Registry No. 1, 20596-52-5; 2, 90150-03-1; dimethylamine–borane, 1838-13-7; *tert*-butylamine–borane, 43795-48-8; benzaldehyde, 100-52-7; 2-undecanone, 112-12-9; acetophenone, 98-86-2; benzophenone, 119-61-9; 4-*tert*-butylcyclohexanone, 98-53-3; 3,3,5-trimethylcyclohexanone, 873-94-9; camphor, 76-22-2; isophorone, 78-59-1; α-ionone, 127-41-3; β-ionone, 79-77-6; benzyl alcohol, 100-51-6; 2-undecanol, 1653-30-1; 1-phenylethanol, 98-85-1; benzhydrol, 91-01-0; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; *cis*-3,3,5-trimethylcyclohexanol, 933-48-2; *trans*-3,3,5-trimethylcyclohexanol, 767-54-4; isoborneol, 124-76-5; isophorol, 470-99-5; α-ionol, 25312-34-9; 6-(2-butenylidene)-1,5,5-trimethylcyclohexene, 55497-53-5; ethyl decanoate, 110-38-3; methyl stearate, 112-61-8; methyl benzoate, 93-58-3; methyl cinnamate, 103-26-4; coumarin, 91-64-5; dihydrocoumarin, 119-84-6; benzyl benzoate, 120-51-4; decanol, 112-30-1; octadecanol, 112-92-5; cinnamyl alcohol, 104-54-1; 3-phenylpropanol, 122-97-4; 3-(*o*-hydroxyphenyl)-1-propanol, 1481-92-1; benzamide, 55-21-0; decanamide, 2319-29-1; acetanilide, 103-84-4; *N*-phenylbenzamide, 93-98-1; *N*-pentyldecanamide, 64891-15-2; *N,N*-dimethylbenzamide, 611-74-5; *N,N*-diethylbenzamide, 1696-17-9; 2,6-dichloro-*N,N*-diethylbenzamide, 10345-78-5; *N,N*-dimethyldecanamide, 14433-76-2; *N,N*-diethyldecanamide, 2602-61-1; *N,N*-diisopropyldecanamide, 57303-36-3; *N,N*-dimethyldodecanamide, 3007-53-2; *N,N*-diethyldodecanamide, 3352-87-2; *N,N*-dimethylcyclohexanecarboxamide, 17566-51-7; *N,N*-diethylcyclohexanecarboxamide, 5461-52-9; benzylamine, 100-46-9; decylamine, 2016-57-1; *N*-ethylaniline, 103-69-5; *N*-phenylbenzylamine, 103-32-2; *N,N*-diethylbenzylamine, 772-54-3; 2,6-dichloro-*N,N*-diethylbenzylamine, 90150-04-2; 2-chloro-*N,N*-diethylbenzylamine, 27958-80-1; *N,N*-diethyldecylamine, 6308-94-7; *N,N*-diisopropyldecylamine, 53137-37-4; *N,N*-diethyldodecylamine, 4271-27-6; cyclohexylmethanol, 100-49-2; (diethylamino)cyclohexylmethane, 90150-05-3; 1-iodonaphthalene, 90-14-2; 1-bromonaphthalene, 90-11-9; 4-bromobiphenyl, 92-66-0; 1-chloronaphthalene, 90-13-1; 1-iododecane, 4292-19-7; 1,2-dodecene epoxide, 2855-19-8; phenylmethanenitrile, 140-29-4; benzonitrile, 100-47-0; nitrobenzene, 98-95-3; benzyl phenyl sulfoxide, 833-82-9; naphthalene, 91-20-3; biphenyl, 92-52-4; *N,N*-dimethyldodecylamine, 112-18-5; 2-hydroxy-*N,N*-dimethyldecanamine, 20542-99-8; 1,2-diamino-1,2-diphenylethane, 5700-60-7; aniline, 62-53-3; azobenzene, 103-33-3; thiophenol, 108-98-5; benzylmercaptan, 100-53-8; benzyl phenyl sulfide, 831-91-4.

Dimethylaluminum Chloride Catalyzed Ene Reactions of Aldehydes. 2.[1] Stereochemistry and Scope

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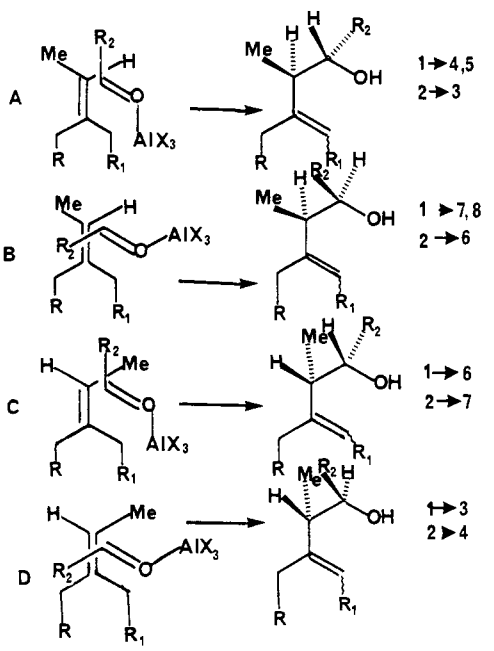
The dimethylaluminum chloride (Me_2AlCl) catalyzed ene reactions of aliphatic aldehydes with (*E*)- and (*Z*)-3-methyl-2-pentene (**1** and **2**) were examined. Complex mixtures of erythro and threo adducts and double-bond position isomers were obtained. Ene reaction of 2-phenylpropionaldehyde with methylenecyclohexane gives a 1.5:1 mixture of diastereomers. Geraniol, linalool, citral, geranylacetone, and 6-methyl-5-hepten-2-one are suitable substrates for Me_2AlCl-catalyzed ene reaction with formaldehyde.

We have recently reported that dimethylaluminum chloride (Me_2AlCl), in equivalent or greater amounts, is a uniquely useful catalyst for the ene reaction of aldehydes with alkenes.[1,3] Proton-initiated rearrangements do not occur since the alcohol–Lewis acid complex produced in the ene reaction reacts rapidly to give methane and a nonacidic aluminum alkoxide.[4] Using the Me_2AlCl as a catalyst, ene adducts can now be obtained in useful yield from aliphatic or aromatic aldehydes and alkenes containing a disubstituted vinylic carbon and from formaldehyde and nonnucleophilic mono- and 1,2-disubstituted alkenes. This extends the scope of Lewis acid catalyzed ene reactions of aldehydes that were previously limited to the reaction of formaldehyde with alkenes containing a disubstituted vinylic carbon and the reactions of reactive electron deficient aldehydes such as chloral or glyoxylate esters.

Uskokovic and Wovkulich have observed a high preference for the transfer of a hydrogen from the alkyl group syn to the vinylic hydrogen in the BF_3-catalyzed ene reaction of formaldehyde with (*E*)- and (*Z*)-ethylidene-2-methylcyclopentane.[5] We have observed similar selectivity

Scheme I



in the Me_2AlCl- and Me_3Al-catalyzed ene reactions of formaldehyde with (*E*)- and (*Z*)-3-methyl-2-pentene.[1] (See Table I.) The preferential abstraction of a hydrogen from the alkyl group syn to the vinylic hydrogen may be due to steric interaction of the Lewis acid, which is exo for steric reasons, with the substituent on the less substituted

(1) Part 1: Snider, B. B.; Rodini, D. J.; Kirk, T. C.; Cordova, R. *J. Am. Chem. Soc.* **1982**, *104*, 555.
(2) Fellow of the Alfred P. Sloan Foundation 1979–1983. Dreyfus Teacher-Scholar 1982–1987.
(3) For related studies see: (a) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426 and references cited therein. (b) Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 464.
(4) Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, T. C.; Deutsch. E. A.; Cordova, R.; Price, R. T. *Tetrahedron* **1981**, *37*, 3927.
(5) Wovkulich, P. M.; Uskokovic, M. R. *J. Org. Chem.* **1982**, *47*, 1600.

0022-3263/84/1949-2443$01.50/0

Table I. Ene Reactions of (*E*)- and (*Z*)-3-Methyl-2-pentene with Aldehydes

alkene	aldehyde RCHO	% yield 3–5, 6–8	% of ene adduct mixture 3	4	5	6	7	8
 1	**a**, R = H	97[a]	20	80[b]	*b*	*c*	*c*	*c*
	b, R = CH_3	13, 34	11	11	3	11	56	3
	c, R = CH_2CH_3	20, 38	15	15	4	9	54	4
	d, R = $CH(CH_3)_2$	53, 8	16	53	16	4	9	0
	e, R = $CH_2CH_2CH_2OCH_3$	24[a]	12	12	*d*	40	36	*d*
 2	**a**, R = H	92[a] (48[e])	55 (75[e])	45 (25[e])	0	*c*	*c*	*c*
	b, R = CH_3	10, 28	5	27	0	10	59	0
	c, R = CH_2CH_3	24, 56	4	29	0	8	59	0
	d, R = $CH(CH_3)_2$	28, 39	9	33	0	3	55	0
	e, R = $CH_2CH_2OCH_3$	30[a]	9	22	0	9	60	0

[a] Total yield. [b] Yield of **4a** and **5a**. [c] Erythro and threo isomers are not possible in this case. [d] These isomers could not be distinguished. [e] Me_3Al was used instead of Me_2AlCl.

end of the double bond. This interaction is minimized if the vinylic substituent is hydrogen (Scheme I, transition state B) rather than an alkyl group (transition state D). The selectivity for the formation of **4a** from (*E*)-3-methyl-2-pentene (**1**) is greater than that for the formation of **3a** from (*Z*)-3-methyl-2-pentene (**2**) since a methylene hydrogen is transferred two to three times as readily as a methyl hydrogen.

We report here a study of the stereochemistry of the ene reaction of other aliphatic aldehydes with **1** and **2** and a study of the ene reactions of formaldehyde with various terpenoids that demonstrates the stability of various reactive functionality to Me_2AlCl.

Results and Discussion

The ene reactions of aliphatic aldehydes with **1** and **2** are more complicated since erythro and threo adducts can be formed and analysis of the various transition states must include the interaction of an alkyl group on the aldehyde with the alkene and must also consider the formation of syn and anti Lewis acid–aldehyde complexes.[6]

To determine the relative importance of various steric interactions, the reactions of **1** and **2** with acetaldehyde, propionaldehyde, and isobutyraldehyde were examined.[7] The results are shown in Table I. The analysis is complicated since six ene adducts can be formed. Fortunately, the threo adducts **3–5** can be easily separated from the erythro adducts **6–8** by medium-pressure liquid chromatography. The threo adducts are less polar since they form a more stable intramolecular hydrogen bond.[8] The ratio of adducts was determined by analysis of the GC of the crude product and purified fractions **3–5** and **6–8**. Analysis of the olefinic region of the NMR spectrum of these samples allowed the assignment of the GC peaks. The analysis of products from **2** was more straightforward since **5** and **8** were not formed due to severe interactions between the methyl groups in the transition state.

The results shown in Table I indicate that the selectivity for the transfer of a hydrogen from the alkyl group syn to the vinylic hydrogen, which was observed with formaldehyde, has now been lost. Scheme I shows the possible transition states for these reactions. It has been assumed that only the more stable anti Lewis acid–aldehyde complex need be considered.[6] It can be seen that transition state B is no longer especially preferred due to the interactions of R_2 and the alkene. In all cases a strong preference is observed for the formation of trisubstituted double bond isomers **4**, **5**, **7**, and **8**. This seems to dominate any overall preference for a specific transition state. The reactions of **2** show no effect with increasing steric bulk of the aldehyde. The reactions of **1** show a marked shift on going from propionaldehyde to isobutyraldehyde. As the bulk of R_2 increases, transition state B that leads to **7** from **1** becomes higher in energy and the major product is formed via transition state A.

The ene reactions of 3-methoxypropionaldehyde[9] were examined in an attempt to generate a chelated aldehyde–Lewis acid complex that would be syn and therefore have different steric requirements. However, the results of the ene reactions of 3-methoxypropionaldehyde with **1** and **2** are very similar to those of propionaldehyde except for the relative amounts of **6** and **7** from **1**. A syn chelated Me_2AlCl complex from 3-methoxypropionaldehyde would have a pentacoordinate aluminum. Since this may not be favorable, we explored the use of glycolaldehyde and 3-hydroxybutyraldehyde as enophiles with a variety of alkylaluminum halide catalysts. In these cases a trivalent aluminum alkoxide is formed from the alcohol and alkylaluminum halide with the loss of an alkane. A syn chelated complex with a tetravalent aluminum should then be formed. Unfortunately, these reactions led to a complex mixture of products.

The reaction of 2-phenylpropionaldehyde with methylenecyclohexane was examined to determine the diastereotopic facial selectivity of the ene reaction. A 1.5:1 mixture of the diastereomers of α-(1-cyclohexenylmethyl)-β-methylbenzeneethanol (**9**) was obtained in 67% yield. Since the selectivity is not high, no attempt was made to determine which isomer predominates.

The Me_2AlCl-catalyzed ene reactions of formaldehyde with several terpenoid substrates was examined to determine the stability of various reactive functional groups to

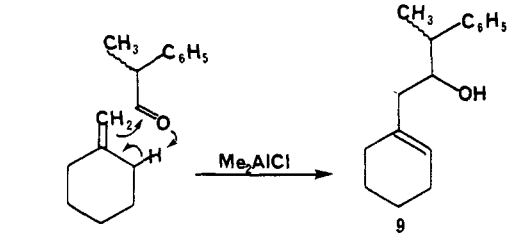
(6) For related studies with chloral see: (a) Gill, G. B.; Wallace, B. *J. Chem. Soc., Chem. Commun.* **1977**, 382. (b) Gill, G. B.; Marrison, K.; Parrot, S. J.; Wallace, B. *Tetrahedron Lett.* **1979**, 4867.

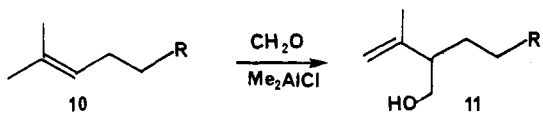
(7) Attempted reaction of pivaldehyde with **1** or **2** gave only the methyl addition product 2,3-dimethyl-2-butanol.

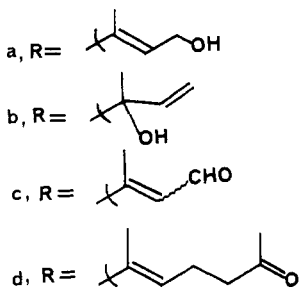
(8) (a) Felkin, H.; Gault, Y.; Roussi, G. *Tetrahedron* **1970**, *26*, 3761. (b) Sicher, J.; Cherest, M.; Gault, Y.; Felkin, H. *Collect. Czech. Chem. Commun.* **1963**, *28*, 72. (c) Fujita, K.; Schlosser, M. *Helv. Chim. Acta* **1982**, *65*, 1258. (d) Hoffmann, R. W.; Zeiss, H.-J. *J. Org. Chem.* **1981**, *46*, 1309.

(9) White, E. R. U.S. Patent 2 967 889; *Chem. Abstr.* **1961**, *55*, 9283c.

Me_2AlCl. Reaction of geraniol (**10a**) with formaldehyde and 2 equiv of Me_2AlCl in CH_2Cl_2 for 5 min at 0 °C gave a 63% yield (72% based on recovered **10a**) of ene adduct **11a**. Similarly, linalool (**10b**) gave a 41% yield (63% based on recovered **10b**) of ene adduct **11b**. The allylic alcohols of **10a** and **10b** are definitely, but not indefinitely, stable to Me_2AlCl. The second equivalent of Me_2AlCl reacts with the allylic alcohol of **10a** or **10b** to give an aluminum alkoxide. The allylic alkoxide is stable for a short time at 0 °C. If the ene reaction is carried out for 1 h at 0 °C, extensive decomposition occurs. Geranyl acetate cannot be used as a substrate for this reaction since the allylic acetate is not stable to Me_2AlCl.





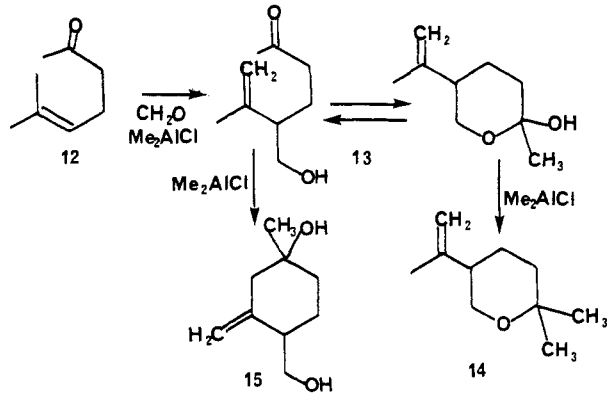


Reaction of citral (**10c**) and formaldehyde, also carried out with 2 equiv of Me_2AlCl since the aldehyde of citral is more basic than formaldehyde, gave a 21% yield of **11c**. Reaction of geranylacetone (**10d**) with formaldehyde and 2 equiv of Me_2AlCl (since the ketone of **10d** is more basic than formaldehyde) gave **11d** in 73% yield (85% based on recovered **10d**). Reaction occurs exclusively at the terminal double bond since the ketone–Me_2AlCl complex inductively deactivates the internal double bond.

The reaction of 6-methyl-5-hepten-2-one (**12**) with formaldehyde and 2 equiv of Me_2AlCl for 5 min at 0 °C gave a 38% yield (51% based on recovered **12**) of ene adduct **13**, which exists as a 60–40 mixture of ketone and hemiketal forms,[10] and 3% of **14**, which is derived from the hemiketal form of **13** by reaction with Me_2AlCl. Reaction of **12** with formaldehyde for 1 h at 25 °C gave a 33% yield (51% based on recovered **12**) of **15**. A second ene reaction has occurred with the ketone of **13** functioning as the enophile.[11]

In conclusion, the ene reactions of **1** and **2** with aliphatic aldehydes give complex mixtures of erythro and threo isomers and double-bond position isomers. The reactions of **10** and **12** demonstrate that allylic alcohols, α,β-unsaturated aldehydes, and ketones are compatable with Me_2AlCl-catalyzed ene reactions of formaldehyde.

(10) Whiting, J. E.; Edward, J. T. *Can. J. Chem.* **1971**, *49*, 3799.
(11) Snider, B. B.; Deutsch, E. A. *J. Org. Chem.* **1983**, *48*, 1822.



Experimental Section

Dimethylaluminum chloride, manufactured by Texas Alkyls Inc., was purchased as 1.14 M solution in heptane from Stauffer Chemical. Some batches contained traces of toluene that reacted to give byproducts. CH_2Cl_2 was distilled from CaH_2. Paraformaldehyde, paraldehyde, and other aldehydes were used without purification. Commercial samples of alkenes were used. Analyses were carried out by Galbraith Laboratories.

General Procedure for Reaction of (*E*)- or (*Z*)-3-Methyl-2-pentene with Acetaldehyde, Propionaldehyde, or Isobutyraldehyde. Alkene (3.1 mmol) and aldehyde (2.8 mmol, paraldehyde was used as a source of acetaldehyde), and CH_2Cl_2 (8 mL) were added to a flame-dried flask under nitrogen. The reaction mixture was cooled to 0 °C and treated with Me_2AlCl (3.66 mL of 1.14 M in heptane, 4.18 mmol). The reaction mixture was stirred for 1 h at 0 °C and quenched with 30 mL of water. The mixture was extracted with three 20-mL portions of ether. The combined organic layers were dried ($MgSO_4$) and evaporated. The reaction mixture was analyzed by NMR spectroscopy and GC on a $^1/_4$ in. × 10 ft 8% UCON LB550 X on Chromosorb WNAW column at 120 °C. The crude product was purified by medium-pressure liquid chromatography on silica gel (4:1 hexane–EtOAc) to give a mixture of less polar threo adducts **3**, **4**, and **5** followed by a mixture of the more polar erythro adducts **6**, **7**, and **8**. The mixtures of **3–5** and **6–8** were analyzed by NMR spectroscopy and GC as above. The GC retention times follow: **3b–8b**, 7.2, 7.8, 7.2, 9.5, 10.4, 11.1 min; **3c–8c**, 9.3, 10.0, 9.3, 11.2, 12.8, 13.7 min; **3d–7d**, 11.0, 12.2, 11.0, 13.5, and 15.8 min. The TLC R_f data in 4:1 hexane–EtOAc follow: **3b–5b**, 0.33; **6b–8b**, 0.21; **3c–5c**, 0.45; **6c–8c**, 0.34; **3d–5d**, 0.56; **6d–7d**, 0.42. The ratio of **3** + **6**:**4** + **5** + **7** + **8** in the crude product and **3**:**4** + **5** and **6**:**7** + **8** in the pure products were determined by analysis of NMR signals of the olefinic hydrogen at δ 4.8 for **3** and **6** and δ 5.2–5.4 for **4**, **5**, **7**, and **8**.

Reaction of 3-Methyl-2-pentene with 3-Methoxypropionaldehyde. (*E*)-3-Methyl-2-pentene (160 mg, 1.9 mmol) and 3-methoxypropionaldehyde[9] (152 mg, 1.7 mmol) were dissolved in 5 mL of CH_2Cl_2 in a flame-dried flask under nitrogen. Me_2AlCl (1.5 mL of 1.14 M in heptane, 1.7 mmol) was added, and the reaction mixture was stirred for 2 h at 0 °C and worked up as described above to give 175 mg of crude product. Medium-pressure liquid chromatography on silica gel (4:1 hexane–EtOAc) gave 74 mg (26% yield) of a mixture of **3e–8e** as indicated in Table I: NMR ($CDCl_3$) δ 5.2 (m, **1**, **4e**, **5e**, **7e**, **8e**) 4.8 (br, **2**, **3e**, **6e**); GC ($^1/_4$ in. × 10 ft, 8% UCON LB550X on Chromosorb WNAW) t_R = 49 (**3e**), 52 (**6e**), 55 (**4e**), and 60 min (**7e**). Only four peaks were observed.

Reaction of (*Z*)-3-methyl-2-pentene was carried out similarly.

Reaction of methylenecyclohexane (0.523 g, 5.5 mmol), **2-phenylpropionaldehyde** (0.670 g, 5 mmol) and Me_2AlCl (4.38 mL of 1.14 M in heptane, 5 mmol) in 15 mL of CH_2Cl_2 for 2 h at 0 °C gave 1.74 g (98%) of crude **9**. Medium-pressure liquid chromatography on silica gel (4:1 hexane–EtOAc) gave 0.806 g (67%) of **9** as a ca. 1.5:1 mixture of diastereomers: NMR ($CDCl_3$) δ 7.2 (m, 5), 5.48 (br, 1), 3.75 (br m, 1), 2.75 (m, 1), 1.4–2.2 (m, 11), 1.30 (d, 3, J = 7 Hz, major isomer), 1.25 (d, 3, J = 7 Hz, minor isomer).

Geraniol (10a) (150 mg, 1 mmol), **paraformaldehyde** (30 mg, 1 mmol), and Me_2AlCl (1.8 mL of 1.14 M in heptane, 2 equiv)

were allowed to react for 5 min at 0 °C in 5 mL of CH_2Cl_2. Normal workup gave 180 mg of crude product that was purified by chromatography on silica gel (ether) to give 19 mg of recovered **10a** and 116 mg (63%, 72% based on recovered **10a**) of pure **11a**: NMR ($CDCl_3$) δ 5.40 (t, 1, J = 7 Hz) 4.92 (br s, 1), 4.83 (br s, 1), 4.12 (d, 2, J = 7 Hz), 3.51 (d, 2, J = 7 Hz), 2.80 (s, 2, OH), 1.66 (br s, 6), 1.3–2.5 (m, 5); IR (neat) 3320 (w), 2930, 1445, 1382, 1048, 1007, 898, 744 cm^{-1}. An analytical sample was prepared by evaporative distillation (90 °C, 0.25 torr). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.56; H, 11.05.

Reaction of linalool (10b) (150 mg, 1 mmol) **with paraformaldehyde** under identical conditions gave 184 mg of crude product. Chromatography on silica gel (1:1 hexane–ether and then ether) gave 33 mg of recovered **10b** and 91 mg (41%, 63% based on recovered **10b**) of **11b**: NMR ($CDCl_3$) δ 5.91 (ddd, 1, J = 10, 17, 1 Hz), 5.18 (dd, 1, J = 17, 1 Hz), 5.03 (dd, 1, J = 10, 1 Hz), 4.92 (br s, 1), 4.81 (br s, 1), 3.53 (d, 2, J = 7 Hz), 2.28 (br s, 2, OH), 1.9–2.4 (m, 1), 1.67 (s, 3), 1.46 (br s, 4), 1.25 (s, 3); IR (neat) 3360, 2935, 1648, 1460, 1417, 1377, 1127, 1055, 1007, 929, 900 cm^{-1}. An analytical sample was prepared by evaporative distillation (95 °C, 0.4 torr). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.53; H, 11.09.

Reaction of citral (10c)(150 mg, 1 mmol, *E–Z* mixture) **with paraformaldehyde** under identical conditions gave 171 mg of crude product. Chromatography on silica gel (1:1 hexane–ether and then ether) gave 35 mg of recovered citral, 20 mg of a mixture of citral and an unidentified compound, and 39 mg (21%) of a mixture of (*E*)- and (*Z*)-**11c**: NMR ($CDCl_3$) δ 10.02 (d, 1, J = 8 Hz, (*E*)-**11c**), 9.52 (d, 1, J = 8 Hz, (*Z*)-**11c**), 5.90 (d, 1, J = 8 Hz), 5.00 (br s, 1), 4.87 (br s, 1), 3.57 (d, 2, J = 7 Hz) 2.7–1.5 (m, 6), 2.17 (s, 3, (*E*)-**11c**), 1.98 (s, 3, (*Z*)-**11c**), 1.70 (s, 3); IR (neat) 3430, 2935, 2870, 1669, 1452, 1383, 1203, 1130, 1082, 1052, 920, 904, 742 cm^{-1}.

Reaction of geranylacetone (10d) (190 mg, 1 mmol) **with paraformaldehyde** under identical conditions gave 213 mg of crude product. Chromatography on silica gel (1:1 hexane–ether) gave 24 mg of recovered **10d** and 163 mg (73%, 85% based on recovered **11d**) of pure **11d**: ^1H NMR ($CDCl_3$) δ 5.09 (t, 1, J = 6 Hz), 4.94 (br s, 1), 4.84 (br s, 1), 3.53 (d, 2, J = 7 Hz), 2.12 (s, 3), 1.68 (s, 3), 1.60 (s, 3), 1.23–2.64 (m, 10); ^{13}C NMR ($CDCl_3$) δ 208.5, 144.8, 135.9, 122.5, 113.2, 63.9, 49.2, 43.5, 36.9, 29.6, 27.3, 22.2, 18.7, 15.7; IR (neat) 3430, 2930, 1712, 1648, 1447, 1364, 1169, 1051, 900 cm^{-1}. An analytical sample was prepared by evaporative distillation (112 °C, 0.15 torr). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.84; H, 10.90.

Reaction of 6-methyl-5-hepten-2-one (12) (126 mg, 1 mmol) **with paraformaldehyde** as described above for 5 min at 0 °C gave 135 mg of crude product. Chromatography on silica gel (9:1 hexane–ether) gave 5 mg of **14**, followed by 23 mg of recovered **12**. Elution with ether gave 52 mg (38%, 51% based on recovered **12**) of **13** as a 60:40 mixture of ketone and hemiketal forms.

The data for **14** follow: NMR ($CDCl_3$) δ 4.77 (br s, 1), 4.72 (br s, 1), 3.3–3.9 (m, 2), 1.2–2.5 (m, 5 with br s at δ 1.56), 1.72 (br s, 3), 1.20 (s, 6).

The data for **13** follow: NMR ($CDCl_3$) δ 4.6–5.0 (m, 2), 3.3–4.0 (m, 0.4 × 2, hemiketal form), 3.54 (d, 0.6 × 2, J = 7 Hz, ketone form), 1.2–2.9 (m, 0.6 × 5 + 0.4 × 7), 2.41 (t, 0.6 × 2, J = 8 Hz, ketone form), 2.12 (s, 0.6 × 3, ketone form) 1.67 (s, 3), 1.41 (s, 0.4 × 3, hemiketal form); IR (neat) 3200–3650, 3075, 2935, 2870, 1717, 1647, 1454, 1377, 1221, 1179, 1136, 1100, 1086, 1053, 980 cm^{-1}.

The identical reaction was carried out for 5 min at 0 °C and then 1 h at 25 °C to give 124 mg of crude product. Chromatography on silica gel (ether) gave 44 mg of recovered **12** followed by 52 mg (33%, 51% based on recovered **12**) of pure **15**: NMR ($CDCl_3$) δ 4.87 (br s, 1), 4.82 (br s, 1), 3.84 (dd, 1, J = 7, 11 Hz), 3.64 (dd, 1, J = 6, 11 Hz), 2.20 (br s, 2), 1.96 (br s, 2, OH), 1.24 (s, 3), 1.2–2.4 (m, 5); IR (neat) 3350, 3075, 2930, 2870, 1651, 1445, 1379, 1128, 1056, 1033, 920, 940 cm^{-1}.

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Registry No. **1**, 616-12-6; **2**, 922-62-3; **3a**, 77103-98-1; **3b**, 90369-32-7; **3c**, 90369-33-8; **3d**, 90369-34-9; **3e**, 90369-35-0; **4a**, 90369-36-1; **4b**, 90369-37-2; **4c**, 90369-38-3; **4d**, 90369-39-4; **4e**, 90369-40-7; **5a**, 90388-39-9; **5b**, 90369-41-8; **5c**, 90369-42-9; **5d**, 90369-43-0; **5e**, 90369-44-1; **6b**, 90369-45-2; **6c**, 90369-46-3; **6d**, 90369-47-4; **6e**, 90369-48-5; **7b**, 90369-49-6; **7c**, 90369-50-9; **7d**, 90369-51-0; **7e**, 90369-52-1; **8b**, 90369-53-2; **8c**, 90369-54-3; **8e**, 90369-29-2; **9** (isomer 1), 90369-29-2; **9** (isomer 2), 90369-56-5; **11a**, 90369-26-9; **11b**, 90369-23-6; **11c** (isomer 1), 90369-24-7; **11c** (isomer 2), 90369-57-6; **11d**, 90369-25-8; **13** (isomer 1), 90369-27-0; **13** (isomer 2), 90369-28-1; **14**, 90369-31-6; **15**, 90369-30-5; Me_2AlCl, 1184-58-3; HCO_2H, 50-00-0; methylenecyclohexane, 1192-37-6; geraniol, 106-24-1; linalool, 78-70-6; citral, 5392-40-5; geranylacetone, 689-67-8; 6-methyl-5-hepten-2-one, 110-93-0; 2-phenylpropionaldehyde, 93-53-8; toluene, 108-88-3; paraformaldehyde, 30525-89-4; paraldehyde, 123-63-7; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; isobutyraldehyde, 78-84-2; 3-methoxypropionaldehyde, 2806-84-0.

Selectivity and Catalysis in Ene Reactions of Diethyl Oxomalonate

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Stereoselectivity, regioselectivity, and structural selectivity of the thermal ene reactions of diethyl oxomalonate are strongly determined by steric approach control. For a series of 1-arylcyclopentenes thermal ene reactions only show a small enhancement of rate by electron-donating substituents ($\rho = -1.2 \pm 0.2$). Lewis acid catalysis is described which allows ene reactions of diethyl oxomalonate under thermally mild conditions. Furthermore, catalysis by $SnCl_4$ profoundly modifies the selectivity of the ene reactions which show a strong enhancement of rate by electron-donating substituents ($\rho = -3.9 \pm 0.3$) for a series of 1-arylcyclopentenes. Structural selectivity can be dramatically reversed by catalysts since the influence of electronic factors is amplified by Lewis acids, and steric approach control becomes less important.

The utility of ene reactions for carbon skeletal construction inheres not only in the efficiency of directly replacing an allylic C–H bond with a C–C bond but also in the regio- and stereospecificity of the operation. Thus, for example, we recently exploited ene reactions of diethyl oxomalonate (**2**) as a key step in new methods for the

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