stirred at −78 °C for 1 h and then allowed to warm to room temperature over 2–3 h. The reaction was quenched by the addition of 1 N HCl (35 mL), and the stirring was continued at room temperature for 5 h, at which time saturated brine (50 mL) was added. The layers were separated, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic fractions were washed with saturated sodium bicarbonate (1 × 50 mL) and dried ($MgSO_4$). The excess solvent was removed under reduced pressure, and the protected aldols **28** were purified by preparative LC by using hexane/ethyl acetate (5:1) as the eluting solvent. Analytical samples were prepared by subsequent bulb-to-bulb distillation (Kügelrohr).

2-(1′-Methoxycarbonyloxybenzyl)-2-(1′-propyl)pentanal (28a): 56%; 120 °C bath (0.05 mm); IR ($CHCl_3$) 1721 cm^{-1}; NMR δ 9.63 (s, 1 H), 7.22 (s, 5 H), 5.80 (s, 1 H), 3.61 (s, 3 H), 2.80–1.67 (comp, 14 H); mass spectrum *m/e* 292, 188, 165, 121 (base). Anal. ($C_{17}H_{24}O_4$) C, H.

1-(1′-Methoxycarbonyloxybutyl)cyclohexanecarboxaldehyde (28b): 45%; 140 °C bath (0.05 mm); IR ($CHCl_3$) 1724 cm^{-1}; NMR δ 9.56 (s, 1 H), 4.95–4.70 (m, 1 H), 3.78 (s, 3 H), 2.28–0.67 (comp, 17 H); mass spectrum *m/e* 242, 138, 112, 81 (base). Anal. ($C_{13}H_{22}O_4$) C, H.

1-(1′-Methoxycarbonyloxybenzyl)cyclohexanecarboxaldehyde (28c): 47%; 180 °C bath (0.05 mm); IR ($CHCl_3$) 1727 cm^{-1}; NMR δ 9.61 (s, 1 H), 7.27 (s, 5 H), 5.58 (s, 1 H), 3.68 (s, 3 H), 2.30–0.70 (comp, 10 H); mass spectrum *m/e* 276, 172, 165, 121 (base). Anal. ($C_{16}H_{20}O_4$) C, H.

1-(1′-Methoxycarbonyloxybenzyl)-3,5,5-trimethylcyclohex-2-enecarboxaldehyde (28d): 59% as 60:40 mixture of diastereomers; 135 °C bath (0.05 mm); IR ($CHCl_3$) 1730 cm^{-1}; NMR δ 9.67 (s, 0.4 H), 9.63 (s, 0.6 H), 7.25 (s, 3.0 H), 7.23 (s, 2.0 H), 5.65 (s, 0.6 H), 5.61 (s, 0.4 H), 3.66 (s, 1.8 H), 3.64 (s, 1.2 H), 2.10–1.18 (comp, 7 H), 0.91 (s, 3 H), 0.68 (s, 3 H); mass spectrum *m/e* 316, 211, 165, 121 (base). Anal. ($C_{19}H_{24}O_4$) C, H.

1-(1′-Methoxymethyloxybenzyl)-3,5,5-trimethylcyclohex-2-enecarboxaldehyde (28e): 42% as 55:45 mixture of diastereomers; 135 °C bath (0.05 mm); IR ($CHCl_3$) 1724 cm^{-1}; NMR δ 9.70 (s, 0.45 H), 9.66 (s, 0.55 H), 7.20 (s, 5 H), 5.82 (br s, 0.45 H), 5.71 (br s, 0.55 H), 4.70 (s, 0.55 H), 4.64 (s, 0.45 H), 4.41 (s, 1.1 H), 4.33 (s, 0.9 H), 3.29 (s, 1.65 H), 3.22 (s, 1.35 H), 2.07–1.14 (comp, 7 H), 0.89 (s, 1.65 H), 0.87 (s, 1.35 H), 0.65 (s, 3 H); mass spectrum *m/e* 212, 196, 105, 45 (base). Anal. ($C_{19}H_{26}O_3$) C, H.

2-Methyl-2-phenyl-3-methoxycarbonyloxyhexanal (28f): 49% as 55:45 mixture of diastereomers; 115 °C bath (0.05 mm); IR ($CHCl_3$) 1721 cm^{-1}; NMR δ 9.46 (s, 0.55 H), 9.44 (s, 0.45 H), 7.30 (s, 2.75 H), 7.27 (s, 2.25 H), 5.65–5.22 (comp, 1 H), 3.68 (s, 1.65 H), 3.50 (s, 1.35 H), 1.49 (s, 3 H), 1.45–0.70 (comp, 7 H); mass spectrum *m/e* 264, 160, 131, 105 (base). Two 2,4-dinitrophenylhydrazones were obtained upon fractional recrystallization (10% aqueous MeOH), mp 139–140 and 146–147 °C. Anal. ($C_{21}H_{24}N_4O_7$) C, H, N.

2-Methyl-3-methoxycarbonyloxy-2,3-diphenylpropanal (28g): 62% as 56:44 mixture of diastereomers; 185 °C bath (0.05 mm); IR ($CHCl_3$) 1730 cm^{-1}; NMR δ 9.59 (s, 1 H), 7.48–6.63 (comp, 10 H), 6.36 (s, 0.56 H), 6.20 (s, 0.44 H), 3.71 (s, 0.56 H), 3.61 (s, 0.44 H), 1.54 (s, 0.56 H), 1.36 (s, 0.44 H); mass spectrum *m/e* 298, 165, 121, 105 (base). Anal. ($C_{18}H_{18}O_4$) C, H.

3-(1′-Methoxycarbonyloxybenzyl)-3-phenyl-2-butanone (28h): 51% as a 55:45 mixture of diastereomers; 200 °C bath (0.05 mm); IR ($CHCl_3$) 1739, 1709 cm^{-1}; NMR δ 7.43–6.58 (comp, 10 H), 6.40 (s, 0.55 H), 6.31 (s, 0.45 H), 3.72 (s, 0.55 H), 3.60 (s, 0.45 H), 2.01 (s, 0.55 H), 1.94 (s, 0.45 H), 1.67 (s, 0.55 H), 1.43 (s, 0.45 H); mass spectrum *m/e* 312, 237, 194 (base), 179, 165. Anal. ($C_{19}H_{20}O_4$) C, H.

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Lewis Acid Induced Conjugate Addition of Alkenes to α,β-Unsaturated Ketones or Aldehydes

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Abstract: α,β-Unsaturated ketones or aldehydes form a 1:2 complex with ethylaluminum dichloride which reacts with alkenes either intermolecularly or intramolecularly to give a zwitterion. The zwitterion collapses reversibly to a cyclobutane in geometrically favorable cases and undergoes hydride and alkyl shifts to generate α,β-unsaturated carbonyl compounds. The intramolecular reactions proceed with high regio- and stereospecificity (e.g., **18** → **20**). The reaction is quite general for a variety of enone and alkene substitution patterns. Other Lewis acids do not give similar reactions. Use of less than 1 equiv of $EtAlCl_2$ in intramolecular reactions gives concerted ene reactions in geometrically favorable cases and complex mixtures of products where an ene reaction cannot occur. In one case, transfer of the β hydrogen of the ethyl group to the carbenium ion of the zwitterion results in reduction to give a saturated ketone.

Introduction

As part of a program designed to explore novel carbon–carbon bond forming reactions of alkenes, we have been exploring the Lewis acid catalyzed reactions of alkynyl and alkenyl esters[2] and alkynyl ketones[3] with alkenes. Ene reaction and stereospecific cycloaddition have been observed. Lewis acid complexes of β-substituted α,β-unsaturated ketones are unreactive toward alkenes. We have found that a complex of these ketones with 2 equiv of $EtAlCl_2$ reacts reversibly with alkenes in a stepwise manner to give a zwitterion. This zwitterion reacts reversibly to give a cyclobutane or undergoes two 1,2-hydride or alkyl shifts to irreversibly generate an α,β-unsaturated carbonyl compound (see Schemes I, II, or III). The intermolecular addition of an enone, as an electrophile, to an alkene has not been observed previously. The specific termination of the reaction by a series of alkyl and hydride shifts is also novel. The absence of polymerization is remarkable.

Complexes of α,β-unsaturated ketones with 2 equiv of $EtAlCl_2$ can also be used as initiators for cation–olefin cyclization, a well-known method for the construction of polycyclic compounds.[4] α,β-Unsaturated ketones have been used as initiators for this reaction, typically by acylation or protonation of the carbonyl group in the presence of a nucleophile.[5] Intramolecular addition

(1) Fellow of the Alfred P. Sloan Foundation, 1979–1981.

(2) (a) Snider, B. B. *J. Org. Chem.* **1974**, *39*, 255. (b) *Ibid.* **1976**, *41*, 3061. (c) Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283.

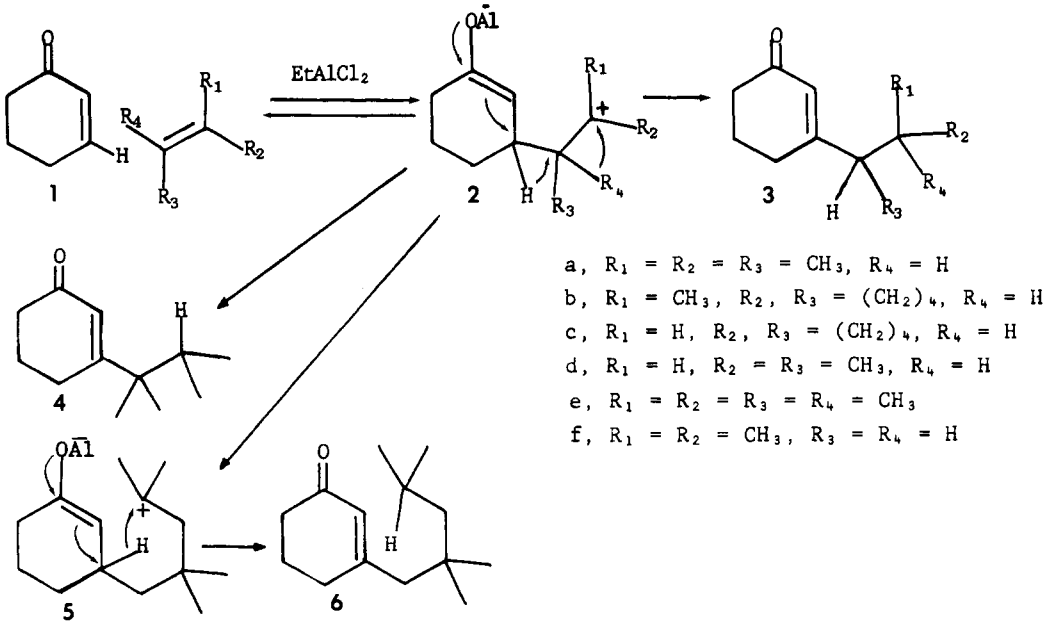
(3) Snider, B. B.; Brown, L. A.; Conn, R. S. E.; Killinger, T. A. *Tetrahedron Lett.* **1977**, 2831.

(4) Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51.

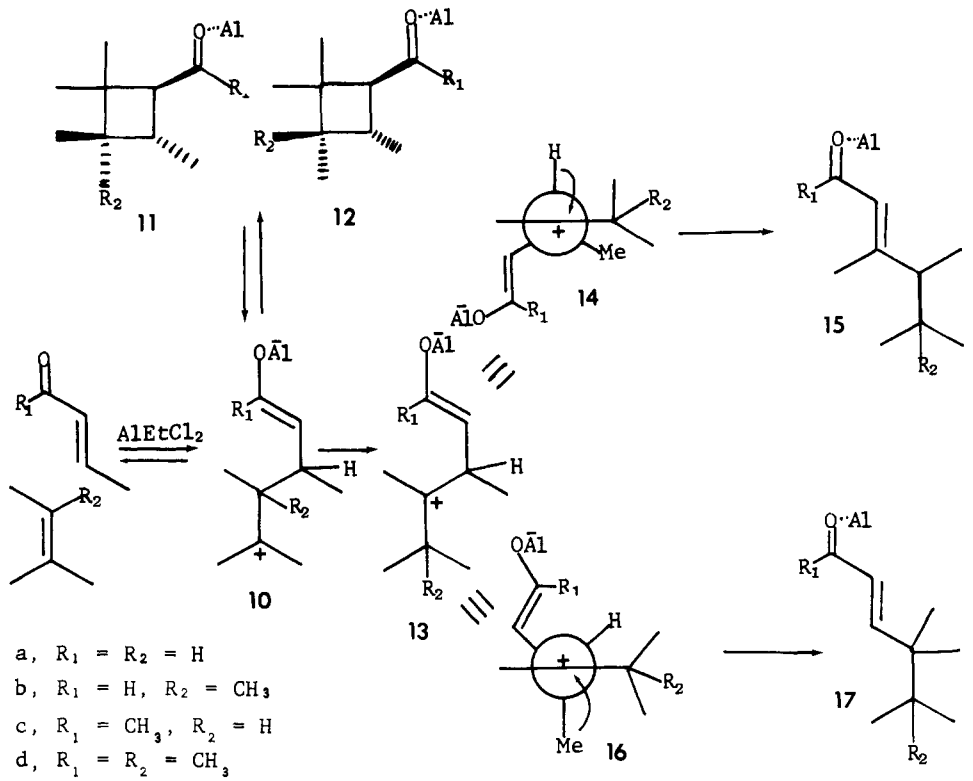
(5) (a) Marshall, J. A.; Wuts, P. G. M. *J. Org. Chem.* **1977**, *42*, 1794. (b) Cooper, J. L.; Harding, K. E. *Tetrahedron Lett.* **1977**, 3321. (c) Dastur, K. P. *J. Am. Chem. Soc.* **1974**, *96*, 2605. (d) Andersen, N. H.; Uh, H.-S. *Tetrahedron Lett.* **1973**, 2079. (e) Naegeli, P. *Ibid.* **1978**, 2127. (f) Harding, K. E.; Puckett, P. M.; Cooper, J. L. *Bioorg. Chem.* **1978**, *7*, 221.

0002-7863/80/1502-5872$01.00/0

Scheme I



Scheme II



of an α,β-unsaturated ketone·$(EtAlCl_2)_2$ complex to the olefin generates a zwitterion which, in the absence of a nucleophile, undergoes a series of 1,2-hydride and/or alkyl shifts to regenerate an enone (see Scheme III).[6] This is a novel termination step for a cation–olefin cyclization. These processes appear to be generally applicable to a wide variety of substitution patterns and of considerable utility in synthesis.

Results and Discussion

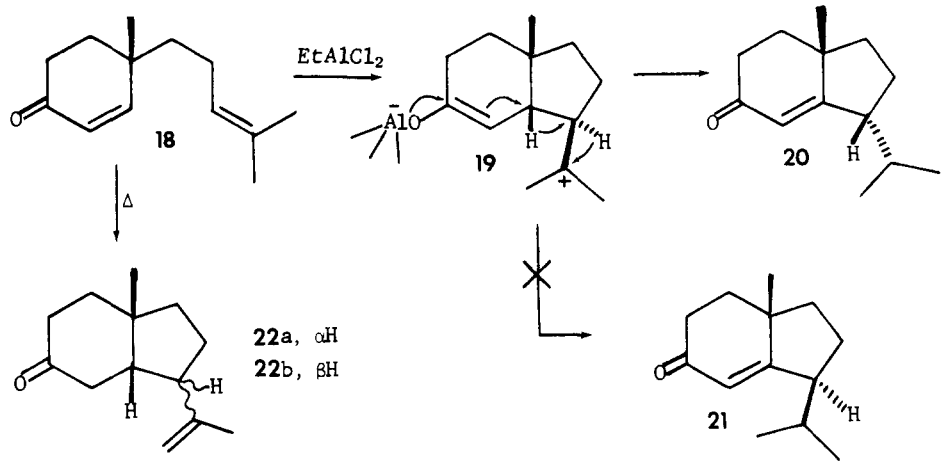
Intermolecular Reactions. The reactions of 2-cyclohexenone (**1**) with various alkenes indicate the effect of alkene substitution on the reactions of the initially formed zwitterion. Treatment of **1** with 1.1 equiv of 2-methyl-2-butene and 1.5 equiv of $EtAlCl_2$ in benzene for 24 h at 25 °C gives an 84% yield of **3a**. The reaction of **1** with 1-methylcyclohexene proceeds analogously, giving an 87% yield of **3b** as a 1:1 mixture of diastereomers.[7] Reaction of cyclohexenone-*3-d*[8] with 2-methyl-2-butene shows that the initially formed zwitterion undergoes two 1,2-hydride shifts, rather than a 1,3-hydride shift, to give the observed product.

(6) A single example has been described.[5e] For related reactions see: (a) Corey, E. J.; Balanson, R. D. *Tetrahedron Lett.* **1973**, 3153. (b) Cookson, R. C.; Smith, S. A. *J. Chem. Soc., Chem. Commun.* **1979**, 145. (c) Baldwin, J. E.; Lusch, M. J. *J. Org. Chem.* **1979**, *44*, 1923. (d) Kulkarni, B. S.; Rao, A. S. *Org. Prep. Proced. Int.* **1978**, *10*, 73. (e) Reaction of *cis*-pseudoionone with $TiCl_4$ gives bicycloionone: Büchi, G.; Koller, E.; Perry, C. W. *J. Am. Chem. Soc.* **1964**, *86*, 5646. Cyclization of pseudoionone and related compounds with $RAlCl_2$ will be reported on shortly. (f) Stork, G.; Marx, M. *J. Am. Chem. Soc.* **1969**, *91*, 2371.

(7) Either (*E*)- or (*Z*)-3-methyl-2-pentene gives an identical 1:1 mixture of the diastereomers of 3-(3-methyl-2-pentyl)-2-cyclohexenone in 86% yield.

(8) Baldwin, J. E.; Kaplan, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3969.

Scheme III



The high regiospecific incorporation of deuterium in **3a** and related stereospecific intramolecular reactions indicates that enolization of the product does not occur under the reaction conditions. Therefore **3b** is probably formed as a kinetically controlled mixture of isomers.

1,2-Disubstituted alkenes react analogously, albeit in lower yield. Reaction of **1**, cyclohexene, and $EtAlCl_2$ (1.5 equiv) for 4 days in CH_2Cl_2[9] gives a 20% yield of **3c**, while *cis*-2-butene gives a 41% yield of **3d**[10] after 2 days in CH_2Cl_2. Formation of **2c** and **2d** is slow since they are secondary carbenium ions. Hydride shifts leading to **3c** and **3d** are clearly favorable.

Reaction of **1** with 2,3-dimethyl-2-butene (2 days) gives two products, both derived from zwitterion **2e** (see Scheme II). A 1,2-methyl shift followed by a 1,2-hydride shift leads to the major product **3e** in 56% yield while a 1,3-hydride shift[11,12] gives rise to the minor product **4** in 14% yield. Cyclohexenone-*3-d* reacts with 2,3-dimethyl-2-butene to give a 4:1 mixture of **3e** and **4** with deuterium in the expected position. The absence of a significant isotope effect on the competition between methyl and hydride shifts is understandable since the secondary isotope effect on the 1,2-methyl shift could be similar to the primary isotope effect on the 1,3-hydride shift.[13]

Isobutylene reacts with **1** to give zwitterion **2f** (see Scheme III). In this case, a 1,2-hydride shift does not occur since it would give a secondary carbenium ion.[14] Instead, **2f** reacts with a second molecule of isobutylene to give **5** which undergoes a well-precedented 1,5-hydride shift[15] to give **6** in 78% yield.

The role of $EtAlCl_2$ in the reaction of **1** with 2-methyl-2-butene was investigated. No reaction occurs with ≤1 equiv of $EtAlCl_2$. The initial rates of the reaction with 1.1, 1.2, and 1.3 equiv of $EtAlCl_2$ are proportional to the excess of $EtAlCl_2$ present. This suggests that the **1**·$EtAlCl_2$ complex formed from the first equivalent of $EtAlCl_2$ interacts with a second molecule of $EtAlCl_2$ to give the active species.[16] Although this reaction may not be unique to $EtAlCl_2$, no **3a** is formed when $AlCl_3$, BF_3·Et_2O, or $SnCl_4$ are used.

Cycloheptenone and cyclopentenone are suitable enones, reacting with 2-methyl-2-butene and $EtAlCl_2$ in benzene for 24 h to give 3-(3-methyl-2-butyl)-2-cycloheptenone (**7**) and 3-(3-methyl-2-butyl)-2-cyclopentenone (**8**) in 74 and 68% yield, respectively. Alkenes containing functional groups are suitable substrates if an additional 1 equiv of catalyst per functional group is used. Citronellyl acetate reacts with **1** and 2.5 equiv of $EtAlCl_2$ to give a 45% yield of 3-(1-acetoxy-3,7-dimethyl-6-octyl)-2-cyclohexenone (**9**).

The reactions of 3-penten-2-one or crotonaldehyde with alkenes give cyclobutanes as well as α,β-unsaturated carbonyl compounds. Crotonaldehyde reacts with 2-methyl-2-butene and 1.5 equiv of $EtAlCl_2$ in benzene for 45 min at 0 °C to give a 63% yield of enal **15a** and a 17% yield of enal **17a**. Reaction for 1.5 h at −80 °C gives a 77% yield of a mixture of 81% of cyclobutane **11a**, 7% of cyclobutane **12a**, 10% of **15a**, and 2% of **17a** (see Scheme II). Collapse of zwitterion **10a** to give cyclobutanes **11a** and **12a** is the kinetically favored process.[17] However, this closure is reversible, and at higher temperatures **10a** is regenerated. Although the formation of cyclobutanes from enones and enamines is well known,[18] the nonphotochemical formation of cyclobutanes from enones and unactivated alkenes has not been observed.[19] These cyclobutanes were previously inaccessible since photochemical [2 + 2] cycloaddition of enones to alkenes is restricted to cyclic enones.[20]

Zwitterions derived from acyclic enones or enals undergo methyl shifts in competition with hydride shifts. The first hydride shift of zwitterion **10a** gives **13a**. The second hydride shift to give **15a** requires that the hydride be eclipsed with both the vacant p orbital of the carbenium ion and the π cloud of the enol. This induces considerable steric hindrance from the interaction of the isopropyl group with the methyl group. This conformation is shown in **14a**. Since this intermediate (**13a**) is flexible, it can also adopt conformation **16a** in which the methyl group is eclipsed with the vacant p orbital. In this conformation the steric interaction, which is between the isopropyl group and a hydrogen, is not significant. A methyl shift in **16a** gives rise to **17a**. Zwitterions derived from **1** cannot give the analogous reaction, ring enlargement, since the ring methylene cannot eclipse with the π cloud of the enol.

The reaction of crotonaldehyde with 2,3-dimethyl-2-butene for 1.5 h at 25 °C gives a 69% yield of **17b**. Reaction for 5 h at −80 to −40 °C gives a 60% yield of **11b** and a 22% yield of **17b**. The absence of **15b** is expected since the steric interaction of the methyl group and *tert*-butyl group in **14b** is severe.

3-Penten-2-one is less reactive than crotonaldehyde, giving a 30% yield of **15c** and a 24% yield of **17c** with 2-methyl-2-butene (48 h, 25 °C). With 2,3-dimethyl-2-butene, 3-penten-2-one gives

(9) With unreactive alkenes, considerable quantities of Friedel–Crafts products are obtained in benzene.

(10) Woods, G. F.; Griswold, Jr., P. H.; Armbrecht, B. H.; Blumenthal, D. I.; Plapinger, R. *J. Am. Chem. Soc.* **1949**, *71*, 2028.

(11) For a discussion of 1,3-hydride shifts see: Fry, J. L.; Karabatsos, G. H. In "Carbonium Ions", Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. II, pp 521–571.

(12) For a related example see: Boelema, E.; Wieringa, J. H.; Wynberg, H.; Strating, J. *Tetrahedron Lett.* **1973**, 2377.

(13) See ref 11, pp 526–527.

(14) See ref 11, pp 523–524.

(15) Hill, R. K.; Carlson, R. M. *J. Am. Chem. Soc.* **1965**, *87*, 2772.

(16) The polymerization of isobutylene by $EtAlCl_2$ is second order in $EtAlCl_2$. Kennedy, J. P. *J. Macromol. Sci. Chem.* **1972**, *6*, 329. Solich, J. M.; Chmelir, M.; Marek, M. *Collect. Czech. Chem. Commun.* **1969**, *34*, 2611.

(17) Cyclobutanes were not observed with cyclic enones. The additional strain of the bicyclic system makes them less stable. It may, however, be possible to isolate them from reactions run at low temperatures.

(18) Cook, A. G. "Enamines"; Mercel Dekker: New York, 1969.

(19) For a slightly related example see ref 6e.

(20) Chapman, O. L.; Weiss, D. S. In "Organic Photochemistry", Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, p 197.

an 80% yield of **11d** after 20 h at 0 °C and a 60% yield of **17d** and a 10% yield of **11d** after 5 days at 25 °C.

Both **11d** and **11c** reopen to the zwitterion **10** under the reaction conditions. Cyclobutane **11d** is re-formed more frequently than **11c**, since the methyl shift required for the formation of **13d** is less facile than the hydrogen shift required for the formation of **13c**. After 4 days with 1.5 equiv of $EtAlCl_2$ at 25 °C, **11d** is converted to an 86:14 mixture of **17d** and **11d**.

The formation of **10d** from 2,3-dimethyl-2-butene and 3-penten-2-one is reversible since treatment of **11d** with 1.5 equiv of $EtAlCl_2$ and 3 equiv of 2-methyl-2-butene for 3 days at 25 °C gives a 56% yield of **15c** and a 28% yield of **17c** as well as an 11% yield of **17d**.

Methyl vinyl ketone (MVK) undergoes different reactions with alkenes. Methyl vinyl ketone is less basic than 3-penten-2-one,[21] giving rise to a more reactive complex which is also more sterically accessible. Therefore the MVK·$EtAlCl_2$ complex (without an additional molecule of $EtAlCl_2$) will react with alkenes to give ene adducts and other products. Better yields of ene adducts are obtained with Me_2AlCl as catalyst.[22] β-Substituted enone·$EtAlCl_2$ complexes are unreactive and appear to require the formation of the enone·$(EtAlCl_2)_2$ complex before reacting with alkenes.

So far we have been unable to obtain products from β,β-disubstituted enones such as mesityl oxide, 3-methylcyclohexenone, or α,β-disubstituted enones or enals such as acetylcyclohexene or tigaldehyde and alkenes. β,β-Disubstituted enones are more basic[21] than β-monosubstituted enones, giving complexes which are less reactive and more sterically hindered. α,β-Disubstituted enones are more hindered. We have observed intramolecular reactions with these types of enones.

Intramolecular Reactions. Enone·$(EtAlCl_2)_2$ complexes can also be used as initiators for cation–olefin cyclizations. The zwitterions which result undergo two 1,2-hydride shifts to regenerate an enone. These reactions are very versatile. They occur with nonnucleophilic terminal alkenes and with β,β-disubstituted and unsubstituted as well as β-substituted α,β-unsaturated ketones.

Treatment of **18**[23,24] with 1.5 equiv of $EtAlCl_2$ in either benzene or CH_2Cl_2 for 3 h at 25 °C gives a virtually quantitative yield of **20**. We believe that the zwitterion **19** is an intermediate. The cis ring fusion and the isopropyl group trans to the cyclohexane should be the most stable, as well as the kinetically favored,[25] configuration of the intermediate. Two 1,2-hydride shifts can give rise to **20**. A 1,3-hydride shift would give rise to **21**, which is not observed. Remarkably, isomerization of **20** to **21** does not occur under these strongly acidic reaction conditions. Use of less than 1 equiv of catalyst results in complex mixtures containing **20** and unidentified byproducts which are saturated ketones, apparently derived from **19** via typical reactions of carbenium ions. Enone **20**, which was previously obtained as a difficultly separable mixture with **21** by a multistep route,[26] is a key intermediate for the synthesis of muurol-3-ene-9-hydroxy-2-one.[26,27] Upon thermolysis (100 h, 240 °C), **18** undergoes the expected ene reaction[28] to give **22** as a 1:1 mixture of isomers.

This cyclization reaction is also of value for the synthesis of six-membered rings. Treatment of **23**[29,30] (as a 1:1 mixture of isomers) with 2 equiv of $MeAlCl_2$ for 2 h at −60 to −15 °C gives a 70% yield of **28** (as a 1:1 mixture of isomers), a 3% yield of **29**, and a 7% yield of ene adduct **26** (as a 1:1 mixture of isomers). We believe that ene adduct **26** is formed by a concerted Lewis acid catalyzed ene reaction.[2,3] In support of this hypothesis, treatment of **23** with 0.9 equiv of $MeAlCl_2$ for 20 h at 25 °C in CH_2Cl_2 gives an 80% yield of **26**. No **28** or **29** is formed. Apparently a **23**·$MeAlCl_2$ complex undergoes an ene reaction. In the presence of more than 1 equiv of $MeAlCl_2$, a **23**·$(MeAlCl_2)_2$ complex is formed which induces formation of zwitterion **24**. Two hydride shifts leading from **24** to **28** are disfavored since the first hydride shift is endothermic[31] and the second hydride shift is unlikely since the ring fusion hydrogen is nearly perpendicular to the π cloud of the enol. Conversion of **24** to the less stable boat conformer **25** makes the second hydride shift which gives **28** geometrically favorable. Isomerization of **28** by KOH in MeOH gives the most stable isomer **29**.[32] As expected, **28b** isomerizes more quickly than **28a**, since formation of the heteroannular dienoate required for the isomerization of **28b** is faster than formation of the homoannular dienoate required for the isomerization of **28a**.

Reaction of **23** with $EtAlCl_2$ is more complicated. Treatment of **23** with 1.5 equiv of $EtAlCl_2$ for 2 h at −15 °C in CH_2Cl_2 gives a 49% yield of a 5:1 mixture of **28a** and **28b**, an 8% yield of **29a**, a 9% yield of **26**, and a 30% yield of **27** (predominantly **27b**). Hydride shifts of the zwitterionic intermediate to give **28** are slow since it must adopt an unstable conformation. Transfer of a β-hydrogen atom of the ethyl group to the carbenium ion of **24**, possibly through a ten-membered ring transition state, gives **27** and ethylene. This process is avoided by the use of $MeAlCl_2$. Isomers **28a** and **27b** predominate, since **25a** (leading to **28a**) is more stable than **25b**, and **24b** (leading to **27b**) is more stable than **24a** owing to steric interactions of the methyl group on the cyclohexane. Hydrogenation of **26** to give **27** confirms the structure assignment.

Other catalysts were also investigated for the cyclization of **23**. BF_3·Et_2O[6d] (1.5 equiv) gives exclusively ene adduct **26**. $SnCl_4$ (2.5 equiv)[5e] gives an 88% yield of **26**, a 7% yield of **28**, and a 4% yield of **29**. As expected, **23** does not undergo an ene reaction on heating, even after 100 h at 250 °C, since formation of cyclohexanes by thermal intramolecular ene reactions is much more difficult than formation of cyclopentanes.[28]

This cyclization reaction also occurs with enones in which the alkene moiety is attached to the carbonyl carbon. Treatment of **30**[33,34] with 1.1 equiv of $EtAlCl_2$ in CH_2Cl_2 at 0 °C gives an 80% yield of **31**. Similarly, **32**[35] gives a 90% yield of a 3:1 mixture of **36** and **37**.[37] This is consistent with a preference for the formation of zwitterion **34** with an equatorial methyl group which gives rise to **36**. The cis enone **33** gives an identical 3:1 mixture

(21) (a) Jensen, J. L.; Thibeault, A. T. *J. Org. Chem.* **1977**, *42*, 2168. (b) Zalewski, R. I.; Dunn, G. E. *Can. J. Chem.* **1970**, *48*, 2538. (c) *Ibid.* **1969**, *47*, 2263. (d) Elegant, L.; Paris, C.; Gal, J. F.; Azzaro, M. *Thermochim. Acta* **1974**, *9*, 210.

(22) Snider, B. B.; Karras, M., unpublished results. We have previously carried out this reaction by using zinc chloride as catalyst.[2a]

(23) Ketone **18** was prepared by an enamine Robinson annelation[24] in 75% yield from the commercially available aldehyde.

(24) Ireland, R. E.; McKenzie, T. C.; Trust, R. I. *J. Org. Chem.* **1975**, *40*, 1007.

(25) Exclusively cis ring fusion occurs in related reactions.[5a,f]

(26) Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1977**, 3107.

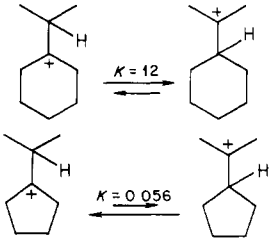
(27) Kuo, Y. H.; Cheng, Y. S.; Lin, Y. T. *Tetrahedron Lett.* **1969**, 2375.

(28) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.

(29) Prepared as a chromatographically separable mixture of α,β- and β,γ-unsaturated ketones by enamine Robinson annelation of citronellal.[24]

(30) Vig, O. P.; Lal, A.; Matta, K. L. *J. Indian Chem. Soc.* **1968**, *45*, 7.

(31) A carbenium ion is more stable on a cyclopentane carbon and less stable on a cyclohexane carbon than on an acyclic carbon as determined by NMR studies. This is responsible for some of the differences in the reactions of **19** and **24**. The actual data are shown below. Saunders, M. personal communication, Yale University, 1980.



(32) Belavadi, V. K.; Kulkarni, S. N. *Indian J. Chem.* **1978**, *16B*, 336; **1976**, *14B*, 901.

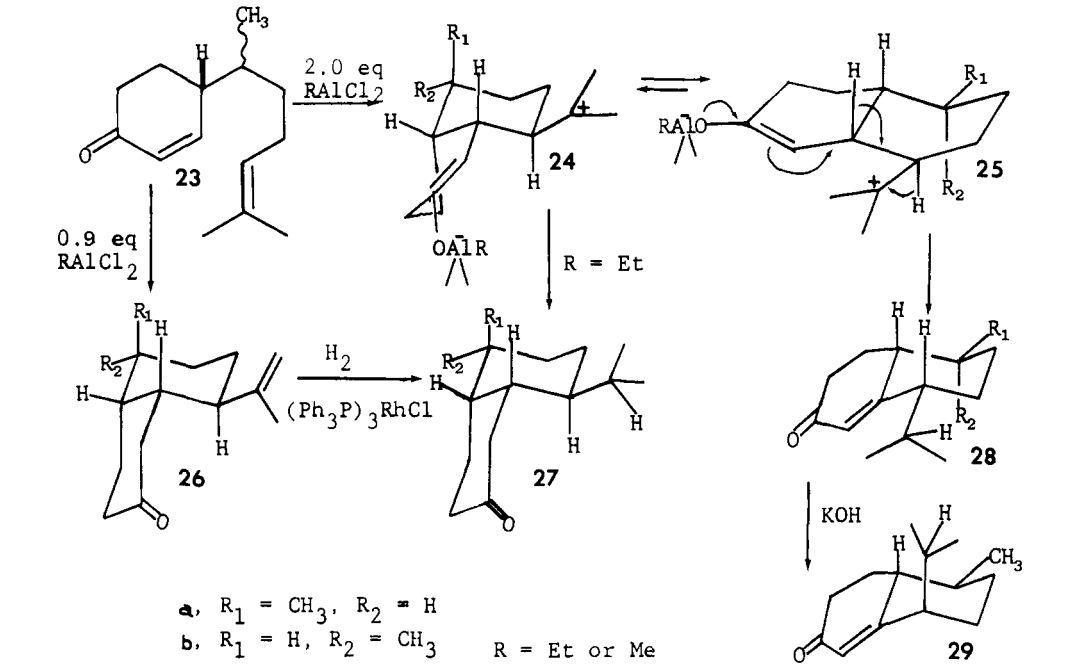
(33) Prepared by addition of 4-methyl-3-pentenylmagnesium bromide[34] to crotonaldehyde, followed by oxidation with Jones reagent.

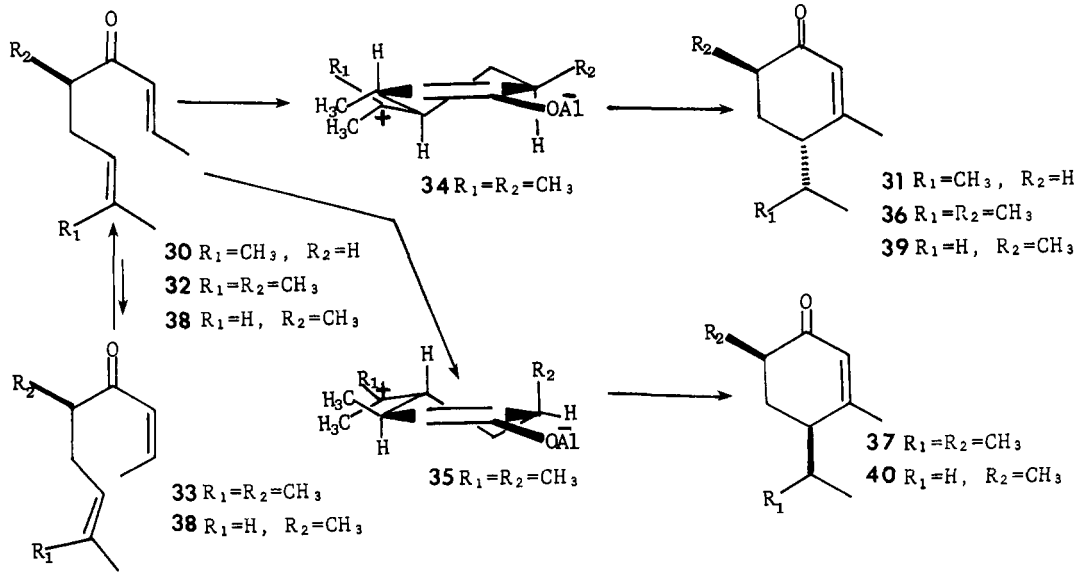
(34) Julia, M.; Julia, S.; Guégan, R. *Bull. Soc. Chim. Fr.* **1960**, 1072.

(35) Enones **32** and **35** and **43** were prepared by addition of 1-propenylmagnesium bromide or vinylmagnesium bromide to 2,5-dimethyl-4-hexenal[36] or 5-methyl-4-hexenal, respectively, followed by oxidation with Jones reagent.

(36) Marbet, R.; Saucy, G. *Helv. Chim. Acta* **1967**, *50*, 2095.

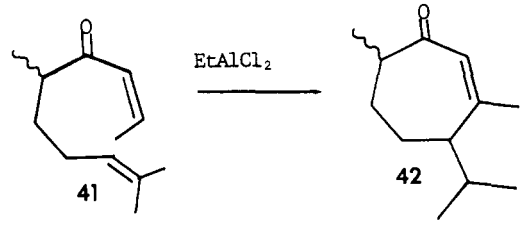
(37) Arnaud, C., Huet, J. *Bull. Soc. Chim. Fr.* **1971**, 4525.





of **36** and **37**. Since the cis methyl group hinders formation of the zwitterion and Lewis acid catalyzed isomerization of α,β-unsaturated ketones is rapid,[38] isomerization of **33** to **32** probably precedes cyclization.

Cyclization of the homologous enone, **41**, gives only a 5% yield of cycloheptenone **42** as a mixture of diastereomers. This reaction appears to be limited to the formation of five- and six-membered rings.

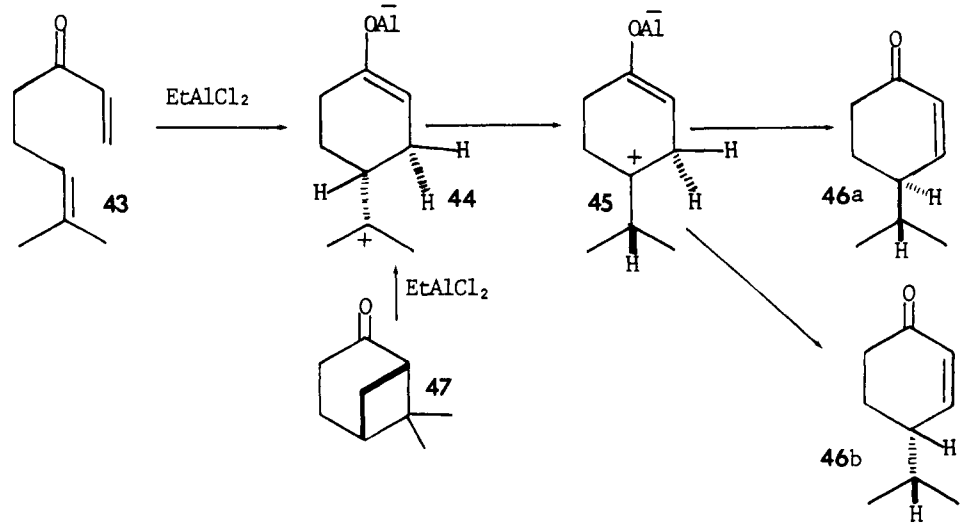


Secondary carbenium ions can also be formed in this reaction. Treatment of **38**[39,40] with 1.1 equiv of $EtAlCl_2$ in CH_2Cl_2 for 70 h at 25 °C gives a 2:1 mixture of **39** and **40** in 46% yield. The formation of a less stable carbenium ion requires longer reaction times and results in lower yields of cyclized products.

β-Unsubstituted enones such as **43**[35] give rise to more complicated mixtures of products. Treatment of **43** with 1.5 equiv of $EtAlCl_2$ in CH_2Cl_2 at 25 °C for 3 h gives a 25% yield of cryptone (**46**). Reactions of β-unsubstituted enones are less selective since the β positions of these enones are sterically more accessible and these enones are less basic than β-substituted enones,[21] giving rise to more reactive Lewis acid complexes. The differing reactivity of **30** and **43** is strictly analogous to that observed with 3-penten-2-one and methyl vinyl ketone (vide supra).

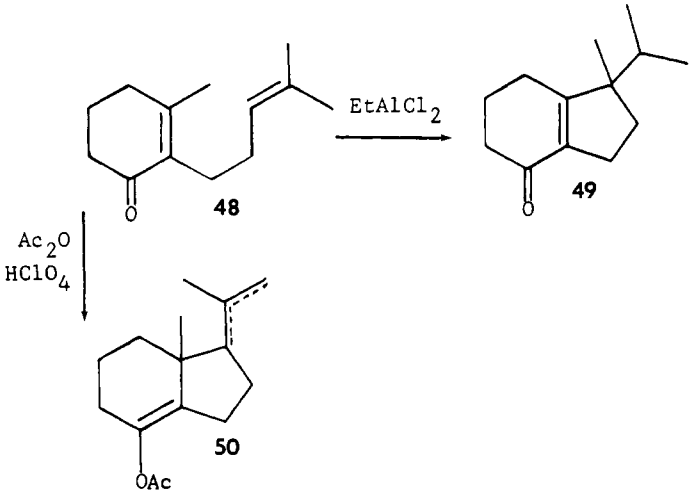
The low yield of **46** obtained from **43** is due to side reactions competing with the formation of **44** since treatment of nopinone (**47**) with $EtAlCl_2$ gives a 90% yield of **46**. If optically active **47** is used, a ≈53:47 mixture of **46a** and **46b** is obtained. The major isomer does result from inversion at the chiral center. This indicates that the hydride shifts are not concerted and that **45**, which is achiral, is an intermediate. Two concerted hydride shifts would give **46a**. Racemization of **44** by ring opening to give **43** and reclosure to **44** are excluded since **43** gives a low yield of **46** and

(38) McGreer, D. E.; Page, B. D. *Can. J. Chem.* **1969**, *47*, 866.
(39) Prepared as a mixture of isomers as for **32** and **33**[35] from 2-methyl-4-hexenal.[40]
(40) Montgomery, L. K.; Matt, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 934.



47 gives a >90% yield of **46**. An alternate possibility—racemization of **46**—is excluded on two grounds. Epimerization is not observed in other cases (i.e., **20** and **28**) where it would lead to mixtures of isomers. Furthermore, if racemization occurred, some of the β,γ isomer would be obtained[41] since it is present to the extent of 40% at equilibrium. It was not observed. Sulfuric acid catalyzed isomerization of cryptone gives a 60:40 mixture of α,β and β,γ isomers.[41]

β-Disubstituted enones are also reactive in these cyclizations, giving rise to zwitterions which undergo successive hydride and methyl shifts. Treatment of **48**[42,43] with 1.3 equiv of $EtAlCl_2$ for 24 h at 25 °C gives a 67% yield of enone **49**. This result is in contrast to previous results obtained by cyclization of **48** with acetylating agents which gives a mixture of enol acetates **50**.[43]



Similarly, cyclization of **51** with 1.5 equiv of $EtAlCl_2$ for 60 h at 25 °C gives 45% of **54**[44] and 15% of **56**.[45] The zwitterion formed in this case, **53**, is symmetrical and can undergo two 1,2-hydride shifts giving **54** or a 1,2-hydride shift followed by a 1,2-methyl shift giving **56**. Since **51** is available in 85% yield by alkylation of Hagemann's ester,[5b] this is a very efficient route to **54**, a key intermediate in Boeckman's synthesis of β-gorgonene.[44] Again cyclization of **51** by acetylation proceeds differently, giving **58**, or **59** in the presence of a large excess of acetate.[5b] The utility of $EtAlCl_2$ is indicated by the fact that **51** does not cyclize on treatment with $BF_3 \cdot Et_2O$ or $SnCl_4$.[5b] Cyclization of **52** gives **55** as a 1:1 mixture of isomers in 70% yield. Since isomerization does not occur in other cases, we believe that this is the kinetic mixture of products. Enone **57** is not formed since the initial hydride shift which gives a tertiary carbenium ion is favored.

Conclusions

An overall mechanism can be constructed from a consideration of all of the above experiments. A 1:2 enone–$EtAlCl_2$ complex reacts with an alkene as an electrophile to form a zwitterion reversibly. This process can be intermolecular or can form a five- or six-membered ring. In geometrically favorable cases, the zwitterion collapses rapidly but reversibly to a cyclobutene. In general, two 1,2-hydride or methyl shifts occur in the zwitterion to generate a new enone. For this process to occur, the intermediate formed from the first shift must be almost as stable as the initially formed zwitterion.

These reactions provide an attractive route to a variety of novel α,β-unsaturated ketones and aldehydes and cyclobutyl ketones and aldehydes. The series of hydride and methyl shifts are similar to processes occurring in the biosynthesis of terpenes and steroids. Further studies on the mechanism and synthetic applications of these reactions are in progress.

Experimental Section

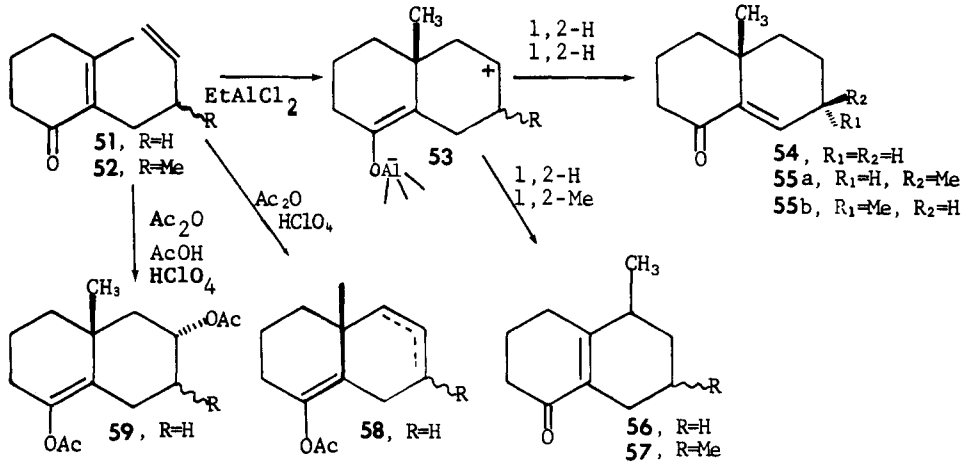
NMR spectra were taken on Varian A-60, Perkin-Elmer R-32, and JEOL FX-90Q spectrometers. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Mass spectra were determined on AEI-MS9 and Du Pont 21-490 mass spectrometers. Combustion analyses were performed by Galbraith Laboratories. All GC analyses were performed on a $^1/_4$ in. × 6 ft 10% XF-1150 column.

Benzene was dried by distillation from sodium benzophenone ketyl. CH_2Cl_2 was dried by distillation from calcium hydride. Ethylaluminum chloride was purchased from Texas Alkyls as a 25.5% solution in heptane (d = 0.772, 1.57 M). Dimethylaluminum chloride was purchased from Texas Alkyls as a 14.6% solution in heptane (d = 0.724, 1.13 M).

All reactions were run under nitrogen in flame-dried glassware. Reagents were added via dry syringes through septa. Intermolecular reactions were worked up by slow addition of 10 mL of saturated sodium dihydrogen phosphate solution followed by addition of just enough 10% hydrochloric acid to dissolve the precipitated alumina. The organic layer was separated and the aqueous layer extracted three times with ether. The combined organic layers were dried ($MgSO_4$) and evaporated. Intramolecular reactions were quenched with ammonium chloride solution and otherwise worked up as described above.

Reaction of 2-Cyclohexenone with 2-Methyl-2-butene. 2-Methyl-2-butene (0.35 g, 5.0 mmol, 1.1 equiv) was added to a solution of 2-cyclohexenone (0.44 g, 4.54 mmol) and $EtAlCl_2$ (4.34 mL of 1.57 M, 6.81 mmol, 1.5 equiv) in 15 mL of benzene. The solution was stirred overnight and worked up in the normal manner to give 0.72 g of crude product which was purified by evaporative distillation (65 °C, 0.05 Torr) to give 0.636 g (84%) of pure **3a**: NMR (CCl_4) δ 5.73 (br s, 1), 0.7–2.7 (m, 8), 1.08 (d, 3, J = 7 Hz), 0.94 (d, 3, J = 6 Hz), and 0.88 (d, 3, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 198.6, 169.9, 125.7, 48.8, 37.7, 31.0, 27.2, 23.0, 21.6, 19.5, and 15.8; IR (neat) 1675 and 1622 cm^{-1}; GC t_R = 7.3

(41) Lewis, K. G.; Williams, G. J. *Aust. J. Chem.* **1968**, *21*, 2467.
(42) Prepared by the procedure of Johnson, W. S.; Dawson, M. I.; Ratcliffe, B. E. *J. Org. Chem.* **1977**, *42*, 153.
(43) Hoffmann, W.; Mueller, N. German Offen. 2 440 406; *Chem. Abstr.* **1976**, *85*, 62734f. Cf. Brunke, E.-J.; Bielstein, H.; Kutschan, R.; Rehme, G.; Schuetz, H.-J.; Wolf, H. *Tetrahedron* **1979**, *35*, 1607.
(44) Boeckman, Jr., R. K.; Silver, S. M. *J. Org. Chem.* **1975**, *40*, 1755.
(45) Bhandari, R. G.; Bhide, G. V. *Chem. Ind. (London)* **1970**, 868.



min (190 °C). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.43; H, 11.06.

The reaction was repeated in an identical manner with 2-cyclohexenone-*3-d*[8] to give after distillation 0.639 g (83%) of 3-(3-methyl-*2-d*-2-butyl)-2-cyclohexenone: NMR ($CDCl_3$) δ 5.88 (t, 1, J = 1 Hz), 1.51–2.63 (m, 7), 1.1 (br s, 3), 0.93 (d, 3, J = 7 Hz), and 0.88 (d, 3, J = 7 Hz); IR (neat) 2130, 1672, and 1618 cm^{-1}; MS m/e (rel intensity) 167 (M^+, 4), 152 (1), 126 (10), 125 (100), 124 (11), 110 (9), 109 (57), 108 (6), 98 (9), 97 (44), 96 (24), and 95 (14). Calcd for $C_{11}H_{17}DO$: mol wt, 167.1420. Found: 167.1423.

Effect of the Amount of $EtAlCl_2$ on the Reaction of 2-Cyclohexenone with 2-Methyl-2-butene. The reaction was carried out as described above, using 1.0 equiv of $EtAlCl_2$. After 24 h no reaction had occurred as determined by GC and TLC. With more than 1 equiv of $EtAlCl_2$ reaction occurred which was monitored by GC (150 °C for 5 min, then 170 °C). With 1.1 equiv of $EtAlCl_2$: time in min (% completion) 60 (17.5), 120 (34.2), 180 (48.5), 300 (63.5), 553 (82.9), and 1115 (94.6). With 1.2 equiv of $EtAlCl_2$: 15 (10.1), 30 (25.1), 40 (29.2), 50 (37.7), 90 (46.7), 120 (55.7), 150 (65.1), 480 (90.5), and 1156 (97.1). With 1.3 equiv of $EtAlCl_2$: 5 (1.8), 10 (9.1), 15 (17.2), 20 (22.2), 25 (22), 30 (27.50), 60 (48.3), 90 (54.4), 120 (61.1), 180 (72), and 1189 (99).

Reaction of 2-Cyclohexenone with 1-Methylcyclohexene. 1-Methylcyclohexene (0.48 g, 5.0 mmol, 1.1 equiv) was allowed to react with 2-cyclohexenone for 24 h as described above. Workup gave 0.86 g of crude product which was purified by evaporative distillation (85 °C, 0.05 Torr) to give 0.76 g (87%) of **3b** as a 1:1 mixture of isomers: NMR (CCl_4) δ 5.84 and 5.77 (2 br s, 1), 0.9–2.5 (m, 16), and 0.83 and 0.80 (2 d, 3, J = 7 Hz); IR (neat) 1675 and 1622 cm^{-1}; GC t_R = 20.7 and 28.4 min (190 °C). Anal. Calcd for $C_{13}H_{20}O$: C, 81.22; H, 10.49. Found: C, 81.21; H, 10.64.

Reaction of 2-Cyclohexenone with Cyclohexene. Cyclohexene (0.41 g, 5.0 mmol, 1.1 equiv) was allowed to react with cyclohexenone for 4 days at 25 °C as described above. Normal workup gave 0.813 g which NMR showed to consist of ≈20% of **3c**, which was isolated by preparative GC: NMR (CCl_4) δ 5.88 (br s, 1), 0.9–2.5 (17, m); IR (neat) 1658 and 1620 cm^{-1}; GC t_R = 20.6 min (190 °C). Calcd for $C_{12}H_{18}O$: mol wt, 178.1358. Found: 178.1352.

Reaction of 2-Cyclohexenone with *cis*-2-Butene. Excess *cis*-2-butene was allowed to react with cyclohexenone for 2 days as described above. Normal workup gave 0.79 g of crude product. Purification by chromatography on silica gel with 5:1 hexane–ethyl acetate as eluent gave 0.27 g (42%) of **3d**: NMR (CCl_4) δ 5.78 (br s, 1), 1.2–2.5 (m, 9), 1.08 (d, 3, J = 6 Hz), 0.87 (t, 3, J = 7 Hz); IR (neat) 1668 and 1620 cm^{-1}; GC t_R = 5.7 min (190 °C). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.86; H, 10.58.

Reaction of 2-Cyclohexenone with 2,3-Dimethyl-2-butene. 2,3-Dimethyl-2-butene (0.42 g, 5.00 mmol, 1.1 equiv) was allowed to react with 2-cyclohexenone for 2 days as described above. Normal workup gave 0.68 g of crude product which was purified by evaporative distillation (70 °C, 0.05 Torr) to give 0.57 g (70%) of a 4:1 mixture of **3e** and **4**. Pure samples were obtained by preparative GC.

The spectral data for **3e**: NMR ($CDCl_3$) δ 5.9 (br s, 1), 1.86–2.5 (m, 7), 1.08 (d, 3, J = 7 Hz), and 0.93 (s, 9); IR ($CDCl_3$) 1660 and 1612 cm^{-1}; GC t_R = 9.2 min (190 °C).

The spectral data for **4**: NMR ($CDCl_3$) δ 5.93 (br s, 1), 1.76–2.5 (m, 7), 1.02 (s, 6), and 0.82 (d, 6, J = 7 Hz); IR ($CDCl_3$) 1650 and 1608 cm^{-1}; GC t_R = 10.3 min (190 °C).

Anal. Calcd for $C_{13}H_{20}O$ (mixture of **4** and **6**): C, 79.94; H, 11.18. Found: C, 79.94; H, 11.30.

The reaction was repeated with 2-cyclohexenone-*3-d* on half the above scale for 5 days at 25 °C. Normal workup gave 0.389 g (92%) of a 4:1 mixture of 3-(3,3-dimethyl-*2-d*-2-butyl)-2-cyclohexenone (*d*-**3e**) and 3-(2,3-dimethyl-*3-d*-2-butyl)-2-cyclohexenone (*d*-**4**) which were separated by preparative GC.

The spectral data for *d*-**3e**: NMR ($CDCl_3$) δ 5.89 (t, 1, J = 1 Hz), 1.83–2.53 (m, 6), 1.08 (br s), and 0.93 (s, 9); IR ($CDCl_3$) 2138, 1660, and 1610 cm^{-1}.

The spectral data for *d*-**4**: NMR ($CDCl_3$) δ 5.94 (br s, 1), 1.78–2.52 (m, 6), 1.02 (s, 6), and 0.82 (br s, 6); IR ($CDCl_3$) δ 2120, 1660, and 1618 cm^{-1}.

Reaction of 2-Cyclohexenone with Isobutylene. Isobutylene (0.54 g, 10.61 mmol, 2.3 equiv) was allowed to react with 2-cyclohexenone for 24 h as described above. Normal workup gave 0.68 g of crude product which was purified by evaporative distillation (65 °C, 0.05 Torr) to give 0.54 g (79%) of **6** which was ≥90% pure by GC: NMR ($CDCl_3$) δ 5.89 (br s, 1), 2.19 (br s, 2), 1.5–2.6 (m, 7), 1.32 (d, 2, J = 6 Hz), 0.96 (s, 6), and 0.95 (d, 6, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 199.5, 164.7, 129.3, 52.2, 51.3, 37.2, 35.6, 32.7, 27.8, 25.5, 24.2, and 23.1; IR (neat) 1672 and 1620 cm^{-1}; MS m/e (rel intensity) 208 (M^+, 3.4), 193 (1.3), 152 (2.5), 151 (6.0), 137 (2.3), 111 (8.8), 110 (100); GC t_R = 14.2 min (190 °C). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.55; H, 11.86.

Reaction of 2-Cyclohexenone with Citronellyl Acetate. A solution of citronellyl acetate (0.52 g, 2.63 mmol), cyclohexenone (0.25 g, 263 mmol), and $EtAlCl_2$ (4.19 mL of 1.57 M, 6.58 mmol, 2.5 equiv) in 8 mL of benzene was stirred for 3 days at 25 °C. Normal workup gave 0.7 g of material which was purified by chromatography on silica gel with 1:1 hexane–ethyl acetate as eluent to give 0.350 g (45%) of 3-(1-acetoxy-3,7-dimethyl-6-octyl)-2-cyclohexenone (**9**): NMR ($CDCl_3$) δ 5.83 (t, 1, J = 1 Hz), 4.06 (t, 2, J = 7 Hz), 2.06 (s, 3), 1.1–2.5 (m, 18), 0.98 (d, 3, J = 7 Hz), 0.90 (d, 3, J = 7 Hz), and 0.83 (d, 3, J = 7 Hz); IR (neat) 1738, 1670, and 1618 cm^{-1}. Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 72.84; H, 10.46.

Reaction of 2-Cycloheptenone with 2-Methyl-2-butene. A solution of cycloheptenone (0.25 g, 2.27 mmol), 2-methyl-2-butene (0.175 g, 2.5 mmol, 1.1 equiv), and $EtAlCl_2$ (2.17 mL of 1.57 M, 3.41 mmol, 1.5 equiv) in 8 mL of benzene was stirred for 24 h at 25 °C. Normal workup gave 0.38 g of material which was purified by evaporative distillation (90 °C, 0.05 Torr) to give 0.30 g (74%) of 3-(3-methyl-2-butyl)-2-cycloheptenone (**7**): NMR (CCl_4) δ 5.79 (br s, 1), 1.48–2.68 (m, 10), 1.08 (d, 3, J = 6 Hz), 0.94 (d, 3, J = 6 Hz), and 0.90 (d, 3, J = 6 Hz); IR (neat) 1662 and 1622 cm^{-1}; GC t_R = 8.4 min (190 °C). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.71; H, 11.29.

Reaction of 2-Cyclopentenone with 2-Methyl-2-butene. Cyclopentenone (0.37 g, 4.54 mmol), 2-methyl-2-butene (0.35 g, 5.00 mmol), and $EtAlCl_2$ (4.34 mL of 1.57 M, 6.81 mmol, 1.5 equiv) were allowed to react for 24 h at 25 °C as described above. Normal workup gave 0.52 g of crude product which was purified by evaporative distillation (65 °C, 0.05 Torr) to give 0.47 g (68%) of 3-(3-methyl-2-butyl)-2-cyclopentenone (**8**): NMR (CCl_4) δ 5.85 (m, 1), 1.5–2.7 (m, 6), 1.13 (d, 3, J = 7 Hz), 0.93 (d, 3, J = 7 Hz), and 0.88 (d, 3, J = 7 Hz); IR (neat) 1710, 1668, and 1612 cm^{-1}; GC t_R = 6.2 min (190 °C). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.88; H, 10.76.

Reaction of Crotonaldehyde with 2-Methyl-2-butene. A solution of crotonaldehyde (0.32 g, 4.54 mmol), 2-methyl-2-butene (0.354 g, 5.0 mmol, 1.1 equiv), and $EtAlCl_2$ (4.34 mL of 1.57 M, 6.81 mmol, 1.5 equiv) in 15 mL of benzene was stirred for 45 min at 25 °C. Normal workup followed by evaporative distillation (65 °C, 0.05 Torr) gave 0.50

g (79%) of an 81:19 mixture of **15a** and **17a** which could be separated by preparative GC.

The spectral data for **15a**: NMR (CCl_4) δ 9.97 (d, 1, J = 8 Hz), 5.78 (dq, 1, J = 8, 1 Hz), 2.12 (d, 3, J = 1 Hz), 1.5–2.1 (m, 1), 1.09 (d, 3, J = 7 Hz), 0.96 (d, 3, J = 7 Hz), and 0.89 (d, 3, J = 7 Hz); IR (CCl_4) 1718, 1678, 1632, and 1605 cm^{-1}; GC t_R = 13.9 min (120 °C).

The spectral data for **17a**: NMR (CCl_4) δ 9.43 (d, 1, J = 8 Hz), 6.63 (d, 1, J = 16 Hz), 5.93 (dd, 1, J = 16, 8 Hz), 1.45–1.9 (m, 1), 1.07 (s, 6), 0.90 (d, 6, J = 7 Hz); IR (CCl_4) 1689 and 1630 cm^{-1}; GC t_R = 9.5 min (120 °C).

Anal. Calcd for $C_9H_{16}O$ (**15a** and **17a**): C, 77.09; H, 11.22. Found: C, 77.00; H, 11.78.

Repetition of the above reaction in 15 mL of CH_2Cl_2 for 1.5 h at −80 °C gave 0.48 g (77%) of a mixture consisting of 81% of **11a**, 7% of **12a** (GC t_R = 6.8 min (120 °C)), 10% of **15a**, and 2% of **17a**. Cyclobutane **11a** was purified by preparative GC.

The spectral data for **11a**: NMR ($CDCl_3$) δ 9.40 (d, 1, J = 6 Hz), 1.53–1.83 (m, 2), 1.36 (dd, 1, J = 6, 6 Hz, C*H*CHO by decoupling), 1.15 (d, 3, J = 6 Hz), 1.04 (s, 6), and 0.87 (d, 3, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 201.6, 45.8, 41.3, 32.6, 30.3, 19.4 (**2**), 13.1, 12.7; IR ($CDCl_3$) 2740, 1690 cm^{-1}; GC t_R = 6.4 min (120 °C). The stereochemistry of the substituents on the cyclobutane of **11a** forces it into a rigid puckered conformation. In this conformation the carbonyl is eclipsed with the α proton. This results in a shielding of the α proton by the carbonyl and in a large coupling constant of the α proton with the aldehyde proton.[46]

On standing in air **11a** oxidized to the corresponding carboxylic acid, mp 70–78 °C. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 68.94; H, 10.35.

Reaction of Crotonaldehyde with 2,3-Dimethyl-2-butene. 2,3-Dimethyl-2-butene (0.42 g, 5.0 mmol) was allowed to react with crotonaldehyde for 1.5 h at 25 °C as described above. Normal workup gave 0.69 g of crude **17b** which was purified by evaporative distillation (60 °C, 0.05 Torr) to give 0.48 g (69%) of pure **17b**: NMR ($CDCl_3$) δ 9.53 (d, 1, J = 7 Hz), 7.00 (d, 1, J = 16 Hz), 6.04 (dd, 1, J = 16, 7 Hz), 1.09 (s, 6), and 0.96 (s, 9); IR (neat) 1692 and 1632 cm^{-1}; GC t_R = 3.2 min (170 °C). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.82; H, 11.81.

Repetition of the above reaction in 16 mL of CH_2Cl_2 for 5 h at −70 to −40 °C gave 0.67 g of crude product. Chromatography on silica gel with 10:1 hexane–ethyl acetate as eluent gave 0.42 g (60%) of **11b** and 0.16 g (22%) of **17b**.

The spectral data for **11b**: NMR (CCl_4) δ 9.76 (d, 1, J = 1.5 Hz), 2.14–2.85 (m, 2), 1.08 (s, 3), 1.05 (s, 3), 0.95 (s, 3), 0.88 (s, 3), and 0.87 (d, 3, J = 6 Hz); IR (neat) 2720, 1728 cm^{-1}; GC t_R = 4.8 min (125 °C).

On standing in air **11b** oxidized to the corresponding acid, mp 69–75 °C. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.32; H, 10.56.

Reaction of 3-Penten-2-one with 2-Methyl-2-butene. A solution of 3-penten-2-one (0.38 g, 4.54 mmol), 2-methyl-2-butene (0.35 g, 5.0 mmol, 1.1 equiv), and $EtAlCl_2$ (4.34 mL of 1.57 M, 6.8 mmol, 1.5 equiv) in 15 mL of benzene was stirred for 2 days at 25 °C. Normal workup gave 0.44 g (61%) of a 5:4 mixture of **15c** and **17c**, which were separated by preparative GC.

The spectral data for **15c**: NMR (CCl_4) δ 5.96 (br s, 1), 2.10 (s, 3), 2.04 (s, 3), 1.5–1.97 (m, 2), 1.04 (d, 3, J = 7 Hz), 0.90 (d, 3, J = 7 Hz), and 0.83 (d, 3, J = 7 Hz); IR (CCl_4) 1682, 1610 cm^{-1}; GC t_R = 4.1 min (140 °C). Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.87; H, 11.74.

The spectral data for **17c**: NMR (CCl_4) δ 6.65 (d, 1, J = 17 Hz), 5.89 (d, 1, J = 17 Hz), 2.18 (s, 3), 1.20–1.7 (m, 1), 1.04 (s, 6), and 0.87 (d, 6, J = 7 Hz); IR (CCl_4) 1698, 1680, 1620 cm^{-1}; GC t_R = 6.1 min (140 °C). Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.55; H, 11.92.

Reaction of 3-Penten-2-one with 2,3-Dimethyl-2-butene. A solution of 3-penten-2-one (0.39 g, 4.54 mmol, 1.0 equiv), 2,3-dimethyl-2-butene (0.42 g, 5.00 mmol, 1.1 equiv), and $EtAlCl_2$ (4.34 mL of 1.57 M, 6.81 mmol, 1.5 equiv) in 15 mL of benzene was stirred for 20 h at 0 °C. Normal workup gave 0.61 g (80%) of a 97:3 mixture of **11d** and **17d**: ^1H NMR ($CDCl_3$) δ 2.59 (d, 1, J = 10 Hz), 2.40 (dq, 1, J = 10, 6 Hz), 2.07 (s, 3), 1.13 (s, 3), 0.96 (s, 3), 0.92 (s, 3), 0.87 (s, 3), 0.84 (d, 3, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 204.0, 60.8, 42.7 (w), 38.6 (w), 35.3, 30.4, 24.1, 22.8, 20.3, 19.8, 12.7; IR (CCl_4) 1702 cm^{-1}; MS m/e (rel intensity) 168 (M^+, 1), 135 (1), 125 (2), 111 (1), 110 (3), 109 (1), 106 (1), 100 (3), 99 (23), 98 (100), 97 (2), 96 (3), 85 (1), 84 (10), 83 (27), 82 (11), 71 (6), 70 (62), 69 (39), 68 (36), 67 (37), 57 (5), 56 (25), 55 (3), 54 (3), 44 (17), 43 (20), 42 (12), and 41 (20); GC t_R = 6.7 min (125 °C). Calcd for $C_{11}H_{20}O$: mol wt, 168.1514. Found: 168.1521.

Repetition of the reaction for 4 days at 25 °C, normal workup, and evaporative distillation (50 °C, 0.05 Torr) gave 0.53 g (70%) of a 6:1 mixture of **17d** and **11d**. Preparative GC gave pure **17d**: NMR (CCl_4) δ 6.97 (d, 1, J = 16 Hz), 6.00 (d, 1, J = 16 Hz), 2.19 (s, 3), 1.2 (s, 6), and 0.9 (s, 9); IR (CCl_4) 1680 and 1620 cm^{-1}; MS m/e (rel intensity) 153 (1.5), 113 (2.6), 112 (21.7), 111 (100), 110 (6), 108 (17), 97 (4), 96 (19), 70 (4), 69 (22), 58 (15), 57 (33), 44 (72), 43 (4), 42 (8), and 41 (23); GC t_R = 14.3 min (125 °C). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.74; H, 12.04.

Reaction of 11d with $EtAlCl_2$. A solution of **11d** (0.18 g, 1.1 mmol, 1.0 equiv) and $EtAlCl_2$ (1.05 mL of 1.57 M, 1.65 mmol, 1.5 equiv) in 2 mL of benzene was stirred at 25 °C. The reaction was monitored by GC. Cyclobutane **11d** was converted exclusively to **17d**. The data: time in h (% **17d**) 0 (<2), 2.5 (5), 18 (8), 42 (27), 67 (66), 99 (86), 113 (94).

Reaction of 11d with $EtAlCl_2$ in the Presence of Excess 2-Methyl-2-butene. $EtAlCl_2$ (0.6 mL of 1.57 M, 0.9 mmol, 1.5 equiv) was added to a solution of **11d** (0.1 g, 0.6 mmol) and 2-methyl-2-butene (0.128 g, 1.8 mmol, 3 equiv) in 1.8 mL of benzene. The solution was stirred for 3 days at 25 °C. Normal workup gave 84 mg of a mixture consisting of 59% **15c**, 30% **17c**, and 11% **17d** as determined by GC analysis (125 °C).

Cyclization of 18. A solution of **18**[23,24] (200 mg, 1.05 mmol) in 5 mL of CH_2Cl_2 was treated with $EtAlCl_2$ (1.00 mL of 1.57 M, 1.57 mmol, 1.5 equiv). After 3 h at 25 °C, the reaction mixture was worked up to give 200 mg of **20** which was >95% pure. Chromatography on silica gel with 2:1 hexane–ethyl acetate as eluent gave 180 mg (90%) of pure **20** which was identical with an authentic sample by NMR and IR spectral comparison.[26]

A solution of **18** (150 mg, 0.78 mmol) in 3 mL of benzene was sealed in a Pyrex tube and heated for 84 h at 240 °C. The benzene was removed and the residue was purified by chromatography on silica gel with 2:1 hexane–ethyl acetate to give 131 mg (87%) of **22a** and **22b** as a 53:47 mixture of isomers. These were separated by preparative GC.

The spectral data for **22a**: NMR (CCl_4) δ 4.71 (br s, 2), 2.4–1.5 (m, 12), 1.67 (3, s), and 1.22 (s, 3); IR (neat) 3040, 1713, and 1645 cm^{-1}; GC t_R = 13 min (170 °C).

The spectral data for **22b**: NMR (CCl_4) δ 4.82 (br s, 1), 4.67 (br s, 1), 2.5–1.6 (m, 12), 1.74 (s, 3), and 1.17 (s, 3); IR 3040, 1713, and 1645 cm^{-1}; GC t_R = 18 min (170 °C). Anal. Calcd for $C_{13}H_{21}O$ (**22a** and **22b**): C, 80.77; H, 10.95. Found: C, 80.54; H, 10.82.

The olefinic methylene of **22a** which is cis to a hydrogen absorbs as a singlet. The olefinic methylene group of **22b** which is cis to an alkyl group absorbs as two singlets. Similar observations have been made for the isomeric 2,3-dimethyl-1-isopropenylcyclopentanes.[47]

Cyclization of 23 with 2.0 Equiv of $MeAlCl_2$. A suspension of $AlCl_3$ (0.12 g, 0.97 mmol) in 2.5 mL of CH_2Cl_2 was treated with Me_2AlCl (0.86 mL of 1.13 M, 0.97 mmol). The solution was cooled to −65 °C and **23** (0.2 g, 0.97 mmol) in 2.5 mL of CH_2Cl_2 was added. The solution was stirred for 3 h, allowing the temperature to slowly rise to −15 °C. Normal workup gave 0.195 g (99%) of crude product which GC showed to consist of 70% **28**, 3% **29**, 7% **26**, and 20% of an unidentified compound. For spectral data see below.

Cyclization of 23 with 1.0 Equiv of $MeAlCl_2$. A suspension of $AlCl_3$ (0.065 g, 0.5 mmol) in 3 mL of CH_2Cl_2 was treated with Me_2AlCl (0.43 mL of 1.13 M, 0.49 mmol). The solution was stirred for 5 min at 25 °C and cooled to −40 °C. Enone **23** (0.2 g, 0.97 mmol) in 2 mL of CH_2Cl_2 was added and the solution warmed to 25 °C. The reaction mixture was kept for 20 h at 25 °C and worked up to give 0.17 g (85%) of pure **26**: NMR (CCl_4) δ 4.82 (br s, 1), 4.73 (br s, 1), 1.0–2.7 (m, 14), 1.64 (br s, 3), and 1.13 and 0.96 (2 d, 3, J = 7 Hz, methyl groups of **26a** and **26b**, respectively); IR (neat) 1715, 1645, and 890 cm^{-1}; MS m/e (rel intensity) 206 (M^+, 17), 188 (7), 165 (7), 164 (13), 151 (7), 150 (6), 149 (10), 148 (19), 123 (100), 122 (31), and 121 (68); GC t_R = 13 min (190 °C). Calcd for $C_{14}H_{22}O$: mol wt, 206.1671. Found: 206.1673.

Cyclization of 23 with 1.5 Equiv of $EtAlCl_2$. A solution of **23** (0.97 mmol) in 5 mL of CH_2Cl_2 at −40 °C was treated with $EtAlCl_2$ (0.93 mL of 1.57 M, 1.46 mmol, 1.5 equiv). The resulting solution was stirred at −15 °C for 2 h and worked up, giving a mixture which was shown by GC to consist of 30% **27** (predominantly **27b**), 9% **26**, 8% **29**, and 49% of a 5:1 mixture of **28a** and **28b**. The mixture was separated by preparative GC.

The spectral data for **27**: NMR (CCl_4) δ 0.55–2.7 (m, 15), 0.89 (d, 3, J = 7 Hz), 0.84 (d, 3, J = 7 Hz), and 0.65 (d, 3, J = 7 Hz); the spectrum seems to be predominantly a single isomer (**27b**) since only three methyl groups are seen; IR 1720 cm^{-1}; MS m/e (rel intensity) 208 (M^+, 9), 152 (6), 151 (10), 124 (8), 123 (11), 110 (12), 107 (9), 98 (5), 97 (33), 96 (45), 95 (12), 93 (6), 83 (12), 82 (8), 81 (17), 79 (12), 77

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(6), 75 (19), and 71 (18); GC t_R = 11.1 min (190 °C). Calcd for $C_{14}H_{24}O$: mol wt, 208.1827. Found: 208.1835.

The spectral data for **28**: NMR (CCl_4) δ 5.82 (br s, 1, **28b**) and 5.68 (br s, 1, **28a**); IR (neat) 1678 and 1615 cm^{-1}; MS *m/e* (rel intensity) 206 (M^+, 27), 166 (18), 165 (83), 164 (82), 163 (51), 161 (8), 150 (34), 149 (54), 136 (53), 135 (44), 131 (37), 124 (26), 123 (73), and 122 (100); GC t_R = 24.3 min (190 °C). Calcd for $C_{14}H_{22}O$: mol wt, 206.1671. Found: 206.1668.

Isomerization of 28. A solution of 0.2 g of crude **28** (obtained from **23** with 2 equiv of $MeAlCl_2$) in 10 mL of 10% KOH in MeOH was stirred overnight. Water was added and the solution extracted with ether which was dried ($MgSO_4$) and evaporated. The residue was purified by filtration through Florisil with ether as eluent to give 0.059 g of **29**: NMR (CCl_4) δ 5.67 (br s, 1); IR (neat) 1678 and 1615 cm^{-1}; MS *m/e* (rel intensity) 206 (M^+, 31), 166 (15), 165 (73), 164 (82), 163 (13), 150 (20), 149 (50), 136 (49), 135 (39), 131 (36), 122 (98), and 121 (92); GC t_R = 21.0 min (190 °C). This material was identical with an authentic sample by spectral comparison.[32]

At shorter reaction times NMR showed only a single absorption at δ 5.67 while GC showed peaks at 21 and 24.3 min. This indicates that **28b**, which absorbs at δ 5.82 in the NMR, isomerizes to **29** faster than **28a** does.

Hydrogenation of 26. Benzene (2.5 mL) was added to 0.087 g (0.2 equiv) of tris(triphenylphosphine)rhodium chloride under hydrogen. Ene adduct **26** (0.096 g, 0.47 mmol, 75% **26b**) in 2.5 mL of benzene was added and the resulting solution stirred for 6 days at 25 °C under hydrogen. The mixture was filtered through Florisil with ether as eluent to give 0.63 g (72%) of **27** which was chromatographically identical with that previously obtained. The NMR showed the absorptions expected for **27b** and an absorption at δ 0.75 (d, 3, J = 7 Hz) which is a methyl group of **27a**.

Cyclization of 30. A solution of **30**[33,34] (100 mg, 0.66 mmol) in 5 mL of CH_2Cl_2 at 0 °C was treated with $EtAlCl_2$ (0.42 mL of 1.57 M, 0.70 mmol). After 1 h at 0 °C, the mixture was worked up to give 90 mg of crude **31** which was purified by chromatography on silica gel with 3:1 hexane–ethyl acetate as eluent to give 81 mg (81%) of pure **31**:[48] NMR (CCl_4) δ 5.71 (br s, 1), 2.0–2.5 (m, 5), 1.99 (s, 3), 1.70 (m, 1), 1.06 (d, 3, J = 7 Hz), 0.87 (d, 3, J = 7 Hz); IR (neat) 1670 and 1618 cm^{-1}.

Cyclization of 32. A solution of **32**[35] (80 mg, 0.48 mmol) in 5 mL of CH_2Cl_2 was treated with $EtAlCl_2$ (0.35 mL of 1.57 M, 0.52 mmol, 1.1 equiv). After 3 h at 25 °C the solution was worked up to give a quantitative crude yield of a 3:1 mixture of **36** and **37**. Purification of the residue by chromatography on silica gel with 3:1 hexane–ethyl acetate gave 64 mg (80%) of a 3:1 mixture of pure **36** and **37**. The isomers were separated by preparative GC.

The spectral data for **36**: NMR (CCl_4) δ 5.80 (br s, 1), 1.2–2.5 (m, 5), 1.93 (s, 3), 1.08 (d, 3, J = 7 Hz), 1.03 (d, 3, J = 7 Hz), and 0.77 (d, 3, J = 7 Hz); IR (neat) 1675 and 1610 cm^{-1}; GC t_R = 18 min (150 °C).

The spectral data for **37**: NMR (CCl_4) δ 5.75 (br s, 1), 1.6–2.4 (m, 5), 1.96 (s, 3), 1.06 (d, 3, J = 7 Hz), 1.04 (d, 3, J = 7 Hz), and 0.94 (d, 3, J = 7 Hz); IR (neat) 1675 and 1610 cm^{-1}; GC t_R = 16 min (150 °C).

Calcd for $C_{11}H_{18}O$: mol wt, 166.1358. Found: 166.1361.

The relative structure assignments of **36** and **37** are based on mechanistic arguments (see Discussion) and analysis of the NMR spectra.[37] The 4-isopropyl group of **31** exists primarily in the pseudoaxial conformation. This results in a large upfield shift of one of the methyls due to shielding by the double bond. In the trans isomer **36** this upfield methyl group (δ 0.77) is observed. In the cis isomer **37**, the isopropyl adopts an equatorial conformation in order to avoid a 1,3-diaxial interaction, and no upfield methyl group is observed.

Cyclization of 33. Treatment of **33** (100 mg) as described above gave, after purification, 81.9 mg (82%) of a 3:1 mixture of **36** and **37**.

Cyclization of 41. A solution of **41**[49] (456 mg, 2.53 mmol) in 25 mL of $CHCl_2$ was treated with $EtAlCl_2$ (4.6 mL of 1.17 M in pentane, 5.2 mmol, 2.1 equiv). TLC showed that the reaction was complete after 5 h. Normal workup gave 131 mg of crude product which was purified by chromatography on silica gel with 4:1 pentane–ether as eluent to give 12 mg (3%) of the trans isomer of **41** and 25 mg (5%) of **46**. The spectral data for **46**: NMR (CCl_4) δ 5.72 (br s, 1), 2.2–2.5 (m, 1), 1.90 (br s, 3), 0.7–2.0 (m, 15); IR (neat) 1670 cm^{-1}; MS *m/e* 180 (M^+), 165, 152, 138, 137, 123, 110, 109, 98, and 95. Calcd for $C_{12}H_{20}O$: mol wt, 180.1514. Found: 180.1523.

Cyclization of 38. A solution of **38**[39,40] (300 mg, 2 mmol) in 10 mL of CH_2Cl_2 was treated with $EtAlCl_2$ (1.4 mL of 1.57 M, 2.2 mmol). The solution was stirred for 70 h at 25 °C and worked up giving 283 mg of crude product. Chromatography of 196 mg of this material on silica gel with 3:1 hexane–ethyl acetate as eluent gave 96% mg (46%) of a 2:1 mixture of **39** and **40**. The spectral data were estimated from the mixture.

The spectral data for **39**: NMR (CCl_4) δ 5.72 (br s, 1), 2.5–1.4 (m, 6), 1.92 (s, 3), 1.04 (d, 3, J = 7 Hz), 1.02 (t, 3, J = 6 Hz); IR (neat) 1670 and 1637 cm^{-1}.

The spectral data for **40**: NMR (CCl_4) δ 5.83 (br s, 1), 2.50–1.40 (m, 6), 1.95 (s, 3), 1.04 (d, 3, J = 7 Hz), and 1.00 (t, 3, J = 6 Hz).

Calcd for $C_{10}H_{16}O$: mol wt, 152.1201. Found: 152.1198.

Cyclization of 43.[35] A solution of **43** (100 mg, 0.73 mmol) in 5 mL of CH_2Cl_2 was treated with $EtAlCl_2$ (0.7 mL of 1.57 M, 1.1 mmol, 1.5 equiv). The mixture was stirred for 3 h at 25 °C and worked up to give 80 mg of crude **46**. The residue was purified by chromatography on silica gel with 3:1 hexane–ethyl acetate as eluent to give 25 mg (25%) of pure **46**: NMR (CCl_4) δ 6.75 (dd, 1, J = 10, 1 Hz), 5.90 (dd, 1, J = 10, 2 Hz), 2.5–1.6 (m, 6), and 1.00 (d, 6, J = 7 Hz); IR (neat) 1680 cm^{-1}. This material is identical with authentic cryptone.[41]

Rearrangement of Nopinone (47). A solution of nopinone[41] (0.5 g, 3.6 mmol) in 12 mL of CH_2Cl_2 was treated with $EtAlCl_2$ (3.44 mL of 1.57 M, 5.4 mmol, 1.5 equiv). The solution was stirred for 3 h at 25 °C and worked up to give 0.49 g (98%) of pure cryptone uncontaminated with unconjugated isomers as determined by the absence of an IR absorption above 1700 cm^{-1}.

(*S,S*)-*l*-Pinene gave nopinone with $[\alpha]^{25}_D$ +31.61° ($CHCl_3$) (lit.[50] $[\alpha]^{25}_D$ +33.99° ($CHCl_3$)). The resulting cryptone had $[\alpha]^{25}_D$ −12.1° ($CHCl_3$), $[\alpha]^{25}_D$ −6.6° (EtOH) (lit.[51] $[\alpha]^{25}_D$ −119.3° (EtOH) for (*R*)-*l*-cryptone). This indicates that a 53:47 mixture of **46a,b** was obtained.

Cyclization of 48.[43] A solution of **42** (200 mg, 1.2 mmol) in 5 mL of CH_2Cl_2 was treated with $EtAlCl_2$ (1 mL of 1.57 M, 1.57 mmol, 1.3 equiv). The mixture was stirred for 24 h at 25 °C and worked up to give 200 mg of crude **49**. Purification of 140 mg by chromatography on silica gel with 3:1 hexane–ethyl acetate as eluent gave 94 mg (67%) of pure **49**: mp 44.5–46 °C; NMR (CCl_4) δ 2.6–1.3 (m, 11), 1.11 (s, 3), 0.93 (d, 3, J = 7 Hz), and 0.78 (d, 3, J = 7 Hz); IR (neat) 1665 and 1635 cm^{-1}; GC t_R = 11.5 min (190 °C). Calcd for $C_{13}H_{20}O$: mol wt, 192.1514. Found: 192.1517.

Cyclization of 51.[5b] A solution of **51**[5b] (200 mg, 1.22 mmol) in 5 mL of CH_2Cl_2 was treated with $EtAlCl_2$ (0.58 mL of 1.57 M, 1.83 mmol, 1.5 equiv). The resulting solution was stirred for 60 h at 25 °C. Normal workup gave 198 mg, which was purified by chromatography on silica gel with 3:1 hexane–ethyl acetate as eluent to give 90 mg (45%) of **54** followed by 30 mg (15%) of **56**. Enone **54** was identical with an authentic sample by spectral comparison.[44] Enone **56** was identical with an authentic sample by spectral comparison.[45]

Cyclization of 52. A solution of **52**[42] (100 mg, 0.56 mmol) in 2.5 mL of CH_2Cl_2 was treated with $EtAlCl_2$ (0.64 mL of 1.57 M, 1.01 mmol, 1.8 equiv). The resulting solution was stirred for 22 h at 25 °C and worked up to give 77 mg (77%) of crude **55**. Evaporative distillation (115 °C, 0.15 Torr) gave 63 mg (63%) of pure **55** as a 1:1 mixture of isomers: NMR (CCl_4) δ 6.17 (d, 0.5, J = 5 Hz, **55b**), 6.09 (br s, 0.5, **55a**), 1.1–3.0 (m, 14), and 1.05 (3, s); IR (neat) 1690 and 1620 cm^{-1}; MS *m/e* 178 (M^+), 163, and 111. Calcd for $C_{12}H_{18}O$: mol wt, 178.1358. Found: 178.1353.

The alkenyl hydrogen of **55b** absorbs as a doublet since the adjacent methine hydrogen is equatorial, giving rise to a small dihedral angle between the hydrogens. The alkenyl hydrogen of **55a** absorbs as a singlet since the adjacent methine hydrogen is axial giving rise to a dihedral angle between the hydrogens of close to 90°.

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