propylamide (2.5 equiv in THF) gave none of the desired rearrangement. Even when the resulting dark-colored hydrolysis products were heated with alcoholic KOH solution (to convert any $ArCHSiMe_3OH$ into $ArCH_2OH$), no *p*-nitrobenzyl alcohol could be detected. The only identifiable product was *p*-nitrophenol.

Heating **3c** (4 mmol) in 10 mL of anhydrous THF with 10 mmol of potassium *tert*-butoxide for 8 h and hydrolysis produced *p*-nitroanisole (35%).

Likewise, letting a suspension of 5 mmol of **3c**, 50 mmol of anhydrous KF, and 2.5 mmol of benzyltriethylammonium chloride in 25 mL of acetonitrile reflux for 24 h and then hydrolyzing gave only a 1:3 mixture of *p*-nitroanisole and **3c**.

b. *p*-Methoxyphenyl Derivative 3b. A solution of 840 mg (4 mmol) of **3b** in 30 mL of anhydrous THF at −78 °C was treated with 10 mmol of *n*-butyllithium in hexane. After 0.5 h at −78 °C the mixture was warmed up to 25 °C over 1 h and stirred a further 16 h. The crude product (309 mg) obtained after the usual hydrolytic workup consisted of over 60% of *p*-methoxyphenol, 10% of **3b**, and 30% of a mixture of 2-ethyl-4-methoxyphenol (**20**) and 4-methoxy-2-[2-(trimethylsilyl)ethyl]phenol (**21**). The latter two components were separated from each other by GLC and the IR spectrum of each displayed a broad band at 3350 cm^{-1}. **20**: NMR ($CDCl_3$) δ 1.12 (t, 3 H, J = 7 Hz), 2.74 (q, 2 H, J = 7 Hz), 3.96 (s, 3 H), 5.57 (br s, 1 H), 6.81 (br s, 3 H). **21**: NMR ($CHCl_3$) δ 0.20 (s, 9 H), 0.8–1.2 (m, 2 H), 2.6–2.9 (m, 2 H), 3.9 (s, 3 H), 4.67 (br s, 1 H), 6.81 (br s, 3 H). No NMR signals characteristic of *p*-dimethoxybenzene or of *p*-methoxybenzyl alcohols were observed in the hydrolysis products.

When 2 mmol of **3b** in 15 mL of anhydrous THF was treated with 5 mmol of *sec*-butyllithium for 16 h at 20–25 °C and then worked up by the usual acidic hydrolysis, a 28% conversion of **3b** to *p*-methoxyphenol was observed.

Rearrangement of 2-Naphthyl (Trimethylsilyl)methyl Ether (3d). A solution of 1.15 g (5 mmol) of **3d** in 40 mL of absolute THF at −78 °C was treated with 12.5 mmol of *sec*-butyllithium in cyclohexane. The reaction mixture was allowed to come to 20–25 °C and stirred there for 12 h. Treatment with water and ether and the usual workup gave an organic product, whose NMR spectrum showed the absence of **3d**. The product was heated to reflux with 600 mg of KOH in 15 mL of methanol for 8 h. Usual workup and column chromatography of the organic product on silica gel with a hexane–ether gradient yielded 62% of 2-naphthalenemethanol, mp 79–80 °C from hexane (lit.[17] 80–80.5 °C).

Rearrangement of 9-Phenanthryl (Trimethylsilyl)methyl Ether (3e). A solution of 2.6 g (8.8 mmol) of **3e** in 40 mL of absolute THF at −78 °C was treated with 23 mmol of *sec*-butyllithium in cyclohexane. The reaction mixture was allowed to come to 20–25 °C and stirred there for 12 h. Usual workup and column chromatography on silica gel gave 0.58 g (32%) of 9-phenanthrenemethanol, mp 148–149 °C (lit.[18] mp 149 °C).

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Registry No. **3a**, 75144-61-5; **3b**, 83693-52-1; **3c**, 83693-53-2; **3d**, 83693-54-3; **3e**, 83693-55-4; **4a**, 17876-95-8; **6a**, 108-95-2; **6b**, 150-76-5; **6c**, 100-02-7; **6d**, 135-19-3; **6e**, 484-17-3; **7**, 2344-80-1; **8**, 17067-65-1; **9**, 83693-56-5; **10**, 5926-35-2; **11**, 83693-57-6; **13**, 83693-58-7; **20**, 13391-32-7; **21**, 83693-59-8; **23**, 66222-29-5; **25**, 83693-60-1; **26**, 1461-25-2; **27**, 5432-02-0; **28**, 83693-61-2; **29**, 100-17-4; benzyl alcohol, 100-51-6; 2-naphthalenemethanol, 1592-38-7; 9-phenanthrenemethanol, 4707-72-6.

(17) Bamberger, E.; Boekmann, O. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 118.
(18) Bachmann, W. E. *J. Am. Chem. Soc.* **1934**, *56*, 1363.

Diels–Alder Reactions of Cycloalkenones. 1. Preparation and Structure of the Adducts[1]

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Uncatalyzed and aluminum chloride induced Diels–Alder reactions of 2-cyclopentenones, 2-cyclohexenones, and 2-cycloheptenones with 1,3-butadiene, isoprene, and (*E*)-piperylene are described. Structure analysis of the adducts and their hydrogenation products by standard means and ^{13}C NMR spectroscopy is presented.

For half a century the Diels–Alder reaction has served as one of the best methods of synthesis of six-membered carbocycles.[4] The ease of the cycloaddition of diene and dienophile (illustrated below, for example, by the production of 1,2,5,6-tetrahydrobenzaldehyde from the interaction of acrolein with 1,3-butadiene), the rapid accumulation of polyfunctionality in a relatively small molecular framework, the extraordinary stereochemical control of the cycloaddition, and the fair predictability of its regiochemistry have contributed to the popularity of the reaction in general organochemical synthesis. In the realm of natural products synthesis, in which a premium is put on the rapidity of construction of polyfunctional, highly bridged carbon, and heteroatom networks, the Diels–Alder reaction has left a special imprint. By the use of cyclic dienes and/or dienophiles facile syntheses of polycycles have emerged. In this connection, however, one highly desirable research goal has remained elusive, i.e., the synthesis of octalones and related bicyclic olefinic ketones by the reaction of conjugated dienes with conjugated cycloalkenones (e.g., the reaction between 1,3-butadiene and 2-cyclohexenone depicted below). Whereas, in principle,

(1) Preliminary communication: Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *Synth. Commun.* **1979**, *9*, 391.
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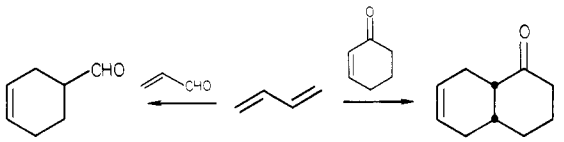
(4) Kloetzel, M. *Org. React.* **1948**, *4*, 1. Holmes, H. L. *Ibid.* **1948**, *4*, 60. Butz, L. W.; Rytina, A. W. *Ibid.* **1949**, *5*, 136. Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16 and references therein. Wollweber, H. "Diels–Alder Reaktion", Georg Thieme Verlag, Stuttgart, 1972. Carruthers, W. "Some Modern Methods of Organic Synthesis", 2nd ed.; Cambridge University Press: Cambridge, 1978; Chapter 3.

0022-3263/82/1947-5056$01.25/0

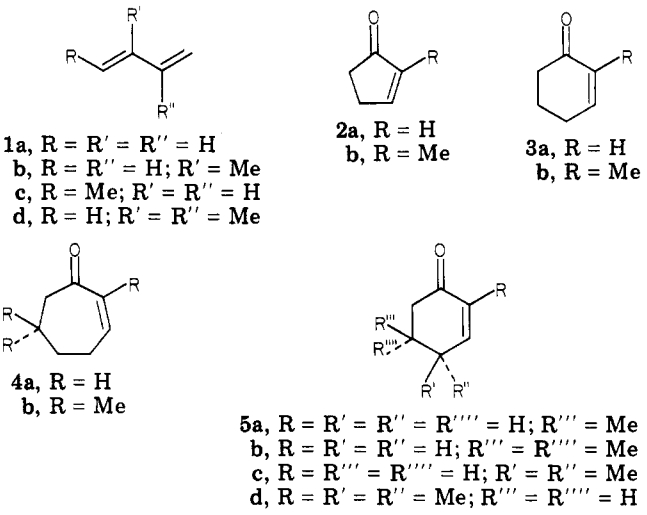


octalone synthesis could have been the route of choice for the construction of decaline-based sesquiterpenes, labdanic and hydrophenanthroid diterpenes, steroids, and tetracyclic and pentacyclic triterpenes, reports of frequently low product yields and the necessity for drastic reaction conditions in the Diels–Alder reaction of cycloalkenones[5,6] have made this reaction unattractive for natural products synthesis. It is intriguing to speculate whether the major advances in steroid synthesis in the 1940s and 1950s might not have followed the Diels–Alder route of fused-ring construction (with dienophiles other than quinones, followed by bridgehead isomerization) instead of the Robinson annelation path, had the early history of the diene synthesis been different.

The 1960 Yates–Eaton discovery of dramatic rate acceleration of enone–diene interactions by Lewis acid catalysis[7] lifted the barrier to the use of conjugated cycloalkenones in cycloadditions, since the problems of the past seemed to be associated with low reaction rates. Early data, generated from acid-catalyzed Diels–Alder reactions, substantiated this surmise.[8] Unfortunately, however, no uniformity of reaction conditions and product yields exists at this time, making reaction predictability uncertain and general adoption of the reaction into the natural products synthesis repertoire unlikely. As a consequence, it has become necessary to carry out an exhaustive, systematic study of all the reaction parameters and to place the reaction on a firm basis of reproducible, experimental routine.

A broad study of the Diels–Alder reactions of 1,3-butadiene (**1a**), isoprene (**1b**), and (*E*)-piperylene (**1c**) (Chart I) with a variety of cycloalkenones in toluene solution under the influence of diverse Lewis acids and an array of reaction conditions was undertaken to determine all reaction constraints. The present paper describes the preparation of the Diels–Alder adducts under optimum product yield conditions and the structure analysis of the adducts. A subsequent publication will deal with the effect of specific reaction parameters on the reaction outcome. Since at an early stage aluminum chloride was found to be the most efficacious catalyst, it was used as the sole catalyst in the synthesis phase of the study, involving cycloadditions of 2-cyclopentenone (**2a**), 2-methyl-2-cyclopentenone (**2b**), 2-cyclohexenone (**3a**), 2-methyl-2-cyclohexenone (**3b**), 2-cycloheptenone (**4a**), and 2,6,6-trimethyl-2-cycloheptenone (**4b**) as well as 5-methyl-2-cyclohexenone (**5a**), 5,5-dimethyl-2-cyclohexenone (**5b**),

Chart I



1a, R = R′ = R″ = H
b, R = R″ = H; R′ = Me
c, R = Me; R′ = R″ = H
d, R = H; R′ = R″ = Me

2a, R = H
b, R = Me

3a, R = H
b, R = Me

4a, R = H
b, R = Me

5a, R = R′ = R″ = R‴′ = H; R‴ = Me
b, R = R′ = R″ = H; R‴ = R‴′ = Me
c, R = R‴ = R‴′ = H; R′ = R″ = Me
d, R = R′ = R″ = Me; R‴ = R‴′ = H

(5) Thus, for example, a reaction of 3.6:1 1,3-butadiene and 2-cyclopentenone at 110 °C in benzene solution for 288 h gave a 29% yield of adducts;[6b] 2:1 1,3-butadiene and 2-cyclohexenone at 190 °C for 72 h gave an 11% yield of adduct;[6e] 2.5:1 1,3-butadiene and 2-methyl-2-cyclohexenone at 230 °C for 7 h gave a 24% yield of adduct;[6x] 2:1 1,3-butadiene and carvone at 190 °C for 60 h yielded 8% of adduct.[6f]

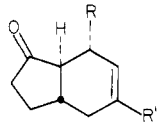
(6) For examples of uncatalyzed diene–cycloalkenone cycloadditions see: (a) Bockemüller, W. *Angew. Chem.* **1938**, *51*, 188. (b) Dane, E. *Ibid.* **1939**, *52*, 655. (c) Dane, E.; Eder, K. *Justus Liebigs Ann. Chem.* **1939**, *539*, 207. (d) Bockemüller, W. U.S. Patent 2179809; *Chem. Abstr.* **1940**, *34*, 1823. (e) Bartlett, P. D.; Woods, G. F. *J. Am. Chem. Soc.* **1940**, *62*, 2933. (f) Nudenberg, W.; Butz, L. W. *Ibid.* **1943**, *65*, 1436. (g) Gaddis, A. M.; Butz, L. W. *Ibid.* **1947**, *69*, 117, 1165, 1203. (h) Nazarov, I. N.; Bergel'son, L. D.; Shmonina, L. I.; Terekhova, I. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1949**, 439; *Chem. Abstr.* **1950**, *44*, 3458. (i) Nazarov, I. N.; Nagibina, T. D. *Zh. Obshch. Khim.* **1950**, *20*, 531. (j) Nazarov, I. N.; Bergel'son, L. D. *Ibid.* **1950**, *20*, 648. (k) Nazarov, I. N.; Terekhova, L. N.; Bergel'son, L. D. *Ibid.* **1950**, *20*, 661. (l) Nazarov, I. N.; Shmonina, L. I. *Ibid.* **1950**, *20*, 876. (m) Nazarov, I. N.; Kuznetsova, A. I.; Gurvich, I. A. *Ibid.* **1952**, *22*, 982. (n) Nazarov, I. N.; Kucherov, V. F.; Terekhova, L. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1952**, 442; *Chem. Abstr.* **1953**, *47*, 5366. (o) Alder, K.; Schumacher, M. *Fortschr. Chem. Org. Naturst.* **1953**, *10*, 75. (p) Nazarov, I. N.; Torgov, I. V.; Zaretskaya, I. I.; Verkholetova, G. P.; Ananchenko, S. N.; Andreev, V. M. *Isv. Akad. Nauk SSSR, Ser. Khim.* **1953**, 78; *Chem. Abstr.* **1954**, *48*, 3324. (q) Nazarov, I. N.; Torgov, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1953**, 901; *Chem. Abstr.* **1955**, *49*, 1083. (r) Nazarov, I. N.; Zaretskaya, I. I.; Verkholetova, G. P.; Torgov, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1953**, 920; *Chem. Abstr.* **1955**, *49*, 1085. (s) Nazarov, I. N.; Verkholetova, G. P.; Torgov, I. V.; Zaretskaya, I. I.; Ananchenko, S. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1953**, 929; *Chem. Abstr.* **1955**, *49*, 1086. (t) Nazarov, I. N.; Shmonina, L. I.; Torgov, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1953**, 1074; *Chem. Abstr.* **1955**, *49*, 2452. (u) Nazarov, I. N.; Gurvich, I. A.; Kuznetsova, I. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1953**, 1091; *Chem. Abstr.* **1955**, *49*, 2456. (v) Nazarov, I. N. Kotlyarevskii, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1953**, 1100; *Chem. Abstr.* **1955**, *49*, 2458. (w) Nazarov, I. N.; Burmistrova, M. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1954**, 56; *Chem. Abstr.* **1955**, *49*, 2457. (x) Dauben, W. G.; Rogan, J. B.; Blanz, E. J., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 6384. (y) Torgov, I. V.; Nazarov, I. N. *Zh. Obshch. Khim.* **1959**, *29*, 787. (z) Sorkina, T. I.; Zaretskaya, I. I.; Torgov, I. V. *Dokl. Akad. Nauk SSSR* **1959**, 129. (a′) House, H. O.; Gannon, W. F.; Ro, R. S.; Wluka, D. J. *J. Am. Chem. Soc.* **1960**, *82*, 1463. (b′) House, H. O.; Rasmusson, G. H. *J. Org. Chem.* **1963**, *28*, 31. (c′) Torgov, I. V.; Sorkina, T. I.; Zaretskaya, I. I. *Bull. Soc. Chim. Fr.* **1964**, 2063. (d′) Zaretskaya, I. I.; Sorkina, T. I.; Tikhomirova, O. B.; Torgov, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1051; *Chem. Abstr.* **1965**, *63*, 8282. (e′) Dunn, G. L.; DiPasquo, V. J.; Hoover, J. R. E. *Tetrahedron Lett.* **1966**, 3737. (f′) Nerdel, F.; Dahl, H. *Justus Liebigs Ann. Chem.* **1967**, *710*, 90.[8f] (g′) Beslin, P.; Block, R.; Moinet, G.; Conia, J.-M. *Bull. Soc. Chim. Fr.* **1969**, 508. (h′) Torii, S.; Kunitomi, T.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2349. (i′) Liu, H. J.; Browne, E. N. C. *Tetrahedron Lett.* **1977**, 2919. In contrast to the behavior of cycloalkenones, cyclic enediones have led to higher yields of Diels–Alder adducts. Cf.: Dane, E.; Schmitt, J. *Justus Liebigs Ann. Chem.* **1938**, *536*, 196; **1939**, *537*, 246. Dane, E. U.S. Patent 2230233; *Chem. Abstr.* **1941**, *35*, 3037. Singh, G. *J. Am. Chem. Soc.* **1956**, *78*, 6109. Kucherov, V. F.; Ivanova, L. N. *Dokl. Akad. Nauk SSSR* **1960**, *131*, 1077. Kucherov, V. F.; Gurvich, I. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1961**, 1152; *Chem. Abstr.* **1961**, *55*, 27421. Zaretskaya, I. I.; Sorkina, T. I.; Torgov, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1058; *Chem. Abstr.* **1965**, *63*, 8282.

(7) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436.

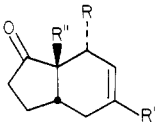
(8) Inter alia: (a) Wenkert, E.; Michalski, C. A., unpublished observations (1968–1969) on Diels–Alder reactions between 1,3-butadiene and methylated 2-cyclohexenones catalyzed by aluminum chloride. (b) Thompson, H. W.; Mellilo, D. G. *J. Am. Chem. Soc.* **1970**, *92*, 3218. (c) Yamamoto, K.; Kawasaki, I.; Kaneko, T. *Tetrahedron Lett.* **1970**, 4850. (d) Harayama, T.; Cho, H.; Ohtani, M.; Inubushi, Y. *Chem. Pharm. Bull. Jpn.* **1974**, *22*, 2784. (e) Kelly, T. R.; McNutt, R. W. *Tetrahedron Lett.* **1975**, 285. (f) Harayama, T.; Cho, H.; Inubushi, Y. *Ibid.* **1975**, 2693. (g) Nagakura, I.; Ogata, H.; Ueno, M.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2995. (h) Oppolzer, W.; Petrzilka, M. *J. Am. Chem. Soc.* **1976**, *98*, 6722. (i) Harayama, T.; Cho, H.; Inubushi, Y. *Chem. Pharm. Bull. Jpn.* **1977**, *25*, 2273. (j) Oppolzer, W.; Petrzilka, M. *Helv. Chim. Acta* **1978**, *61*, 2755. (k) Harayama, T.; Cho, H.; Takatani, M.; Inubushi, Y. *Abstracts of the 21st Symposium* on the *Chemistry of Natural Products*, Sapporo, Japan, **1978**, p 455. (l) Harayama, T.; Takatani, M.; Inubushi, Y. *Chem. Pharm. Bull. Jpn.* **1979**, *27*, 726; *Abstracts of the 22nd Symposium* on the *Chemistry of Natural Products*, Fukuoka, Japan, 1979, p 596. (m) Liu, H.-J.; Browne, E. N. C. *Tetrahedron Lett.* **1977**, 2919. (n) Liu, H.-J.; Browne, E. N. C. *Can. J. Chem.* **1979**, *57*, 377. (o) *Ibid.* **1981**, *59*, 601.

4,4-dimethyl-2-cyclohexenone (**5c**), and 2,4,4-trimethyl-2-cyclohexenone (**5d**).

The interaction of 2-cyclopentenone (**2a**) with 1,3-butadiene (**1a**) yielded a ca. 1:1 mixture of hydrindanones **6a**[6b'] and **7a**,[6b',9] with isoprene (**1b**) a ca. 1:2 mixture of



6a, R = R′ = H
b, R = H; R′ = Me
c, R = Me; R′ = H

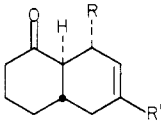


7a, R = R′ = R″ = H
b, R = R″ = H; R′ = Me
c, R′ = R″ = H; R = Me
d, R = R′ = H; R″ = Me
e, R = H; R′ = R″ = Me
f, R = R″ = Me; R′ = H

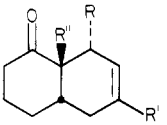
methylhydrindanones **6b** and **7b**, and with (*E*)-piperylene (**1c**) a 200:1 mixture of methylhydrindanones **6c**[6b'] and **7c**[6b',10] (see Table I). The acidic medium had induced isomerization of the primary products, the cis adducts **7**. Equilibration of the three isomer pairs with sodium methoxide in methanol solution led to equilibrium values of ca. 1, 1, and >70 for **6a/7a**[6b'], **6b/7b**, and **6c/7c**,[6b'] respectively.

Reactions of 2-methyl-2-cyclopentenone (**2b**) with 1,3-butadiene (**1a**), isoprene (**1b**), and (*E*)-piperylene (**1c**) led to ketones **7d–f**, respectively. The optimum yields of Diels–Alder adducts emanating from both cyclopentenones (**2a,b**) and the three dienes were in the 73–95% range.[11]

Acid-induced interaction of 2-cyclohexenone (**3a**) with 1,3-butadiene (**1a**) afforded a 9:1 mixture of octalones **8a**[12,13] and **9a**,[6e] with isoprene (**1b**) a 18:1 mixture of ke-



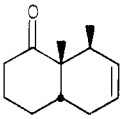
8a, R = R′ = H
b, R = H; R′ = Me
c, R = Me; R′ = H



9a, R = R′ = R″ = H
b, R = R″ = H; R′ = Me
c, R′ = R″ = H; R = Me
d, R = R′ = H; R″ = Me
e, R = H; R′ = R″ = Me
f, R = R″ = Me; R′ = H

tones **8b** and **9b**,[14] and with (*E*)-piperylene (**1c**) a ca. 1:2 mixture of octalones **8c** and **9c**. Equilibration of the three pairs of isomeric adducts by the aforementioned procedure gave trans/cis equilibrium constants of ca. 9, 50, and 20, respectively.

The reactions of 2-methyl-2-cyclohexenone (**3b**) with the dienes **1a,b** afforded octalones **9d**[6g,f] and **9e**,[8g,15] whereas the involvement of the dienophile with (*E*)-piperylene (**1c**) produced a ca. 2:1 mixture of octalones **9f**[6g] and **10**.[15] The formation of the latter ketone constitutes the sole stereo-



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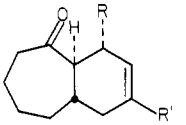
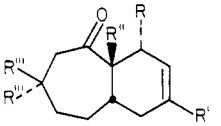
chemical exception among the present cycloadditions of (*E*)-piperylene (**1c**) and stands in contrast to the behavior of 2-methyl-2-cyclopentenone (**2b**, vide supra) and the methylated 2-cycloheptenone (**4b**, vide infra) toward this diene. This seeming violation of the Diels–Alder endo addition rule may reflect a larger, unfavorable, nonbonded interaction between the methyl functions of the dienophile and diene in the endo transition state of the six-membered ring ketone–acid complex than that found in the five- and seven-membered-ring complexes. The yields of the Diels–Alder products from both cyclohexenones (**3a,b**) were 70–93%.[11]

The cycloaddition of 2-cycloheptenone (**4a**) and 1,3-butadiene (**1a**) produced a 1:12 mixture of hydrobenzosuberones **11a** and **12a**, isoprene (**1b**), a 1:45 mixture of ketones **11b** and **12b**, and (*E*)-piperylene (**1c**) a ca. 1:200 mixture of ketones **11c** and **12c**. Base-catalyzed equili-



11a, R = R′ = H
b, R = H; R′ = Me
c, R = Me; R′ = H

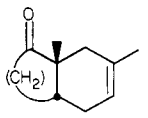


12a, R = R′ = R″ = R‴ = H
b, R = R″ = R‴ = H; R′ = Me
c, R = Me; R′ = R″ = R‴ = H
d, R = R′ = H; R″ = R‴ = Me
e, R = H; R′ = R″ = R‴ = Me
f, R = R″ = R‴ = Me; R′ = H

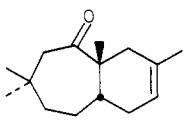
bration of the three adduct isomer pairs revealed trans/cis equilibrium ratios of >50, 15, and 20, respectively. It is noteworthy that, in contrast to the isomerization behavior of the hydroindanones and octalones without angular methyl groups, structurally similar hydrobenzosuberones underwent acid-induced isomerization in the cycloaddition process very slowly.

The cycloadditions of 2,6,6-trimethyl-2-cycloheptenone (**4b**) with the standard three dienes (**1a–c**) resulted in the formation of ketone **12d–f**, respectively. The optimum yields for both seven-membered-ring ketones ranged from 73% to 98%.[11]

In order to have a direct comparison of the efficacy of the Diels–Alder reaction catalyzed by Lewis acids vs. that of the uncatalyzed, traditional process, the thermal interaction of each of the dienes (**1a–c**) with each of the α,β-unsaturated ketones was investigated. As inspection of Table I indicates, the uncatalyzed reactions led to low product yields and required high temperatures and long reaction times. As a comparison of the regioisomer product ratios for the catalyzed vs. uncatalyzed reactions of isoprene (**1b**) and the three 2-methylated cycloalkenones suggests, aluminum chloride catalysis affects strongly the regiochemistry of the diene synthesis with isoprene (**1b**). The latter is oriented in the transition state of the catalyzed process in such a manner as to respond best to the greater electron demand of the ketone–acid complex.[16]



13a, $x = 2$
b, $x = 3$



14

(9) Granger, R.; Nau, P. F. G.; Francois, C. *Bull. Soc. Chim. Fr.* **1962**, 1902.

(10) This compound could not be isolated from the mixture. It was assumed to be the bridgehead isomer of the nearly sole product (**6c**) on the basis of its constituting 30% of the reaction mixture after 20 h of reaction time and its subsequent diminution with concomitant buildup of the major product.

(11) These are yields based on gas chromatographic analysis. The yields of isolated products averaged 6% lower than these values.

(12) Ireland, R. E.; Marshall, J. A. *J. Org. Chem.* **1962**, *27*, 1620.

(13) Acklin, W.; Prelog, V.; Schenker, F.; Serdarevic, B.; Walter, P. *Helv. Chim. Acta* **1965**, *48*, 1725.

(14) Whereas it was not isolated, this substance was identified by its representing 87% of the reaction mixture after 20 h of reaction and diminishing thereafter in favor of its trans isomer (**8b**).

(15) In previous studies[6g,8g] of the reactions of 2-methyl-2-cyclohexenone (**3b**) with isoprene (**1b**) and (*E*)-piperylene (**1c**) under the influence of aluminum chloride, the adducts were reported erroneously to be regioisomeric with structures **9e** and **10**, respectively.

Table I. Thermal and Aluminum Chloride Catalyzed Diels–Alder Reactions of Dienes 1 with Cycloalkenones 2-4[a]

	thermal reaction		products			catalyzed reaction		products		
	temp	time	yield		ratio	temp	time	yield		ratio
1a-2a	110	228	29	6a, 7a	1:1.5	70	5	95	6a, 7a	1.2:1
1a-3a	185	72	11	8a, 9a[b]	9:1	70	22	84	8a, 9a[b]	9:1
1a-4a	150	65	15	11a, 12a	1:1.7	25	15	98	11a, 12a	1:12
1a-2b	150	142	40	7d		70	17	92	7d	
1a-3b	200	38	42	9d		70	10	93	9d	
1a-4b	150	144	6	12d		25	18	95	12d	
1b-2a	150	142	29[c]	6b, 7b	1:1	50	71	80	6b, 7b	1:1.7
1b-3a	150	142	20[c]	8b, 9b[b]	5:1	40	140	70	8b, 9b[b]	18:1
1b-4a	150	72	16[c]	11b, 12b	1:2.3	25	87	73	11b, 12b	1:45
1b-2b	200	24	20	7e, 13a	*e*	40	40	73	7e, 13a	*e*
1b-3b	150	142	20	9e, 13b[d]	*e*	25	17	79	9e, 13b[d]	*e*
1b-4b	150	96	14	12e, 14[d]	*f*	25	8	90	12e	
1c-2a	150	55	70[g]	6c, 7c[b]	2.2:1	40	81	77	6c, 7c[b]	200:1
1c-3a	150	142	46[g]	8c, 9c	1:1	40	96	81	8c, 9c	1:1.8
1c-4a	150	48	24[g]	11c, 12c	1:>200	25	32	80	11c, 12c	1:>200
1c-2b	200	55	60[g]	7f		40	31	80	7f	
1c-3b	150	142	32	9f, 10	2.2:1	25	11	92	9f, 10	2.2:1
1c-4b	150	96	48[g]	12f		25	6	85	12f	

[a] Temperature in °C; time in hours; yields, in percent. [b] Structure based on the observation of its concentration decrease with time in the catalyzed reaction, commensurate with a concentration increase of its trans-bridgehead isomer. [c] Two compounds of unknown constitution account for 12%, 8%, and 5% of the cited yields in the **1b-2a**, **1b-3a**, and **1b-4a** reactions, respectively. [d] Most likely structure. [e] The **7e-13a** and **9e-13b** ratios in the thermal process are 1.2 and 1.9, respectively, and in the catalytic process 6.3 and 32, respectively. [f] **12e-14** ratio of 1.8. [g] Compounds of unknown constitution account for 17%, 11%, 4%, 10%, and 10% of the cited yields in the **1c-2a**, **1c-3a**, **1c-4a**, **1c-2b**, and **1c-4b** reactions, respectively.

Table II. ^{13}C Chemical Shifts of *trans*-Hydrindanones 6 and 22 and *trans*-Hydrobenzosuberones 11 and 28[a]

	shift									
carbon	6a[b]	6b	6c[b]	22a[b,c]	22b[b]	11a	11b	11c	28a[d]	28b
C(1)	217.7	218.2	217.4	217.7	217.4	215.9	215.9	214.9	216.7	215.4
C(2)	50.5	50.8	56.7	55.3	59.9	54.7	54.5	62.1	57.5	62.6
C(3)	24.8	24.6	31.9	24.8	32.8	29.2	29.3	33.5	29.6	33.0
C(4)	125.6	119.9	133.4	25.4	35.9	125.1	118.9	132.2	25.3	34.0
C(5)	126.3	133.8	124.8	25.7	25.7	126.7	133.6	125.4	26.1	25.5
C(6)	32.0	37.1	31.9	32.4	32.2	33.5	38.3	33.5	34.7	34.5
C(7)	38.3	39.1	38.3	43.1	42.9	36.4	36.6	36.8	40.4	40.4
C(8)	27.4	27.5	27.0	27.5	26.9	35.2	35.1	34.4	37.6	37.8
C(9)	36.8	37.4	36.9	36.8	36.9	28.7	28.7	27.9	28.5	26.6
C(10)						26.1	25.9	26.4	25.5	24.2
C(11)						40.9	40.7	40.9	42.2	43.5
Me		23.3	19.4		19.0		22.8	19.6		20.2

[a] The δ values are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. The arbitrary carbon numbering is based on formula **30**. [b] Reference 6b'. [c] References 20 and 21. [d] References 22 and 23.

Besides the Diels–Alder reactions of the cycloalkenones **2–4**, the aluminum chloride catalyzed reactions of the substituted 2-cyclohexenones **5a–d** were investigated also. Their reactions with 1,3-butadiene (**1a**) produced a 4:1 mixture (80%) of octalones **15a**[8d] and **16a** (Chart II), a 20:1 mixture (69%) of ketones **15b** and **16b**, a 100:1 mixture (87%) of ketones **15c** and **16c**,[17] and, finally, octalone **16d** (80%), respectively. The reactions of 4,4-dimethyl-2-cyclohexenone (**5c**) with isoprene (**1b**) and (*E*)-piperylene (**1c**) afforded a 1.2:1 mixture (75%)[18] of octalones **17c** and **18c**[17] and a 1:2.3 mixture (90%) of ketones **19c** and **20c**, respectively. Base-induced equilibration of the adducts derived from the cyclohexenones **5a–c** gave trans/cis equilibrium constants of 4, 25, >70, >70, and >70, respectively.

Finally, one example of the acid-catalyzed Diels–Alder reaction of 2,3-dimethylbutadiene (**1d**) was studied. Its involvement with 2-methyl-2-cyclohexenone (**3b**) led to octalone **21** in 80% yield.

Most Diels–Alder adducts derived from 1,3-butadiene (**1a**) and (*E*)-piperylene (**1c**) were hydrogenated in order to facilitate the structure analysis of the bicyclic ketones described above. The resultant perhydroindanones, decalones, and perhydrobenzosuberones are illustrated by formulas **22–29** (Chart III).

Structure Analysis by ^{13}C NMR Spectroscopy

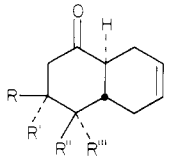
The carbon shift assignment of the *trans*-hydrindanones **6** and **22** and the *trans*-hydrobenzosuberones **11** and **28** followed a first-order analysis and is presented in Table II. The shift assignment was buttressed by an Yb(DPM)$_3$-induced shift study on every ketone. Whereas most shifts follow expected patterns, a comparison of the δ values of the cycloheptanone carbons of bicycles **11** with those of bicycles **28** reveals strong shift perturbations as

(16) Whereas the 2-methyl-2-cyclopentenone-based regioisomer **13a** could be isolated and characterized by ^{13}C NMR spectroscopy, the low yields of **13b** and **14** precluded their identification. Their structures thus are proposed by analogy with the constitution of ketone **13a**.

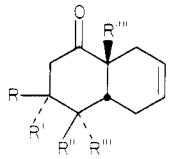
(17) The low yield of these isomers precluded their isolation. The suggestion of their being the primary Diels–Alder adducts, i.e. the *cis*-octalones, is based on the observation of their presence in appreciable quantity in reaction mixtures at an early reaction stage and their diminution with time being accompanied by a buildup of their trans isomers.

(18) The overall yield includes a 10% component, consisting of two substances of unknown constitution (possibly regioisomers of **17c** and **18c**).

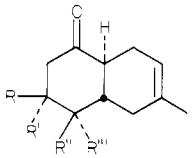
Chart II



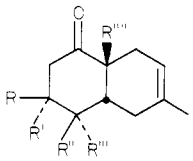
15a, R = Me; R′ = R″ = R‴ = H
b, R = R′ = Me; R″ = R‴ = H
c, R = R′ = H; R″ = R‴ = Me



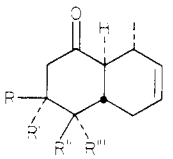
16a, R = Me; R′ = R″ = R‴ = R⁗ = H
b, R = R′ = Me; R″ = R‴ = R⁗ = H
c, R = R′ = R⁗ = H; R″ = R‴ = Me
d, R = R′ = H; R″ = R‴ = R⁗ = Me



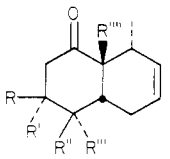
17a, R = Me; R′ = R″ = R‴ = H
b, R = R′ = Me; R″ = R‴ = H
c, R = R′ = H; R″ = R‴ = Me

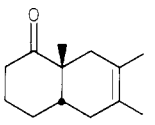


18a, R = Me; R′ = R″ = R‴ = R⁗ = H
b, R = R′ = Me; R″ = R‴ = R⁗ = H
c, R = R′ = R⁗ = H; R″ = R‴ = Me
d, R = R′ = H; R″ = R‴ = R⁗ = Me



19a, R = Me; R′ = R″ = R‴ = H
b, R = R′ = Me; R″ = R‴ = H
c, R = R′ = H; R″ = R‴ = Me

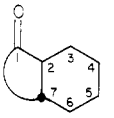




21

20a, R = Me; R′ = R″ = R‴ = R⁗ = H
b, R = R′ = Me; R″ = R‴ = R⁗ = H
c, R = R′ = R⁗ = H; R″ = R‴ = Me
d, R = R′ = H; R″ = R‴ = R⁗ = Me

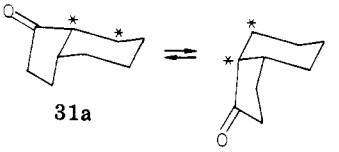
a consequence of the introduction of a distant double bond into the adjoining six-membered ring. The double bond causes the customary homoallyl shielding effect on the bridgehead carbons,[19] attenuated, however, at the α-keto methine of the hydrobenzosuberones.



30

A standard shift analysis of the *trans*-octalones **8**, **15**, **17**, and **19** and *trans*-α-decalones **24** and **26**, aided by a lanthanide shift study on every ketone, yielded the signal assignment depicted in Table III. Comparison of δ values of the two sets of compounds reveals that the introduction of a double bond produces not only the expected homoallyl effect on the bridgehead carbons but also general shielding throughout the ring system, presumably due to overall bond angle reorganization. Introduction of an equatorial methyl group at the site peri to the keto function of the octalones and decalones causes general deshielding of all cyclohexanone ring carbons, undoubtedly the consequence of ring deformation induced by the nonbonded interaction of the carbonyl oxygen with the methyl function. The minimization of the latter interaction in the hydrindanones, due to the orientation of the carbonyl oxygen away from the neighboring six-membered ring, results in only minimal shift perturbation of the cyclopentanone ring carbons on introduction of the equatorial methyl group peri to the carbonyl function (vide supra). The exhaustive chemical shift study of the trans isomers of the hydrindanone, hydrobenzosuberone, and octalone Diels–Alder products and their dihydro derivatives assures their regiochemical and stereochemical assignments. Furthermore, the aforegoing ^{13}C NMR investigation substantiates also the structure assignment of the cis bicyclic ketones, whose relationship to the above trans isomers was established by chemical means (vide supra).

Table IV presents the carbon shift assignment for the *cis*-hydrindanones **7**, **13a**, and **23** and *cis*-hydrobenzosuberones **12** and **29**. The bicyclic ketones without angular methyl substituents, i.e., the cis bicycles which have been correlated chemically with their trans isomers (vide supra), reveal their cis configuration by general shielding of at least the six-membered-ring methylenes. An $Yb(DPM)_3$-induced shift study of the hydrindanones confirms their expected predilection toward conformation **31b**, in which



31a

31b

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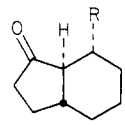
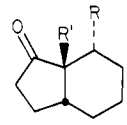
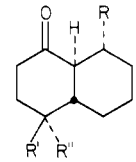
Chart III



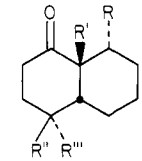
22a, R = H
b, R = Me



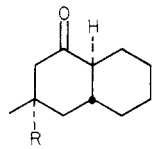
23a, R = R′ = H
b, R = H; R′ = Me
c, R = R′ = Me



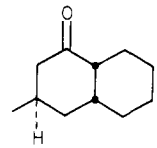
24a, R = R′ = R″ = H
b, R = Me; R′ = R″ = H
c, R = H; R′ = R″ = Me
d, R = R′ = R″ = Me



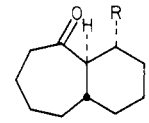
25a, R = R′ = R″ = R‴ = H
b, R = Me; R′ = R″ = R‴ = H
c, R = R″ = R‴ = H; R′ = Me
d, R = R′ = Me; R″ = R‴ = H
e, R = R′ = H; R″ = R‴ = Me
f, R = R″ = R‴ = Me, R′ = H
g, R = H; R′ = R″ = R‴ = Me



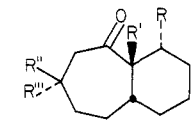
26a, R = H
b, R = Me



27



28a, R = H
b, R = Me



29a, R = R′ = R″ = R‴ = H
b, R = Me; R′ = R″ = R‴ = H
c, R = H; R′ = R″ = R‴ = Me
d, R = R′ = R″ = R‴ = Me

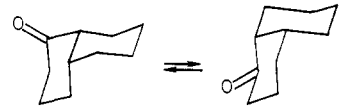
Table III. ^{13}C Chemical Shifts of *trans*-Octalones 8, 15, 17, and 19 and *trans*-Decalones 24 and 26[a]

	shift													
carbon	8a[b,c]	8b	8c	15a[d]	15b	15c	17c[e]	19c	24a[c,f,g]	24b[h]	24c	24d	26a	26b[i]
C(1)	211.1	211.7	211.4	211.7	210.9	210.9	211.9	211.6	211.7	212.5	212.2	213.0	212.1	211.6
C(2)	49.8	50.0	58.0	49.8	49.1	44.8	45.0	52.9	54.6	61.7	49.2	55.8	54.7	54.0
C(3)	24.1	24.5	29.0	23.8	24.1	24.9	25.2	29.4	24.8	30.0	25.6	30.2	24.6	24.6
C(4)	125.3	119.6	132.6	125.3	125.5	124.8	119.1	131.9	25.1	34.5	25.1	34.3	25.1	25.2
C(5)	124.6	131.9	123.2	124.9	125.0	124.6	132.1	123.3	25.4	25.1	25.9	25.2	25.4	25.6
C(6)	32.9	38.1	32.9	33.0	33.2	26.3	31.5	26.1	34.0	34.0	27.5	27.4	34.0	34.1
C(7)	39.7	40.2	40.8	34.3	35.4	46.7	47.3	48.0	44.6	45.8	52.2	53.2	38.9	40.0
C(8)	32.2	32.4	32.9	37.7	45.5	32.0	32.2	32.8	32.7	33.5	32.6	33.2	38.4	46.2
C(9)	25.6	25.9	27.0	30.3	35.4	40.8	41.1	42.6	26.1	27.7	41.7	43.7	30.6	35.6
C(10)	41.3	41.8	42.8	47.5	54.4	37.6	37.9	39.1	41.4	43.0	38.1	39.8	47.5	54.4
Me		23.0	20.9				23.2	21.4		20.8		21.2		
α-Me					31.8	18.9	19.0	19.6			19.2	19.5		32.0
β-Me				18.4	25.2	28.5	28.7	28.9			28.6	28.8	19.0	25.8

[a] The δ values are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. The arbitrary carbon numbering is based on formula **30**. The Me values refer to shifts of the diene-derived methyl groups and the α- and β-Me values to those of enone-derived methyl functions. [b] Reference 12. [c] Reference 13. [d] Reference 8d. [e] Reference 8o. [f] References 21, 22, and 24-26. [g] References 27 and 28. [h] Reference 29. [i] Reference 30.

the carbonyl group is disposed axially toward the cyclohexane or cyclohexene nucleus. This displacement of the conformational equilibrium is noticeable especially for the dimethylated ketone **23c** (i.e., **31b**, methyl groups on starred carbons). The chemical shift designation of the angularly methylated Diels–Alder adducts, derived from isoprene (**1b**) and (*E*)-piperylene (**1c**), is in accord with the assignment of their regiochemistry. Whereas the stereochemistry of the secondary methyl group of the (*E*)-piperylene-based hydrindanones was made secure by the lanthanide shift study, the stereochemistry of the same site in the hydrobenzosuberones derived from (*E*)-piperylene (**1c**) is difficult to designate on the basis of the data at hand in view of the unpredictability of the conformation of the latter compounds. Thus the structures of ketones **12f** and **29d** remain tenuous and based solely on analogy with the stereochemistry of ketones **12c** and **29b** as well as other major Diels–Alder products of (*E*)-piperylene (**1c**).

The *cis*-octalones **9**, **10**, **16**, **20**, and **21** and *cis*-α-decalones **25** and **27** were subjected to standard carbon shift analysis and lanthanide shift investigation. The results are listed in Table V. The combined studies left no doubt regarding the stereostructures of all bicyclic ketones and contributed to the understanding of their favored conformations. Thus, ketones **9c,f**, **16a**, **20c**, **25d,f**, and **27** could be shown to favor one (i.e., **32b**) of the two possible



32a **32b**

cis-α-decalone conformations on the basis of consideration of the shielding effects expected from syn-gauche, nonbonded, carbon–hydrogen interactions. The ^{13}C NMR spectral analysis of the Diels–Alder adducts of 2-methyl-2-cyclohexenone (**3b**) and (*E*)-piperylene (**1c**) settles their regiochemistry, i.e., structures containing vicinal methyl groups, and shows the two products (**9f** and **10**) to be epimeric at the site of attachment of the secondary methyl group. Since the lanthanide shift values of ketone **9f** fit well those calculated for the compound in a **32b**-like conformation, the stereochemistry of its unusual isomer (**10**) is assured.

Experimental Section

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra of carbon tetrachloride solutions were recorded on a Perkin-Elmer 257 spectrophotometer. GC analyses were executed on a Carlo Erba GI

Table IV. ^{13}C Chemical Shifts of *cis*-Hydrindanones 7, 13a, and 23 and *cis*-Hydrobenzosuberones 12 and 29[a]

carbon	shift																
	7a[b]	7b	7d	7e	7f	13a	23a[b,c]	23b[d]	23c	12a	12b	12c	12d	12e	12f	29a[e]	29b	29c	29d
C(1)	218.5	219.1	220.1	220.6	222.2	221.2	219.5	222.0	221.7	214.2	214.4	211.1	217.3	217.1	215.7	215.6	214.4	216.7	214.9
C(2)	46.5	46.2	45.4	45.3	48.9	46.6	49.3	48.1	51.5	49.2	49.1	52.7	47.5	47.2	51.1	52.1	53.2	49.2	53.4
C(3)	20.9	21.5	27.2	27.9	34.9	32.2	22.4	29.4	38.1	25.9	25.7	34.3	29.8	29.7	36.1	23.9	34.7	28.2	39.0
C(4)	124.3	118.4	122.4	116.4	129.9	129.4	22.7	22.1	31.6	124.9	118.6	131.1	124.0	118.0	130.8	25.4	28.4	21.6	27.8
C(5)	124.8	131.8	123.9	130.7	122.3	118.0	23.9	22.3	23.7	124.8	131.6	124.0	122.9	129.5	121.2	21.4	22.5	20.8	21.7
C(6)	25.3	30.6	24.6	29.6	25.1	25.4	28.0	26.7	29.7	31.4	36.5	28.2	31.3	36.0	30.3	33.8	25.6	30.2	29.1
C(7)	31.6	32.6	39.7	40.5	40.9	39.5	36.0	24.2	44.5	33.6	33.8	35.5	38.9	38.7	37.2	35.5	36.8	41.5	41.9
C(8)	26.1	26.2	24.6	24.7	25.7	24.5	25.5	22.9	24.0	32.9	32.7	35.3	29.5	29.9	30.3	31.2	34.7	29.1	30.5
C(9)	33.6	33.9	35.0	35.1	37.7	35.2	34.6	34.8	35.2	27.1	27.3	23.3	42.6	42.7	40.9	28.9	24.6	44.5	39.7
C(10)										23.8	23.8	23.8	33.6	33.6	33.6	25.7	29.4	34.1	33.2
C(11)										43.3	43.3	45.4	51.5	51.6	51.9	42.1	45.3	50.9	53.8
Me		23.6		23.4	23.0	23.6			21.9		23.3	17.2		23.3	28.2		19.3		26.9
ang Me			19.4	19.4	18.7	19.7		21.2	16.0				24.4	24.4	18.3			23.0	17.3
gem-Me_2													27.1, 32.1	26.9, 32.2	29.3, 30.6			25.7, 33.2	29.8, 29.9

[a] The δ values are in parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. The arbitrary carbon numbering is based on formula **30**. The Me values refer to the shifts of the diene-derived methyl groups. [b] References 6b and 9. [c] References 31 and 32. [d] References 33 and 34. [e] References 22 and 23.

chromatograph with a 1-, 2-, or 3-m 20% LAC 728 column (internal standards: *m*- and *p*-methoxyacetophenone and *p*-chloroacetophenone). Absorption chromatography was carried out on neutral alumina columns. ^1H NMR spectra were run on carbon tetrachloride solutions with Me_4Si as the internal standard (δ 0) and registered on a JEOL JNM-60 HI spectrometer. The ^{13}C NMR spectra were taken on a Varian XL-100-15 FT-NMR spectrometer. All solid Diels–Alder adducts were crystallized from pentane and the 2,4-dinitrophenylhydrazones from absolute ethanol. (The 2,4-dinitrophenylhydrazones of some of the angularly unmethylated bicycles **7**, **9**, **12**, **16**, **18**, and **20** were not prepared because of bridgehead epimerization of the ketones during derivatization.)

General Procedure. Uncatalyzed Diels–Alder Reactions. The diene (3 equiv) was poured into a solution of 50 mg of cycloalkenone and 1 mg of hydroquinone in 0.05 mL of dry toluene at 20 °C in a small heating tube, and the latter was sealed and heated at 110, 150, 185, or 200 °C in a heating bath. For analysis an internal standard was added to the mixture and the latter exposed to the chromatograph. All data are reported in Table I.

Catalyzed Diels–Alder Reactions. All operations involving the preparation of the starting reaction mixtures were executed in a drybox. A solution of the cycloalkenone in 1 mL of toluene was added to anhydrous aluminum chloride at 10 °C and the mixture stirred at the experimentally found most suitable temperature (i.e., the complexation temperature) and for the experimentally found optimum length of time (i.e., the complexation time). At the end of the required time period the diene in toluene (enough solvent to form a 5-mL volume for the combined solutions) was added at room temperature, the reaction vessel stoppered, and the mixture heated. For analysis a solution of internal standard (vide supra) in toluene was poured into ice–water, a 1-mL aliquot of the reaction mixture (at different reaction times) added, and the mixture extracted with ether. The extract was washed with 10% sodium bicarbonate solution, dried over anhydrous sodium sulfate, and evaporated. The residue was injected into the gas chromatograph.

In the experiments designed for product isolation, rather than product analysis, the analytically found optimum reaction conditions were followed, the above workup was reproduced, and the products were purified by column chromatography, distillation, or crystallization. The yields of isolated products were ca. 6% lower than those based on GC analysis. The reaction conditions are detailed in Table VI. The products of unknown constitution and new data on known substances are described below.

Hydrindanone 6b: IR 1750 (s, C=O) cm^{-1}; ^1H NMR δ 1.70 (s, 3, Me), 5.35 (br s, 1, olefinic H). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.80; H, 9.45.

Hydrindanone 7b: IR 1750 (s, C=O), 1637 (w, C=C) cm^{-1}; ^1H NMR δ 1.66 (s, 3, Me), 5.36 (br s, 1, olefinic H). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.20; H, 9.30.

Hydrindanone 7d: IR 1740 (s, C=O), 1655 (w, C=C) cm^{-1}; ^1H NMR δ 1.01 (s, 3, Me), 5.56 (br s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 175–176 °C. Anal. Calcd for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 57.80; H, 5.60; N, 17.40.

Hydrindanone 7e: IR 1750 (s, C=O) cm^{-1}; ^1H NMR δ 0.97 (s, 3, Me), 1.67 (s, 3, olefinic Me), 5.25 (br s, 1, olefinic H). 2,4-Dinitrophenylhydrazone, mp 142–143 °C. Anal. Calcd for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 59.00; H, 5.60; N, 16.50.

Hydrindanone 7f:[36] IR 1745 (s, C=O), 1665 (w, C=O) cm^{-1}; ^1H NMR δ 0.97 (d, 3, J = 6 Hz, Me), 1.05 (s, 3, Me), 5.57 (br s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 220–222 °C. Anal. Calcd for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 59.60; H, 5.80; N, 16.70.

Octalone 8a:[12,13] mp 46–47 °C: IR 1720 (s, C=O) cm^{-1}; ^1H NMR δ 1.0–2.6 (m, 12, 5 CH_2, 2 CH), 5.65 (br s, 2, olefinic Hs). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.40; H, 9.30. 2,4-Dinitrophenylhydrazone, mp 195–196 °C.

Octalone 8b: IR 1720 (s, C=O) cm^{-1}; ^1H NMR δ 1.62 (s, 3, Me), 5.30 (br s, 1, olefinic H). 2,4-Dinitrophenylhydrazone, mp

(36) Conia, J.-M.; Moinet, G. *Bull. Soc. Chim. Fr.* **1969**, 500.

Table V. ^{13}C Chemical Shifts of *cis*-Octalones 9, 10, 16, 20, and 21 and *cis*-Decalones 25 and 27[a]

	shift													
carbon	9c	9d[b]	9e[c]	9f[c]	10	16a	16d	20c	21	25c[d]	25d	25f	25g	27
C(1)	210.2	213.5	214.7	213.6	214.3	210.5	214.6	210.6	214.7	215.0	215.0	212.6	215.7	212.1
C(2)	53.2	47.2	47.0	50.2	51.1	47.0	46.2	49.2	48.2	49.0	51.9	50.9	48.3	48.7
C(3)	32.2	30.6	31.3	38.5	31.4	23.3	32.5	32.6	37.4	33.8	42.9	35.5	34.2	26.1
C(4)	130.6	122.3	116.4	130.9	128.9	124.4[e]	122.8	130.7	120.9	22.6	29.0	28.7	21.1	21.9
C(5)	123.0	123.4	130.3	122.0	123.3	124.5[e]	125.1	123.0	122.1	24.9	26.5	26.7	23.8	24.9
C(6)	25.8	27.5	32.7	27.3	28.2	26.7	22.5	24.6	34.5	26.2	26.7	24.1	24.5	29.2
C(7)	39.1	40.4	41.3	42.0	42.9	34.9	47.6	49.5	41.4	44.4	47.5	53.4	51.5	39.1
C(8)	29.5	27.3	27.6	25.4	27.5	38.4	33.4	33.2	27.5	28.6	22.9	33.4	33.7	39.7
C(9)	24.4	24.7	24.9	23.0	25.7	30.7	40.3	36.6	24.9	22.6	30.8	35.7	37.3	29.4
C(10)	42.8	36.6	36.8	38.9	37.2	49.3	34.4	39.3	36.9	37.6	39.4	39.8	34.7	49.8
Me	17.4		23.4	23.4	14.6			17.7	18.7 18.7		23.9	19.9		
ang Me		19.8	20.1	17.7	14.3		22.8		20.4	25.5	16.7		26.9	
α-Me							20.5	26.6				26.9	27.4	
β-Me						22.3	31.7	27.2				28.0	31.5	22.3

[a] The δ values are in parts per million downfield from Me_4Si; δ(Me_4Si) = δ($CDCl_3$) + 76.9 ppm. The arbitrary carbon numbering is based on formula **30**. The Me values refer to the shifts of the diene-derived methyl groups. [b] References 6g,f'. [c] Reference 8g. [d] References 30, 33, 34a,c, and 35. [e] Signals may be interchanged.

Table VI. Reaction Conditions of the Diels–Alder Reactions of Dienes 1 with Cycloalkenones 2–5 Catalyzed by Aluminum Chloride[a,b]

	ratios			complexation		reaction		
	diene/ketone	$AlCl_3$/ketone	ketone concn	temp	time	temp	time	product yield
1a-2a	13	0.90	0.10	70	15	70	5	95
1b-2a	15	0.20	0.10	70	15	50	71	80
1c-2a	9	0.25	0.10	70	15	40	81	77
1a-2b	3	0.90	0.10	22	40	70	17	92
1b-2b	15	0.25	0.20	22	40	40	40	73
1c-2b	3	0.25	0.15	22	40	40	31	80
1a-3a	3	0.50	0.10	22	40	70	22	84
1b-3a	3	0.25	0.10	22	40	40	140	70
1c-3a	3	0.25	0.10	22	40	40	96	81
1a-5a	3	0.90	0.10	22	40	70	11	80
1a-5b	3	0.90	0.10	22	40	70	65	69
1a-5c	3	0.90	0.20	22	40	40	47	87
1b-5c	15	0.25	0.10	22	40	40	80	75
1c-5c	3	0.25	0.10	22	40	40	48	90
1a-3b	3	0.90	0.20	22	12	70	10	93
1b-3b	3	0.25	0.20	22	12	25	17	79
1c-3b	3	0.25	0.20	22	12	25	11	92
1a-5d	3	0.90	0.10	22	40	70	51	80
1a-4a	6	0.90	0.20	22	40	25	15	98
1b-4a	6	0.25	0.20	22	40	25	87	73
1c-4a	3	0.25	0.20	22	40	25	32	80
1a-4b	3	0.90	0.40	22	40	25	18	95
1b-4b	3	0.25	0.20	22	40	25	8	90
1c-4b	3	0.25	0.20	22	40	25	6	85

[a] Ratios of equivalents; ketone concentration in molarity; temperature in °C; complexation time in minutes; reaction time in hours; product yield in percent. [b] Product ratios listed in Table I and the discussion.

198–199 °C. Anal. Calcd for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 59.40; H, 5.75; N, 16.00.

Octalone 8c: IR 1720 (s, C=O) cm^{-1}; ^1H NMR δ 0.94 (d, 3, *J* = 6 Hz, Me), 5.37 (br s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 186–187 °C. Anal. Calcd for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 58.80; H, 5.80; N, 16.40.

Octalone 9c: IR 1723 (s, C=O) cm^{-1}; ^1H NMR δ 1.27 (d, 3, *J* = 6 Hz, Me), 5.37 (br s, 2, olefinic Hs). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.10; H, 9.90.

Octalone 9d:[6g,f,29] bp 70 °C (0.8 torr); IR 1705 (s, C=O), 1655 (w, C=C) cm^{-1}; ^1H NMR δ 1.03 (s, 3, Me), 5.55 (br s, 2, olefinic Hs). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.60; H, 9.70. 2,4-Dinitrophenylhydrazone, mp 163–164 °C.

Octalone 9e:[15] IR 1705 (s, C=O) cm^{-1}; ^1H NMR δ 1.02, 1.65 (s, 3 each, Me), 5.23 (br s, 1, olefinic H). 2,4-Dinitrophenyldrazone, mp 174–175 °C. Anal. Calcd for $C_{18}H_{22}O_4N_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.30; H, 6.20; N, 15.80.

Octalone 9f:[15] IR 1720 (s, C=O) cm^{-1}; ^1H NMR δ 1.15 (d, 3, *J* = 6 Hz, Me), 1.30 (s, 3, Me), 5.45 (br s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 201 °C dec. Anal. Calcd for $C_{18}H_{22}O_4N_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.40; H, 6.25; N, 15.85.

Octalone 10:[15] IR 1715 (s, C=O) cm^{-1}; ^1H NMR δ 0.75 (d, 3, *J* = 6 Hz, Me), 0.87 (s, 3, Me), 5.45 (br s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 173–174 °C. Anal. Calcd for $C_{18}H_{22}O_4N_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.20; H, 6.25; N, 15.80.

Hydrobenzosuberone 11a: mp 45–46 °C; IR 1705 (s, C=O); 1650 (w, C=C) cm^{-1}; ^1H NMR δ 1.1–2.8 (m, 14, 6 CH_2, 2 CH), 5.59 (br s, 2, olefinic Hs). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.40; H, 9.80. 2,4-Dinitrophenylhydrazone, mp 150–151 °C.

Hydrobenzosuberone 12a: IR 1705 (s, C=O), 1655 (w, C=C) cm^{-1}; ^1H NMR δ 1.3–2.8 (m, 14, 6 CH_2, 2 CH), 5.52 (br s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 115–118 °C. Anal. Calcd for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 59.20; H, 5.80; N, 16.30.

Hydrobenzosuberone 11b: IR 1715 (s, C=O) cm^{-1}; ^1H NMR δ 1.65 (s, 3, Me), 5.27 (br s, 1, olefinic H). 2,4-Dinitrophenylhydrazone, mp 149–151 °C. Anal. Calcd for $C_{18}H_{22}O_4N_4$: C, 60.32;

H, 6.19; N, 15.63. Found: C, 60.20; H, 6.20; N, 15.57.

Hydrobenzosuberone 12b: IR 1720 (s, C=O) cm^{-1}; ^1H NMR δ 1.62 (s, 3, Me), 5.25 (br s, 1, olefinic H). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.80; H, 10.20.

Hydrobenzosuberone 11c: IR 1715 (s, C=O), 1655 (w, C=C) cm^{-1}; ^1H NMR δ 0.88 (d, 3, J = 6 Hz, Me), 5.42 (br s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 141–142 °C. Anal. Calcd for $C_{18}H_{22}O_4N_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.60; H, 6.20; N, 15.40.

Hydrobenzosuberone 12c: IR 1715 (s, C=O) cm^{-1}; ^1H NMR δ 0.97 (d, 3, J = 6 Hz, Me), 5.42 (br s, 2, olefinic Hs). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.95; H, 10.20.

Hydrobenzosuberone 12d: bp 82 °C (0.1 torr); IR 1700 (s, C=O), 1660 (w, C=C) cm^{-1}; ^1H NMR δ 0.86, 1.00, 1.03 (s, 3 each, Me), 5.53 (br s, 2, olefinic Hs). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.50; H, 10.60. 2,4-Dinitrophenylhydrazone, mp 194–195 °C.

Hydrobenzosuberone 12e: mp 41–42 °C; IR 1700 (s, C=O) cm^{-1}; ^1H NMR δ 0.87, 1.00, 1.05 (s, 3 each, Me), 1.65 (s, 3, olefinic Me), 5.25 (br s, 1, olefinic H). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.60; H, 11.00. 2,4-Dinitrophenylhydrazone, mp 183–185 °C.

Hydrobenzosuberone 12f: IR 1700 (s, C=O), 1666 (w, C=C) cm^{-1}; ^1H NMR δ 0.92, 0.97, 1.03 (s, 3 each, Me), 1.15 (d, 3, J = 6 Hz, Me), 5.47 (br, s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 203–204 °C. Anal. Calcd for $C_{21}H_{28}O_4N_4$: C, 62.98; H, 7.05; N, 13.99. Found: C, 62.70, H, 7.10; N, 14.10.

Octalone 15a:[8d] mp 42–43 °C; IR 1705 (s, C=O), 1655 (w, C=C) cm^{-1}; ^1H NMR δ 0.96 (d, 3, J = 6 Hz, Me), 5.67 (m, 2, olefinic Hs). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.70; H, 10.00. 2,4-Dinitrophenylhydrazone, mp 158–160 °C.

Octalone 16a: IR 1720 (s, C=O), 1666 (w, C=C) cm^{-1}; ^1H NMR δ 1.04 (d, 3, J = 6 Hz, Me), 5.58 (m, 2, olefinic Hs). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.75; H, 9.90.

Octalone 15b: bp 56–58 °C (0.2 torr); IR 1715 (s, C=O), 1655 (w, C=C) cm^{-1}; ^1H NMR δ 0.89, 1.05 (s, 3 each, Me), 5.54 (br s, 2, olefinic Hs). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85, H, 10.18. Found: C, 80.30; H, 10.20. 2,4-Dinitrophenylhydrazone, mp 162–164 °C.

Octalone 15c: mp 70–71 °C: IR 1715 (s, C=O), 1660 (w, C=C) cm^{-1}; ^1H NMR δ 1.01, 1.09 (s, 3 each, Me), 5.54 (br s, 2, olefinic Hs). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.60; H, 10.25. 2,4-Dinitrophenylhydrazone, mp 173–174 °C.

Octalone 16d: mp 60 °C; IR 1710 (s, C=O), 1660 (w, C=O) cm^{-1}; ^1H NMR δ 0.98, 1.03, 1.09 (s, 3 each, Me), 5.57 (br s, 2, olefinic Hs). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.80; H, 10.50. 2,4-Dinitrophenylhydrazone, mp 171–173 °C.

Octalone 17c: mp 69–70 °C; IR 1705 (s, C=O) cm^{-1}; ^1H NMR δ 1.01, 1.10 (s, 3 each, Me), 1.62 (s, 3, olefinic Me), 5.25 (br s, 1, olefinic H). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.60; H, 10.40. 2,4-Dinitrophenylhydrazone, mp 209–210 °C.

Octalone 19c: IR 1715 (s, C=O), 1670 (w, C=C) cm^{-1}; ^1H NMR δ 1.00 (d, 3, J = 6 Hz, Me), 1.02, 1.15 (s, 3 each, Me), 5.42 (br s, 2, olefinic Hs). 2,4-Dinitrophenylhydrazone, mp 163–164 °C. Anal. Calcd for $C_{19}H_{24}O_4N_4$: C, 61.27; H, 6.50; N, 15.05. Found: C, 61.60; H, 6.60, N, 15.20.

Octalone 20c: IR 1725 (s, C=O), 1660 (w, C=C) cm^{-1}; ^1H NMR δ 1.00, 1.37 (s, 3 each, Me), 1.20 (d, 3, J = 6 Hz, Me), 5.40 (br s, 2, olefinic Hs). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.00; H, 10.30.

Octalone 21. Aluminum chloride (0.15 equiv) and 1 equiv of 2-methyl-2-cyclohexenone (**3b**, 0.3 M solution) interacted at 22 °C for 12 min. After the addition of 3 equiv of 2,3-dimethyl-1,3-butadiene (**1d**) the reaction was continued at 25 °C for 20 h, leading to ketone **21**: 80% yield; bp 80 °C (4 torr); IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 1.02 (s, 3, Me), 1.60, 1.60 (s, 3 each, olefinic Me). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.80; H, 10.40. 2,4-Dinitrophenylhydrazone, mp 174–175 °C.

Epimerizations of Diels–Alder Adducts. A solution of 40 mg of cis and/or trans, angularly unsubstituted, bicyclic ketone and sodium methoxide (from 0.25 g of sodium) in 15 mL of dry methanol was stirred under nitrogen at room temperature up to the time of equilibrium establishment, as seen by GC monitoring. The product ratios, detailed in the discussion, are based on GC analysis.

Hydrogenations of Diels–Alder Adducts. The reduction of the bicyclic, olefinic ketones was carried out in dry ethanol solution over 10% palladium/charcoal and was followed by the usual workup. In the case of ketones **12f** and **19d** the catalyst was replaced by platinum oxide in view of the occurrence of palladium-induced rearrangements under the hydrogenatioin conditions.

Hydrindanone 22b:[6b',36] IR 1740 (s, C=O) cm^{-1}; ^1H NMR δ 1.18 (d, 3, J = 6 Hz, Me). 2,4-Dinitrophenylhydrazone, mp 198–200 °C. Anal. Calcd for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.06; N, 16.86. Found: C, 58.30; H, 6.00; N, 16.70.

Hydrindanone 23b:[33,34] mp 31–32 °C; IR 1730 (s, C=O) cm^{-1}; ^1H NMR δ 1.00 (s, 3, Me). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.70; H, 10.70. 2,4-Dinitrophenylhydrazone, mp 143–144 °C.

Hydrindanone 23c:[36] IR 1750 (s, C=O) cm^{-1}; ^1H NMR δ 1.05 (s, 3, Me), 1.15 (d, 3, J = 6 Hz, Me). 2,4-Dinitrophenylhydrazone, mp 133–134 °C. Anal. Calcd for $C_{17}H_{22}O_4N_4$: C, 58.94; H, 6.40; N, 16.18. Found: C, 59.20; H, 6.40; N, 16.10.

Decalone 25d:[15] IR 1715 (s, C=O) cm^{-1}; ^1H NMR δ 1.10 (d, 3, J = 6 Hz, Me), 1.32 (s, 3, Me). 2,4-Dinitrophenylhydrazone, mp 188–189 °C. Anal. Calcd for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.10; H, 6.70; N, 15.60.

Decalone 26a, mp 30 °C; IR 1702 (s, C=O) cm^{-1}; ^1H NMR δ 1.10 (d, 3, J = 5 Hz, Me). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.80; H, 10.80. 2,4-Dinitrophenylhydrazone,[37] mp 157–158 °C.

Decalone 27: IR 1705 (s, C=O) cm^{-1}; ^1H NMR δ 0.96 (d, 3, J = 5 Hz, Me). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.20; H, 10.85.

Decalone 24c: IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 1.00, 1.09 (s, 3 each, Me). 2,4-Dinitrophenylhydrazone, mp 218–220 °C. Anal. Calcd for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.00; H, 6.80; N, 15.70.

Decalone 24d: IR 1715 (s, C=O) cm^{-1}; ^1H NMR δ 0.90 (d, 3, J = 6 Hz, Me), 0.95, 1.10 (s, 3 each, Me). 2,4-Dinitrophenylhydrazone, mp 190–191 °C. Anal. Calcd for $C_{19}H_{26}O_4N_4$: C, 60.94; H, 7.00; N, 14.96. Found: C, 61.00; H, 7.05; N, 14.80.

Decalone 25f: IR 1715 (s, C=O) cm^{-1}; ^1H NMR δ 0.96 (d, 3, J = 6 Hz, Me), 1.09, 1.29 (s, 3 each, Me). Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.80; H, 11.35.

Decalone 25g: IR 1700 (s, C=O) cm^{-1}; ^1H NMR δ 1.00, 1.15, 1.15 (s, 3 each, Me). 2,4-Dinitrophenylhydrazone, mp 141–143 °C. Anal. Calcd for $C_{19}H_{26}O_4N_4$: C, 60.94; H, 7.00; N, 14.96. Found: C, 61.00; H, 7.05; N, 15.00.

Hydrobenzosuberone 28b: IR 1713 (s, C=O) cm^{-1}; ^1H NMR δ 0.75 (d, 3, J = 6 Hz, Me). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.10; H, 11.20.

Hydrobenzosuberone 29b: IR 1710 (s, C=O) cm^{-1}; ^1H NMR δ 0.92 (d, 3, J = 6 Hz, Me). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.70; H, 11.10.

Hydrobenzosuberone 29c, mp 43 °C: IR 1695 (s, C=O) cm^{-1}; ^1H NMR δ 0.91, 1.00, 1.04 (s, 3 each, Me). Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.30; H, 11.70. 2,4-Dinitrophenylhydrazone, mp 184–185 °C.

Hydrobenzosuberone 29d: IR 1700 (s, C=O) cm^{-1}; ^1H NMR δ 0.94, 1.00, 1.04 (s, 3 each, Me), 1.20 (d, 3, J = 3 Hz, Me). 2,4-Dinitrophenylhydrazone, mp 140–141 °C. Anal. Calcd for $C_{21}H_{30}O_4N_4$: C, 62.66; H, 7.51; N, 13.92. Found: C, 62.90; H, 7.50; N, 13.80.

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Registry No. **1a**, 106-99-0; **1b**, 78-79-5; **1c**, 2004-70-8; **1d**, 513-81-5; **2a**, 930-30-3; **2b**, 1120-73-6; **3a**, 930-68-7; **3b**, 1121-18-2; **4a**, 1121-66-0; **4b**, 35836-89-6; **5a**, 7214-50-8; **5b**, 4694-17-1; **5c**, 1073-13-8; **5d**, 13395-71-6; **6a**, 25050-74-2; **6b**, 83586-03-2; **6c**, 83586-04-3; **7a**, 53921-54-3; **7b**, 83586-05-4; **7d**, 17428-89-6; **7d**·DNP, 17428-92-1; **7e**, 83586-06-5; **7e**·DNP, 83586-07-6; **7f**,

(37) Thin-layer chromatography of this derivative showed it to be slightly impure with the derivative of decalone **27**. Preparation of the latter led to the same mixture.

22643-67-0; **7f**·DNP, 22643-68-1; **8a**, 70749-11-0; **8a**·DNP, 83586-08-7; **8b**, 83586-09-8; **8b**·DNP, 83586-10-1; **8c**, 83586-11-2; **8c**·DNP, 83586-12-3; **9a**, 70749-10-9; **9c**, 83586-13-4; **9d**, 18174-04-4; **9d**·DNP, 83586-14-5; **9e**, 83586-15-6; **9e**·DNP, 83586-16-7; **9f**, 22645-08-5; **9f**·DNP, 83586-17-8; **10**, 83586-18-9; **10**·DNP, 83586-19-0; **11a**, 70708-57-5; **11a**·DNP, 83586-20-3; **11b**, 59456-40-5; **11b**·DNP, 83586-21-4; **11c**, 83586-22-5; **11c**·DNP, 83586-23-6; **12a**, 70708-57-5; **12a**·DNP, 83586-24-7; **12b**, 83586-25-8; **12c**, 83586-26-9; **12d**, 83586-27-0; **12d**·DNP, 83586-28-1; **12e**, 83586-29-2; **12e**·DNP, 83586-30-5; **12f**, 83586-31-6; **12f**·DNP, 83586-32-7; **15a**, 54812-89-4; **15a**·DNP, 83586-33-8; **15b**, 83586-34-9; **15b**·DNP, 83586-35-0; **15c**, 83586-36-1; **15c**·DNP, 83615-33-2; **16a**, 83648-02-6; **16d**, 83586-37-2; **16d**·DNP, 83586-38-3; **17c**, 83586-39-4; **17c**·DNP, 83586-40-7; **19c**, 83586-41-8; **19c**·DNP, 83586-42-9; **20c**, 83586-43-0; **21**, 83586-44-1; **21**·DNP, 83586-45-2; **22c**, 22643-74-9; **22c**·DNP, 22643-78-3; **23b**, 13025-91-7; **23b**·DNP, 83586-46-3; **23c**, 22647-26-3; **23c**·DNP, 22643-65-8; **24e**, 83586-47-4; **24e**·DNP, 83586-48-5; **24f**, 83586-49-6; **24f**·DNP, 83586-50-9; **25d**, 22645-06-3; **25d**·DNP, 22645-07-4; **25f**, 83586-51-0; **25g**, 83586-52-1; **25g**·DNP, 83586-53-2; **26a**, 83586-54-3; **26a**·DNP, 83586-55-4; **27**, 83586-56-5; **28b**, 83586-57-6; **29b**, 83586-58-7; **29c**, 83586-59-8; **2c**·DNP, 83586-60-1; **29d**, 83586-61-2; **29d**·DNP, 83586-62-3; $AlCl_3$, 7446-70-0.

Hydroboration. 61. Diisopinocampheylborane of High Optical Purity. Improved Preparation and Asymmetric Hydroboration of Representative Cis-Disubstituted Alkenes

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The convenient preparation of diisopinocampheylborane of high enantiomeric purity (99.1%) utilizing the commercially available relatively stable borane–methyl sulfide and α-pinene of 92% enantiomeric purity is described. Methyl sulfide liberated in the hydroboration step interferes with the equilibration needed to improve the optical purity of the reagent. However, this difficulty is readily overcome by removal of methyl sulfide under vacuum following hydroboration of the α-pinene. The reagent is then equilibrated in THF with 15% excess α-pinene at 0 °C for 3 days. During this equilibration period, the major isomer becomes incorporated selectively into the reagent. This high optical purity diisopinocampheylborane has been utilized for asymmetric hydroboration of representative cis-disubstituted alkenes such as *cis*-2-butene, *cis*-3-hexene, *cis*-2-pentene, norbornene, norbornadiene, *cis*-4,4-dimethyl-2-pentene, and *cis*-propenylbenzene. Oxidation of the intermediate organoboranes provides the corresponding alcohols in enantiomeric purities of 60–98%.

Diisopinocampheylborane (Ipc_2BH) is perhaps one of the most versatile chiral reagents readily available for laboratory use. It has been applied to the synthesis of many chiral products such as alcohols, halides, amines, ketones, hydrocarbons, and α-amino acids. It has been also applied for the kinetic resolution of alkenes, dienes, and allenes.[2]

In the early exploration of the characteristics of the hydroboration reaction, we were content with the 87% optical purity of 2-butanol realized in the hydroboration of *cis*-2-butene with Ipc_2BH generated from sodium borohydride in situ in diglyme.[3] Disappointingly, a somewhat lower optical purity of 2-butanol (78% ee) was achieved when the hydroboration was carried out with borane in the more convenient solvent tetrahydrofuran (THF). The less gratifying result was attributed to the greater solubility of Ipc_2BH in THF, resulting in a greater dissociation into the less desirable $IpcBH_2$ of the Ipc_2BH present. In diglyme the reagent exists predominantly as the crystalline material, with minimal dissociation.

A more systematic study of the preparation of Ipc_2BH in THF was carried out more recently.[4] It was found that the reaction of α-pinene with BH_3·THF proceeds rapidly to triisopinocampheyldiborane or monoisopinocampheylborane ($IpcBH_2$), named as the monomer. This species reacts faster than Ipc_2BH with the olefin. It has been established that $IpcBH_2$ on hydroboration–oxidation gives alcohols of configuration opposite[3,6] to that produced by Ipc_2BH. Therefore, a good asymmetric hydroboration cannot be achieved with such a mixture of reagents. In order to suppress the formation of monoisopinocampheylborane, 15% excess α-pinene was used for the preparation of Ipc_2BH. A fortuitous development was the discovery that equilibration of such reaction mixtures at 0 °C for 3 days resulted in the formation of Ipc_2BH, more optically pure than the initial α-pinene. The longer reaction time was accompanied by the selective incorporation of the major isomer of α-pinene into the crystalline reagent, with concurrent accumulation of the minor isomer in the solution. This preparation of Ipc_2BH of high optical purity, however, suffers from a serious limitation. It involves the use of concentrated solutions of borane in THF (2.26 M) and α-pinene of relatively high optical purity (97.4% ee). Neither of these materials is currently available commercially, thereby limiting application of this desirable chiral reagent. Moreover, the high optical purity Ipc_2BH has been applied only for the hydroboration of *cis*-2-butene[4] and *cis*-3-hexene.[6] It appeared desirable to test it more broadly.

In the recent past, borane–methyl sulfide[5] (BMS), because of its several advantages over BH_3·THF or BH_3·DG, has become a key source for the preparation of synthetically useful organoboranes. The present study, therefore, reports the use of commercially available[7] borane–methyl

(1) Postdoctoral research associates on Grant 2 R01 GM 10937-19 from the National Institutes of Health.

(2) For a recent review on "Asymmetric Syntheses via Chiral Organoborane Reagents", see: Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, *37*, 3547.

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(7) Borane–methyl sulfide (BMS) and (+)-α-pinene ($[\alpha]^{23}_D$ +47.1° (neat), 92% ee) are available from the Aldrich Chemical Co., Inc.

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