h, the ¹H NMR showed the addition to be complete and that only 20% of the adduct had decomposed; use of AIBN (0.05 equiv) at 60–62 °C for 5 h gave rise to a fairly pure adduct with a melting range of 32–47 °C. ¹H NMR: δ 3.72 (s, 2 H), 2.71 (s, 1 H), 2.67 (s, 1 H), 2.43 (s, 2 H), 2.28 (s, 1 H), 2.23 (s, 1 H), 2.0–1.7 (m, 8 H). ¹³C NMR: δ 97.67 (CCl₃), 77.80 (C₂), 61.78 (CH₂CCl₃), 39.69 (C_{1,3}), 39.20 (C₆), 34.94 (C_{8,10}), 34.69 (C_{4,9}), 26.83 (C_{5,7}).

2-Methylene-5-phenyladamantane (6). The procedure is similar to Olah's.³⁸ Methyl triphenylphosphonium bromide (1.89 g, 5.3 mM), dried over P₂O₅ at 85 °C overnight, was covered with ether (25 mL) freshly distilled from sodium benzophenone ketyl and treated with *n*-butyllithium (2.4 M in hexane, 2.2 mL, 5.3 mM) with stirring under nitrogen. The salt dissolved in a half hour to give a brick-red solution. 5-Phenyladamantanone (1 g, 4.4 mM) in ether (20 mL) was added in 15 min at room tem-

perature; then, the mixture was refluxed for 20 h. After the addition of water (40 mL) and filtration to remove the phosphine oxide, the usual workup furnished 1.22 g of a viscous liquid which solidified after chromatography (silica gel, hexane). Yield: 0.95 g (96%). Mp: 28–29 °C. ¹H NMR: δ 7.36–7.15 (m, 5 H), 4.58 (s, 2 H), 2.65 (s, 2 H), 2.2–1.8 (m, 11 H). ¹³C NMR: δ 156.87 (C₂), 150.10 (C₁), 128.12 (C_m), 125.65 (C_p), 124.84 (C_o), 101.42 (=CH₂), 44.89 (C_{4,9}), 42.65 (C₆), 39.27 (C_{1,3}), 38.71 (C_{8,10}), 36.38 (C₅), 28.89 (C₇). High resolution MS: calcd 224.1565, found 224.1564.

2-Bromo-5-phenyl-2-(2,2,2-trichloroethyl)adamantanes (7). Treatment of olefin 6 with BrCCl₃ and initiator AIBN as described above (10 h) gave a viscous, liquid product essentially free of olefins. ¹H NMR: δ 7.39–7.21 (m), 3.76 (s), 3.72 (s), 2.93–1.82 (m). ¹³C NMR: δ 149.10, 148.69, 128.34, 128.20, 126.10, 125.89, 124.77, 124.55, 97.61, 97.45, 76.45, 76.36, 61.70, 61.47, 45.50, 44.46, 40.51, 40.42, 40.08, 39.62, 35.39, 35.30, 34.16, 33.87, 27.45, 27.40. The CH₂CCl₃ peaks at δ 3.76 and 3.72 were in a 64:36 ratio. Dissolution of the mixture in acetone-*d*₆-D₂O (5:1, v/v) and monitoring of these peaks at 21 °C showed that the major peak at δ 3.76 vanished roughly 10 times faster than the minor one; it was gone after 24 h, at which point the 3.72 peak was at about 30% of its original intensity. Three signals grew in simultaneously at δ ~6.5; their relative intensities change, and after 4 days only one was left, at δ 6.30.

Acknowledgment. W. le N. thanks the NSF for supporting this work. We thank Mr. Haifang Li for assistance with some of the NMR spectra.

Supplementary Material Available: Calculated and observed chemical ¹³C shifts of *E*- and *Z*-2 and their dependence on added shift reagent and the ¹³C spectra of mixtures of *E*- and *Z*-2 and of *E*- and *Z*-7 (3 pages). Ordering information is given on any current masthead page.

(38) Olah, G. A.; Krishnamurthy, V. V. *J. Am. Chem. Soc.* 1982, 104, 3987.

Stereochemistry of Nucleophilic Addition to Several Rigid, Sterically Unbiased 7-Norbornanones

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Received July 16, 1990

A stereochemical investigation is reported of the reactions of lithium aluminum hydride (LAH) and of methyllithium with three sterically unbiased, rigid ketones: tetracyclo[7.4.0.0^{2,7}.0^{6,10}]trideca-3,12-dien-8-one (2), pentacyclo[6.5.0.0^{4,12}.0^{6,10}.0^{9,13}]tridecan-11-one (3), and pentacyclo[6.5.0.0^{4,12}.0^{6,10}.0^{9,13}]trideca-2,6-dien-11-one (4). Various proton NMR techniques were brought to bear upon the dual problems of characterization and analysis of the mixtures of epimeric alcohols obtained. The results can be interpreted in terms of transition-state hyperconjugation. A comparison with literature data on other endo-substituted 7-norbornanones points up the need, in studies of electronically controlled face selection, for probes that not only have sterically equivalent faces but are also conformationally rigid.

Introduction

Face selection in additions to trigonal carbon is at the heart of stereogenesis, and much attention has been lavished on it.¹ A multitude of factors can influence it; they include steric effects, conformations of the flanking groups, complexation of reagents, deviations from planarity, product stability, and electronic effects. Studies of these factors have usually depended on choices of substrates, the faces of which are equivalent, as much as possible, with

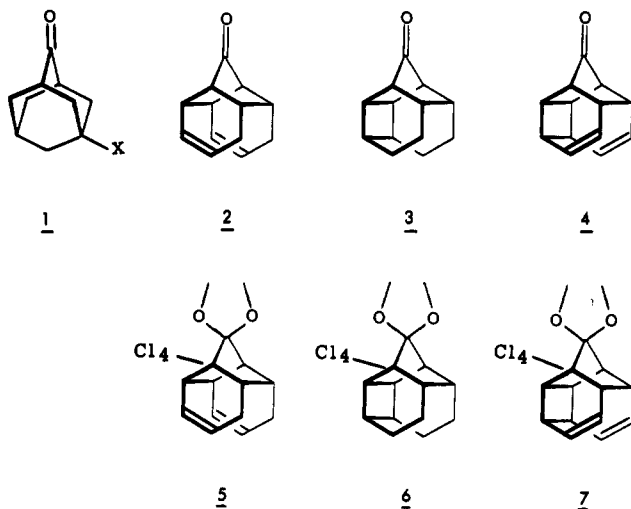
respect to each of the other effects. Cyclic and polycyclic ketones and their reactions with reducing and alkylating agents have therefore been prominent in these studies. We presently report our results observed in the LAH reduction and methylation with MeLi of several 7-norbornanones and compare them with others known to have been stud-

(1) For informative recent summaries and lead references, see: (a) Fraser, R. R.; Stanculescu, M. *J. Am. Chem. Soc.* 1987, 109, 1580. (b) Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* 1987, 109, 3353. (c) Macaulay, T. B.; Fallis, A. G. *J. Am. Chem. Soc.* 1988, 110, 4074. (d) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* 1989, 111, 8447.

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ied. Appropriately endo-2,3-disubstituted 7-norbornanones have in common with our recently studied²⁻⁴ 5-substituted adamantan-2-ones the advantageous features of steric equivalence of the two faces and the absence of conformational uncertainty; furthermore, they offer the advantage that the substituents are closer to the site of action and hence, may induce larger ratios.⁴ The norbornanones 2-4 had recently become accessible⁵ via simple conversions of the protected tetrachloro derivatives 5-7, albeit in such small quantities (5-10 mg) that the analysis and configurational assignments of the six alcohols obtained by reduction and methylation posed special problems; we exclusively depended on the ¹H NMR spectra.

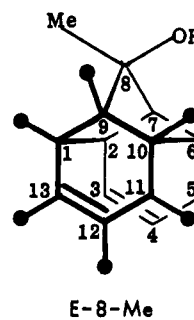


Results

Reaction of 2 with MeLi in ether at 0 °C furnished in 98% yield a mixture of (*E*)- and (*Z*)-8-Me, which we did not attempt to separate. The two methyl ¹H NMR peaks were sufficiently distinct to allow integration, giving a ratio of 61:39. Addition of small and carefully measured quantities of a Eu(fod)₃ solution revealed the usual dependencies of the chemical shifts upon the concentrations. The data were plotted, and the initial slopes were estimated by a graphical method. A two-dimensional COSY spectrum was recorded for the solution containing 0.19 equiv of the shift reagent. With the exception of the *exo*- and *endo*-methylene proton signals, which could not be discerned, a complete correlation of all peaks and of all hydrogen atoms could be constructed on the basis of the chemical shift values, their sensitivities to the shift reagent, the intensities of the signals, and the strength of the couplings as judged from the COSY results; these findings are shown in Table I. The major alcohol was found to have the *E* configuration.

The reduction of 2 with LAH was also quantitative. The ratio of alcohols (*E*)- and (*Z*)-8-H in this case was based on the integration of the H_{1,2} and H_{6,10} signals. The assignment of all signals followed lines similar to those used in the methylation study. The Eu(fod)₃-induced shifts were much stronger in the secondary alcohols, as expected; the much lower concentrations required led to virtually straight-line dependencies. The assignment of configu-

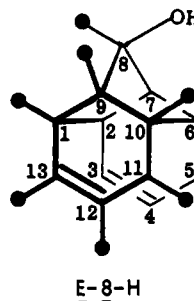
Table I. Proton NMR Results for (*E*)- and (*Z*)-8-Me



proton	<i>E</i>			<i>Z</i> ^a		
	CS ^b	slope ^c	COSY ^d	CS ^b	slope ^c	COSY ^d
Me	1.50	6.69		1.47	6.85	
H ₉	1.55	6.55	1, 10	1.55	6.67	1, 10
H ₁	2.76	3.19	9, 13	3.07	8.07	9 ^e
H ₁₃	5.34	1.51	1, 11, 12	5.45	1.55	11, 12 ^e
H ₁₂	5.71	1.19	11, 13	5.71	1.19	11, 13
H ₁₁	2.03	1.55	10, 11, 12	2.00	1.68	10, 12, 13
H ₁₀	2.72	7.70	9, 13	2.43	3.67	9, 11

^a Me and OH reversed. ^b Chemical shift (ppm) relative to SiMe₄. ^c Slopes of plots of CS vs amount of Eu(fod)₃ added. The lines are essentially straight, and the data were least-squared on that basis. Each entry is the result of four to six measurements; the correlation coefficients equal 0.987 ± 0.003. ^d This column shows the numbers of the protons that are coupled to the proton in question. ^e The coupling of H₁ and H₁₃ was not observed.

Table II. Proton NMR Results for (*E*)- and (*Z*)-8-H



proton	<i>E</i>			<i>Z</i> ^a		
	CS ^b	slope ^c	COSY ^d	CS ^b	slope ^c	COSY ^{d,e}
H ₈	4.17	25.4		4.17	24.9	
H ₉	1.88	13.9	1, 10	1.88	13.7	1, 10
H ₁	2.56	5.76	9, 13	2.94	15.8	9, 13
H ₁₃	5.33	2.75	1, 11, 12	5.49	4.24	1, 11
H ₁₂	5.71	2.86	11, 13	5.71	2.86	11
H ₁₁	2.05	4.68	10, 11, 12	1.97	3.05	10, 12, 13
H ₁₀	2.63	16.4	9, 11	2.29	5.75	9, 11

^a H₈ and OH reversed. ^{b-d} See Table I. ^e The coupling of H₁₂ and H₁₃ was not observed.

ration is at once obvious from the fact that, in the major isomer, the signal for the H_{6,10} protons is shifted much more strongly than that in the minor one and that the opposite is true for the H_{1,2} peaks. The conclusion is that the *E* isomer is again the major product (57:43); the details are shown in Table II.

Ketone 3 in the same way gave essentially quantitative yields of small amounts of mixtures of alcohols (*E*)- and (*Z*)-9-Me and of (*E*)- and (*Z*)-9-H. The presence of the two pairs of diastereotopic methylene hydrogens greatly complicated assignments; thus, a preliminary COSY spectrum of the secondary alcohol mixture yielded coupling between H₁₁ and H_{10,12} in the major isomer as the only useful information. Fortunately, it proved possible in this instance

- (2) Cheung, C. K.; Tseng, L. T.; Lin, M.-h.; Srivastava, S.; le Noble, W. *J. Am. Chem. Soc.* 1986, 108, 1598.
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 (4) Lin, M.-h.; Silver, J. E.; le Noble, W. *J. Org. Chem.* 1988, 53, 5155.
 (5) Mehta, G.; Padma, S. *J. Am. Chem. Soc.* 1987, 109, 2212; *J. Org. Chem.* 1988, 53, 4890.
 (6) Cahn, R. S. *J. Chem. Educ.* 1964, 41, 116.

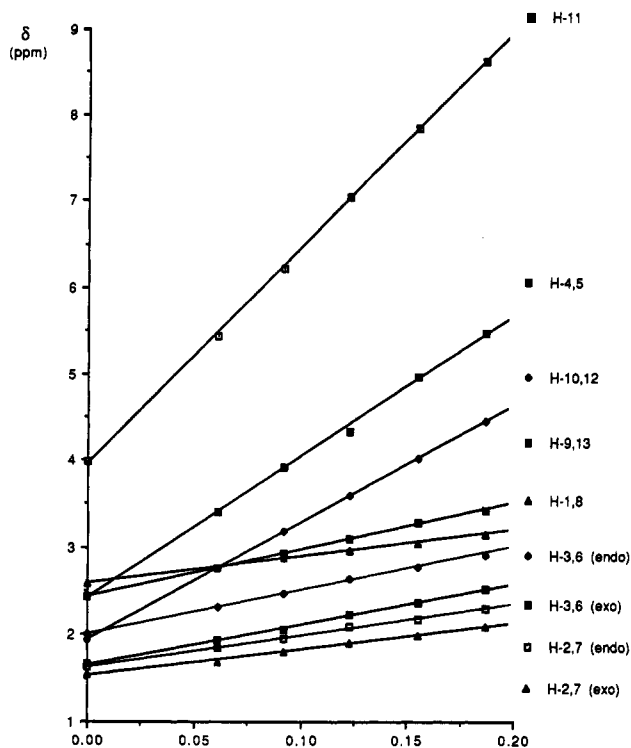


Figure 1. Effect of increasing concentrations of $\text{Eu}(\text{fod})_3$ on the chemical shifts of the protons in compound (*E*)-9-H. See Table III for the structure; r is the molar ratio of the shift reagent to the alcohol.

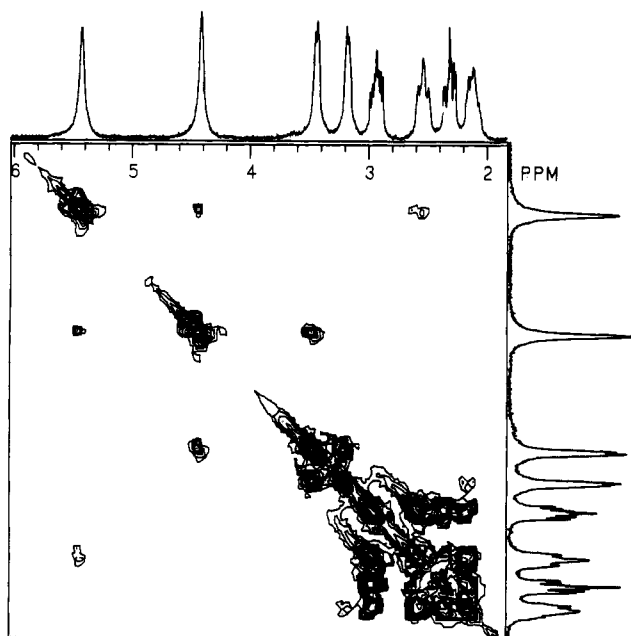
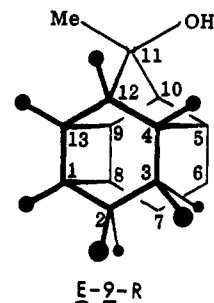


Figure 2. COSY spectrum of (*E*)-9-H in the presence of 20 mol % $\text{Eu}(\text{fod})_3$. The H_{11} and $\text{Eu}(\text{fod})_3$ signals are outside the range shown. The eight protons representing the eight signals are identified in Figure 1 and Table III.

to isolate a small amount of this alcohol by means of column chromatography. The addition of $\text{Eu}(\text{fod})_3$ enabled us to see all of the nine CH proton signals in this molecule; the plot supporting this claim is shown in Figure 1. The solution with the highest concentration of added shift reagent was used to record the COSY spectrum, which is shown in Figure 2; it allowed complete assignments including both pairs of exo and both pairs of endo hydrogens.

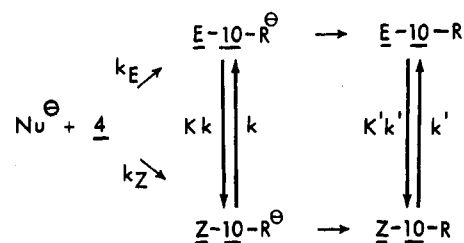
Table III. Proton NMR Results for (*E*)-9-R^a



proton	R = Me		COSY ^d	R = H	
	CS ^b	slope ^c		CS ^b	slope ^c
Me (H_{11})	1.27	8.16	(12)	3.99	25.4
12	1.57	7.63	4, (11), 13	1.93	13.6
13	3.55	3.88	1, 12	2.43	5.01
1	2.55	2.00	2, 13	2.58	3.08
2-X	1.45	1.58	1,2-N, 3-X, 3-N	1.55	2.98
2-N	1.64	1.78	2-X, 3-X, 3-N	1.63	3.57
3-X	1.64	1.58	2-X, 2-N, 3-N, 4	1.66	4.66
3-N	1.99	1.58	2-X, 2-N, 3-X	2.01	4.91
4	2.55	8.85	3, 12	2.43	16.4

^a C_1 has priority over C_3 in the sequence rule when it applies to atoms with multiple linkings. ^b Chemical shifts. ^c See footnote c in Table I; the correlation constants averaged 0.999. ^d The COSY results apply to both R = H and R = Me except for H_{11} and H_{12} .

Scheme I



Critical in this process was an MM2 calculation of the dihedral angles between $\text{H}_{4,5}$ and endo $\text{H}_{3,6}$ and between $\text{H}_{1,8}$ and endo $\text{H}_{2,7}$. They were found to be close to 90° (84° and 88° , respectively); couplings between these atoms are indeed absent from the COSY spectrum. Expanded spectra show the signals of the endo hydrogens as ddd patterns, while the exo atoms give rise to more complex multiplets. The 67:33 *E*:*Z* ratio of the alcohols was based on integration of the two well-separated H_{11} signals; assignment of the other peaks due to the minor isomer was not pursued. Our study of the mixture of the tertiary alcohols followed the same lines, a small amount of the *E* isomer being available after chromatography. The *E*:*Z* ratio in this instance, also 67:33, was based on the methyl signals (Table III).

The mixtures of products 10-R obtained from ketone 4 posed yet another challenge: both pairs of alcohols are subject to a degenerate Cope rearrangement interconverting *E* and *Z*. This was obvious from the fact that the epimeric ratios depended on the time allotted for reaction and on that elapsed before analysis. Chromatographic separation was obviously ruled out. Furthermore, since the alcohols are present as the alkoxides in the reaction mixtures (in ether) in which they are formed, but as the neutral species (in CDCl_3) after workup, it was necessary to assess the equilibration rates of both forms. Fortunately, these rates were in all instances found to be substantially slower than the formation rates, and it proved possible to obtain the original isomer ratios by extrapolation (see Scheme I).

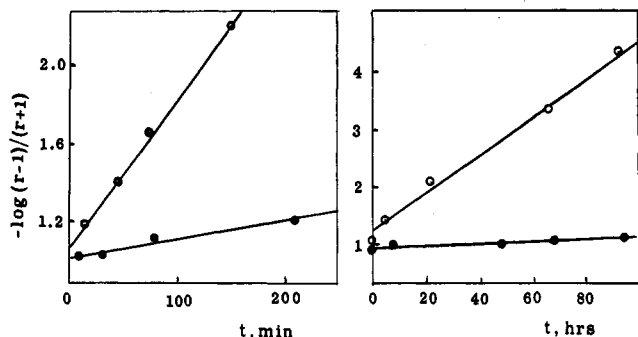
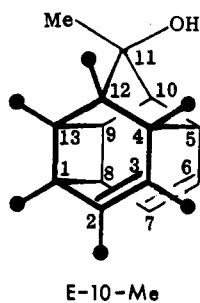


Figure 3. Variation of S vs t : left, for the anions; right, for the neutral alcohols. Key: filled circles, tertiary alcohols; open circles, secondary alcohols.

Table IV. Proton NMR Results for (*E*)- and (*Z*)-10-Me



proton	<i>E</i>			<i>Z</i>	
	CS	slope	COSY ^a	CS	slope
Me	1.38	7.36		1.51	8.91
12	1.54	6.92	4, 13	1.60	8.02
13	2.80	3.52	1, 12	3.02	8.33
1	3.22	1.78	2, 13	3.28	2.07
2	5.74	1.36	1, 3	5.74	1.36
3	6.21	1.36	2, 4	6.12	1.88
4	3.12	8.19	3, 12	2.80	4.33

^a COSY results apply to both epimers. Other comments are as in Table I.

For the secondary alcohols, the H_{11} signals served as a yardstick for r , the variable ratio $E:Z$; for the tertiaries, the vinyl signals of $H_{3,6}$ were so employed. Note that $r_0 = k_E/k_Z$; eq 1 describes the equilibration process (the

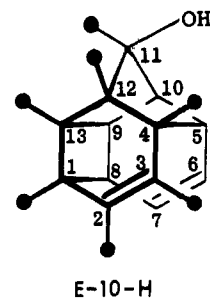
$$\frac{Kr - 1}{r + 1} = \frac{Kr_0 - 1}{r + 1} e^{-(K+1)kt} \quad (1)$$

derivation is given in the supplementary material). Equation 1 applies when $k \ll k_E$ and k_Z and $e^{-(k_E+k_Z)t} \approx 0$. In the case in which K equals unity (the alcohols do reach exactly equal concentrations after several weeks), this expression simplifies to eq 2, where $S = -\log(r - 1)/(r + 1)$

$$S = S_0 + 2kt \quad (2)$$

1) and $S_0 = -\log(r_0 - 1)/(r_0 + 1)$. A plot of S vs t should give a straight line with slope $2k$ and intercept S_0 , from which we can calculate r_0 . The plots, shown in Figure 3, yield the following information: The $E:Z$ ratio in the reduction is 67:33; that in the methylation equals 68:32. The equilibration rates during the formation reaction at 0 °C are 6.1×10^{-5} and $7.8 \times 10^{-6} \text{ s}^{-1}$ for the reduction and methylation, respectively, and during storage in CDCl_3 at room temperature (21 °C), 6×10^{-6} and $3 \times 10^{-7} \text{ s}^{-1}$, respectively. The anions equilibrate 2 orders of magnitude faster than the neutral alcohols (if one allows for the temperature difference). The equilibration provided one benefit: it allows us to guarantee that the face selections observed with 4 are not driven by product stability control.

Table V. Proton NMR Results for (*E*)- and (*Z*)-10-H



proton	<i>E</i>		COSY ^a	<i>Z</i>	
	CS	slope		CS	slope
11	4.21	28.1	12	4.17	32.0
12	1.84	14.9	4, 11, 13	1.91	17.2
13	2.71	6.15	1, 12	2.94	18.1
1	3.23	3.48	2, 13	3.30	6.06
2	5.74	3.34	1, 3	5.74	3.90
3	6.22	4.67	2, 4	6.09	3.15
4	3.03	17.3	3, 12	2.63	7.16

^a COSY results apply to both epimers. Other comments are as in Table I.

Table VI. Product Distribution in the Reactions of LAH and MeLi with Ketones 2-4

ketone	reagent	% alcohol	
		<i>E</i>	<i>Z</i>
2	LAH	57	43
	MeLi	61	39
3	LAH	67	33
	MeLi	67	33
4	LAH	67	33
	MeLi	68	32

Direct equilibration of two epimers has only rarely² been possible in our previous studies; hence, 10-H and 10-Me are welcome examples of this.

The ^1H NMR assignments were made in a manner similar to that used for alcohols 8; the $\text{Eu}(\text{fod})_3$ and COSY studies were done with mixtures that had only minimally equilibrated. The data are summarized in Tables IV and V.

Discussion

The stereochemical results gathered in Table VI can be explained with the hypothesis of transition-state hyperconjugation, an idea that was first advanced by Cieplak⁷ to account for the fact that small nucleophiles tend to attack rigid cyclohexanones at the axial face. We have since applied it to account for the stereochemistry of nucleophilic addition to adamantanones.²

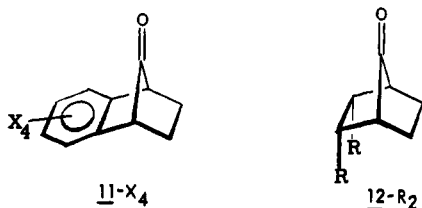
As applied to 2 the notion is that the electrons of the σ bonds antiparallel to the incipient bond delocalize to some extent into the newly forming antibonding orbital σ^{*} . This interaction stabilizes the transition state. Since this phenomenon is possible at either side, the favored face is the one opposite the more electron-rich vicinal bonds. The sp^2 character of the vinyl bonds should render them electron withdrawing to those of the methylene groups; as a result, the nucleophile should favor the anti face and thus produce more of the *E* alcohols, as is observed. As we have pointed out earlier,² this description resembles Winstein's

(7) Cieplak, A. S. *J. Am. Chem. Soc.* 1981, 103, 4540. A corollary of this hypothesis is that the effect should be strongest for early transition states since the energy difference between σ^{*} and σ^* should be minimal then; however, there is little if any experimental support for this extrapolation (see ref 4).

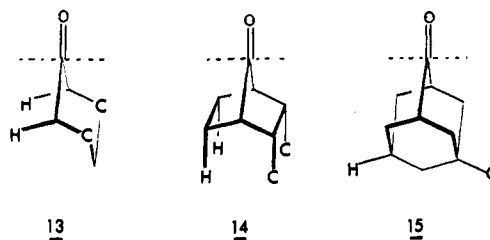
σ participation in carbocations.⁸

In a similar vein, the cyclobutano annelation in **3** should impart greater s character into the flanking vicinal bonds on that side,⁹ and hence we consider the excess E alcohols produced in that case reasonable also; in fact, the $E:Z$ ratio is somewhat larger in this case. In **4**, the E alcohols predominate also, and perhaps do so to a degree somewhat greater than might have been expected if one assumes that the cyclobutane and vinyl moieties are unaffected by one another's presence.

The literature on the subject of addition by LAH and MeLi to 7-norbornanones deals mostly with exo-substituted structures clearly producing sterically controlled results. The one example instructive from our present point of view is Oda's series of benzonorbornenones **11-X₄**.¹⁰ LAH reduction led to $E:Z$ ratios of 81:19, 95:5, and 100:0 when X is H, Cl, and F, respectively; that result is clearly in accord with transition-state hyperconjugation.



When we focus our attention on the literature on endo-substituted 7-norbornanones, the picture that emerges is not quite simple and straightforward.^{10,11} Chasman and Gassman found that *endo,endo*-2,3-dimethyl-7-norbornanone (**12-Me**) with LAH gave an $E:Z$ ratio of 45:55; evidently, the methyl groups function as weak donors. This fact is troublesome since part of the controversy¹² that has developed around Cieplak's suggestion centers on his need to adopt the Baker-Nathan order of donor abilities in order to explain the behavior of cyclohexanones; i.e., hydrogen is the better donor. Similarly, we have interpreted Whiting's data¹³ and our own, in 5-alkyl-substituted 2-adamantyl cations and 2-adamantanones,^{2,14} respectively, on the basis of the same assumption. It seems possible that the electron-donating or -withdrawing character of an alkyl group in this connection depends on the number of intervening bonds (two in **13**, three in **14**, and four in **15**), or on the dihedral angles, but there is no compelling a priori reason that is apparent to us.¹⁵ The other literature now available¹¹ is concerned



with the compounds **12**-(C₂H₅)₂, -(CH₂OCH₃)₂, -(CH=CH₂)₂, and -(COOCH₃)₂. The first three of these give excess Z product, and only **12**-(COOCH₃)₂ produces a large excess of E alcohols. In the series **12**-(C₂H₅)₂, **12**-(CH₂OCH₃)₂, and **12**-(COOCH₃)₂, the $E:Z$ ratio clearly goes in the direction that we would predict (e.g., for MeLi, 21:79, 34:66, and 90:10, respectively); however, it is hard to see how methoxymethyl can function as a σ donor. The LAH datum for **12**-(CH=CH₂)₂ ($E:Z$ = 35:65) stands in apparent contrast with that of **2**.

The origin of these difficulties may lie in the conformational freedom of these substituents of **12**. There are many discussions in the literature¹⁶ of the connection between hyperconjugation and conformation, and it may be best at present to restrict discussions of electronic effects of face selection to probes in which not only the carbonyl-flanking groups but also distant face-differentiating groups are held in rigid and well-known positions. Finally, with the ratios observed here as close to unity as they are, the possibility of inadvertent steric differences between the two faces should not be overlooked either. In particular, the incorporation of a cyclobutyl ring in **9** and **10** may have caused hydrogen atoms C₉H and C₁₃H to be bent a bit further apart, slightly facilitating access to the e face of the carbonyl group.

Experimental Section

Materials. Ketone **2** was prepared from the 1,2,7,9-tetrachloro dimethyl ketal precursor **5** described earlier,⁵ as follows. The hydrodechlorination was carried out on a 100-mg scale with a 2-fold excess of lithium metal cut into small pieces, in THF solution (8 mL) containing some *tert*-butyl alcohol, by 2-h reflux under nitrogen. After workup, silica gel chromatography with 2% ethyl acetate in hexane gave the ketal of **2** in 84% yield (recrystallized from hexane): mp 63–64 °C; IR (KBr) ν_{\max} 3025, 2925, 1120, 1060 cm⁻¹; ¹H NMR (100 MHz, CDCl₃) δ 5.69 (2 H, ddd, $J_1 = 10$ Hz, $J_2 = J_3 = 3$ Hz), 5.48–5.24 (2 H, m), 3.30 (3 H, s), 3.28 (3 H, s), 2.78 (2 H, br s), 2.5 (2 H, br s), 1.98 (4 H, br s), 1.88 (2 H, m); ¹³C NMR (25 MHz, CDCl₃) δ 128.2, 127.0, 111.9, 50.3 (2 C), 40.4, 39.3, 31.7, 23.4. Anal. Calcd. for C₁₅H₂₀O₂: C, 77.25; H, 8.68. Found: C, 77.43; H, 8.71.

Hydrolysis was accomplished by stirring a solution of 50 mg of the ketal with 200 mg of Amberlyst-15 and a drop of water at room temperature for several hours. Filtration through Celite and silica gel chromatography gave **2** in 87% yield (recrystallized from hexane): mp 105 °C, **2** rearranges slowly to the Cope isomer; IR (KBr) ν_{\max} 3025, 2925, 1760, 1440 cm⁻¹; ¹H NMR (100 MHz, CDCl₃) δ 5.79 (2 H, ddd, $J_1 = 10$ Hz, $J_2 = J_3 = 3$ Hz), 5.6–5.36, (2 H, m), 2.84 (2 H, br s), 2.63 (2 H, br s), 2.1 (4 H, m), 1.88 (2 H, m); ¹³C NMR (25.0 MHz, CDCl₃) δ 127.1, 126.5, 42.9, 31.9, 29.4, 21.9; HRMS (M⁺) for C₁₃H₁₄O, calcd 186.1045, found 186.1041.

The ketones **3** and **4** were prepared similarly from the 9,10,12,13-tetrachloro dimethyl ketals **6** and **7**.^{5,17}

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The ketal of **3** was obtained in 86% yield (recrystallized from hexane): mp 89.5–90 °C; IR (KBr) ν_{\max} 2950, 1450, 1300, 1095, 1055, 920 cm^{-1} ; ^1H NMR (100 MHz, CDCl_3) δ 3.3 (3 H, s), 3.26 (3 H, s), 2.56 (4 H, br s), 2.32 (2 H, br s), 2.1–1.3 (10 H, series of m). Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}$: C, 76.88; H, 9.46. Found: C, 76.33; H, 9.60.

Hydrolysis gave **3** in 96% yield (recrystallized from hexane): mp 160 °C (sublimes), 200 °C dec; IR (KBr) ν_{\max} 2925, 1755, 1450, 1120, 690 cm^{-1} ; ^1H NMR (100 MHz, CDCl_3) δ 2.76 (4 H, s), 2.48 (2 H, br s), 2.2–1.4 (10 H, series of m); ^{13}C NMR (25.0 MHz, CDCl_3) δ 214.3, 48.5, 29.5, 27.0, 16.5, 16.2. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.93; H, 8.57. Found: C, 82.45; H, 8.86.

The ketal of **4** was obtained in 70% yield and recrystallized from dichloromethane–hexane: mp 92 °C; IR (KBr) ν_{\max} 3050, 2950, 1440, 1380, 1300, 1060, 690 cm^{-1} ; ^1H NMR (100 MHz, CDCl_3) δ 6.24–6.0 (2 H, m), 5.8–5.5 (2 H, m), 3.38–3.1 (2 H, m), 3.3 (3 H, s), 3.26 (3 H, s), 2.84 (4 H, m), 1.86 (2 H, m); ^{13}C NMR (25.0 MHz, CDCl_3) δ 131.9, 128.7, 113.9, 50.8, 50.4, 41.2, 40.2, 38.5, 33.9. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88. Found: C, 78.07; H, 7.76.

Hydrolysis as above gave **4** in 90% yield (recrystallized from dichloromethane–hexane): mp 165 °C; IR (KBr) ν_{\max} 3025, 2950, 1760, 1380, 1130, 690 cm^{-1} ; ^1H NMR (100 MHz, CDCl_3) δ 6.3–6.06 (2 H, m), 5.9–5.64 (2 H, m), 3.44 (2 H, m), 2.94 (4 H, m), 1.74 (2

H, br s); ^{13}C NMR (25.0 MHz, CDCl_3) δ 213.6, 129.4, 129.1, 43.7, 39.5, 37.3, 28.8. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}$: C, 84.75; H, 6.57. Found: C, 84.52; H, 6.51.

The conversions of **2–4** into the alcohols with LAH and MeLi were carried out in ether under nitrogen at 0 °C. After aqueous workup, drying, and evaporation of solvent, the yields were essentially quantitative. The product ratios were determined by means of ^1H NMR experiments on a QE-300 NMR spectrometer operating at 300.15 MHz as described in the text. For the shift reagent studies, a carefully weighed amount of the alcohol or alcohol mixture was dissolved in a known amount of CDCl_3 , and NMR spectra were measured after additions of various amounts of a CDCl_3 solution of $\text{Eu}(\text{fod})_3$ of known strength. After each addition, the volume was reduced to the original by applying a vacuum.

The MM2 calculation with energy minimization was carried out with the MACRO Model V.2.5 program developed by C. Still, Department of Chemistry, Columbia University.

Acknowledgment. The work at Stony Brook was supported by the National Science Foundation, and that at Hyderabad was supported by the University Grants Commission. We thank the reviewers for their careful examination of this paper.

Supplementary Material Available: The derivation of eqs 1 and 2 and ^{13}C NMR spectra of **3** and its ketal (6 pages). Ordering information is given on any current masthead page.

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Highly Selective Trapping of Unsymmetrical Pentadienyl Anions by Silicon and Tin Electrophiles. Marked Contrast between Kinetic and Thermodynamic Control of Product Composition

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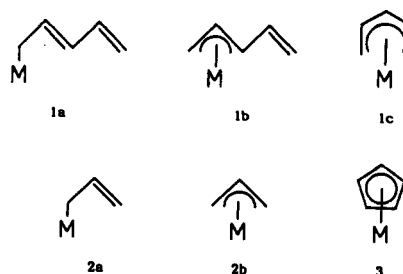
Received August 2, 1990

The nucleophilic reaction of lithium and potassium salts of five pentadienyl anions bearing sterically and/or coordinatively different groups at their unsymmetrical 2-position toward Me_3SiCl and Me_3SnBr is described. When the anion of the potassium salt was trapped by Me_3SiCl , (*Z*)-4-substituted-pentadienylsilanes were obtained with high selectivity (87–100%). The lithium salt, however, gave a mixture of (*E*)- and (*Z*)-4-substituted-pentadienylsilanes. The coupling reaction proceeds under kinetic control, because the product composition from Si trapping reflected the structure of the parent dienyli anion and the steric interaction between the incoming Me_3Si group and the substituent on the anion. In contrast, when the anion was trapped by Me_3SnBr under the identical conditions, (*Z*)-2-substituted-pentadienyltins were formed with 60–96% selectivity. Only relatively small changes in product composition, as a function of the cation or the substituent on the anion, were observed. These results could be explained by thermodynamic controlling factors, including a 1,5- Me_3Sn shift, and a redistribution of pentadienyl groups under basic conditions.

Introduction

In recent years, much attention has been paid to the chemistry of pentadienylmetals **1**.² They can be regarded as both extended analogues of allylmetals **2** and acyclic analogues of cyclopentadienylmetals **3**. The majority are fluxional molecules. The existence of various coordination modes, η^1 -, η^3 -, and η^5 -forms (corresponding to **1a**, **1b**, and **1c**, respectively), and the equilibria among them make extensive exploitation of pentadienylmetal chemistry difficult. Only the simplest pentadienylmetals, or their

symmetrically substituted homologues, have been studied in order to avoid complexity.



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In organic synthesis, main group metal derivatives of pentadienes have been utilized as pentadienyl anions or