NMR ($CDCl_3$) δ 5.36 (s, 1 H), 6.64–7.66 (m, 13 H).

9-Fluorenyl 2-Fluoroethyl Sulfoxide (3d). Mixtures of methylene chloride–ethyl acetate (17:1, 12:1, and 5:1) were used for gradient elution. There was obtained 0.64 g (49%) of **3d**: mp 126–128 °C; IR (Nujol) 1060 and 1050 cm^{-1} (overlapping C–F and S=O absorptions); ^1H NMR ($CDCl_3$) δ 1.85 (complex m, 2 H), 4.5 (complex m, 2 H), 5.48 (s, 1 H), 7.32–7.95 (m, 8 H). The signals centered at δ 1.85 and 4.5 are very complex because the protons of both methylenes are diastereotopic, and there is coupling between the fluorine and each proton, as well as between protons. Anal. Calcd for $C_{15}H_{13}FOS$: C, 69.21; H, 5.03. Found: C, 68.94; H, 4.96.

Methyl α-(9-Fluorenylsulfinyl)acetate (3e). Gradient elution with 10:1 and 5:1 methylene chloride–ethyl acetate gave 0.84 g (59%) of **3e**; mp 81–83 °C; IR (Nujol) 1730 (C=O) and 1050 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 2.55 (quartet, 2 H), 3.57 (s, 3 H), 5.41 (s, 1 H), 7.3–8.0 (m, 8 H). Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.12; H, 4.92. Found: C, 66.79; H, 4.87.

9-Fluorenyl Cyanomethyl Sulfoxide (3f). Methylene chloride–ethyl acetate mixtures (12:1, 10:1, and 7:1) were employed for gradient elution. There was obtained 0.63 g (50%) of **3f**: mp 111–113 °C; IR (Nujol) 2240 (CN), 1050 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 2.58 (poorly resolved quartet, 2 H), 5.47 (s, 1 H), 7.35–8.05 (m, 8 H). Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.13; H, 4.37. Found: C, 70.56; H, 4.45.

Kinetics of H/D Exchange of 3 As Followed by ^1H NMR. The sulfoxides **3** each have a singlet due to the 9-H in the region δ 5.2–5.5. The H/D exchange of this proton was monitored by measuring the integrated intensity of this signal, relative to that of an internal standard, as a function of time. In most cases the signal used as an internal standard was the singlet at δ 3.3 due to the small amount of CH_3OD present in the CD_3OD used as solvent. In those cases where other resonances in the sulfoxide might cause some interference with the accurate measurement of the integrated intensity of this peak, small amounts (10–30 μL) of a stock solution of cyclohexane in CD_3OD were added prior to the initiation of the exchange reaction and the cyclohexane singlet (δ 1.43) was used as the internal standard.

The general procedure for the kinetic runs was as follows. Diazabicyclooctane (DABCO), purified as described in an earlier publication,[14] was dissolved in CD_3OD (99.5 atom % D, Aldrich) to make a 0.10 M stock solution. A 0.10 M stock solution of CF_3CO_2D (Aldrich) in CD_3OD was also prepared. The 9-fluorenyl sulfoxide (**3**) was weighed out and dissolved in 0.90–0.99 mL of CD_3OD to which had been added 3–75 μL (depending on the DABCO-D^+ concentration desired) of the 0.10 M stock solution of CF_3CO_2D in CD_3OD. If needed 10–30 μL of the stock solution of cyclohexane in CD_3OD was added at this point. The solution was placed in an NMR tube in the thermostated probe (25 °C) of a Chemagnetics A200 NMR spectrometer, and the exchange reaction was initiated by the addition of an amount (6–150 μL) of the 0.10 M stock solution of DABCO equal to twice the volume of 0.1 M CF_3CO_2D solution added initially. In the runs with **3f** the volume of DABCO solution used was only 1.5 times the volume of CF_3CO_2D solution, since in that case a 1:2 DABCO–DABCO-D^+ buffer was desired. At appropriate time intervals after the initiation of the reaction, spectra were obtained and stored. After sufficient time the singlet for the 9-H disappeared completely. A plot of log (I/I_0) vs time was made for each run, where I and I_0 are the integrated intensities of the 9-H singlet relative to the internal standard at times t and zero, respectively. The experimental first-order rate constant for exchange (k_1) was then evaluated from the slope of this plot.

Kinetics of DABCO-Catalyzed Sulfine Formation from 4 in CD_3OD. The formation of sulfine **6** from ester **4** in CD_3OD in the presence of DABCO was studied in 1:1 DABCO–DABCO-D^+ buffers using procedures outlined in an earlier paper.[2] The rates were all measurable by conventional ultraviolet spectrophotometry.

(14) Kice, J. L.; Weclas, L. *J. Org. Chem.* **1985**, *50*, 32.

The Anti-Selective Michael Addition of Allylic Organometals to Ethylidenemalonates and Related Compounds

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The reaction of ethylidenemalonates **3a** and α-cyanocrotonates **3b** with crotylorganometals **2** such as B, Ti, Zr, and Sn reagents produced the anti adduct **4** predominantly. Similarly, the Michael addition of γ-alkoxy-substituted allylmetals **6** to **3** gave the anti adduct **7** preferentially. The Michael addition of crotyltin **2e** and (γ-(methoxymethoxy)allyl)tin **6d** to nitroolefins **20** again produced the anti isomers (**21** and **23**, respectively) predominantly. The anti preference was also observed in the reaction of crotyltin **2e** with α,β-unsaturated ketones. The selectivity difference between the allylic organometal additions (anti selectivity) and the enolate additions (syn or anti selectivity) is demonstrated.

The diastereofacial control between two adjacent substituents in the acylic system **1** continues to be of current

1

1a; X=Y=Me
b; X=C, Y=O, N, ···
c; X=Y=O, N, ···

importance in organic synthesis. The stereocontrol between X = carbon and Y = heteroatoms (**1b**) or between X = Y = heteroatoms (**1c**) may be achieved by various excellent methods.[1] At the outset of our work, the method for diastereofacial control between two adjacent alkyl groups, e.g., **1a**, seemed to be inadequate despite the frequent occurrence of such a stereodefined unit in important natural products.[2] One of the previous methods for this stereocontrol was based on intramolecular reactions such

(1) Review articles: (a) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 489. (c) Seebach, D.; Weidmann, B.; Widler, L. *Modern Synthetic Methods*; **1983**, *3*, 217. Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31. (d) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556. (e) Hoppe, D. *Ibid.* **1984**, *23*, 932. (f) Mulzer, J. *Nachr. Chem. Tech. Lab.* **1984**, *32*, 16. (g) McGarvey, G. J.; Kimura, M.; Oh, T.; Williams, J. M. *J. Carbohydr. Chem.* **1984**, *3*, 125. (h) Heathcock, C. H. in *Comprehensive Carbanion Chemistry*; Durst, T., Buncel, E., Eds.; Elsevier: New York, 1984. (i) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1. (j) Mukaiyama, T. *Org. React. (N.Y.)* **1982**, *28*, 203. (k) Masamune, S.; Choy, W.; Peterson, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. (l) Nakai, T.; Mikami, K. *Chem. Rev.* **1986**, *86*, 885. (m) Bartlett, P. D. *Tetrahedron* **1980**, *36*, 2.

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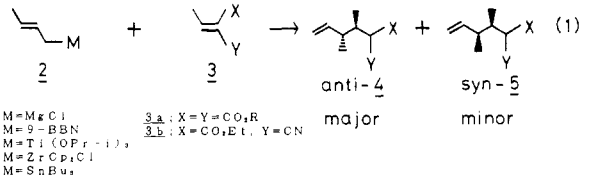
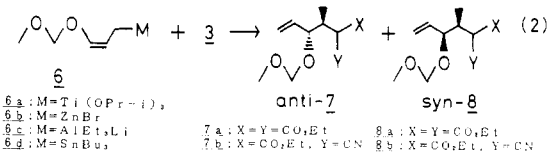
as ester enolate and thio Claisen rearrangements.[3] In 1981, Seebach reported an intermolecular diastereoselective Michael addition of enamines to nitroolefins.[4a] He also investigated the diastereoselectivity in the Michael addition of lithium enolates, silyl enol ethers, and related nucleophiles to nitroolefins.[4b-d] In 1984, Yamaguchi reported high diastereoselective Michael addition of ester and amide enolates to α,β-unsaturated carbonyl compounds.[4e-i] Similar types of reactions were further studied in detail primarily by Mukaiyama and Heathcock.[4j-s]

Previously, we reported the anti-selective condensation between crotyl organometallic compounds **2** and ethylidenmalonates **3a** (eq 1).[5] We now report the full details



(1)

of that work together with the diastereoselective addition of γ-alkoxy-substituted allylic organometallic compounds **6** to **3** (eq 2). Further, we report the Lewis acid mediated Michael addition of allylic tin reagents to nitroolefins and α,β-unsaturated ketones.



(2)

Results and Discussion

Diastereoselective Michael Addition of Crotylorganometals to Enoates. The reaction of crotyl Grignard reagents with ethyl crotonate did not give the Michael adduct but produced the 1,2-adduct exclusively.[6] It had been reported that the conjugate addition took place in the reaction of crotyl Grignard reagents with isopropylidenemalonates having two electron-withdrawing groups.[6] We examined the stereoselectivity in the 1,4-addition of various crotylorganometals to prochiral Michael acceptors. The results are summarized in Table I. The anti isomer **4** was produced predominantly regardless of crotylmetals.

Table I. Anti-Selective Reactions of 2 with 3

entry	crotylmetal 2, M	Michael acceptor 3, R	reactn condn[a]	anti-4:syn-5[b]	total isolated yield, %
1	MgCl	**3a**, Me	A	60:40	80
2	MgCl	**3a**, Et	A	60:40	66
3	MgCl	**3a**, *i*-Pr	A	60:40	80
4	MgCl	**3b**,	A	72:28	60
5	9-BBN	**3a**, Me	B	80:20	75
6	9-BBN	**3a**, Et	B	90:10	80
7	9-BBN	**3a**, *i*-Pr	B	85:15	80
8	Ti(O-*i*-Pr)$_3$	**3a**, Me	C	75:25	85
9	Ti(O-*i*-Pr)$_3$	**3a**, Et	C	90:10	80
10	Ti(O-*i*-Pr)$_3$	**3a**, *i*-Pr	C	85:15	80
11	Ti(O-*i*-Pr)$_3$	**3a**, Et	C	80:20	66
12	$ZrCp_2Cl$	**3a**, Et	D	80:20	80
13	$ZrCp_2Cl$	**3b**,	D	80:20	80
14	$SnBu_3$/$TiCl_4$	**3a**, Et	E	87:13	95
15	$SnBu_3$/$SnCl_4$	**3a**, Et	E	90:10	52
16	$SnBu_3$/$AlCl_3$	**3a**, Et	E	80:20	94
17	$SnBu_3$/$TiCl_4$	**3b**,	E	80:20	86

[a] A: The reaction was carried out in ether at −78 °C for 0.5 h and then quenched either at −78 °C (entries 1–3) or at 0 °C (entry 4). B: The reaction was conducted in CH_2Cl_2 at 25 °C for 12 h. C: The reaction was conducted in ether at −78 °C for 1 h and then quenched at 0 °C. D: The reaction of entry 12 was carried out in THF at 0 °C for 1 h and then quenched at 25 °C. The reaction of entry 13 was carried out at 25 °C for 12 h. E: Lewis acid–CH_2Cl_2 solution was added at −78 °C to a CH_2Cl_2 solution of substrates and the reaction was quenched at 0 °C. [b] By ^1H NMR analysis.

The reaction of crotyltitanium or 9-BBN reagent gave **4** with high diastereoselectivity (entries 6 and 9), while the reaction of the Grignard reagent resulted in low stereoselectivity. The steric bulk of the ester group did not exert a strong influence upon the selectivity; the methyl, ethyl, and isopropyl esters of **3a** exhibited similar diastereoselectivity as shown in entries 1–3, 5–7, and 8–10. The reaction of α-cyanocrotonate **3b** proceeded slowly in comparison with that of **3a**, but almost the same anti selectivity was produced (entries 4, 11, and 13). Addition to **3b** did not take place with crotyl-9-BBN and the adduct could not be obtained. The Lewis acid mediated Michael addition of crotyltributyltin produced the anti adduct predominantly irrespective of the type of Lewis acids and Michael acceptors (entries 14–17). Titanium tetrachloride was the most suitable activator among the Lewis acids examined. No reaction took place with $BF_3{\cdot}OEt_2$. Although the reaction of **3a** with crotyltin–$SnCl_4$ gave the adducts in 52% yield, the reaction of **3b** with the same reagent did not occur.

The stereochemistry of the adducts were determined as shown in Scheme I. Decarboxylation of *anti*-**4a** (R = Et) produced **9**. Hydroboration–oxidation of **9**, followed by oxidation with CrO_3 gave the corresponding acid **10**, which was converted into the ester **11**. Comparison of the ^{13}C NMR data with an authentic sample[2a] indicated the anti structure. The structure of *syn*-**5a** (R = Et) was confirmed by a similar procedure. The stereochemistry of the corresponding methyl and isopropyl esters was assigned by comparing ^1H NMR chemical shift data with those of the ethyl ester. The chemical shift data of the C-3 and C-4 methyl protons of **4a** and **5a** (Me, Et, and *i*-Pr) are listed in Table II. Two methyl protons of **4a** always appeared

(2) For faranal, see: (a) Baker, R.; Billington, D. C.; Ekanayake, N. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1387. (b) Knight, D. W.; Ojhara, B. *Tetrahedron Lett.* **1981**, *22*, 5101. For ikarugamycin, see: (c) Kurth, M. J.; Burns, D. H.; O'Brien, M. J. *J. Org. Chem.* **1984**, *49*, 733. For steroid side chain, see: (d) Gebreyesus, T.; Djerassi, C. *Tetrahedron Lett.* **1982**, *23*, 4427.

(3) For example: (a) Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668. (b) Tamaru, Y.; Furukawa, Y.; Mizutani, M.; Kitao, O.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 3631. (c) Beslin, P.; Metzner, P.; Vallee, Y.; Vialle, J. *Tetrahedron Lett.* **1983**, *24*, 3617. (d) Denmark, S. E.; Harmata, M. A. *J. Org. Chem.* **1983**, *48*, 3369. (e) Danishefsky, S.; Tsuzuki, K. *J. Am. Chem. Soc.* **1980**, *102*, 6891.

(4) (a) Seebach, D.; Golinski, *J. Helv. Chim. Acta* **1981**, *64*, 1413. (b) Häner, R.; Laube, T.; Seebach, D. *Chimia* **1984**, *38*, 255. (c) Seebach, D.; Beck, A. K.; Golinski, J.; Hay, J. N.; Laube, T. *Helv. Chim. Acta* **1985**, *68*, 162. (d) Seebach, D.; Brook, M. A. *Ibid.* **1985**, *68*, 319. (e) Yamaguchi, M.; Tsukamoto, M.; Hirao, I. *Chem. Lett.* **1984**, 375. (f) Yamaguchi, M.; Tsukamoto, M.; Tanaka, S.; Hirao, I. *Tetrahedron Lett.* **1984**, *25*, 5661. (g) Yamaguchi, M.; Hasebe, K.; Tanaka, S.; Minami, T. *Ibid.* **1986**, *27*, 959. (h) Yamaguchi, M.; Tsukamoto, M.; Hirao, I. *Tetrahedron Lett.* **1985**, *26*, 1723. (i) Review; Yamaguchi, M. *J. Syn. Org. Chem. Jpn.* **1986**, *44*, 405. (j) Stevens, R. W.; Mukaiyama, T. *Chem. Lett.* **1985**, 855. (k) Mukaiyama, T.; Tamura, M.; Kobayashi, S. *Ibid.* **1986**, 1017. (l) Hashimoto, Y.; Mukaiyama, T. *Ibid.* **1986**, *1623*. (m) Mukaiyama, T.; Tamura, M.; Kobayashi, S. *Ibid.* **1986**, 1817. (n) Minowa, N.; Mukaiyama, T. *Ibid.* **1987**, 1719. (o) Heathcock, C. H.; Norman, M. H.; Uehling, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 2797. (p) Heathcock, C. H.; Henderson, M. A.; Oare, D. A.; Sanner, M. A. *J. Org. Chem.* **1985**, *50*, 3019. (q) Heathcock, C. H.; Oare, D. A. *Ibid.* **1985**, *50*, 3022. (r) Heathcock, C. H.; Ueling, D. E. *Ibid.* **1986**, *51*, 279. (s) Oare, D. A.; Heathcock, C. H. *Tetrahedron Lett.* **1986**, *27*, 6169. (t) Yoshikoski, A.; Miyashita, M. *Acc. Chem. Res.* **1985**, *18*, 284.

(5) Yamamoto, Y.; Nishii, S.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 386.

(6) Holmberg, G. A.; Sjöholm, R. *Acta Chem. Scand.* **1970**, *24*, 3490.

Table II. Selected NMR Spectral Data of 4a and 5a

R	C-3 and C-4 methyl protons, δ from TMS	
	anti-**4a**	*syn*-**5a**
Me	0.88, 1.06	0.93, 0.96
Et	0.89, 1.05	0.94, 0.97
i-Pr	0.89, 1.05	0.94, 0.96

at the highest and lowest field, and those of **5a** appeared between these two extremes.

The stereochemistry of **4b** and **5b** was determined in a similar manner as shown in Scheme I. Decarboxylation of **4b** (R = Et) gave **12**, which was converted to **9** via hydrolysis–esterification. The Michael adducts to **3b** possessed three chiral centers and thus potentially had four pairs of diastereomers. We were concerned with the chiral centers of C-3 and C-4, and hence the diastereomer ratios listed in Table I were obtained after the decarboxylation–hydrolysis–esterification; the ratios of **9** and its epimer were listed. The diastereomer ratio of **4b** and **5b** in entry 4, which was determined by 400-MHz ^{1}H NMR spectroscopy, was 47:25:20:8. Accordingly, epimerization does not take place during the decarboxylation–hydrolysis–esterification.

The anti selectivity can be explained by either an acyclic or an eight-membered cyclic transition state. Although two possible conformations, crown and boat-chair, are conceivable in the eight-membered transition state, the former is generally more stable than the latter.[7] In the crown conformations, it seems that **13** is destabilized in comparison with **14** owing to the pseudoaxial Me group (Scheme II). The comparative stabilities of **13** and **14** should be sensitive to variations of size in the alkoxycarbonyl groups, which is not observed as stated above (Table I). Further, the Lewis acid mediated addition of crotyltin, which proceeds through an acyclic transition state,[1a,8] produces again the anti selectivity. Taken together, the reaction must proceed through the acyclic transition state, in which it is clear that **15** is more stable than **16** for steric reasons. The gauche interaction between two methyl groups in **16** must destabilize this transition state.

The ratio of *E*/*Z* of crotyl-9-BBN is ca. 70/30.[9] The ratio of *E*/*Z* of crotyltin used here is ca. 75/25. In Scheme II, consideration based upon *E*-allylic metals is made. Therefore, it is desirable to examine the conjugate addition with allylic organometals having *Z* geometry in order to know both the stereoselectivity and the transition-state geometry.

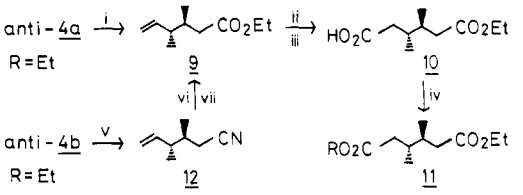
Diastereoselective Michael Addition of (γ-Alkoxyallyl)organometals. Since it was previously demonstrated that (γ-alkoxyallyl)metals **6** took *Z* geometry owing to the strong coordination ability of the oxygen atom toward metals,[10] and since the *Z* geometry of the tin derivative was confirmed as mentioned later, the Michael addition of **6** was examined, and the results are summarized in Table III. Synthetically, this type of reaction (eq 2) is important since the conjugate adducts (**7** and **8**) possess a 1,4-dioxygen substituted structure and can be easily converted to homoaldol derivatives.

Table III. Anti-Selective Reactions of 6 with 3

entry	(alkoxyallyl)-metal 6, M	Michael acceptor	reactn condn[a]	*anti*-**7**: *syn*-**8**[b]	total isolated yield, %
1	$Ti(O\text{-}i\text{-}Pr)_3$	**3a**	A	87:13	83
2	$Ti(O\text{-}i\text{-}Pr)_3$	**3b**	A	85:15	59
3	ZnBr	**3a**	A	50:50	42
4	$Al^-Et_3Li^+$	**3a**	A	50:50	48
5	$SnBu_3/TiCl_4$	**3a**	B	85:15	34
6	$SnBu_3/SnCl_4$	**3a**	B	92:8	10

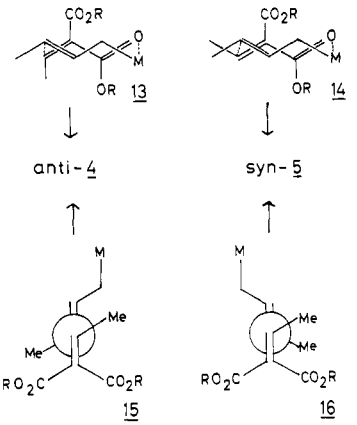
[a] A: The reaction was conducted in THF at −78 °C and then quenched at 0 °C. B: The reaction was conducted in CH_2Cl_2 at −78 °C and quenched at −30 °C. [b] By ^{1}H NMR analysis.

Scheme I[a]



[a] (i) Me_4NOAc–hexamethylphosphoramide, 110 °C, 10 h, 90%; (ii) $BH_3{\cdot}SMe_2$–tetrahydrofuran, then $NaOH\text{–}H_2O_2$, 92%; (iii) $CrO_3\text{–}H_2SO_4$–acetone, 80%; (iv) ROH–TsOH–C_6H_6, reflux, 10 h, 90%; (v) NaCl–H_2O–dimethyl sulfoxide, 150 °C, 1 h, 80%; (vi) 5 M KOH–$HOCH_2CH_2OH$, 120 °C, 2 h; (vii) EtOH–TsOH–C_6H_6, reflux, 10 h, 78%.

Scheme II



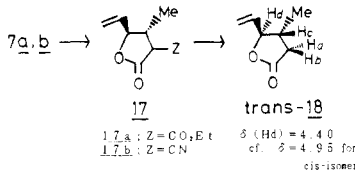
A fairly high anti/syn ratio was obtained with the titanium reagent (entries 1 and 2), but no selectivity was observed with the zinc and aluminum reagents (entries 3 and 4). In contrast to these reagents, ((methoxymethoxy)allyl)tributyltin could be isolated as a stable form.[11] The *Z* geometry was confirmed by the coupling constant of olefinic vicinal protons; $J_{H\text{-}H}$ = 6.1 Hz. Here again, the anti isomer was produced predominantly (entries 5 and 6), though the desired adducts were obtained in low yields. If higher temperature and prolonged reaction time were employed, the methoxymethyl group was removed during the reaction and complex mixtures of products were obtained. With $BF_3{\cdot}OEt_2$, the reaction did not occur at all. The addition of the tin reagent to **3b** did not take place even with the aid of $TiCl_4$.

The anti selectivity of **6** is presumably a reflection of an acyclic transition state, because the tin reagent in the

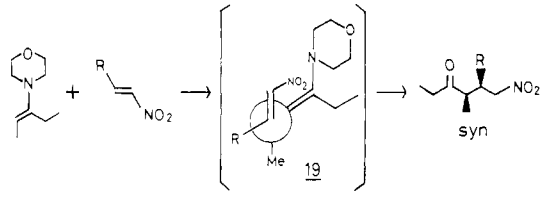
(7) Allinger, N. L. *J. Am. Chem. Soc.* **1959**, *81*, 5727. Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357.
(8) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107.
(9) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969.
(10) Yamamoto, Y.; Saito, Y.; Maruyama, K. *J. Organomet. Chem.* **1985**, *292*, 311.
(11) For γ-oxygen-substituted allylic tins, see: (a) Koreeda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, *28*, 143. (b) Keck, G. E.; Abbott, D. E.; Wiley, M. R. *Ibid.* **1987**, *28*, 139. (c) Yamamoto, Y.; Taniguchi, K., unpublished data. For α-oxygen-substituted allylic tins, see: (d) Marshall, J. A.; DeHoff, B. S.; Crooks, S. L. *Tetrahedron Lett.* **1987**, *28*, 527. (e) Hull, C.; Mortlock, S. V.; Thomas, E. J. *Ibid.* **1987**, *28*, 5343.

presence of Lewis acids produces the anti isomer. Consequently, the anti diastereoselectivity is produced in the Michael addition regardless of the geometry of the allylic double bond (eq 1 and 2).

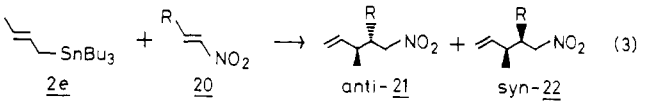
The stereochemistry of the adducts was determined as follows. Deprotection of the methoxymethyl group with 3 N HCl lead to rapid lactonization, giving **17** in essentially quantitative yield. Decarboxylation of **17a** or hydrolysis–decarboxylation of **17b** produced *trans*-**18**. Quite similarly, *syn*-**8** was converted to the corresponding cis lactone (*cis*-**18**). The proton at C-4 of *trans*-**18** appeared at higher field than that of *cis*-**18**, owing to the shielding effect of the vicinal methyl substituent.

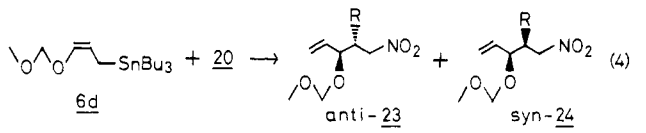


Michael Addition to Nitroolefins. The stereoselective Michael addition to nitroolefins has been reported previously,[4a-d,j,t] and high syn selectivity is produced in the conjugate addition of enamines to nitroolefins.[4a-d]. The syn selectivity is explained by an acyclic synclinal model (**19**), in which there is some favorable interaction between



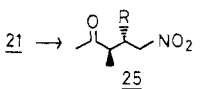
the nitro group and the nitrogen lone pair of the enamine group. This syn selectivity is opposite to the anti selectivity of conjugate addition of allylmetals to enoates. Therefore, we examined the reaction of allylmetals with nitroolefins (eq 3 and 4). The results are summarized in Table IV.





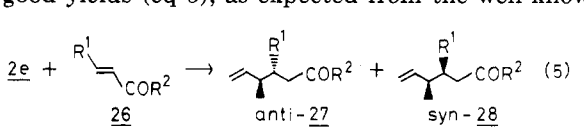
Although the selectivity was not as high as that observed in reactions with **3a** and **3b**, the anti preference was observed except entry 3. The addition of **6d** was accomplished by use of $TiCl_4$; other Lewis acids were ineffective to promote the reaction. This anti selectivity is different from the observation made by Seebach in the enamine addition but is similar to the observation by Mukaiyama[4j] in the tin enolate Michael addition. The reason for this difference is not clear at present. An antiperiplanar transition state similar to the model depicted in Scheme II might be involved, instead of an synclinal transition state.

The stereochemistry of **21** was determined by converting to the nitro ketone **25**. Wacker oxidation[12] of **21** produced



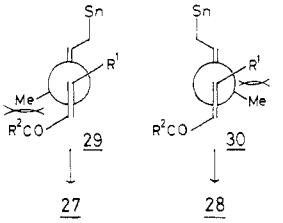
25 (R = Ph and Me) in good yields. The ^1H NMR data of **25** were compared with those of authentic samples. We thank Professor Seebach for providing us with ^1H NMR data of **25** and its epimer.

Michael Addition to α,β-Unsaturated Ketones. The addition of crotyltin **2e** to α,β-unsaturated ketones **26** proceeded quite smoothly and gave the adducts **27** and **28** in good yields (eq 5), as expected from the well-known



Michael addition of allylsilanes.[13] The diastereoselectivities are summarized in Table V. The addition was accomplished even by use of $BF_3 \cdot OEt_2$, which was ineffective for the addition of crotyltin **2e** to nitroolefins. However, use of $SnCl_4$ did not give the desired adducts. Here again, the anti selectivity was obtained regardless of the substituents of **26**, although the selectivity itself was not so high. When the yields of 1,4-adducts were low (entries 2, 6, and 7), the starting ketones were recovered and no 1,2-addition took place.

The stereochemistry of **27** (R^1 = Me) was determined by comparison with an authentic sample which was prepared through the reaction of **12** with PhMgBr followed by hydrolysis. The stereochemistries of **27** (R^1 = Ph) and **28** were not determined unambiguously but assigned by considering their ^1H NMR spectra.



The anti selectivity can be explained by an acyclic antiperiplanar model (**29**), which is essentially equal to **15**. There is a gauche interaction between R^1 and Me in **30**, while there is a long distance interaction between R^2CO and Me in **29**. Therefore, it is likely that **29** is more favorable than **30**. The energy difference between **29** and **30** seems to be small, since the conjugate addition to enones results in low diastereoselectivity.

Summary. Regardless of the reagent types and the reagent geometry, and regardless of the substrate structures, the anti selectivity is produced and hence the stereochemistry can be explained uniformly by an acyclic antiperiplanar transition state. On the other hand, the stereoselectivity of the enolate addition or enamine addition highly depends upon the structures of both substrates and reagents. The addition of (*E*)-enamines to (*E*)-nitrooolefins produces the syn selectivity, which is accounted for by an acyclic synclinal transition state.[4a,14] The lithium enolate addition to enoates or enones exhibits either syn or anti selectivity.[4j] The selectivity is dictated by a number of factors, such as the enolate geometry, the geometry of the double bond of the Michael acceptors, the

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Table IV. Anti-Selective Reactions of 2e and 6d with 20[a]

entry	allylmetal	20, R	Lewis acid	anti:syn[b]	total isolated yield, %
1	**2e**	Ph	$TiCl_4$	70:30	53
2	**2e**	Ph	$TiCl_2(O\text{-}i\text{-}Pr)_2$	65:35	67
3	**2e**	Ph	$AlCl_3{\cdot}OEt_2$	45:55	92
4	**6d**	Ph	$TiCl_4$	64:36	40
5	**2e**	Me	$TiCl_4$	69:31	35
6	**2e**	Me	$TiCl_2(O\text{-}i\text{-}Pr)_2$	59:41	29
7	**2e**	Me	$AlCl_3{\cdot}OEt_2$	54:46	42
8	**6d**	Me	$TiCl_4$	65:35	36

[a] The reaction was carried out in CH_2Cl_2 at −78 °C for 2 h and then quenched at −60 °C. [b] By ^1H NMR analysis.

Table V. Anti-Selective Reactions of 2e with 26

entry	26 R^1	26 R^2	Lewis acid	reactn condn[a]	*anti*-**27**: *syn*-**28**[b]	total isolated yield, %
1	Me	Me	$TiCl_4$	A	72:28	64
2	Me	Me	$AlCl_3{\cdot}OEt_2$	A	68:32	15
3	Me	Ph	$TiCl_4$	A	58:42	77
4	Me	Ph	$BF_3{\cdot}OEt_2$	B	62:38	60
5	Ph	Me	$TiCl_4$	A	61:39	95
6	Ph	Me	$BF_3{\cdot}OEt_2$	B	62:38	40
7	Ph	Ph	$BF_3{\cdot}OEt_2$	B	57:43	48

[a] A: at −78 °C in CH_2Cl_2 for 1–2 h. B: at room temperature in CH_2Cl_2 for 16 h. [b] By ^1H NMR analysis.

substituents of substrates and reagents, and reaction conditions. Both acyclic synclinal and antiperiplanar transition-state models are proposed. In contrast to these complex behaviors of enolates and related compounds, the reactions of allylic organometals are so far straightforward and can be understood simply by an acyclic antiperiplanar model.

Experimental Section

General information concerning instrumentation and materials is described previously.[15] Diethyl ethylidenemalonate was purchased from Aldrich Chemical Co. Inc. Dimethyl (**3a**, R = Me) and diisopropyl ethylidenemalonates (**3a**, R = *i*-Pr) were prepared according to the literature.[16] **3a** (R = Me): bp 105 °C/18 mmHg; ^1H NMR (CCl_4) δ 1.97 (3 H, d, *J* = 7.3 Hz), 3.78 (3 H, S), 3.84 (3 H, s), 7.13 (1 H, q, *J* = 7.3 Hz); IR (neat) 1430, 1635, 1720, 2950 cm^{-1}; exact mass calcd for $C_7H_{10}O_4$ *m/z* 158.0579, found *m/z* 158.0589. **3a** (R = *i*-Pr): bp 125 °C/18 mmHg; ^1H NMR (CCl_4) δ 1.27 (6 H, d, *J* = 6.1 Hz), 1.31 (6 H, d, *J* = 6.4 Hz), 1.94 (3 H, d, *J* = 7.3 Hz), 5.09 (1 H, hept, *J* = 6.1 Hz), 5.19 (1 H, hept, *J* = 6.4 Hz); IR (neat) 1095, 1220, 1255, 1370, 1460, 1715, 2980 cm^{-1}: exact mass calcd for $C_{11}H_{18}O_4$ *m/z* 214.1206, found *m/z* 214.1208. **Ethyl α-cyanocrotonate (3b)** was prepared according to the literature:[17] ^1H NMR (CCl_4) δ 1.35 (3 H, t, *J* = 7.2 Hz), 2.23 (3 H, d, *J* = 7.0 Hz), 4.31 (2 H, q, *J* = 7.2 Hz), 7.73 (1 H, q, *J* = 7.0 Hz); IR (neat) 1370, 1430, 1620, 1720, 2230, 2980 cm^{-1}; exact mass calcd for $C_7H_9NO_2$ *m/z* 139.0634, found *m/z* 139.0634. The geometry of **3b** was determined to be *E* by nondecoupling ^{13}C NMR measurement; the carbon–vinyl proton coupling constant $^3J_{CN-H}$ = 13.7 Hz, while $^3J_{CO-H}$ = 3.5 Hz. **β-Nitrostyrene (20**, R = Ph) was purchased from Aldrich Chemical Co. Inc. **(*E*)-1-Nitropropene (20**, R = Me) was prepared by the nitroaldol reaction between nitromethane and acetaldehyde,[18] followed by dehydration of the resulting nitroaldol:[19] bp 70 °C/20 mmHg, 60% yield (overall); ^1H NMR (CCl_4) δ 1.96 (3 H, dd, *J* = 1.8, 7.3 Hz), 7.02 (1 H, dq, *J* = 1.8, 13.4 Hz), 7.29 (1 H, dq, *J* = 7.3, 13.4 Hz); IR (neat) 1520, 1655 cm^{-1}. **α,β-Unsaturated ketones 26** were purchased and used without further purification. Crotylorganometals[15,20] **2a–e** and β-alkoxy-substituted allylmetals **6a–c**[20] were prepared as described previously. (3-(Methoxymethoxy)-2-propenyl)tributyltin (**6d**) was prepared by the reaction of the corresponding lithium derivative with tributyltin chloride:[20,21] bp 160 °C/1 mmHg, 90% yield; ^1H NMR (CCl_4) δ 0.80–1.80 (27 H, m), 1.70 (2 H, d, *J* = 8.8 Hz), 3.40 (3 H, s), 4.65 (1 H, dt, *J* = 6.1, 8.8 Hz), 4.77 (2 H, s), 5.96 (1 H, d, *J* = 6.1 Hz).

Reaction of 2 with 3. The following procedure for the preparation of **4a** and **5a** (R = Et) is representative (procedure A in Table I). To a solution of 1 mmol of **3a** (R = Et) (0.185 mL) dissolved in 5 mL of dry ether was added 1.1 mmol of **2a** dissolved in dry ether under N_2 at −78 °C. After 30 min, the reaction was quenched with a saturated NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were dried over $MgSO_4$ and concentrated. The crude product was purified by short column chromatography on silica gel (hexane:ether = 10:1 as eluant). Procedure B was carried out similarly except for the quenching method. The reaction was quenched with 1 mL of MeOH and 2 mmol of monoethanolamine (0.12 mL). The solvents were removed under vacuum, and hexane (15 mL) was added to the resulting viscous yellow oil. The hexane solution was separated and the reaction mixture was extracted three times with hexane. The combined hexane solution was condensed and purified. Procedures C and D were essentially same as procedure A. Procedure E was conducted as follows. To a solution of 1 mmol of **3a** (R = Et) dissolved in 5 mL of dry CH_2Cl_2 was added 1.1 mmol of **2e** (0.44 mL) under N_2 at −78 °C. Subsequently 1.1 mmol of $TiCl_4$–CH_2Cl_2 solution (1.1 mL) was added and the reaction mixture was allowed to warm up to 0 °C and stirred for 4 h. The reaction was quenched with a saturated NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic layers were dried over $MgSO_4$ and evaporated. The tin residue was removed by a short silica gel column by using hexane as an eluant, and then the crude product was purified by flash column chromatography on silica gel (hexane:ether = 10:1).

Ethyl 2-(ethoxycarbonyl)-3,4-dimethyl-5-hexenoate: ^1H NMR (CCl_4) δ of *anti*-**4a** (R = Et) 0.89 (3 H, d, *J* = 6.7 Hz), 1.05 (3 H, d, *J* = 6.4 Hz), 3.32 (1 H, d, *J* = 9.5 Hz); δ of *syn*-**5a** (R = Et) 0.94 (3 H, d, *J* = 6.4 Hz), 0.97 (3 H, d, *J* = 6.4 Hz), 3.42 (1 H, d, *J* = 7.3 Hz); the following signals were observed in both isomers, 1.27 (6 H, t, *J* = 7.2 Hz), 1.31–1.44 (1 H, m), 2.21–2.32 (1 H, m), 4.18 (4 H, q, *J* = 7.2 Hz), 4.95–5.05 (2 H, m), 5.62–5.77 (1 H, m); IR (CCl_4) 1375, 1470, 1640, 1735, 1755, 2990 cm^{-1}; exact mass calcd for $C_{13}H_{22}O_4$ *m/z* 242.1519, found *m/z* 242.1517.

Methyl 2-(methoxycarbonyl)-3,4-dimethyl-5-hexenoate: ^1H NMR (CCl_4) δ of *anti*-**4a** (R = Me) 0.88 (3 H, d, *J* = 6.7 Hz), 1.06 (3 H, d, *J* = 6.7 Hz), 3.36 (1 H, d, *J* = 9.5 Hz); δ of *syn*-**5a** (R = Me) 0.93 (3 H, d, *J* = 6.7 Hz), 0.96 (3 H, d, *J* = 6.4 Hz), 3.47 (1 H, d, *J* = 7.6 Hz); the following signals were observed in both isomers, 2.20–2.33 (2 H, m), 3.72 (3 H, s), 3.73 (3 H, s), 4.94–5.05 (2 H, m), 5.61–5.70 (1 H, m); IR (CCl_4) 1430, 1720, 1750, 2950 cm^{-1}; exact mass calcd for $C_{11}H_{18}O_4$ *m/z* 214.1205, found *m/z* 214.1204.

Isopropyl 2-(isopropoxycarbonyl)-3,4-dimethyl-5-hexenoate: ^1H NMR (CCl_4) δ of *anti*-**4a** (R = *i*-Pr) 0.89 (3 H, d, *J* = 7.0 Hz), 1.05 (3 H, d, *J* = 6.4 Hz), 3.24 (1 H, d, *J* = 9.5 Hz); δ of *syn*-**5a** (R = *i*-Pr) 0.94 (3 H, d, *J* = 6.7 Hz), 0.96 (3 H, d, *J* = 6.4 Hz), 3.34 (1 H, d, *J* = 7.3 Hz); the following signals were observed in both isomers, 1.24 (6 H, d, *J* = 5.8 Hz), 1.25 (6 H, d, *J* = 5.5 Hz), 2.22–2.31 (2 H, m), 4.95–5.09 (4 H, m), 5.62–5.70 (1 H, m); IR (CCl_4) 1460, 1720, 1740, 2970 cm^{-1}; exact mass calcd for $C_{15}H_{26}O_4$ *m/z* 270.1832, found *m/z* 270.1843.

Ethyl 3,4-Dimethyl-5-hexenoate (9). Decarboxylation of **4a** (R = Et) was accomplished by the reported procedure.[22] **9** was

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obtained in 65% yield: ^{1}H NMR (CCl_4) δ of anti isomer 0.89 (3 H, d, J = 7 Hz), 1.01 (3 H, d, J = 7 Hz), 1.24 (3 H, t, J = 7 Hz), δ of syn isomer 0.88 (3 H, d, J = 7 Hz), 0.98 (3 H, d, J = 7 Hz), 1.26 (3 H, t, J = 7 Hz); the following signals were observed in both isomers, 1.91–2.40 (4 H, m), 4.07 (2 H, q, J = 7 Hz), 4.82–5.08 (2 H, m), 5.50–5.84 (1 H, m); IR (CCl_4) 1455, 1730, 2930, 2960 cm^{-1}.

5-(Ethoxycarbonyl)-3,4-dimethylpentanoic Acid (10). The usual hydroboration–oxidation[23] of **9** produced the corresponding alcohol in 92% yield: ^{1}H NMR (CCl_4) δ 0.79–0.92 (6 H, m), 1.23 (3 H, t, J = 7 Hz), 1.38–1.80 (3 H, m), 1.84–2.44 (3 H, m), 3.08 (1 H, br), 3.47–3.67 (2 H, m), 4.06 (2 H, q, J = 7 Hz). Without further purification, this alcohol was oxidized with CrO_3–H_2SO_4–acetone,[24] and **10** was obtained in 80% yield: ^{1}H NMR (CCl_4) δ 0.80–1.08 (6 H, m), 1.27 (3 H, t, J = 7 Hz), 1.45–1.82 (1 H, m), 1.99–2.60 (5 H, m), 4.09 (2 H, q, J = 7 Hz), 9.28 (1 H, br). Esterification of **10** was performed according to the reported procedure.[25] **11** was obtained in 90% yield: ^{1}H NMR (CCl_4) δ of *anti*-**11** (meso) 0.93 (6 H, d, J = 6.1 Hz); δ of syn isomer (racemic) 0.88 (6 H, d, J = 6.4 Hz); the following signals were observed in both isomers, 1.25 (6 H, t, J = 7.0 Hz), 1.99–2.15 (4 H, m), 2.30–2.36 (2 H, m), 4.13 (4 H, q, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) *anti*-**11** 13.719, 16.072, 34.102, 37.820, 59.629, 172.437; syn isomer 13.719, 14.357, 33.616, 39.004, 59.629, 172.270; IR (CCl_4) 1370, 1460, 1730, 2980 cm^{-1}.

Ethyl 2-cyano-3,4-dimethyl-5-hexenoate (4b and 5b): ^{1}H NMR (CCl_4) of four diastereomeric mixtures, δ 0.96–1.11 (6 H, m), 1.31–1.35 (3 H, m), 2.04–2.26 (2 H, m), 3.32–3.76 (1 H, m), 4.23–4.30 (2 H, m), 5.06–5.20 (2 H, m), 5.56–5.70 (1 H, m); IR (CCl_4) 1460, 1640, 1740, 2260 cm^{-1}; exact mass calcd for $C_{11}H_{17}NO_2$ m/z 195.1259, found m/z 195.1259.

3,4-Dimethyl-5-hexenenitrile (12). Decarboxylation of a mixture of **4b** and **5b** was carried out as described in the literature.[26] **12** was obtained in 80% yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ of *anti*-**12** 1.031 (3 H, d, J = 6.7 Hz), 1.041 (3 H, d, J = 6.7 Hz), 1.82–1.88 (1 H, m); δ of syn isomer 1.025 (3 H, d, J = 6.1 Hz), 1.093 (3 H, d, J = 7.0 Hz), 1.71–1.79 (1 H, m); the following signals were observed in both isomers 2.10–2.41 (3 H, m), 5.05–5.09 (2 H, m), 5.58—5.68 (1 H, m); IR (CCl_4) 1460, 1640, 1695, 2250 cm^{-1}; exact mass calcd for $C_8H_{13}N$ m/z 123.1048, found m/z 123.1053. Hydrolysis of **12** was carried out according to the literature procedure.[27] 3,4-Dimethyl-5-hexenoic acid was obtained: ^{1}H NMR (CCl_4) δ 0.95–1.05 (6 H, m), 1.52–2.60 (4 H, m), 4.82–5.08 (2 H, m), 5.47–5.82 (1 H, m), 10.95 (1 H, br). Esterification of this acid gave **9**.

Reaction of 6 with 3. The following procedure for preparation of **7** and **8** through the titanium reagent is representative. To a solution of 3 mmol of allyl methoxymethyl ether (0.33 mL) dissolved in 5 mL of dry THF was added 1 equiv of *n*-BuLi under N_2 at −78 °C. The mixture was stirred for 30 min at −30 °C and then cooled to −78 °C. Titanium chlorotriisopropoxide (1 equiv) was added and the substrate (1 mmol) was added after 10 min. The resulting mixture was allowed to warm to 0 °C and was stirred for 6 h. The reaction was quenched with a saturated aqueous NH_4Cl solution. The usual workup procedure was used to isolate the product.

Ethyl 2-(ethoxycarbonyl)-4-(methoxymethoxy)-3-methyl-5-hexenoate: ^{1}H NMR (CCl_4) δ of *anti*-**7a** 0.99 (3 H, d, J = 7.0 Hz), 1.27 (3 H, t, J = 7.0 Hz), 1.28 (3 H, t, J = 7.0 Hz), 2.41–2.50 (1 H, m), 3.37 (3 H, s), 3.63 (1 H, d, J = 6.4 Hz), 3.96 (1 H, dd, J = 7.9 Hz), 4.16–4.23 (4 H, m), 4.50 (1 H, d, J = 6.7 Hz), 4.67 (1 H, d, J = 6.7 Hz), 5.22–5.32 (2 H, m), 5.57–5.66 (1 H, m); δ of *syn*-**8a** 1.00 (3 H, d, J = 6.7 Hz), 1.27 (3 H, t, J = 7.0 Hz), 1.28 (3 H, t, J = 7.0 Hz), 2.41–2.50 (1 H, m), 3.36 (3 H, s), 3.50 (1 H, d, J = 8.9 Hz), 4.09 (1 H, dd, J = 4.3, 7.0 Hz), 4.16–4.23 (4 H, m), 4.51 (1 H, d, J = 6.7 Hz), 4.62 (1 H, d, J = 6.7 Hz), 5.22–5.32 (2 H, m), 5.70–5.79 (1 H, m); IR (CCl_4) 910, 1090, 1150, 1725, 1740, 2980 cm^{-1}; MS, m/z 288 (M^+).

Ethyl 2-cyano-4-(methoxymethoxy)-3-methyl-5-hexenoate: ^{1}H NMR (CCl_4) δ of four diastereomeric mixtures of **7b** and **8b** 1.03–1.19 (3 H, m), 1.33–1.34 (3 H, m), 2.33–2.53 (1 H, m), 3.41–3.43 (3 H, s, 4 peaks), 3.85–4.01 (1 H, m), 4.23–4.32 (3 H, m), 4.47–4.54 (1 H, m), 4.68–4.74 (1 H, m), 5.32–5.42 (2 H, m), 5.53–5.62 (1 H, m); IR (CCl_4) 1090, 1250, 1360, 1455, 1735, 2240, 2920, 2970 cm^{-1}; MS, m/z 241 (M^+).

3-Methyl-5-hexen-4-olide (18). To a solution of 0.45 mmol of a mixture of **7a** and **8a** dissolved in 10 mL of methanol was added 0.6 mL of 3 N HCl. The mixture was refluxed for 1 h and then cooled to room temperature. The reaction mixture was extracted with ether, and the organic layer was washed with brine, dried over $MgSO_4$, and condensed. The deprotected crude product (**17a**) was decarboxylated according to the reported procedure.[26] The lactone **18** was obtained in 59% overall yield: ^{1}H NMR (CCl_4) δ of *trans*-**18** 1.16 (3 H, d, J = 6.4 Hz), 2.17–2.34 (2 H, m, H_a and H_c), 2.69 (1 H, dd, J = 7.5, 16.6 Hz, H_b), 4.40 (1 H, dd, J = 6.9, 7.8 Hz, H_b), 5.28–5.41 (2 H, m), 5.81–5.89 (1 H, m); δ of the cis isomer 1.03 (3 H, d, J = 6.4 Hz), 2.17–2.34 (2 H, m), 2.63–2.73 (1 H, m), 4.95 (1 H, dd, J = 5.5, 6.4 Hz), 5.28–5.41 (2 H, m), 5.81–5.89 (1 H, m); IR (CCl_4) 930, 990, 1160, 1220, 1430, 1460, 1780, 2980 cm^{-1}; exact mass calcd for $C_7H_{10}O_2$ m/z 126.0680, found m/z 126.0680. Deprotection of **7b** and **8b** was carried out as described above, and the resulting crude **17b** was hydrolyzed according to the reported procedure.[27] The desired product **18** was obtained in 38% overall yield.

Reaction of 2e and 6d with 20. The Lewis acid mediated conjugate additions of the allylic tin reagents were carried out in a similar manner as described in Table I, procedure E.

3-Methyl-5-nitro-4-phenyl-1-pentene: ^{1}H NMR (CCl_4) δ of *anti*-**21** (R = Ph) 1.00 (3 H, d, J = 6.7 Hz), 2.49–2.57 (1 H, m), 3.47–3.53 (1 H, m), 4.65 (1 H, dd, J = 8.7, 12.7 Hz), 4.73 (1 H, dd, J = 6.9, 12.7 Hz); δ of *syn*-**22** (R = Ph) 0.85 (3 H, d, J = 6.7 Hz), 2.39–2.45 (1 H, m), 3.22–3.28 (1 H, m), 4.53 (1 H, dd, J = 10.5, 12.7 Hz), 4.74 (1 H, dd, J = 4.9, 12.7 Hz); the following signals were observed in both isomers, 5.01–5.16 (2 H, m), 5.52–5.76 (1 H, m), 7.12–7.33 (5 H, m); IR (CCl_4) 680, 1375, 1445, 1545, 2910, 2960, 3030, 3050 cm^{-1}; MS, m/z 205 (M^+).

3,4-Dimethyl-5-nitro-1-pentene: ^{1}H NMR (CCl_4) δ of **21** (R = Me) 1.00 (3 H, d, J = 6.7 Hz), 1.08 (3 H, d, J = 7.0 Hz); δ of **22** (R = Me) 1.03 (3 H, d, J = 7.0 Hz), 1.07 (3 H, d, J = 6.7 Hz); the following signals were observed in both isomers, 2.16–2.43 (2 H, m), 4.12–4.29 (1 H, m), 4.38–4.49 (1 H, m), 5.05–5.13 (2 H, m), 5.66–5.76 (1 H, m); IR (CCl_4) 1370, 1450, 1545, 2960, 2980 cm^{-1}; MS, m/z 143 (M^+).

3-Methyl-5-nitro-4-phenyl-2-pentanone: ^{1}H NMR (CCl_4) δ of *anti*-**25** (R = Ph) 1.21 (3 H, d, J = 7.3 Hz), 1.94 (3 H, s), 2.99 (1 H, dq, J = 7.3, 7.6 Hz), 3.78 (1 H, ddd, J = 5.2, 7.6, 9.6 Hz), 4.70 (1 H, dd, J = 9.6, 12.8 Hz), 4.78 (1 H, dd, J = 5.2, 12.8 Hz), 7.15–7.35 (5 H, m); δ of *syn*-**25** (R = Ph) 0.98 (3 H, d, J = 7.3 Hz), 2.23 (3 H, s), 2.98 (1 H, dq, J = 7.3, 9.1 Hz), 3.68 (1 H, ddd, J = 4.9, 8.5, 9.1 Hz), 4.62 (1 H, dd, J = 4.9, 12.5 Hz), 4.67 (1 H, dd, J = 8.5, 12.5 Hz), 7.15–7.35 (5 H, m); IR (CCl_4) 685, 1375, 1540, 1700, 2920, 2970, 3030, 3070 cm^{-1}.

3,4-Dimethyl-5-nitro-2-pentanone: ^{1}H NMR (CCl_4) δ of *anti*-**25** (R = Me) 1.06 (3 H, d, J = 6.4 Hz), 1.16 (3 H, d, J = 6.8 Hz), 2.20 (3 H, s); δ of *syn*-**25** (R = Me) 1.01 (3 H, d, J = 6.8 Hz), 1.13 (3 H, d, J = 6.8 Hz), 2.21 (3 H, s); the following signals were observed in both isomers, 2.59–2.69 (2 H, m), 4.24–4.50 (2 H, m); IR (CCl_4) 1360, 1380, 1550, 1700, 2920, 2960 cm^{-1}.

3-(Methoxymethoxy)-5-nitro-4-phenyl-1-pentene: ^{1}H NMR (CCl_4) δ of *anti*-**23** (R = Ph) 3.30 (3 H, s), 4.25 (1 H, dd, J = 7.6, 7.6 Hz), 4.48 (1 H, d, J = 6.7 Hz), 4.67 (1 H, d, J = 6.7 Hz), 4.72 (1 H, dd, J = 9.5, 13.1 Hz), 4.96 (1 H, dd, J = 5.5, 13.1 Hz); δ of *syn*-**24** (R = Ph) 3.19 (3 H, s), 4.29 (1 H, dd, J = 7.3, 8.5 Hz), 4.48 (1 H, d, J = 7.0 Hz), 4.64 (1 H, d, J = 7.0 Hz), 4.71 (1 H, dd, J = 6.4, 13.1 Hz), 4.84 (1 H, dd, J = 6.4, 13.1 Hz); the following signals were observed in both isomers, 3.65–3.73 (1 H, m), 5.09–5.29 (2 H, m), 5.47–5.60 (1 H, m), 7.20–7.32 (5 H, m); IR (CCl_4) 1450, 1550, 2920, 2960 cm^{-1}; MS, m/z 251 (M^+).

3-(Methoxymethoxy)-4-methyl-5-nitro-1-pentene: ^{1}H NMR (CCl_4) δ of *anti*-**23** (R = Me) 1.04 (3 H, d, J = 6.8 Hz), 2.52 (1 H, m), 3.37 (3 H, s), 3.90 (1 H, m); δ of *syn*-**24** (R = Me) 0.91 (3 H, d, J = 7.7 Hz), 2.58 (1 H, m), 3.35 (3 H, s), 4.05 (1 H, m); the following signals were observed in both isomers, 4.17–4.28 (1 H,

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m), 4.49-4.72 (3 H, m), 5.26-5.36 (2 H, m), 5.60-5.69 (1 H, m); IR (CCl_4) 1095, 1150, 1380, 1460, 1550, 2920, 2950 cm^{-1}; MS m/z 189 (M^+).

Reaction of 2e with 26. The conjugate addition of crotyltin to α,β-unsaturated ketones was carried out in a similar procedure as described in Table I, procedure E.

4,5-Dimethyl-6-hepten-2-one: ^1H NMR (CCl_4) δ of *anti*-**27** ($R^1 = R^2 = Me$) 0.85 (3 H, d, $J = 6.7$ Hz), 0.99 (3 H, d, $J = 7.0$ Hz), 2.12 (3 H, s); δ of *syn*-**28** ($R^1 = R^2 = Me$) 0.87 (3 H, d, $J = 7.0$ Hz), 0.97 (3 H, d, $J = 6.4$ Hz), 2.11 (3 H, s); the following signals were observed in both isomers, 1.97-2.25 (3 H, m), 2.42-2.54 (1 H, m), 4.94-5.01 (2 H, m), 5.63-5.74 (1 H, m); IR (CCl_4) 1450, 1710, 2960 cm^{-1}; MS, m/e 140 (M^+).

3,4-Dimethyl-1-phenyl-5-hexen-1-one: ^1H NMR ($CDCl_3$, 400 MHz) δ of *anti*-**27** ($R^1 = Me$, $R^2 = Ph$) 0.918 (3 H, d, $J = 6.7$ Hz), 1.045 (3 H, d, $J = 6.7$ Hz); δ of *syn*-**28** ($R^1 = Me$, $R^2 = Ph$) 0.924 (3 H, d, $J = 6.7$ Hz), 1.033 (3 H, d, $J = 6.4$ Hz); the following signals were observed in both isomers, 2.11-2.21 (1 H, m), 2.22-2.29 (1 H, m), 2.65-2.73 (1 H, m), 2.97-3.08 (1 H, m), 4.97-5.04 (2 H, m), 5.71-5.82 (1 H, m), 7.43-7.60 (3 H, m), 7.92-7.95 (2 H, m); IR (CCl_4) 680, 740, 1445, 1580, 1595, 1680, 2960 cm^{-1}; MS, m/z 202 (M^+).

5-Methyl-4-phenyl-6-hepten-2-one: ^1H NMR (CCl_4) δ of *anti*-**27** ($R^1 = Ph$, $R^2 = Me$) 0.95 (3 H, d, $J = 7.0$ Hz), 2.02 (3 H, s), 2.38-2.45 (1 H, m), 2.79-2.83 (2 H, m), 3.16-3.22 (1 H, m); δ of *syn*-**28** ($R^1 = Ph$, $R^2 = Me$) 0.79 (3 H, d, $J = 6.7$ Hz), 1.94 (3 H, s), 2.27-2.34 (1 H, m), 2.64-2.87 (2 H, m), 2.95-3.00 (1 H, m); the following signals were observed in both isomers, 4.89-5.07 (2 H, m), 5.54-5.70 (1 H, m), 7.07-7.29 (5 H, m); IR (CCl_4) 690, 905, 1160, 1355, 1450, 1715, 2960, 3040, 3080 cm^{-1}; MS, m/z 202 (M^+).

4-Methyl-1,3-diphenyl-5-hexen-1-one: ^1H NMR (CCl_4) δ of *anti*-**27** ($R^1 = R^2 = Ph$) 1.00 (3 H, d, $J = 6.7$ Hz), 2.51-2.56 (1 H, m); δ of *syn*-**28** ($R^1 = R^2 = Ph$) 0.84 (3 H, d, $J = 6.7$ Hz), 2.40-2.46 (1 H, m); the following signals were observed in both isomers, 3.19-3.46 (3 H, m), 4.91-5.10 (2 H, m), 5.59-5.77 (1 H, m), 7.11-7.57 (8 H, m), 7.81-7.91 (2 H, m); IR (CCl_4) 690, 905, 1000, 1370, 1440, 1595, 1680, 2970, 3040 cm^{-1}; MS, m/z 264 (M^+).

Preparation of an Authentic Sample of 27 ($R^1 = Me$, $R^2 = Ph$). To a solution of 0.3 mmol (0.036 mL) of **12** dissolved in 3 mL of dry THF was added 5 equiv of PhMgBr dissolved in dry THF under N_2 at -78 °C. The mixture was stirred for 3 days at room temperature. The reaction was quenched with aqueous HCl, and the mixture was refluxed for 2 h. The reaction mixture was cooled, washed with a saturated aqueous $NaHCO_3$ solution, dried over $MgSO_4$, condensed, and purified by short silica gel column chromatography by using hexane-ether (20:1) as eluant. The desired ketone was obtained in 41% yield along with 41% recovered **12**.

Notes

Metal-Ammonia Reduction of Triphenylene

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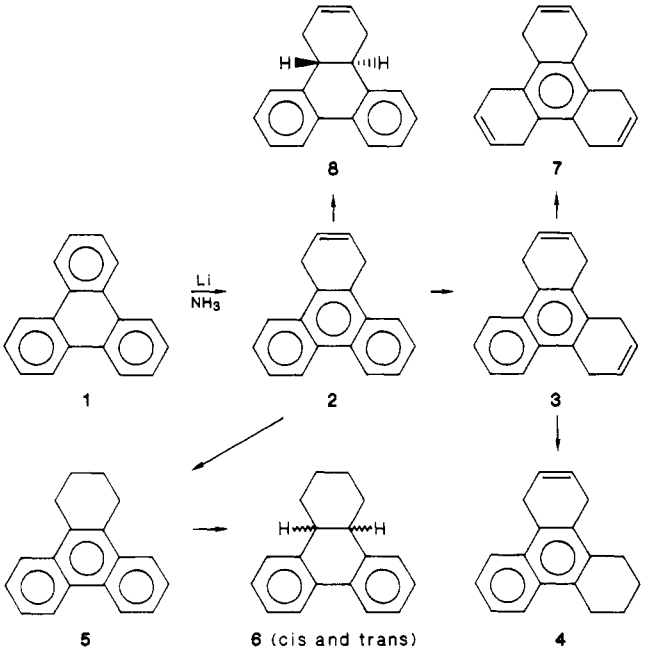
The reaction of polynuclear aromatic hydrocarbons with alkali metals in liquid ammonia provides a useful method for the preparation of hydroaromatics.[1] As outlined in eq 1, the aromatic, ArH, reacts with metal to form a radical

$$ArH + e^- \rightleftarrows [ArH]^{\bullet -} \overset{e^-}{\rightleftarrows} [ArH]^{2-} \xrightarrow{NH_3} [ArH_2]^- \xrightarrow{H^+} ArH_3 \quad (1)$$

anion which is not protonated in the absence of protic cosolvents (e.g., alcohols)[2] but goes on to furnish the considerably more basic dianion. For most two-, three-, and four-ring polynuclears, the dianion is protonated by ammonia, resulting in a monoanion which persists until the reaction is quenched with water, ammonium chloride, etc.[2,3] Regiochemistry in this reaction is dictated by the position of protonation in the dianion which is generally considered to occur at the position of highest electron density.[4] However, as we have noted previously,[5] it appears that in certain instances protonation does not occur at the (calculated) position of highest electron density but rather at a position so as to produce the most stable monoanion.[6] Herein, we report such an example which has also resulted in the isolation of a number of new and interesting hydrocarbons.

Scheme I



The reaction of triphenylene (1) with a slight excess of lithium metal in anhydrous ammonia/THF (2:1) furnished

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