mixture was distributed between ether and water and then the organic phase was separated, dried (MgSO₄), and evaporated. The crude products were then purified by flash chromatography (20% EtOAc-hexane) and recrystallized from hexane or pentane.

3b: 83% from 1b, crystallized directly from 1:1 EtOH-5% HCl; mp 143-144 °C; TLC, IR, NMR, and MS identical with those of 3b isolated by the THF method. After recrystallization from hexane it exhibited the same melting behavior as in the THF method, melting at 144 °C, resolidifying, and melting again at 151-152 °C.

3c: 54% from 1c (flash chromatography); mp 83–84 °C; IR (CHCl₃) 1600 (C—N) cm⁻¹; NMR (CDCl₃) δ 2.14 (6 H, s, CH₃), 7.20–7.85 (7 H, m, Ar H); MS(EI), m/e (relative intensity) 223 (M⁺, 100), 222 (M⁺ – H, 62). Anal. Calcd for C₁₅H₁₃NO: C, 80.69; H, 5.87; N, 6.27. Found: C, 81.09; H, 6.20; N, 6.25.

3d: 70% from 1d (flash chromatography); mp 92–93 °C; IR (CHCl₃) 1610 (C=N), cm⁻¹; NMR (CDCl₃) δ 7.40–7.75 (m, Ar H); MS(EI), *m/e* (relative intensity) 265 (M⁺, ³⁷Cl, 63), 263 (M⁺, 100), 237 (M⁺ - CO, ³⁷Cl, 50), 235 (M⁺ - CO, 78). Anal. Calcd for C₁₃H₇Cl₂NO: C, 59.11; H, 2.67; N, 5.30. Found: C, 58.96; H, 2.65; N, 5.26.

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[1,2]-Intramolecular Ene Reactions

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The intramolecular ene reaction has been elaborated into a versatile synthetic method. In a recent review,¹ Oppolzer and Snieckus enumerate three variants of the reaction in which the enophile is linked by a bridge to the olefinic terminal (type I), central atom (type II), or allylic terminal (type III) of the ene component. However, there are in principle six types of intramolecular ene reactions, since the bridge can be attached at either of two positions on the enophile as well as the three possible positions on the ene unit (see Scheme I). The type of intramolecular ene reaction can be specified by the attachment point of the bridge to the ene and enophile units, respectively. Using this terminology Oppolzer and Snieckus' type I becomes [1,1], type II becomes [2,1], and type III becomes [3,2]. [3,1]-Intramolecular ene reactions must result in the formation of a large ring and are therefore entropically unfavorable, but [1,2]- and [2,2]-intramolecular ene reactions are plausible (see Scheme II).

The electronically favored [1,2] adduct 2 has been obtained as the minor component of a mixture with the geometrically favored [1,1] adducts 3 in the thermal ene reaction of $1.^2$ Lewis acid catalysis of this reaction would be expected to enhance electronic effects and lead selectively to 2, but a stepwise reaction leading to the formation



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of 4-isopropyl-2-cyclohexenone via two 1,2-hydride shifts results.³ [1,2] and [1,1] adducts have been obtained as mixtures from the $MgBr_2$ -catalyzed intramolecular ene reaction of 4 at 140 °C.⁴

We set out to develop substrates that would undergo [1,2]- and [2,2]-intramolecular ene reactions selectively. Methyl 3,7-dimethyl-2-methylene-6-octenoate (7) was



chosen since Lewis acid catalysis should favor the [1,2] reaction and α,β -unsaturated esters are less susceptible to competing stepwise reactions than α,β -unsaturated ketones. Furthermore, the relative stereochemistry of the two chiral centers formed in the reaction should provide mechanistic information.

Condensation of the lithium enolate of methyl citronellate (5) with N,N-dimethylmethyleneammonium iodide gives a 66% yield (93% based on recovered 5) of 6, which is treated sequentially with methyl iodide and DBU to give a 63% yield of 7.⁵

Treatment of 7 with 0.93 equiv of $EtAlCl_2$ in CH_2Cl_2 at 40 °C for 5 days gives an 82% yield of a single [1,2] adduct (8) as determined by GC and ¹³C NMR analysis. The stereochemistry of 8 was established by spectroscopic analysis and chemical transformations. Epimerization of 8 with sodium methoxide in methanol for 5 days at reflux,⁶ followed by reesterification with diazomethane, gives a

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26% yield of 9 as the only volatile product. This suggests that 9 has all three substituents equatorial, since the other pair of diastereomers, with the methyl and isopropenyl group cis, would be present in comparable amounts at equilibrium.⁶ The ¹³C NMR spectra of 8 and 9 fit well with those calculated for the most stable conformer when literature data for *cis*- (both conformers) and *trans*-1-isopropenyl-4-methylcyclohexane⁷ and shifts resulting from axial and equatorial carbomethoxy groups on cyclohexane rings⁸ are used.

The formation of 8 as a single isomer suggests that the reaction is concerted. Examination of models indicates that the boatlike transition state 10 leading to 8 should



be favored over either chairlike transition state 11 due to unfavorable steric interactions between the indicated axial hydrogen and the methyl group. Formation of 8 via a stepwise mechanism seems less likely but cannot be ruled out. Cyclization would be expected to give 12 with the substituents trans and diequatorial. An intermolecular proton transfer, which seems unlikely in the presence of EtAlCl₂, should lead to a mixture of 8 and 9 with 8 predominating.⁹ Intramolecular proton transfer would require a high-energy conformational change.

The exclusive formation of the [1,2]-ene adduct 8 is a result of the electronic effects of Lewis acid catalysis. In general, the geometry of the transition states will always favor the formation of [1,1] rather than [1,2] adducts. [1,2]adducts will be observed as major products only in those cases where Lewis acid catalysis is used and the substitution of the enophile is such that only the [1,2] reaction is catalyzed. The [1,1] adduct 13 would be expected to be the major product from 7 in a thermal ene reaction. It is not observed here since the position of the ester group precludes Lewis acid catalysis of this reaction.



Methyl 6-methyl-2-methylene-6-heptenoate (14) was prepared as a substrate for a [2,2]-intramolecular ene reaction. Although examination of models indicates that



the transition state leading to 15 is strain free, the reaction could not be accomplished with Lewis acid catalysis. Depending on the reaction conditions, starting material was recovered or complex mixtures were obtained.

Experimental Section

NMR spectra were taken on a Varian EM-390 or Bruker WH-90 spectrometer. EtAlCl₂ was purchased as a 25% solution in heptane from Alfa. Analyses were performed by Galbraith Laboratories.

Methyl 3,7-Dimethyl-2-methylene-6-octenoate (7). Butyllithium (2.7 mL of 1.6 M in hexane, 4.3 mmol) was added to a solution of diisopropylamine (440 mg, 4.4 mmol) in 10 mL of THF at 0 °C under nitrogen in a flame-dried flask. The solution was stirred for 30 min and cooled to -78 °C. Methyl citronellate (5, 670 mg, 3.6 mmol) in THF (5 mL) was added over 10 min. After 15 min, dimethylmethyleneammonium iodide (1.21 g, 6.5 mmol) was added and the solution was allowed to warm to 25 °C over 2.5 h. The reaction was quenched with water and extracted with ether. The combined organic layers were extracted with 1 M hydrochloric acid, dried (Na_2SO_4), and evaporated to give 225 mg (34%) of 80% pure recovered 5. The hydrochloric acid layer was made basic by slow addition of sodium bicarbonate and extracted twice with methylene chloride. The combined organic layers were dried (K_2CO_3) and evaporated to give 575 mg (66%) of 6.

Crude 6 was dissolved in MeOH (2 mL), and methyl iodide (2.3 g, 16 mmol) was added. The reaction mixture was stirred for 40 h, evaporated in vacuo, and treated with THF (10 mL) and DBU (1.0 g, 7 mmol). The solution was stirred for 2 days and treated with pentane and water. The organic layer was separated, dried (MgSO₄), and evaporated to give 430 mg of crude 7. Evaporative distillation (74 °C, 3.6 torr) gave 299 mg (63% from 6) of pure 7: NMR (CCl₄) δ 6.06 (d, 1, J = 2 Hz), 5.04 (br t, 1, J = 7 Hz), 1.66 (br s, 3), 1.57 (br s, 3) 1.2–1.6 (m, 2), 1.07

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(d, 3, J = 7 Hz); IR (neat) 1720, 1625 cm⁻¹. The data correspond well to those previously reported for the ethyl ester.¹⁰

Methyl $(1\alpha, 2\alpha, 5\beta)$ -2-Methyl-5-(1-methylethenyl)cyclohexanecarboxylate (8). Ester 7 (32 mg, 0.16 mmol) was dissolved in 1 mL of methylene chloride in a flame-dried flask under nitrogen. EtAlCl₂ (0.1 mL of 1.5 M in heptane, 0.15 mmol) was added and the reaction mixture was refluxed for 5 days. Ether and water were added. The organic layer was dried (MgSO₄) and evaporated to give 28 mg of crude 8. Flash chromatography on silica gel (99:1 pentane-ether) gave 26 mg (82%) of pure 8: NMR (CCl₄) δ 4.63 (s, 2), 3.62 (s, 3), 2.63 (br, 1), 1.1–2.4 (m, 8), 1.70 (br s, 3), 0.97 (d, 3, J = 6 Hz); ¹³C NMR (CDCl₃) δ 139.1 (C=), 108.4 (=CH₂), 50.9 (OCH₃), 44.9 (C₁), 39.2 (C₅), 33.8 (C₂*), 33.5 (C₆*), 31.2 (C₄), 29.7 (C₃), 21.1 (CH₃), 19.5 (CH₃); IR (neat) 3090, 2930, 1735, 1645, 1160, 890, 760 cm⁻¹; GC (10 ft × $^{1}/_{4}$ in, 10% Carbowax 20 M, 150 °C) $t_{\rm R}$ 13 min. Anal. Calcd for C₁₂H₂₀O₂: C, 73.47; H, 10.27. Found: C, 73.25; H, 10.30.

Methyl $(1\beta,2\alpha,5\beta)$ -2-Methyl-5-(1-methylethenyl)cyclohexanecarboxylate (9). Ester 8 (50 mg, 0.26 mmol) was dissolved in 3 mL of 0.5 M sodium methoxide in methanol and heated at reflux for 5 days. The solution was acidified with 1 M hydrochloric acid and extracted with ether. The organic layer was dried (Na_2SO_4) and evaporated to give 77 mg of a mixture of acid and ester. The crude product was treated with diazomethane at 0 °C in ether until the yellow color persisted. The solvent was removed in vacuo to give 45 mg of crude 9. Medium pressure chromatography on silica gel (99:1 pentane-ether) gave 14 mg (28%) of pure 9: NMR (CDCl₃) δ (4.63 (br s, 2), 3.67 (s, 3), 1.1–2.3 (m, 9), 1.70 (br s, 3), 0.87 (d, 3, J = 7 Hz): ¹³C NMR (CDCl₃) δ 176.3 (C=O), 149.4 (C=), 108.8 (C=CH₂), 51.3 (OCH₃ and C₁), 44.4 (C₅), 34.8 (C₂*), 34.4 (C₃*), 34.2 (C₆*), 31.2 (C₄), 20.8 (CH₃), 20.4 (CH₃); IR (neat) 3090, 2930, 1740, 1650, 890 cm⁻¹; GC (10 ft × ¹/₄ in. 10% Carbowax 20 M, 150 °C) $t_{\rm R}$ 15 min.

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Synthesis of 1,4-Dinitrocubane

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In continuation of a program on the synthesis of energetic compounds with good thermal stability and high density,¹ we undertook the synthesis and characterization of 1,4-dinitrocubane. So far as we are aware, nitrocubanes have not been reported previously. The compound nearest to this class is a nitroperchlorohomocubane, a substance of much less strain energy, prepared by Scherer and Lunt.²

Eaton and Cole first entered the cubane series in 1964 with the synthesis of the 1,4-diacid.³ This compound is



Figure 1. The approximately hexagonally packed [100] sheet of 1,4-dinitrocubane. The dashed lines define the unit cell.



available in substantial quantities; several pounds have been made at the University of Chicago over the years. An early attempt to prepare diaminocubane via Curtius rearrangement of the diacyl azide was abandoned when the first sample of the crystalline azide exploded violently. After Yamada's method using diphenylphosphoryl azide for the direct conversion of carboxylic acids to carbamates became available,⁴ the project was reopened successfully. Thus, treatment of cubane-1,4-dicarboxylic acid with diphenylphosphoryl azide and triethylamine in *tert*-butyl alcohol at reflux gives 1,4-bis[(tert-butoxycarbonyl)amino]cubane in nearly quantitative yield (Chart I). This method avoids completely the sensitive diacyl azide. Hydrolysis and decarboxylation of the carbamate gives 1,4-diaminocubane dihydrochloride, a stable, high-melting, white solid. The corresponding free amine is less stable, decomposing on standing overnight. The crude amine is thus best oxidized directly. After trying many reagents we settled on *m*-chloroperbenzoic acid, stabilized by 4,4'-thiobis(2-tert-butyl-6-methylphenol), in refluxing dichloroethane. This gave 1,4-dinitrocubane in 40% yield, sufficient for our purposes.

Differential scanning calorimetry showed that there was no obvious decomposition of dinitrocubane below its 260 °C melting point.⁵ As cubane itself decomposes slowly at temperatures above 200 °C,⁶ the strongly electron withdrawing nitro groups seem to stabilize the cubane system, althouth obviously this is a difficult comparison to quantify experimentally. Minimum energy reaction path calculations of the activation energy for ring opening in cubane and several nitro derivatives of cubane via Dewar's UMINDO/3 method indicate that nitro-group sub-

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