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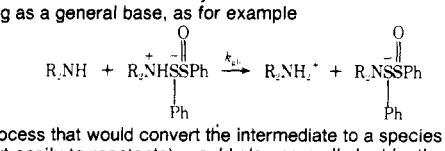

(a process that would convert the intermediate to a species that could not revert easily to reactants), would also normally be kinetically significant and would lead to the presence of a term in the rate expression dependent on $[R_2NH]$.[2] While such a term is observed in the reaction of **1** with hydrazine, it is not found in the reaction of either piperidine or morpholine with **1**.
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Rearrangements in Lewis Acid Catalyzed Diels–Alder Reactions. Route to Substituted Bicyclo[2.2.1]heptanones

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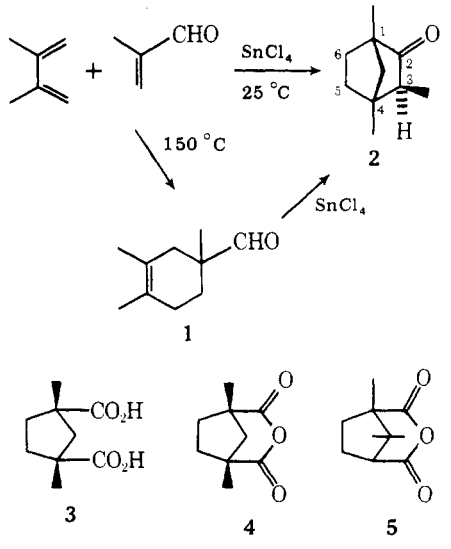
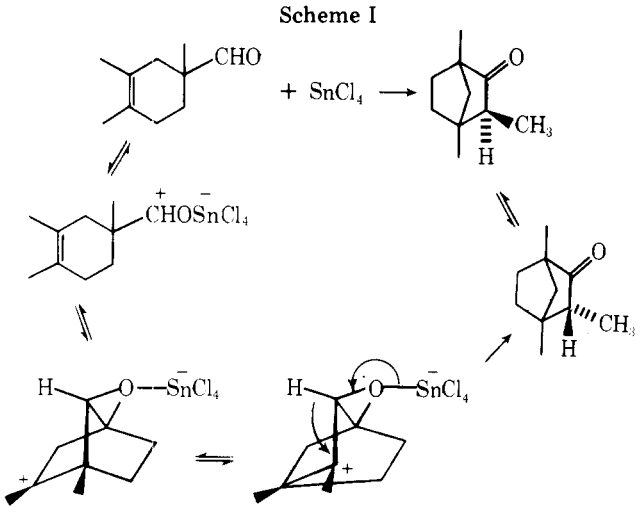
Diels–Alder adducts of 2,3-disubstituted butadienes and methacrolein were smoothly rearranged with $SnCl_4$ to substituted bicyclo[2.2.1]heptanones. The structures of the products have been examined, and the scope of this reaction has been investigated.

In connection with other work[1] we required the cyclohexenylcarboxaldehyde **1** and attempted to prepare it by $SnCl_4$-catalyzed Diels–Alder reaction of 2,3-dimethylbutadiene and methacrolein[2] at 25 °C (benzene). However an isomeric substance (58%), bp 54.5–55 °C (5.2 mm), with a pronounced camphoraceous odor was obtained. That this material probably derived from the expected adduct **1** was demonstrated by the preparation of **1** via conventional thermal cycloaddition (150 °C) and subsequent treatment with $SnCl_4$, which gave the same isomeric substance (66%). The isomer **2** contained a five-membered ketone, ν_{max} 1740 cm^{-1}, and three methyl groups, as shown by the NMR spectrum which contained two sharp methyl singlets and also a methyl doublet (J = 7 Hz) compatible with structure **2**. On base-catalyzed deuterium exchange (NaOMe, DOMe) this last methyl signal was replaced by a singlet, as the substance exchanged one proton for deuterium, being otherwise recovered unchanged. Aqueous nitric acid[3] provided a symmetrical dicarboxylic acid **3** which was readily dehydrated (acetyl chloride) to a six-membered cyclic anhydride **4**, ν_{max} 1760 and 1800 cm^{-1} (intensity ratio 3:2). These carbonyl absorptions were essentially identical with those of camphoric anhydride (**5**).[4] These data establish structure **2**, and we assign the exo configuration to the methyl group at C-3 as a result of the deu-

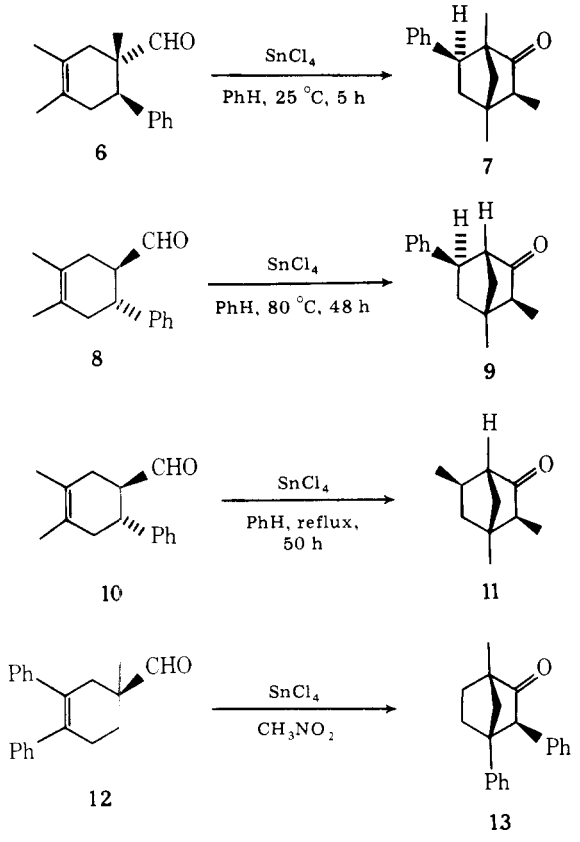


1 2 3 4 5

Scheme I

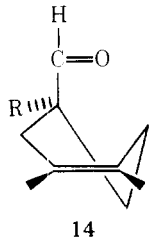


Scheme II



terium exchange experiment, which when conducted with MeOH enabled recovery of unchanged **2** under conditions in which exchange was proceeding (vide supra). We propose the mechanism of Scheme I to account for this observation.

In an attempt to establish the scope of this process, we observed preparatively useful conversions in four other cases (Scheme II) in which we assign the C-3 substituent to the exo configuration, by analogy with the above. In each case the



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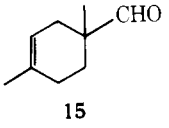

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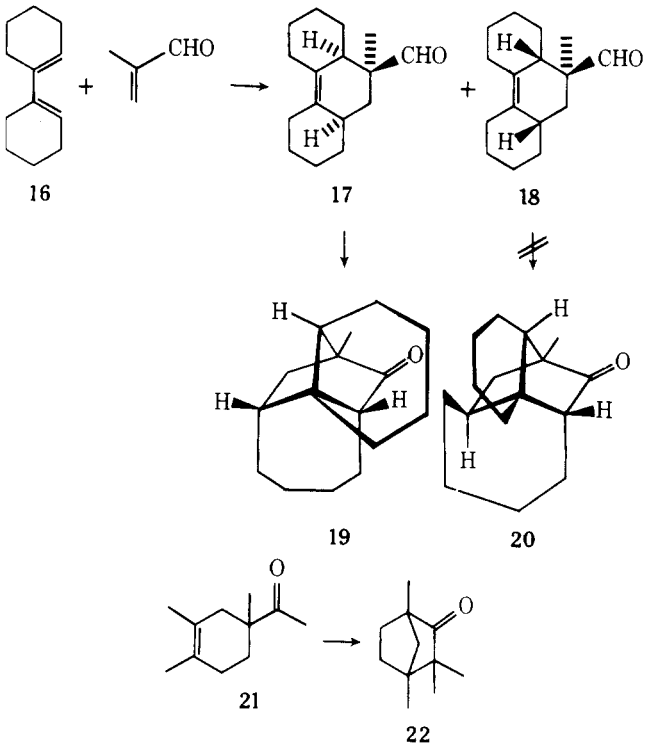
starting material was prepared by the obvious Diels–Alder reaction. Two general features of these reactions were worthy of note. Firstly, adducts **8** and **10,** lacking an α-methyl group with respect to the carboxaldehyde, required more vigorous conditions to effect rearrangement. This may result from reduced populations of the quasi-axial aldehyde, as **14,** necessary for the first ring closure. Secondly, the double bond is tetrasubstituted in all successful cases, which is consistent with the postulated ionic mechanism (Scheme I).[5] Thus, the adduct of methacrolein and isoprene, presumably **15,**[6] did not rearrange in nitromethane containing $SnCl_4$.

The thermal addition of diene **16** to methacrolein gave a pair of isomers in a 9:1 ratio (NMR).[7] Reaction of this mixture with $SnCl_4$ in benzene caused rearrangement only of the major



isomer, with the minor constituent being unaffected. On the basis of our proposed mechanism (Scheme I), this behavior would be anticipated since only adduct **17,** expected from the endo rule, could rearrange to a relatively strain-free ketone **19.** The other isomer, exo adduct **18,** would yield the ketone **20,** containing the highly strained trans-oriented bridge between the 3 and 5 positions of the bicyclo[2.2.1]heptanone.

In order to determine whether these rearrangements were restricted to aldehyde adducts, we prepared ketone **21**[9] and subjected it to a variety of reaction conditions. Little or no change occurred with $SnCl_4$/benzene (80 °C) and $AlCl_3$/mesitylene (168 °C); however, $SnCl_4$/nitromethane (101 °C) gave a moderate amount of rearrangement and with $AlCl_3$/decalin (190 °C) a 1:1 mixture of starting material and product ketone **22** was observed. More efficient reaction was achieved with $AlCl_3$ in refluxing heptane or xylene, but even so small amounts of starting material were always observed.[10]

Experimental Section[11]

General Preparation of Diels–Alder Adducts. A solution of the appropriate diene (0.10 mol), α,β-unsaturated aldehyde (0.10 mol), and 0.1–0.25 g of hydroquinone in 50 mL of solvent was heated under N_2 in a rocking autoclave. After being cooled, the solvent was removed and the residue distilled.

1,3,4-Trimethyl-3-cyclohexenyl-1-carboxaldehyde (1). $CH_2{=}C(CH_3)CHO$ and $CH_2{=}C(CH_3)C(CH_3){=}CH_2$ gave (150 °C, 5 h, PhH) 9.85 g (65%) of **1** as a pale yellow liquid: bp 66–70 °C (5.4–5.6 mm) [lit.[12] bp 64–67 °C (5 mm)]; IR (neat) 1720 (C=O), 2700, 2900 (CHO) cm^{-1}; NMR (90 MHz, CCl_4) δ 1.01 (s, 3 H, CH_3), 1.63 (broad

s, 6 H, $=CCH_3$), 1.1–2.5 (m, 6 H, aliphatic CH), 9.40 (s, 1 H, CHO); MS *m/e* (rel intensity) 152 (M^+, 22), 137 (M − CH_3, 20), 123 (M − CHO, 51), 109 (54), 91 (25), 81 (50), 67 (52), 55 (30), 43 (75), 41 (78), 39 (67), 29 (CHO^+, 100).

6-Phenyl-1,3,4-trimethyl-3-cyclohexenyl-1-carboxaldehyde (6). PhCH=$C(CH_3)$CHO (Aldrich) and $CH_2=C(CH_3)C(CH_3)=CH_2$ gave (200 °C, 12 h, PhMe) 17.895 g (78%) of crude dark brown liquid. Fractionation separated 10.52 g (72%) of unreacted α-methylcinnamaldehyde, bp 63–94 °C (0.40–0.45 mm), and then 2.786 g (12%) of **6** as a yellow liquid: bp 96–109 °C (0.15–0.19 mm); IR (neat) 1720 (C=O), 2700 (CHO), 1595, 1492, 715 (Ph–) cm^{-1}; NMR (90 MHz, CCl_4) δ 0.82 (s, 3 H, CH_3), 1.68 (broad s, 6 H, $=CCH_3$), 1.5–2.6 (m, 4 H, $=CCH_2$), 3.13 (t, *J* = 6 Hz, 1 H, PhC**H**CH_2), 7.14 (m, 5 H, ArH), 9.33 (s, 1 H, CHO, apparently a single isomer); MS *m/e* (rel intensity) 228 (M^+, 22), 213 (M − CH_3, 6), 199 (M − CHO, 25), 186 (69), 143 (68), 124 (60), 109 (52), 108 (69), 105 (54), 91 (100), 77 (30), 67 (22), 51 (20), 43 (36), 41 (54), 39 (39).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.19; H, 8.86.

3,4-Dimethyl-6-phenyl-3-cyclohexenyl-1-carboxaldehyde (8). Freshly distilled *trans*-PhCH=CHCHO (0.10 mol) and $CH_2=C(CH_3)C(CH_3)=CH_2$ (0.15 mol) gave (200 °C, 12 h, PhMe) 19.026 g (89%) of **8** as a viscous pale yellow liquid: bp 103–118.5 °C (0.30–0.35 mm) [lit.[13] bp 164.5–166 °C (3.5 mm)]; IR (neat) 1720 (C=O), 2730, 2840 (CHO), 1600, 1495, 775, 715 (Ph–) cm^{-1}; NMR (CCl_4) δ 1.65 (broad s, 6 H, $=CCH_3$), 1.8–3.5 (m, 6 H, aliphatic CH), 7.13 (s, 5 H, ArH), 9.23 and 9.40 (each a doublet, *J* = 2 Hz, 1 H total, CHO, ca. 4:1 ratio of **8** and cis isomer, respectively); MS *m/e* (rel intensity) 214 (M^+, 35), 199 (M − CH_3, 5), 196 (M − H_2O, 5), 183 (76), 172 (38), 131 (37), 115 (31), 95 (44), 94 (66), 91 (100), 82 (41), 77 (39), 67 (68), 51 (28), 41 (46), 39 (39).

3,4,6-Trimethyl-3-cyclohexenyl-1-carboxaldehyde (10). *trans*-CH_3CH=CHCHO and $CH_2=C(CH_3)C(CH_3)=CH_2$ gave (180 °C, 12 h, PhH) 5.981 g (39%) of **10** as a pale yellow liquid: bp 72.5–77.5 °C (5.3 mm) [lit.[14] bp 90–93 °C (15 mm)]; IR (neat) 1720 (C=O), 2710, 2840 (CHO) cm^{-1}; NMR (90 MHz, CCl_4) δ 1.01 (broadened d, *J* = 5.5 Hz, 3 H, C**H**$_3$CH), 1.61, 1.63 (overlapping s, 6 H, $=CCH_3$), 1.5–2.5 (m, 6 H, aliphatic CH), 9.51 (d, *J* = 2 Hz, 1 H, CHO; small doublet at 9.59 due to ≤5% of cis isomer); MS *m/e* (rel intensity) 152 (M^+, 17), 137 (M − CH_3, 6), 134 (M − H_2O, 2), 121 (44), 107 (29), 91 (25), 81 (45), 67 (65), 55 (46), 43 (62), 41 (100), 39 (74).

3,4-Diphenyl-1-methyl-3-cyclohexenyl-1-carboxaldehyde (12). Attempted dehydration of 2,3-diphenyl-2,3-butanediol[14,15] according to Alder and Haydn[16] gave primarily pinacol rearrangement product (3,3-diphenyl-2-butanone) and only small amounts of 2,3-diphenyl-1,3-butadiene. In one attempt, the crude product from 30.12 g (0.125 mol) of diol was chromatographed on ~600 g of Merck silica gel 60 (70–230 mesh), eluting rapidly with 3:1 hexane/PhH to separate early fractions containing 3.366 g (13%) of slightly impure diene as a low melting yellow solid: IR (neat) 1600, 920 (C=CH_2), 1575, 1495, 795, 720 (Ph–) cm^{-1}; NMR (CCl_4) δ 5.22 (d, *J* = 2 Hz, 2 H, C=CH), 5.42 (d, *J* = 2 Hz, 2 H, C=CH), 6.95–7.40 (m, 10 H, ArH). After refluxing 2.909 g (14.1 mmol) of this diene and 0.1 g of hydroquinone in $CH_2=C(CH_3)$CHO (0.141 mol) under N_2 (24 h) failed to cause complete consumption of diene, the mixture was heated in a rocking autoclave (15 h, 170 °C). The resulting 11.108 g of dark brown liquid was chromatographed on ~400 g of Merck silica gel 60 (70–230 mesh), eluting with CH_2Cl_2 to separate 1.901 g (49%) of **12** as a yellow liquid that solidified upon standing. Attempted recrystallization from a variety of solvents was unsuccessful. Distillation gave 1.468 g (38%) of purified **12**: bp 145–155 °C (0.35 mm); IR (melt) 1720 (C=O), 2710 (CHO), 3060, 3025 (ArH), 1600, 1495, 770, 710 (Ph–) cm^{-1}; NMR (CCl_4) δ 1.15 (s, 3 H, CH_3), 1.2–3.2 (m, 6 H, aliphatic CH), 6.97 (m, 10 H, ArH), 9.52 (s, 1 H, CHO); MS *m/e* (rel intensity) 276 (M^+, 32), 248 (M − CO, 23), 247 (M − CHO, 20), 205 (15), 172 (26), 129 (37), 115 (40), 104 (40), 91 (100), 77 (30), 43 (23).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.10; H, 7.35.

1,2,3,4,5,6,7,8,8a,9,10,10a-Dodecahydro-9-methyl-9-phenanthrenecarboxaldehyde (17 and 18). Diene **16**[17] (0.10 mol) and $CH_2=C(CH_3)$CHO (0.10 mol) gave (12 h, 180 °C, PhH) 12.628 g (54%) of a mixture of the isomers: bp 101–116 °C (0.06 mm) [lit.[7] bp 135–140 °C (0.5 mm)]; IR (neat) 1725 (C=O), 2710 (CHO), 2940, 2870, 1515, 1460, 1380, 1260, 930, 880 cm^{-1}; NMR (CCl_4) δ 0.70–2.3 (broad multiplet, 21 H, aliphatic CH, including a small CH_3 singlet at 0.87 and a large CH_3 singlet at 1.05), 2.65, 2.83 (broad doublet, 2 H, allylic methine), 9.16 and 9.33 (singlets, 1 H, total, CHO, ca. 1:9 ratio of **18**/**17**):[7] MS *m/e* (rel intensity) 232 (M^+, 15), 203 (M − CHO, 42), 189 (16), 175 (10), 162 (74), 147 (21), 133 (28), 119 (28), 105 (46), 94 (61), 91 (84), 81 (61), 79 (89), 77 (51), 67 (63), 55 (63), 43 (29), 41 (100), 39 (42).

1,3-*exo*-4-Trimethylbicyclo[2.2.1]heptan-2-one (2). Directly from Methacrolein and Diene. Following the procedure of Berkowitz and Grenetz,[2] an ice-cold solution of 7.009 g (0.10 mol) of $CH_2=C(CH_3)$CHO in 50 mL of PhH under N_2 was treated with 3.621 g (13.9 mmol) of $SnCl_4$ added dropwise over 2–3 min (mild exotherm, temperature kept below 10 °C). After cooling again to ice temperature, a solution of 8.215 g (0.10 mol) of $CH_2=C(CH_3)C(CH_3)=CH_2$ in 15 mL of PhH was added dropwise over ~10 min, maintaining the temperature at 10–20 °C. The resulting yellow solution was stirred for an additional 15 min with ice bath cooling and then allowed to warm to room temperature and stirred for another 5 h. The clear dark brown solution was then poured into ice water, and the organic phase was separated and washed successively with portions of 5% HCl, saturated $NaHCO_3$, and brine. Drying and concentration gave a golden yellow liquid which was distilled to separate 8.770 g (58%) of ketone **2** as a water-white liquid: bp 54.5–55 °C (5.2 mm); IR (neat) 1740 (C=O), 2970, 2880, 1460, 1380, 967 cm^{-1}; NMR (90 MHz, CCl_4) δ 0.97 (d, *J* = 7 Hz, 3 H, C**H**$_3$CHC=O), 1.10 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3), 1.2–2.0 (m, 7 H, aliphatic CH, including a partially overlapped quartet at 1.83, *J* = 7 Hz, due to CHC=O); MS *m/e* (rel intensity) 152 (M^+, 17), 137 (M − CH_3, 3), 123 (1), 109 (14), 95 (100), 94 (34), 82 (18), 81 (23), 69 (21), 67 (26), 55 (16), 53 (17), 41 (48), 39 (32).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.64; H, 10.72.

Attempted Epimerization of 2 and Formation of 2-d_1. A solution of NaOMe, prepared from 23 mg (1.0 mmol) of Na, and 761 mg (5.0 mmol) of **2** in 25 mL of MeOH, was stirred at room temperature under N_2. After 48 h the solution was partitioned between brine and CH_2Cl_2 and the combined organic layers were washed with brine, dried, and concentrated to leave 714 mg (94%) of pale yellow liquid, the IR, NMR (90 MHz), and mass spectra of which were identical with those of **2**. Treatment of **2** in the same manner with NaOMe in MeOD for 48 h gave, after the addition of D_2O, extraction with CH_2Cl_2, drying, and concentration, 658 mg (86-) of **2**-d_1 as a pale yellow liquid: IR (neat) 1740 (C=O), 2970, 2880, 1460, 1380, 1015 cm^{-1}, fingerprint region (600–1400 cm^{-1}) distinctly different from that in the spectrum of **2**; NMR (90 MHz, CCl_4) δ 0.94 (broadened singlet, 3 H, CH_3CDC=O), 1.08 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.2–2.0 (m, 6 H, aliphatic CH, *no* quartet at 1.83 due to CHC=O); MS *m/e* (rel intensity) 153 (M^+, 10), 138 (M − CH_3, 2), 124 (<1), 110 (13), 95 (100), 94 (36), 82 (22), 81 (20), 70 (22), 67 (20), 55 (15), 53 (16), 42 (28), 41 (51), 39 (35).

Degradation of 2 to *cis*-1,3-Dimethylcyclopentane-1,3-dicarboxylic Acid (3). A heterogeneous mixture of 4.120 g (27.1 mmol) of **2** and 60 mL of 7.9 M HNO_3 was heated at reflux[3] (bath temperature 110–115 °C) for 3 h to produce a homogeneous solution from which a solid separated upon cooling. After the reaction mixture was made basic (pH 10) with 10% NaOH and washed with Et_2O, the resulting aqueous solution was acidified (≤pH 1) with concentrated HCl and extracted with Et_2O. The combined extracts from the acidic mixture were washed with brine, dried, and concentrated to give 4.152 g (82%) of **3** as a pale yellow solid, mp 100–107 °C. Recrystallation from H_2O gave analytically pure **3** as a white powder: mp 116.5–118 °C; IR ($CHCl_3$) 2350–3600 (carboxyl OH), 1702 (C=O), 1470, 1410, 1310, 1230, 1095, 1055, 940 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.38 (s, 6 H, CH_3), 1.5–1.9 (m, 3 H, aliphatic CH), 2.1–2.6 (m, 2 H, aliphatic CH), 3.0 (d, *J* = 14 Hz, 1 H, proton at C-2 syn to the carboxyls, one-half of an AB quartet), 11.74 (s, 2 H, carboxyl protons); MS *m/e* (rel intensity) 187 [M + 1, 1 (no M^+)], 169 (M + 1 − H_2O, 2), 142 (M + 1 − CO_2H, 8), 141 (M − CO_2H, 7), 123 (8), 95 (100), 87 (15), 81 (17), 67 (13), 56 (17), 55 (18), 45 (38), 43 (35), 41 (32), 39 (29).

Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.22; H, 7.80.

Conversion of 3 into Anhydride 4. A suspension of 372 mg (2.0 mmol) of **3** in 475 mg (6.0 mmol) of acetyl chloride was refluxed for 1 h with protection from atmospheric moisture and then cooled in an ice bath. The resulting crystals were filtered, washed with hexane, and dried to give 252 mg (75%) of **4** as fine needles, mp 94.5–99 °C. An analytical sample was recrystallized from CCl_4 to give a white powder: mp 99.5–100 °C; IR ($CHCl_3$) 1760 and 1800 (3:2 ratio, anhydride C=O), 1015, 1003 (C–O), 1453, 1390, 1160 cm^{-1}; NMR ($CDCl_3$) δ 1.43 (s, 6 H, CH_3), 1.5–2.4 (m, 6 H, aliphatic CH); MS *m/e* (rel intensity) 169 [M + 1, <1, (no M^+)], 141 (M + 1 − CO, < 1), 124 (6), 109 (2), 96 (23), 81 (100), 69 (42), 53 (25), 41 (74), 39 (64); ^{13}C NMR ($CDCl_3$) 20.18, 35.44, 45.31, 48.69, 172.73 ppm.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.11; H, 7.19.

Similar treatment of 4.005 g (20.0 mmol) of *d*-camphoric acid with 7.006 g (90.0 mmol) of AcCl at reflux for 1.25 h gave 3.530 g (97%) of

5 as white needles, mp 222–223.5 °C (lit.[4b] mp 223.5–224.5 °C). The IR spectrum of this material in $CHCl_3$ showed anhydride C=O at 1760 and 1805 cm^{-1} (3:2 ratio).

$SnCl_4$-Catalyzed Rearrangement of Diels–Alder Adducts. General Procedure. A solution of the 3-cyclohexenyl-1-carboxaldehyde in PhH or CH_3NO_2 under N_2 was cooled in an ice bath, and $SnCl_4$ was added dropwise via a syringe. After being stirred at ice-bath temperature for 0.5 h, the reaction solution was warmed and stirred at room temperature or refluxed for an appropriate period of time. The resulting usually dark solution was then partitioned between ice-cold saturated aqueous NH_4Cl and PhH (or Et_2O when CH_3NO_2 was the reaction solvent). The combined extracts were washed with successive portions of 5% HCl, saturated aqueous $NaHCO_3$ (or 5% NaOH to remove CH_3NO_2), and brine. Drying and concentration gave crude material that was purified by distillation or recrystallization.

Rearrangement of 1 to 2. Treatment of 1.522 g (10.0 mmol) of 1 in 5 mL of PhH with 365 mg (1.4 mmol) of $SnCl_4$ (5 h, room temperature) gave 1.004 g (66%) of **2**, bp 57–58.5 °C (5.7 mm).

6-Phenyl-1,3,4-trimethylbicyclo[2.2.1]heptan-2-one (7). Treatment of 1.412 g (6.2 mmol) of **6** in 2.5 mL of PhH with 182 mg (0.7 mmol) of $SnCl_4$ (5 h, room temperature) gave 1.298 g (92%) of **7** as a viscous pale yellow liquid, bp 101–104 °C (0.20–0.25 mm), that solidified upon standing for several months. Recrystallization from hexane gave large white prisms: mp 45.5–47 °C; IR (neat) 1738 (C=O), 3030, 1600, 1495, 767, 719 (Ph–), 1455, 1380, 1317, 973 cm^{-1}; NMR (90 MHz, CCl_4) δ 0.63 (s, 3 H, CH_3), 1.07 (d, J = 7 Hz, 3 H, $CH_3CHC{=}O$), 1.28 (s, 3 H, CH_3), 1.5–2.4 (m, 5 H, aliphatic CH), 2.5–2.75 (m, 1 H, CHAr), 7.20 (broadened singlet, 5 H, ArH); MS *m/e* (rel intensity) 228 (M^+, 35), 213 (M − CH_3, 2), 185 (2), 171 (91), 170 (100), 155 (15), 143 (29), 131 (36), 115 (32), 91 (93), 77 (40), 41 (91), 39 (41).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.05; H, 9.00.

3,4-Dimethyl-6-phenylbicyclo[2.2.1]heptan-2-one (9). Treatment of 2.143 g (10.0 mmol) of **8** in 10 mL of PhH with 365 mg (1.4 mmol) of $SnCl_4$ and stirring at room temperature for 48 h gave, after workup, 2.156 g of a mixture of roughly equal amounts of **8** and **9**. Refluxing this mixture in 10 mL of PhH (48 h) with another 365 mg of $SnCl_4$, however, effected essentially complete conversion of **8** to **9**, giving 2.165 g of crude liquid product. Distillation gave 1.532 g (72%) of **9** as a yellow liquid: bp 118–123 °C (0.6 mm); IR (neat) 1740 (C=O), 3030, 1600, 1500, 778, 713 (Ph–), 1360, 1028 cm^{-1}; NMR (90 MHz, CCl_4) δ 0.97 and 1.01 (each a doublet, J = 7 Hz, 3 H total, $CH_3CHC{=}O$, ca. 16:84 ratio of *endo/exo*-phenyl-**9** respectively), 1.22 (s, 3 H, CH_3), 1.3–2.3 (m, 5 H, aliphatic CH), 2.63 (broad singlet, ~0.85 H, bridgehead CH of *exo*-phenyl-**9**), 2.93 (m, 1 H, ArCH), 7.19 (s, 5 H, ArH); MS *m/e* (rel intensity) 214 (M^+, 51), 199 (M − CH_3, 3); 185 (7), 157 (63), 156 (100), 143 (25), 129 (36), 117 (65), 115 (50), 104 (31), 95 (26), 91 (62), 77 (32), 67 (30), 55 (22), 53 (20), 51 (26), 41 (51), 39 (34).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.93; H, 8.28.

3,4,6-Trimethylbicyclo[2.2.1]heptan-2-one (11). Treatment of 761 mg (5.0 mmol) of **10** in 5 mL of PhH with 267 mg (1.0 mmol) of $SnCl_4$ (reflux, 50 h) gave, after workup, 693 mg (91%) of dark brown liquid. Distillation gave 405 mg (53%) of **11** as a clear liquid with a pronounced camphoraceous odor: bp 67–68 °C (6.0 mm); IR (neat) 1740 (C=O), 1460, 1380 cm^{-1}; NMR (90 MHz, CCl_4) δ 0.92 (d, J = 7 Hz, 3 H, CH_3), 1.07 (d, J = 7 Hz, 3 H, CH_3), 1.19 (s, 3 H, bridgehead CH_3), 1.40 (broadened doublet, J = 10 Hz, 1 H), 1.5–2.5 (m, 6 H, aliphatic CH, including a broadened singlet at 2.16, ~1 H, due to the bridgehead CH); MS *m/e* (rel intensity) 152 (M^+, 12), 137 (M − CH_3, 3), 123 (5), 109 (13), 95 (83), 94 (81), 81 (41), 69 (62), 67 (48), 55 (51), 43 (31), 41 (100), 39 (50).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.67; H, 10.40.

3,4-Diphenyl-1-methylbicyclo[2.2.1]heptan-2-one (13). Treatment of 138 mg (0.5 mmol) of **12** in 5 mL of PhH with 26 mg (0.1 mmol) of $SnCl_4$ (24 at room temperature, and then 24 h at reflux) failed to produce any observable rearrangement. The recovered **12** was therefore refluxed in 5 mL of $MeNO_2$ with 26 mg of $SnCl_4$ (24 h) to yield, after workup, 143 mg of dark brown liquid that solidified upon standing. This was recrystallized from hexane (decolorized with carbon) to give 90.4 mg (66%) of **13** as a pale yellow-orange solid, mp 109.5–113 °C. Further recrystallization (hexane) gave an analytical sample of pale yellow crystals: mp 113.5–114.5°C; IR (CCl_4) 1742 (C=O), 3030, 1600, 1500, 710 (Ph–), 1450, 1330, 1070 cm^{-1}; NMR (90 MHz, CCl_4) δ 1.28 (s, 3 H, CH_3), 1.4–2.5 (m, 6 H, aliphatic CH, including a broadened doublet, J = 10 Hz, of ~1 H at 2.22), 3.39 (broadened singlet, 1 H, $ArCHC{=}O$), 6.57 (m, 2 H, ortho ArH of C-4 phenyl), 6.96 (m, 2 H, ortho ArH of C-3 phenyl), 7.12 (m, 6 H, ArH); MS *m/e* (rel intensity) 276 (M^+, 27), 261 (M − CH_3, 14), 157 (100), 143 (33), 129 (23), 115 (42), 91 (65), 77 (25), 65 (19), 55 (16), 51 (25), 41 (23), 39 (27).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29.

Rearrangement of 17/18. Treatment of 2.324 g (10.0 mmol) of the **17/18** mixture prepared above in 20 mL of PhH with 534 mg (2.05 mmol) of $SnCl_4$ (20 h, room temperature) gave 2.287 g of partially rearranged material containing ca. 50% total aldehyde and 50% rearrangement product (by NMR). Only the more abundant isomer appeared to be undergoing rearrangement, however. Further treatment with 534 mg of $SnCl_4$ in 25 mL of PhH (5 h, reflux) gave, after workup, 2.279 g (98%) of a tea-colored liquid which contained almost none of the more abundant aldehyde isomer. Distillation gave 1.614 g (69%) of pale yellow liquid, bp 112.5–116.5 °C (0.40 mm), which was shown by NMR to contain ca. 15% of the less abundant aldehyde isomer (**18**[6]) and 85% of the rearrangement product **19**: IR (neat) 1737 cm^{-1} (C=O); NMR (CCl_4) δ 0.6–2.6 (broad multiplet, 24 H, aliphatic CH, including a small CH_3 singlet at 0.92 due to unreacted **18** and a large CH_3 singlet at 1.00 due to **19**), 917 (s, ~0.15 H, CHO of unreacted **18**); MS *m/e* (rel intensity) 232 (M^+, 22), 203 (17), 189 (14), 174 (31), 161 (27), 150 (100), 135 (23), 119 (20), 105 (39), 93 (43), 91 (76), 81 (42), 79 (76), 77 (49), 67 (67), 55 (70), 42 (71), 41 (96), 39 (52).

$SnCl_4$-Catalyzed Diels–Alder Reaction between Isoprene and Methacrolein. A solution of 7.009 g (0.10 mol) of methacrolein and 3.621 g (13.9 mmol) of $SnCl_4$ in 50 mL of PhH was treated with 6.812 g (0.10 mmol) of isoprene in 15 mL of PhH. After 5 h of stirring at room temperature, workup gave 17.80 g of crude yellow-green liquid. Distillation gave 2.757 g (20%) of Diels–Alder adduct that appeared to be a single compound, presumably **15**,[6] bp 52.5–57 °C (5.6 mm) [lit.[18] bp 42 °C (5 mm)]. No rearrangement product was observed. IR (near) 1723 (C=O), 2715 (CHO), 3020 (=CH), 2975, 2930, 1450, 1380, 1072, 925, 780 cm^{-1}; NMR (CCl_4) δ 1.00 (s, 3 H, CH_3), 0.8–2.8 [m, 9 H, aliphatic CH, including a broad singlet at 1.62 (allylic CH_3)], 5.28 (m, 1 H, =CH), 9.28 (s, 1 H, CHO); MS *m/e* (rel intensity) 139 (M + 1, 69.9), 138 (M^+, 100), 123 (M − CH_3, 28), 109 (M − CHO, 55), 95 (78), 81 (29), 67 (66), 55 (32), 43 (87), 41 (48), 39 (35).

Attempted Rearrangement of 15. Treatment of 691 mg (5.0 mmol) of **15** in 5 mL of $MeNO_2$ with 200 mg (0.77 mmol) of $SnCl_4$ (5 h, room temperature) gave, after workup, 571 mg (83%) of pale orange liquid. IR and NMR analyses failed to show any evidence of rearrangement.

Attempted Lewis Acid Catalyzed Rearrangement of 21. A. With $SnCl_4$. Treatment of 166 mg (1.0 mmol) of **21**[9] and 267 mg (1.0 mmol) of $SnCl_4$ in 5 mL of PhH (29 h, room temperature) gave 142 mg (86%) of pale golden yellow liquid whose IR spectrum was identical with that of the starting material. This material (0.93 mmol) was therefore refluxed with 67 mg (0.26 mmol) of $SnCl_4$ in 5 mL of $MeNO_2$ (48 h) to give 113 mg (80%) of dark brown liquid. IR analysis showed a second carbonyl absorption at 1738 cm^{-1}, as would be expected for rearrangement product **22**, of approximately one-half the intensity of the original carbonyl at 1704 cm^{-1} due to **21**.

B. With $AlCl_3$. A suspension of ~27 mg (0.2 mmol) of $AlCl_3$ in a solution of 166 mg (1.0 mmol) of **21** in 5 mL of $MeNO_2$ was refluxed under N_2 for 48 h and then poured into a mixture of 5 mL of 10% HCl and an equal volume of ice. The mixture was extracted with Et_2O (3 × 10 mL), and the combined ether extracts were washed successively with 5% NaOH (2 × 10 mL) and brine (20 mL), dried, and concentrated to leave 161 mg (97%) of brown liquid. IR and NMR analyses showed that essentially no rearrangement had taken place. This material was therefore refluxed with 95 mg (0.71 mmol) of $AlCl_3$ in 5 mL of $pHCH_3$ for 14 h and then poured into a mixture of 5 mL of 10% HCl and an equal volume of ice. Separation of the organic layer and extraction of the aqueous layer with PhH (2 × 10 mL) followed by washing of the combined organic layers with brine (15 mL), drying, and concentration gave 115 mg (69%) of golden brown liquid with a pronounced camphor-like odor. IR and NMR analyses showed this to be largely bicycloheptanone **22** containing a small amount of **21**.

Other reactions were carried out by refluxing a mixture of 166 mg (1.0 mmol) of **21** with ~27 mg (0.2 mmol) of $AlCl_3$ in 5 mL of the specified solvent under N_2 for the specified time. The reaction was then worked up by quenching into a mixture of 5 mL of 10% HCl and an equal volume of ice, extracting with CH_2Cl_2 (3 × 10 mL), washing with brine (10 mL), drying, and removing the solvents. In 1,3,5-$Me_3C_6H_3$ (24 h) virtually no rearrangement was observed as shown by IR. Refluxing for 14 h in decalin gave a mixture of decalin and product after evaporation of CH_2Cl_2. The decalin was removed by a short filtration chromatography on silica gel eluting the decalin with hexane. Elution with MeOH then gave 106 mg (64%) of golden yellow liquid which was shown by IR to be a mixture of approximatley equal

amounts of **21** and **22**. In heptane (24 h) 168 mg (101%) of yellow-green liquid was isolated that was found to be mostly **22** with a small amount of **21** remaining. Refluxing in xylene (24 h) gave 103 mg (62%) of yellow liquid that was determined to be a similar mixture consisting mostly of **22** with a minor amount of **21**.

A purified sample of ketone **22** was obtained by preparative GLC, collecting from a 10 ft × 0.25 in. 10% Se-30 on AW-DMDCS Chromosorb P column at 150 °C: IR (CCl_4) 1738 (C=O), 1460, 1380, 1030 cm^{-1}; NMR (MHz, CCl_4) δ 0.92 (s, 6 H, CH_3), 1.08 (s, 6 H, CH_3), 1.2–2.0 (m, 6 H, aliphatic CH); MS *m/e* (rel intensity) 166 (M^+, 8.3), 151 ($M - CH_3$, 1.6), 148 (1.5), 133 (7.7), 123 (7.9), 95 (100), 83 (51), 82 (38), 81 (34), 67 (17), 55 (45), 53 (17), 43 (15), 41 (73), 39 (43); ^{13}C NMR ($CDCl_3$) 14.79, 16.35, 19.47, 20.96, 24.21 (weak), 32.98, 33.24, 47.39, 49.60, 54.54, 223.58 ppm.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.81; H, 10.83.

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Registry No.—1, 40702-26-9; **2**, 69461-51-4; **2**-d_1, 69461-52-5; **3**, 69461-53-6; **4**, 69461-54-7; **5**, 595-29-9; **6**, 69461-55-8; **7**, 69461-56-9; *trans*-**8**, 39163-52-5; *cis*-**8**, 69461-57-0; *endo*-**9**, 69461-58-1; *exo*-**9**, 69483-65-4; *trans*-**10**, 39163-50-3; *cis*-**10**, 69461-59-2; **11**, 69461-60-5; **12**, 69461-61-6; **13**, 69461-62-7; **15**, 993-44-8; **16**, 1128-65-0; **17**, 21449-49-0; **18**, 21390-38-5; **19**, 69461-63-8; **21**, 69461-64-9; **22**, 69461-65-0; methacrolein, 78-85-3; 2,3-dimethyl-1,3-butadiene, 513-81-5; α-methylcinnamaldehyde, 101-39-3; *trans*-3-phenyl-2-propanol, 14371-10-9; *trans*-2-butenal, 123-73-9; 2,3-diphenyl-2,3-butanediol, 1636-34-6; 2,3-diphenyl-1,3-butadiene, 2548-47-2; *d*-camphoric acid, 124-83-4.

References and Notes

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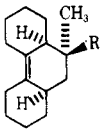
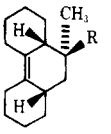
(5) A referee suggested that a nonstereospecific cyclization of the aldehyde would eliminate the need for subsequent epimerization α to the ketone function. This possibility is not excluded by our data.

(6) For examples of similar Diels–Alder reactions in which Lewis acid catalysis favors a 1,4-disubstitution product such as **15** over a 1,3-disubstitution product, see (a) T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 1121 (1966); (b) T. Kojima and T. Inukai, *ibid.*, **35**, 1342 (1970); **36**, 924 (1971); (c) W. Kreiser, W. Haumesser, and A. F. Thomas, *Helv. Chim. Acta*, **57**, 164 (1974).

(7) Christol et al. also report obtaining a mixture of two isomers under similar conditions (160 °C, 8 h in PhMe) in a ratio of 80:20.[8a] Although their mixture has physical and spectral properties very similar to those of the Diels–Alder product which we prepared, they assign structure **18** to the *major* isomer and **17** to the *minor* isomer, in opposition to our structural assignments. Their stereochemical proof relies on a series of correlations leading through the alcohols Ia and Ib back to the acids IIa and IIb, whose structures were determined by lactonization experiments.[8a] Unless an inadvertant transposition of the isomers took place at some stage of this experimental work (particularly possible with alcohols Ia and Ib, whose reported melting points and spectral data are very similar), the difference in structural assignments is not readily explained on the basis of the available data.



Ia, R = CH_2OH
IIa, R = CO_2H



Ib, R = CH_2OH
IIb, R = CO_2H

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(11) Reactions involving air- or moisture-sensitive substances were conducted in a static, slightly positive-pressure nitrogen atmosphere. Reactions involving aqueous workup usually employed a final wash of the combined organic extracts with a saturated aqueous NaCl solution (brine). Drying was then carried out over anhydrous $MgSO_4$ unless otherwise stated, and the solvent was removed at ≤40 °C on a rotary evaporator at water aspirator pressure. Analytical thin-layer chromatography was performed on Merck precoated silica gel 60F-254 TLC plates with visualization under a UV lamp or by I_2 vapor. Melting points were taken on a Thomas-Hoover apparatus in open capillary tubes, and melting points and boiling points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 700 infrared spectrophotometer and were calibrated against polystyrene. Proton NMR spectra were obtained at 60 MHz, unless otherwise stated, on a Varian Associates T-60 or a Perkin-Elmer R-20B or R-24B spectrometer; 90-MHz spectra were recorded on a Perkin-Elmer R-22 spectrometer. Chemical shifts are reported in δ values, parts per million (ppm) relative to Me_4Si as an internal standard. The notations given in parentheses are the multiplicity of the signal (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), the coupling constants if applicable, the number of protons, and the assignment, if made. Mass spectra were determined on a Varian MAT-44 quadrupole mass spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX60Q FT-NMR instrument at 15 MHz with complete proton decoupling.

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