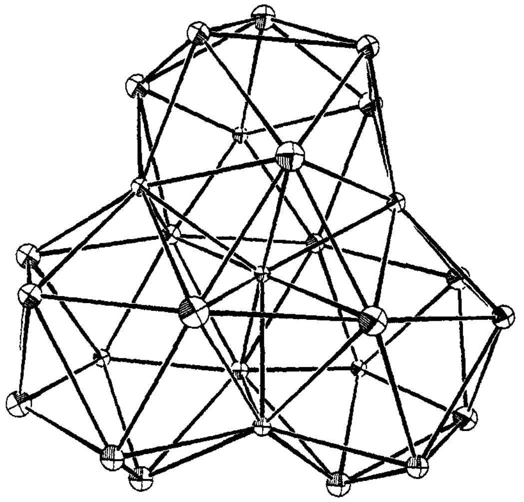

Figure 3. Condensed unit of three boron icosahedra, B_{28}-(C_{3v}), found in β-rhombohedral boron.

$P6_3/mmc$. The alternative operator, a 3_1 normal to the layer, produces a three-layer framework structure with the full cubic symmetry of the group $Fd\bar{3}m$. This is the framework both of α-AlB_{12} and of β-B_{105}-($R\bar{3}m$). It should be mentioned that these frameworks can be derived equally well through formal layer twin operators.[8]

Further insight into the relationships among the structures can be achieved by focusing upon still another structural unit in which 12 interbonded icosahedra define the vertices of a regular truncated tetrahedron. Both frameworks can be generated in detail by appropriately sharing hexagonal faces of this elegant B_{144}-(T_d) unit. Each of the large holes thus defined has 12 internally directed, unsatisfied bonds that sharply delimit the size, the geometry, and the symmetry of the structural units contained therein. In λ-AlB_{12}, the holes are alternately occupied by one of two novel structural units condensed from boron icosahedra (Figure 2). They fully satisfy the internal bonding and interlink in a subsidiary framework through the open hexagonal faces. Along with some attendant deviations from ideality, this reduces the overall symmetry of the structure to $P2_12_12_1$. Similarly, in α-AlB_{12}, the B_{20}-(C_2) unit lies on the twofold axis of the hole in the $Fd3m$ framework and the symmetry of the structure is reduced to $P4_32_12$. Finally and dramatically, the B_{28}-(C_{3v}) unit[4] (Figure 3) occupies the same tetrahedral hole in the β-B_{105}-($R\bar{3}m$) structure, preserves one of the threefold axes of $Fd3m$, and produces the observed rhombohedral symmetry.

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Supplementary Material Available. Tables of atomic positional parameters and temperature factors and of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

References and Notes

(1) I. Higashi, T. Sakurai and T. Atoda, *J. Solid State Chem.*, **20**, 67 (1977).
(2) A single-crystal structure analysis of BeB_6 has been completed in this laboratory; the details will be reported elsewhere. For the preparation, see D. E. Sands, C. F. Cline, A. Zalkin and C. L. Hoenig, *Acta Crystallogr.*, **14**, 309 (1961).
(3) R. E. Hughes, C. H. L. Kennard, D. B. Sullenger, H. A. Weakliem, D. E. Sands, and J. L. Hoard, *J. Am. Chem. Soc.*, **85**, 361 (1963).
(4) J. L. Hoard and R. E. Hughes in "The Chemistry of Boron and its Compounds", E. L. Muetterties, Ed., Wiley, New York, N.Y., 1967.
(5) C. P. Talley, B. Post, and S. LaPlaca in "Boron-Synthesis, Structure and Properties", J. A. Kohn, W. F. Nye, and G. K. Gaule, Ed., Plenum Press, New York, N.Y., 1960.
(6) A number of related non-stoichiometric aluminum borides are being analyzed structurally in this laboratory as are several nonstoichiometric metal borides based upon the β-rhombohedral boron structure. For the latter, see, for example, S. Andersson and B. Callmer, *J. Solid State Chem.*, **10**, 219 (1974).
(7) J. A. Kohn and D. W. Eckart, *Zeit. Kristallogr.*, Bd **116**, 134 (1961).
(8) See ref 4. Also see L.-T. Tai, Ph.D. Thesis, Cornell University, 1969, wherein the basic framework of γ-AlB_{12} is fully described. When this was combined with features of the condensed icosahedral unit in α-AlB_{12}, the full structure systematically unfolded.
(9) J. L. Hoard, D. B. Sullenger, C. H. L. Kennard, and R. E. Hughes, *J. Solid State Chem.*, **1**, 268 (1970).
(10) F. C. Frank and J. S. Kasper, *Acta Crystallogr.*, **12**, 483 (1959).

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Three-Carbon Annulation. Formation of Five-Membered Rings from Olefins via Diels–Alder Reactions

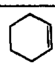
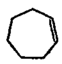
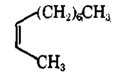
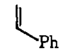
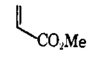
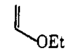
Sir:

Owing to the increasing appearance of cyclopentane rings in large numbers of natural products, especially those of biological importance, great effort has recently been expended to develop new synthetic methods for the construction of five-membered-ring systems.[1-8] Although many of these newly developed methods very successfully prepare five-membered rings, they are often not applicable to the closely related problem of three-carbon annulation, i.e., the attachment of a three-carbon unit to two adjacent carbons of a cyclic or acyclic precursor to form a cyclopentane ring, i.e., [3 + 2 → 5]. No good general method exists for this transformation, although the two corresponding ones, [2 + 2 → 4] (photochemical cyclization of two olefins) and [2 + 4 → 6] (Diels–Alder reaction), are quite well known and are of great synthetic utility. We wish now to report the successful accomplishment of this goal of three-carbon annulation, namely, a highly versatile process for the formation of cyclopentanones from olefins in good overall yields via a Diels–Alder reaction as the key step.

The direct attachment of a three-carbon unit to an olefin by some cycloaddition process has been reported previously in the literature.[1-8] However, in nearly all cases, the double bond was activated by electron-donating substituents (usually ketone derivatives such as enol acetate,[2] enamine,[3] trimethylsilyl enol ether,[4] or enolate of β-keto ester[5] or via ketones themselves[1,6]) or electron-withdrawing substituents (normally α,β-unsaturated esters[7] or sulfoxides[8]). To impart the greatest generality to the method, we desired to place as few restrictions as possible on the nature of the olefinic substrate so that not only electron-rich and electron-poor olefins but even simple unsubstituted olefins would afford good yields of the final cyclopentanone products. For this reason we have developed a method using the very highly reactive compound, dimethoxytetrachlorocyclopentadiene (**1**) as the diene component in a Diels–Alder reaction. The remarkable reactivity of this molecule in cycloaddition reactions was first recognized by McBee,[9] who observed that even simple olefins such as allyl alcohol, allyl bromide, and indene gave good yields of cycloadducts. Much subsequent effort has extended the scope of this facile cycloaddition reaction to include a large variety of olefins and alkynes.[10-12]

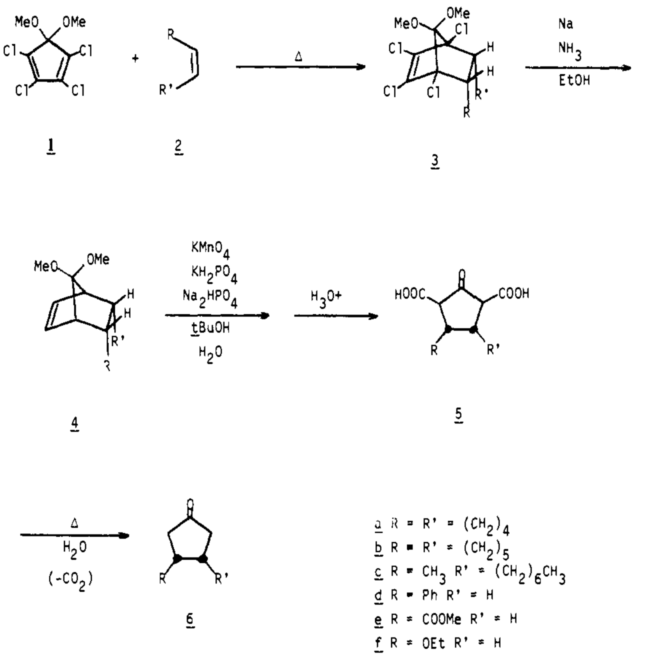
The general method is outlined in Scheme I; the yields obtained in its application to a variety of olefins are listed in Table I. When the diene **1** is heated in the presence of the olefins **2a–f**, high yields of the Diels–Alder adducts **3a–f** are formed.[13] Replacement of all the chlorine atoms in compounds **3a–f** by

Table I. Three-Carbon Annulation. Formation of Cyclopentanones from Olefins[a]

Starting material	% yield (mp, °C) of **3**	% yield of **4**	% yield of **5**	% yield of **6**	% overall yield **2–6**
 **2a**	77 (79)[b]	87	70	80[c]	37
 **2b**	75 (96–97)	86	70	85[d]	38
 **2c**	71 (liq)	86	52	69	22
 **2d**	97 (74–75)[e]	76	72	75[f]	40
 **2e**	95 (liq)	74[g]	70[g]	71[g,h]	34
 **2f**	86 (liq)	73	67	*i*	*i*

[a] Yields given are for isolated products. [b] Reference 10j. [c] *cis*-Bicyclo[4.3.0]nonan-8-one (6a) is known: P. S. Engel and H. Ziffer, *Tetrahedron Lett.*, 5181 (1969); J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Am. Chem. Soc.*, 98, 6529 (1976), and references in both. [d] *cis*-Bicyclo[5.3.0]decan-9-one (6b) is known: R. Granger, H. Orzalesi, and J. P. Chapat, *Bull. Soc. Chim. Fr.*, 1951 (1967); A. M. Islam and R. A. Raphael, *J. Chem. Soc.*, 3151 (1955). [e] Reference 9. [f] 3-Phenylcyclopentanone (6d) is known: H. A. Weidlich and G. H. Daniels, *Chem. Ber.*, 72, 1590 (1939); W. Baker and W. G. Leeds, *J. Chem. Soc.*, 974 (1948). [g] Since reduction of the tetrachloro ester with sodium in ammonia/*tert*-butyl alcohol gave the primary alcohol (an example of the Bouveault–Blanc reduction), the ester 3e was first hydrolyzed to the acid (mp 163 °C, 97% yield) and then reduced to 5e (mp 78–79 °C). Bisdecarboxylation then gave the acid 6e (mp 65 °C). [h] Cyclopentanone-3-carboxylic acid (6c) is known: for several references, see P. Dowd, G. Senqupta and K. Sachdev, *J. Am. Chem. Soc.*, 92, 5726 (1970) [i] Warming in water afforded not only decarboxylation but also elimination of ethanol to give cyclopentenone as the major product, along with a small amount of 3-ethoxycyclopentanone 6f.

Scheme I

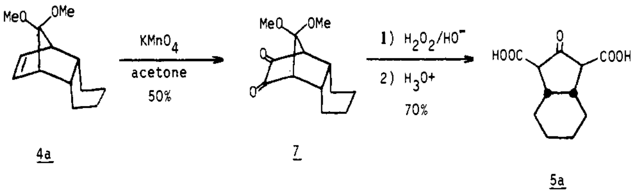


hydrogen was smoothly affected by reduction with sodium in liquid ammonia/ethanol to furnish **4a–f.** Using liquid ammonia as a solvent gives significantly higher yields than the normal reduction procedure which uses a tetrahydrofuran/*tert*-butyl alcohol solvent system.[11] Oxidation of the norbornene-type double bond proved to be the most difficult step in this four-step sequence. Many reagents and procedures afforded unsuccessful results and only after much experimentation were the following optimum conditions determined. Reaction of **4a–f** with potassium permanganate in a pH 7 buffer system (Na_2HPO_4, KH_2PO_4) with *tert*-butyl alcohol as cosolvent for about 1 h afforded the keto diacids **5a–f** after acidic workup in yields ranging from 52 to 72%. The final step of this sequence to the cyclopentanones **6a–e** involves bisdecarboxylation of the keto diacids **5a–f** which was effected by warming **5a–f** in water. This succeeded for all except the 3-ethoxy compound **5f** which underwent facile loss of ethanol under all decarboxylation conditions to afford cyclopentenone. Thus, the cyclopentanones **6a–e** are formed from the olefins **2a–e** via four steps in overall yields of 22–40%.

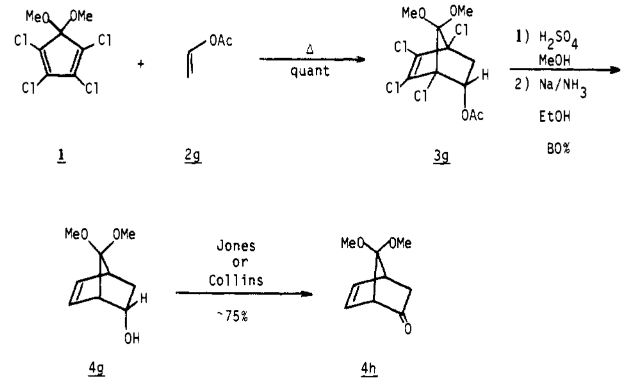
Originally we had planned to transform the tetrachloro adducts **3a–f** directly into the cyclopentanones **6a–f** via essentially one step. We had hoped that ozonolysis of the chloro olefin would give the ozonide which, upon workup with zinc in warm aqueous hydrochloric acid, would afford the desired cyclopentanones via the sequence ozonide, diacid chloride, diacid, hydrolysis of ketal to ketone, decarboxylation of bis β-keto acids, and final reduction of α-chloro ketone by zinc and acid. This ambitious plan failed when we were unable to effect ozonolysis of the very electron-deficient dichloro olefin under various forcing conditions (e.g., the double bond survives untouched in ozone-saturated solutions of dichloromethane or methanol at room temperature for several hours). This failure necessitated the alternative three-step method described herein.

The stereochemistry of the Diels-Alder adducts **3d–f** can be readily assigned as endo from the coupling constants of the endo and exo protons in ^1H NMR. The NMR spectrum of each of these three compounds exhibits an ABX-type spectrum[14] which is totally analogous in line shape and amplitude to that reported by Anet[15] for the corresponding endo adducts in the hexadeuterionorbornene system. The NMR spectra of the cyclohexene, cycloheptene, and *cis*-2-decene adducts **3a–c** do not allow one to determine their stereochemistry; however, we assume that these are also endo by analogy to the many endo adducts of this type known in the literature.[12]

Other methods for oxidation of the norbornene double bond in **4a–f** were attempted (O_3, Jones; $KMnO_4$, $NaIO_4$; H_2O_2, ^-OH; etc.), but in all cases the overall yields of the keto diacids **5a–f** were lower than those with the conditions described above. Furthermore, in some cases different products were obtained. For example, treatment of the reduced cyclohexene adduct **4a** with $KMnO_4$ in acetone afforded in 50% yield the α-diketone **7** (mp 91–92 °C; IR 1760, 1820 cm^{-1}). Further oxidation of **7** to the diacid **5a** could be accomplished in 70% yield by treatment with hydrogen peroxide followed by aqueous acidic workup.



The intermediates in this sequence can be converted into other functionalized molecules which may be useful for further synthetic transformations. For example, the Diels–Alder reaction between **1** and vinyl acetate **2g** (R = OAc; R′ = H) afforded the crude endo[14] acetate **3g** in quantitative yield. Acid-catalyzed hydrolysis and dissolving metal reduction gave the dechlorinated alcohol **4g** in 80% yield. Collins or Jones oxidation of **4g** furnished the ketone **4h** in ≃75% yield. The use of highly functionalized molecules of this type is under investigation in our laboratories.



Acknowledgement. We wish to acknowledge support of this project by a Frederick G. Cottrell Grant from the Research Corporation.

References and Notes

(1) (a) For a good summary of the newer methods, see B. M. Trost and D. E. Kelley, *J. Am. Chem. Soc.*, **98**, 248 (1976); (b) for other examples, see R. A. Ellison, *Synthesis*, 397 (1973).
(2) (a) E. Wenkert, R. A. Mueller, E. J. Reardon, Jr., S. S. Sathe, D. J. Scharf, and G. Tosi, *J. Am. Chem. Soc.*, **92**, 7428 (1970); (b) J. E. McMurry and T. E. Glass, *Tetrahedron Lett.*, 2575 (1971).
(3) R. Noyori, K. Yokoyama, S. Makino, and Y. Hayakawa, *J. Am. Chem. Soc.*, **94**, 1772 (1972).
(4) M. Miyashita, T. Yanami, and A. Yoshikoshi, *J. Am. Chem. Soc.*, **98**, 4679 (1976).
(5) P. L. Fuchs, *J. Am. Chem. Soc.*, **96**, 1607 (1974).
(6) B. M. Trost and M. J. Bogdanowicz, *J.Am. Chem. Soc.*, **95**, 5311 (1973).
(7) J. P. Marino and W. B. Mesbergen, *J. Am. Chem. Soc.*, **96**, 4050 (1974).
(8) R. F. Romanet and R. H. Schlessinger, *J. Am. Chem. Soc.*, **98**, 3701 (1974).
(9) E. T. McBee, W. R. Diveley, and J. E. Burch, *J. Am. Chem. Soc.*, **77**, 385 (1954).
(10) (a) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966). (b) P. Kniel, *Helv. Chim. Acta*, **46**, 492 (1963); **48**, 837 (1965). (c) A. Roedig, H.-H. Bauer, G. Bonse, and R. Ganns, *Chem. Ber.*, **107**, 558 (1974). (d) K. H. Büchel and A. Conte, *ibid.*, **100**, 863 (1967). (e) S.-H. Dai and W. R. Dolbier, Jr., *J. Am. Chem. Soc.*, **94**, 3946 (1972). (f) D. Seyferth and A. B. Evnin, *ibid.*, **89**, 1468 (1967). (g) H. J. Callot and C. Benezra, *Can. J. Chem.*, **48**, 3382 (1970). (h) J. W. Wilt and E. Vasilianskas, *J. Org. Chem.*, **35**, 2410 (1970). (i) W. G. Dauben and L. N. Reitman, *ibid.*, **40**, 835 (1975). (j) P. E. Hoch, *ibid.*, **26**, 2066 (1961).
(11) (a) L. A. Paquette and I. R. Dunkin, *J. Am. Chem. Soc.*, **97**, 2243 (1975); (b) R. Bicker, H. Kessler, and A. Stiegel, *Chem. Ber.*, **107**, 3053 (1974); (c) H.-D. Martin and H. L. Grafetstatter, *ibid.*, **107**, 680 (1974); (d) R. K. McCulloch, A. R. Rye, and D. Wege, *Aust. J. Chem.*, **27**, 1929 (1974); (e) D. Wege and S. P. Wilkinson, *ibid.*, **26**, 1751 (1973); (f) H. Tanida, T. Irie, and K. Tori, *Bull. Chem. Soc. Jpn.*, **45**, 1999 (1972); (g) R. W. Hoffmann and F. Frickel, *Synthesis*, 444 (1975).
(12) (a) K. Mackenzie, *Tetrahedron Lett.*, 1203 (1974); (b) J. R. Wiseman and B. P. Chong, *ibid.*, 1619 (1969); (c) C. L. Perrin and M.-T. Hsia, *ibid.*, 751 (1975); (d) M. S. Salakhov, N. A. Alekperov, P. M. Poladov, Y. S. Salakhova, M. M. Guseinov, and V. F. Kucherov, *Zh. Org. Khim.*, **9**, 942 (1973); (e) J. W. Wilt and V. P. Narutis, *J. Org. Chem.*, **40**, 2542 (1975); (f) R. I. Kagi and B. L. Johnson, *Aust. J. Chem.*, **28**, 2175 (1975); (g) J. B. Bremner, Y. Hwa, and C. P. Whittle, *ibid.*, **27**, 1597 (1974); (d) J. F. Monthony, C. M. Beechan, W. H. Okamura, *Tetrahedron*, **28**, 4285 (1972).
(13) All new compounds had spectral properties in complete accord with the assigned structures. The keto diacids **5a–f** were unstable solids with large melting point ranges. For identification they were converted (CH_2N_2, ether) into their trimethylated (tetramethylated for **5e**) derivatives (enol ether diesters). These had properties in accord with the assigned structures.
(14) **3d:** NMR (CCl_4) δ 6.9–7.3 (m, 5 H), 3.65 (dd, 1 H), 3.63 (s, 3 H), 3.53 (s, 3 H), 2.72 (dd, 1 H), 2.16 (dd, 1 H). **3e:** NMR ($CDCl_3$) δ 3.67 (s, 3 H), 3.59 (s, 3 H), 3.53 (s, 3 H), 3.4 (dd, 1 H), 2.51 (dd, 1 H), 2.20 (dd, 1 H). **3f:** NMR ($CDCl_3$) δ 4.23 (dd, 1 H), 3.58 (q, 2 H, J = 7 Hz), 3.58 (s, 3 H), 3.55 (s, 3 H), 2.58 (dd, 1H), 1.69 (dd, 1 H), 1.20 (t, 3H, J = 7 Hz). **3g:** NMR (CCl_4) δ 5.39 (dd, 1 H), 3.63 (s, 3 H), 3.58 (s, 3 H), 2.81 (dd, 1 H), 2.06 (s, 3 H), 1.68 (dd, 1 H).
(15) F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *J. Am. Chem. Soc.*, **89**, 4431 (1967).

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Ordering the Reactivity of Photogenerated, 17 Valence Electron, Metal Carbonyl Radicals

Sir:

We report herein the first ordering of reactivity of metal carbonyl radicals generated by the photoinduced cleavage of metal–metal bonds. There now exist a number of reports[1–7] showing the importance of photoinduced homolytic metal–metal bond cleavage in complexes like $M_2(CO)_{10}$ and $MM'(CO)_{10}$ (M, M′ = Mn, Re);[1–4] $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W);[5,6] $M(CO)_5M'(CO)_3(\eta^5\text{-}C_5H_5)$[7] (M = Mn, Re; M′ = Mo, W); and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$.[8] In these and related systems[9] radical cross coupling and halogen atom abstraction reactions have been used to implicate the photogeneration of 17e metal radicals such as $M(CO)_5$ and $M(CO)_3(\eta^5\text{-}C_5H_5)$ and the like; reactions 1[7] and 2[1b] are illustrative.

$$(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5 \xrightarrow[\text{isooctane}]{h\nu} (\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6 + Mn_2(CO)_{10} \quad (1)$$

$$Mn_2(CO)_{10} \xrightarrow[Ph_3CCl]{\text{UV}} 2Mn(CO)_5Cl + 2\cdot CPh_3 \quad (2)$$

Coupling of the radicals has been shown to occur at an essentially diffusion controlled rate.[6] Photogenerated $W(CO)_3(\eta^5\text{-}C_5H_5)$ radicals have been shown[10] to react bimolecularly with CCl_4, $CHCl_3$, and CH_2Cl_2 with bimolecular rate constants of 1.5×10^4, ~21, and <0.6 M^{-1} s^{-1}, respectively. In this communication we present results for the irradiation of heterodinuclear complexes which enable us to conveniently order the reactivity of 17e metal carbonyl radicals toward halogen atom donors.

We have studied the photochemistry of the M–M′ bonded complexes listed in Table I, and the chemistry is largely as schemed in reaction 3