J = 7), 1.25 (s, 3); ^{13}C NMR 213.9, 171.6, 61.6, 58.8, 46.9, 44.0, 37.4, 24.3, 14.0, 12.8.

The data for **68**: ^{1}H NMR 5.80 (tdd, 1, J = 6.6, 10.3, 17), 5.06 (br d, 1, J = 17), 5.01 (br d, 1, J = 10.3), 4.27 (q, 2, J = 7.2), 2.97 (td, 1, J = 7.4, 18), 2.68 (td, 1, J = 7.4, 18), 2.38 (br dt, 2, J = 7.4, 7.4), 1.83 (s, 3), 1.30 (t, 3, J = 7.2); ^{13}C NMR 200.5, 168.0, 136.4, 115.6, 70.7, 62.9, 36.8, 27.9, 24.4, 18.8; IR (neat) 1760, 1740 cm^{-1}. Anal. Calcd for $C_{10}H_{15}ClO_3$: C, 54.92; H, 6.91; Cl, 16.21. Found: C, 54.83; H, 6.81; Cl, 16.32.

Ethyl 2-Chloro-2-methyl-3-oxo-6-heptenoate (68). A solution of **35a** (0.058 g, 0.313 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (0.168 g, 0.626 mmol), and $CuCl_2$ (0.042 g, 0.313 mmol) in 3 mL of acetic acid was stirred at 25 °C for 22 h. Workup afforded 0.059 g (85%) of crude **68**.

Acknowledgment. We are grateful to the National Science Foundation and National Institutes of Health for generous financial support.

Registry No. **1c**, 134906-06-2; **6c**, 134906-08-4; **9**, 93185-10-5; **12**, 41079-58-7; **17**, 120790-38-7; **22**, 134906-38-0; **23a**, 134906-09-5; **23b**, 134906-14-2; **26b**, 134906-16-4; **27a**, 134906-10-8; **27a-d_1**, 134906-13-1; **27b**, 134906-15-3; **28a**, 134906-11-9; **28a-d_1**, 134906-12-0; **29a**, 134906-17-5; **29b**, 134906-20-0; **29c**, 134906-22-2; **31a**, 134906-18-6; **31c**, 134906-24-4; **32a**, 134906-19-7; **32b**, 134906-21-1; **34c**, 134906-23-3; **35a**, 87027-59-6; **38a**, 134906-27-7; **39a**, 134906-11-9; **41**, 134906-26-6; **42a**, 134906-25-5; **43a**, 134906-10-8; **48b**, 111086-20-5; **50b**, 111086-22-7; **51b**, 134906-18-6; **52b**, 134906-31-3; **54b**, 134906-30-2; **55b**, 134906-29-9; **56b**, 134906-32-4; **57b**, 134906-28-8; **58**, 111086-21-6; **60**, 134906-33-5; **64**, 134906-34-6; **65**, 134938-20-8; **66**, 134906-35-7; **67**, 134906-36-8; **68**, 134906-37-9; $Mn(OAc)_3$, 993-02-2; ethanol, 64-17-5; acetic acid, 64-19-7; methyl 2-allylacetoacetate, 3897-04-9; 3-chloro-2-((2-methoxyethoxy)methoxy)propene, 134906-07-3.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of **27a** and **28a**, **31a** and **32a**, **31c** and **34c**, **38a**, **39a** and **43a**, **41** and **42a**, **51a**, **52a** and **57a**, **50a**, **54a** and **56a**, **55a** and **58**, and **60** (17 pages). Ordering information is given on any current masthead page.

π-Selective Dichlorocyclopropanation and Epoxidation of 9-Chloro-1,4,5,8-tetrahydro-4a,6a-methanonaphthalene. Controlled Synthesis of the C9 Epimers of (1aα,2aα,6aα,7aα)-1,8,8-Trichloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methanocyclopropa[*b*]naphthalene

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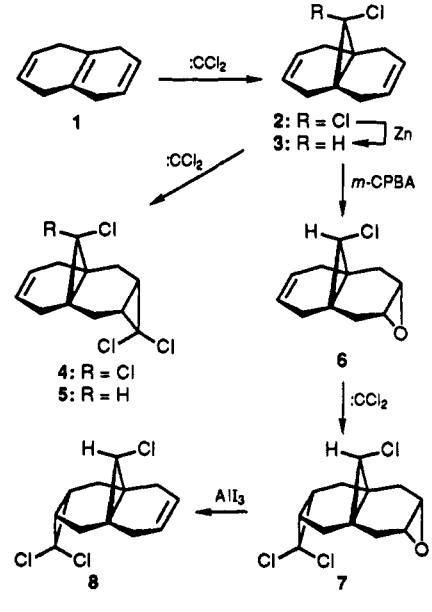
Dichlorocarbene addition to the 9-chloromethanonaphthalene **3** shows remarkable π-selectivity; syn trichloride **5** is the only monoadduct isolated (72%). Epoxidation likewise yields the syn epoxide **6** (78%), which, on dichlorocyclopropanation and deoxygenation, gives the epimeric trichloride **8**. The regioselectivities are in accord with PM3-derived molecular electrostatic potentials.

In connection with our ongoing program on cyclopropanarene chemistry,[1] we had need[2] of the epimeric tetracyclic trichlorides **5** and **8** as well as the known[3] tetrachloro homologue **4**. Our strategy was based upon dichlorocyclopropanation and half-reduction protocols commencing with isotetralin (**1**), and in bringing this work to fruition we have discovered remarkably high π-selectivity in additions to the unsymmetrical diene **3** (Scheme I). The results are compatible with depletion of electron density from the π-bond remote from the chloro substituent such that addition is to the syn double bond; the expected[4-6] high stereoselection of addition to the α-face of the molecule is observed.

Dichlorocarbene addition to **1** affords **2**[3,4] which when separately subjected to further controlled addition gives **4** in 80% (optimized) yield (Scheme I). In our hands this procedure minimizes the amount of unwanted **9** from addition to the three double bonds and is an improvement

Scheme I



on the published[4] method. Half-reduction of **2** affords chloropropelladiene **3** almost quantitatively (Zn/EtOH/KOH is superior to Bu_3SnH). When dichlorocarbene is added to **3**, syn trichloride **5** (72%) and the diadduct **10** (23%) are the only products isolated. Although the NMR

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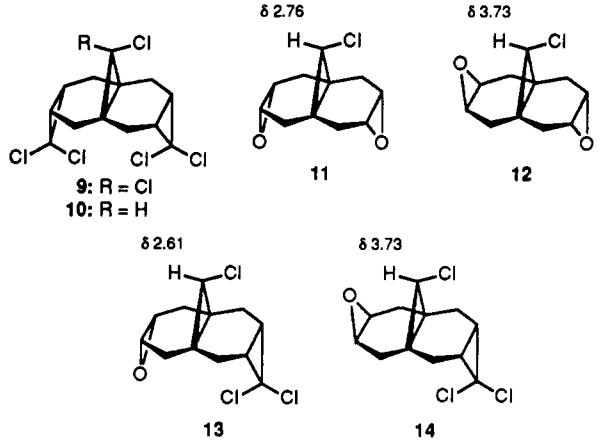
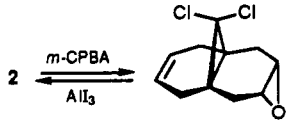
0022-3263/91/1956-5553$02.50/0

spectral characteristics of 5 support its structure, e.g., the >CHCl proton is essentially unaffected by dichlorocyclopropanation (δ(5) 3.14; δ(3) 3.28), the assignment required confirmation and the structure of 5 is secure from X-ray methods. The anti trichloro epimer 8 was not detected, nor was it formed upon attempted epimerization of 5 with various bases.



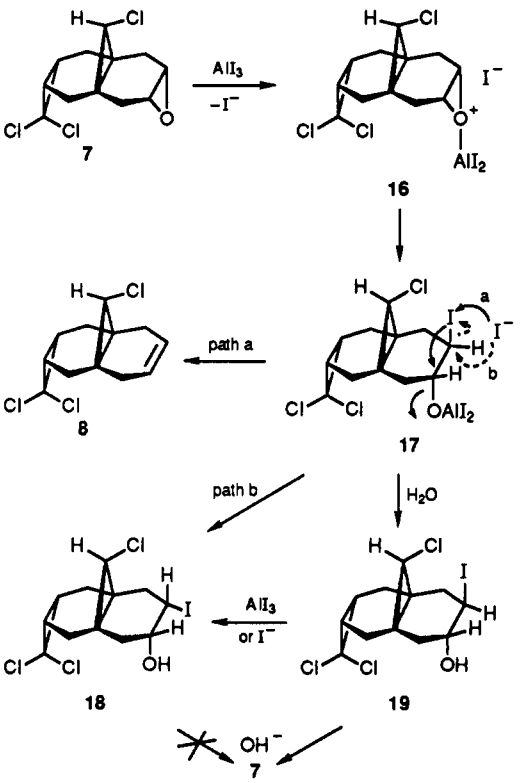
Our approach to 8 employs analogous addition of an electrophilic reagent to 3. Thus epoxidation gives the α-epoxide 6 (78%) together with a ca. 1:2 inseparable mixture (5%) of diepoxides 11 and 12. The >CHCl and allylic protons of 6 appear at almost identical positions to those of 3 (Δδ +0.1 ppm), and of the diepoxides, the structure with the bridge proton and oxygen atom proximal is assigned by virtue of the deshielding[7] this proton receives (δ(11) 2.76; δ(12) 3.73). These receive support from almost identical resonance positions in the (separable) epoxides 13 (40%) and 14 (34%) formed from 5 under the same conditions (δ(13) 2.61; δ(14) 3.73). Dichlorocarbene addition to epoxide 6 gives 7, the CHCl epimer of 13, in 74% yield. In our hands attempted scale up of the reaction beyond 0.5 g of substrate results in 7 as the *minor* (~25%) product of reaction and the pentachloride 10 as the major (~50%) component. Resubjection of 7 to the reaction conditions affords 10 as the sole product of reaction. The one-pot conversion of epoxides into dichlorocyclopropanes is not new[8] and likely involves initial complexation of the carbene with the oxygen atom, ejection of $COCl_2$, and addition of excess reagent to the double bond thus formed.

Useful deoxygenation of epoxides with aluminum triiodide has been reported recently[9] and the value of the reagent in the present series was established by the almost quantitative regeneration of 2 from epoxide 15. Applied



to 7 to complete the synthetic route to 8, the reagent proves equally effective and the anti trichloro compound is formed in 91% yield (path a, Scheme II). However, it is critical that the temperature does not exceed 32 °C, otherwise cis iodohydrin 18 is formed (path b, Scheme II). We presume that complex 16 is opened to 17, the fate of which is to give 8 by elimination (at lower temperature) and 18 by S_N2 displacement (and ultimately hydrolysis) above 32 °C (Scheme II). If the reactions are quenched with water after 5 min, the isomeric iodohydrin 19 is isolated. This last compound must be trans-diaxially substituted as it regenerates epoxide 7 upon treatment with hydroxide ion, a feature not observed for 18. Inadvertent formation of either 18 or 19 is not irretrievable as both compounds give the required olefin 8 (~85%) upon treatment with zinc in methanol (the Boord reaction[10]). This reaction is not stereospecific but of the E1cB type.

Scheme II



The high π-selectivity[11] recorded herein for 3 is at first surprising. The separation of the π-bonds and the bridge sp^3 carbon atom (C9) is greater than that in the anti 7-substituted norbornenes. These latter compounds are well known to receive anchimeric assistance from the anti π-bond with formation of a 2π3C delocalized ion.[12] Nonetheless, and despite the fact that the conformations of the two six-membered rings in 3 are predicted to be nonequivalent, the depletion of electron density from the π-bond exo to the chlorine substituent is found[13] to be fully consistent with PM3-derived molecular electrostatic potentials (MEP).[14] Chloro diene 3 shows a significant

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negative distortion of the MEP toward the π-bond endo to the chlorine substituent and this is attributed[13] to an antiperiplanar stabilization of the exo π-bond by interaction with the C–Cl σ* orbital.[15] This increase in electron density toward the endo π-bond accounts for the observed selectivity of this bond to the electrophilic carbene and peracid as recorded above.

Experimental Section

For general methods and procedures, see ref 5. Column, radial, and thin layer chromatographies employed silica, Kieselgel 60 PF_{254}, and Kieselgel GF_{254}, respectively, with light petroleum ether elution unless otherwise stated.

9,9-Dichloro-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene (2). A. Via Dichlorocarbene Addition. The procedure recently described[5] was followed exactly: 43 g, 64%; mp 87–89 °C (lit.[3] mp 88–89 °C).

B. Via Deoxygenation of 15. To a stirred solution of **15** (57 mg, 0.25 mmol) in MeCN (4 mL) was added a 0.6 M solution of aluminum triiodide (2.5 mL, 0.3 mmol, freshly prepared from aluminum foil and iodide[16] in benzene).[9] After 20 h the solution was poured into water (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic extracts were washed with thiosulfate (25 mL) and water (2 × 25 mL) and dried ($MgSO_4$). Concentration under vacuum to an oily solid and radial chromatographic separation gave **2** as colorless needles (methanol) (41 mg, 78%); mp, 86–87 °C (lit.[3] mp 88–89 °C).

9-Chloro-1,4,5,8-tetrahydro-4a,8a-methanonaphthalene (3). A suspension of zinc dust (14 g, 0.21 g atom), **2** (5 g, 23 mmol), and KOH pellets (7.5 g, 0.13 mol) in ethanol (200 mL) was heated at reflux for 24 h. After cooling, CH_2Cl_2 (200 mL) was added, the mixture was filtered, and the filtrate was washed with HCl (2 M, 60 mL). The aqueous phase was extracted (CH_2Cl_2, 2 × 100 mL), and the combined organic phases were washed with water (2 × 100 mL) and saturated NaCl solution (100 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum to an oil. Column chromatography afforded the title compound **3** (3.86 g, 92%) as a white solid (mp 25–28 °C) with spectral data in accord with those described,[17] this was used without further purification.

(1aα,2aα,6aα,7aα)-1,1,8,8-Tetrachloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1*H*-cyclopropa[*b*]naphthalene (4). Aqueous NaOH (50%, 5 mL) was added dropwise to a solution of **2** (1 g, 4.6 mmol) and benzyltriethylammonium chloride (BTEAC) (20 mg) in $CHCl_3/CH_2Cl_2$ (1:1, 6 mL). After stirring for 4 h, conventional workup[5] gave an off-white solid. Light petroleum ether was added and hexachloride **9** (86 mg, 5%) removed by filtration, mp 266–267 °C dec (lit.[4] mp 268–270 °C dec). Concentration of the filtrate and crystallization of the solid (methanol) gave **4** (1.10 g, 80%), mp 134–135° (lit.[4] mp 135 °C).

(1aα,2aα,6aα,7aα)-1,1,8-Trichloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methano-1*H*-cyclopropa[*b*]naphthalene (5). To a stirred solution of **3** (0.75 g, 4.2 mmol) and BTEAC (20 mg) in $CHCl_3/CH_2Cl_2$ (1:10, 20 mL) was added 50% aqueous NaOH (15 mL). After the solution was stirred at rt for 7 h, conventional workup[5] and preparative TLC (petroleum ether) gave band A (R_f 0.75), which afforded **5** as colorless needles (methanol) (612 mg, 72%): mp 68–69 °C; ^1H NMR δ 1.61–2.42 (m, 10 H), 3.13 (s, H 8), 5.41–5.50 (m, H4/H5); ^{13}C NMR δ 20.7 (C2a/C6a), 21.6/26.0/31.8, C1a/C2/C3/C6/C7/C7a), 41.0 (C8), 65.2 (C1), 124.4 (C4/C5). Anal. Calcd for $C_{12}H_{13}Cl_3$: C, 54.7; H, 5.0; Cl, 40.2. Found: C, 54.7; H, 5.0; Cl, 40.3. Concentration of the mother liquor gave unchanged **3** (0.09 g, 12%).

Band B (R_f 0.5) gave **(1aα,2aα,3aα,4aα,5aα,6aα)-1,1,4,4,7-pentachlorooctahydro-1*H*,3*H*-methanodicyclopropa[*b*,*g*]naphthalene (10)** (331 mg, 23%) (white needles, CH_2Cl_2/methanol): mp 179–180 °C; ^1H NMR δ 1.38–1.74 (m, 8 H), 2.04–2.24 (m, 4 H), 2.84 (s, H7); ^{13}C NMR δ 17.6 (C2a/C5a), 20.8/23.9/24.7/25.7 (C1a/C2/C3/C3a/C4a/C5/C6/C6a), 64.6 (C1), 67.0 (C4). Anal. Calcd for $C_{13}H_{13}Cl_5$: C, 45.1; H, 3.7; Cl, 51.2. Found: C, 45.3; H, 3.5; Cl, 50.9.

Attempted epimerizations of stereoisomer **5** with DBU, Et_3N, and $MeNH_2$ returned **5** (90–95%).

(1aα,2aα,6aα,7aα)-8-Chloro-1a,2,3,6,7,7a-hexachloro-2a,6a-methanonaphtho[2,3-*b*]oxirene (6). To a solution of **3** (5 g, 28 mmol) in CH_2Cl_2 (150 mL) was added, at −10 °C over 1 h, *m*-CPBA (6 g, 134 mmol) in the same solvent (75 mL). After the solution was warmed to rt and mechanically stirred for 20 h, CH_2Cl_2 (100 mL) and water (100 mL) were added. The separated organic phase was washed with NaOH (2 M, 50 mL) and water (2 × 50 mL), dried ($MgSO_4$), filtered, and concentrated to a yellow oil. Column chromatography afforded unchanged **3** (0.76 g, 15%) and (light petroleum ether/ethyl acetate; 4:1) **6** (3.6 g, 78%) as white needles (light petroleum ether): mp 55.5–56 °C; ^1H NMR δ 2.08 (d, J = 15.9 Hz, 2 H), 2.14 (d, J = 15.9 Hz, 2 H), 2.18 (m, 2 H), 2.45 (m, 2 H), 3.12 (bs, H1a/H7a), 3.24 (s, H8), 5.47 (m, H4/H5); ^{13}C NMR δ 19.7 (C2a/C6a), 24.7/25.2 (C2/C3/C6/C7), 42.0 (C8), 50.7 (C1a/C7a), 124.5 (C4/C5). Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.2; H, 6.5; Cl, 18.0. Found: C, 67.2; H, 6.6; Cl, 17.9.

Further elution gave a 1:2 (NMR) mixture of diepoxides **11** and **12** as white crystals (light petroleum ether); mp 127–128 °C; ^1H NMR δ 1.70–2.42 (m, 12 H), 2.76 (s, ~0.3 H, C*H*Cl for **11**), 3.0–3.11 (m, 6 H), 3.23 (s, ~0.7 H, C*H*Cl for **12**); ^{13}C NMR δ 17.3/17.6 (q), 26.8/27.0/31.0 (4 × CH_2), 43.4/44.7 (2 × CHCl), 48.1/50.3/50.7 (2 × HC–O–CH). Anal. Calcd for $C_{11}H_{13}ClO_2$: C, 62.1; H, 6.2; Cl, 16.7. Found: C, 62.3; H, 6.3; Cl, 16.7.

(1aα,2aα,3aα,4aα,5aα,6aα)- and (1aβ,2aα,3aα,4aα,6aβ)-4,4,7-Trichlorooctahydro-2a,5a-methano-3*H*-cyclopropa[6,7]naphtho[2,3-*b*]oxirenes (13 and 14). Epoxidation of **5** (100 mg, 0.4 mmol) with *m*-CPBA (120 mg, 0.7 mmol) as described above for **3** but with radial chromatography (light petroleum/ethyl acetate; 9:1) gave (i) **13** (26 mg, 40%) as white needles (light petroleum ether) [mp 120–121 °C; ^1H NMR δ 1.60–1.70 (m, 4 H), 1.75 (d, J = 16.4 Hz, 2 H), 2.22–2.30 (m, 2 H), 2.32 (dd, J = 4.8, 15.5 Hz, 2 H), 2.61 (s, H7), 2.96 (d, J = 4.8 Hz, H1a/H6a); ^{13}C NMR δ 18.3 (C2a/C5a), 21.8/30.4 (C2/C3/C5/C6), 25.5 (C3a/C4a), 42.3 (C7), 48.4 (C1a/C6a), 64.8 (C4). Anal. Calcd for $C_{12}H_{13}Cl_3O$: C, 51.6; H, 4.7; Cl, 38.0. Found: C, 51.6; H, 4.8; Cl, 37.8.] and (ii) **14** (22 mg, 34%) as needles (light petroleum ether) [mp 107–108 °C; ^1H NMR δ 1.62–1.68 (m, 2 H), 1.72 (bd, J = 15.4 Hz, 2 H), 1.99 (bd, J = 15.8 Hz, 2 H), 2.18 (bd, J = 15.3 Hz, 2 H), 2.54 (bd, J = 15.8 Hz, 2 H), 3.04 (s, H1a/H6a), 3.73 (s, H7); ^{13}C NMR δ 18.9 (C2a/C5a), 22.1/30.1 (C2/C3/C5/C6), 25.7 (C3a/C4a), 43.0 (C7), 50.8 (C1a/C6a), 65.1 (C4). Anal. Calcd for $C_{12}H_{13}Cl_3O$: C, 51.6; H, 4.7; Cl, 38.0. Found: C, 51.5; H, 4.6; Cl, 38.2.].

(1aα,2aα,3aα,4aα,5aα,6aα)-4,4,7-Trichloro-1a,2,3,3a,4a,5,-6,6a-octahydro-2a,5a-methano-3*H*-cyclopropa[6,7]naphtho-[2,3-*b*]oxirene (7). Dichlorocyclopropanation of **6** (0.5 g, 2.5 mmol) using $CHCl_3$ (30 mL), NaOH (50%, 30 mL), and BTEAC (20 mg) over 24 h as described for **3** above but with radial chromatography (light petroleum ether/ethyl acetate; 4:1) afforded **7** (540 mg, 78%) as colorless needles (light petroleum ether): mp 86–87 °C; ^1H NMR δ 1.47–1.58 (m, 4 H), 1.90 (d, J = 16.0 Hz, 2 H), 2.07 (bd, J = 16.0 Hz, 2 H), 2.25–2.34 (m, 2 H), 2.92 (s, H7), 3.06 (bs, H1a/H7a); ^{13}C NMR δ 16.2 (C2a/C5a), 23.7 (C3a/C4a), 25.3/25.7 (C2/C3/C5/C6), 44.4 (C7), 50.7 (C1a/C6a), 66.7 (C4). Anal. Calcd for $C_{12}H_{13}Cl_3O$: C, 51.6; H, 4.7; Cl, 38.0. Found: C, 51.5; H, 4.7; Cl, 38.0.

Scale-up to 1 g gave pentachloropropellane **10** (0.94 g, 50%) and **7** (0.35 g, 25%). Resubjection of **6** to the reaction conditions yielded **10** (68%).

(1aα,2aα,6aα,7aα)-8,8-Dichloro-1a,2,3,6,7,7a-hexahydro-2a,6a-methanonaphtho[2,3-*b*]oxirene (15). Epoxidation of **2** (1.0 g, 4.7 mmol) in CH_2Cl_2 (100 mL) at 0 °C with *m*-CPBA (0.85 g, 4.9 mmol) in CH_2Cl_2 (30 mL) as described for **3** above gave in order of elution from column chromatography (light petroleum ether/ethyl acetate, 7:1) **15** (0.84 g, 78%) as white needles (methanol) [mp 119–120 °C; ^1H NMR δ 2.00–2.52 (m, 8 H), 3.10 (m, H1a/H7a), 5.47 (bs, H4/H5); ^{13}C NMR δ 23.9 (C2a/C6a), 29.2/31.1 (C2/C3/C6/C7), 50.3 (C1a/C7a), 73.4 (C8), 122.9 (C4/C5). Anal. Calcd for $C_{11}H_{12}Cl_2O$: C, 57.2; H, 5.2; Cl, 30.7. Found: C, 57.3; H, 5.3; Cl, 30.4.] and **(1aα,2aα,3aα,4aα,5aα,6aα)-7,7-dichlorooctahydro-2a,5a-**

(15) A CF_3 substituent is expected[13] to display even greater π-selectivity.

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methanonaphtho[2,3-*b*:6,7-*b*']bisoxirene (0.10 g, 5.6%) (white needles, methanol); mp 218–219 °C (lit.[4] mp 218–220 °C).

(1aα,2aα,6aα,7aα)-1,1,8-Trichloro-1a,2,3,6,7,7a-hexahydro- and (1aα,2aα,4β,5β,6aα)-4-Hydroxy-5-iodo-1,1,8-trichlorooctahydro-2a,6a-methano-1*H*-cyclopropa[*b*]naphthalene (8 and 18). Deoxygenation of **7** (50–600 mg, 0.18–2.2 mmol) was effected with an excess of aluminum triiodide as described for **15** above, but with column in place of radial chromatography during workup.

A. At 30–32 °C for 20 h: **8** (0.52 g, 91%) as colorless needles (methanol); mp 106–107 °C ^{1}H NMR δ 1.40–1.50 (m, 4 H), 2.01 (bd, J = 16.7 Hz, 2 H), 2.26 (bd, J = 16.7 Hz, 2 H), 2.35–2.40 (m, 2 H), 2.93 (s, H8), 5.53 (bs, H4/H5); ^{13}C NMR δ 18.0 (C2a/C6a), 23.6 (C1a/C7a), 24.5/27.4 (C2/C3/C6/C7), 41.5 (C8), 67.2 (C1), 123.9 (C4/C5). Anal. Calcd for $C_{12}H_{13}Cl_3$: C, 54.7; H, 5.0; Cl, 40.3. Found: C, 54.7; H, 4.8; Cl, 40.2.

B. At 35 °C for 24 h (light petroleum ether/ethyl acetate, 6:1) in order of elution: **8** (11.8 mg, 25%) and **18** (36.5 mg, 50%) as colorless needles (CH_2Cl_2/light petroleum ether); mp 146–147 °C dec; ^{1}H NMR δ 1.50–1.77 (m, 5 H), 2.15 (dd, J = 5.4, 14.4 Hz, 1 H), 2.28 (dd, J = 4.5, 15.7 Hz, 1 H), 2.30–2.40 (m, 3 H), 2.52 (dd, J = 15.7, 4.5 Hz, 1 H), 2.95 (s, H8), 3.07 (bd, J = 7.13 Hz, H4), 4.40–4.48 (m, H5); ^{13}C NMR δ 19.5/19.9 (C2a/C6a), 23.9 (C1a/C7a), 25.4/25.6 (C2/C7), 35.0/36.3 (C3/C6), 36.3 (C2), 40.7 (C8), 40.8 (C5), 67.0 (C1), 69.2 (C4). Anal. Calcd for $C_{12}H_{14}Cl_3OI$: C, 35.4; H, 3.9; Cl, 26.10; I, 31.1. Found: C, 35.4; H, 3.6; Cl, 25.9; I, 31.0.

C. At 45 °C and 80 °C: **8** (10%) and **18** (60%), and only **18** (80%), respectively.

D. As in A above but with workup after 15 min: trans iodohydrin **19** (0.5 g, 95%) as colorless needles (CH_2Cl_2/light petroleum ether); mp 151–152 °C dec; ^{1}H NMR δ 1.25–1.75 (m, 5 H), 2.30–2.61 (m, 5 H), 2.86 (s, H8), 3.80–3.90 (m, H4/H5); ^{13}C NMR δ 22.1/22.9 (C2a/C6a), 23.3 (C1a/C7a), 24.2/25.2 (C2/C7), 35.0/39.7 (C3/C6), 39.5 (C5), 42.0 (C8), 66.7 (C1), 72.6 (C4). Anal. Calcd for $C_{12}H_{14}Cl_3OI$: C, 35.4; H, 3.9; Cl, 26.1; I, 31.1. Found: C, 35.4; H, 3.6; Cl, 26.1; I, 31.1.

Treatment of **19** with either AlI_3 or I^- under the same conditions gives the cis isomer **18** (92%); **19** is stable in the solvent at 36 °C.

Treatment of 18 and 19 with Sodium Hydroxide. Iodohydrin (20 mg, 0.05 mmol) and NaOH pellets (0.4 g, 10 mmol) in 1,4-dioxane (3 mL) were stirred at 30 °C for 1 h. The reaction mixture was partitioned between light petroleum ether/water (100 mL, 1:1). The organic phase was separated, washed (water, 2 × 20 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum to a solid.

A. From 18: unchanged starting material (85–93%) even after 24 h.

B. From 19: epoxide **7** (15 mg, 74%), identical with that described above, was obtained as a white solid.

Boord Reactions of 18 and 19. A mixture of the iodohydrin (100 mg, 0.25 mmol) and zinc dust (0.5 g, 7.7 mmol) was refluxed in methanol (6 mL) for 24 h, cooled to rt, CH_2Cl_2 (75 mL) was added, and the mixture was filtered. The organic phase was separated, washed with HCl (2 M, 10 mL) and water (2 × 10 mL), then dried ($MgSO_4$), filtered, and concentrated under vacuum. Crystallization of the solid (methanol) gave **8** (58 mg, 90% from **18**) (60 mg, 90% from **19**).

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Registry No. **2**, 39623-22-8; **3**, 18963-51-4; **4**, 102618-60-0; **5**, 102618-68-8; **6**, 135257-80-6; **7**, 135257-81-7; **8**, 135356-60-4; **9**, 102680-43-3; **10**, 135257-82-8; **11**, 135257-83-9; **12**, 135356-61-5; **13**, 135356-62-6; **14**, 135356-63-7; **15**, 135257-84-0; **18**, 135257-85-1; **19**, 135356-64-8; aluminum triiodide, 7784-23-8; (1aα,2aα,3aα,4aα,5aα,6aα)-7,7-dichlorooctahydro-2a,5a-methanonaphtho[2,3-*b*:6,7-*b*']bisoxirene, 102618-62-2.

Supplementary Material Available: All X-ray data, including a PLUTO plot of **5** (7 pages). Ordering information is given on any current masthead page.

Reaction of Diethyl Phosphorochloridite with Enolates: A General Method for Synthesis of β-Keto Phosphonates and α-Phosphono Esters through C–P Bond Formation

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The reaction of ketone enolates with diethyl phosphorochloridite, followed by air oxidation of the immediate reaction products, has proven to be a general and convenient method for preparation of β-keto phosphonates. Fourteen β-keto phosphonates have been prepared by this method, in an average yield greater than 60%. This procedure also appears to be applicable to preparation of both α-phosphono aldehydes and α-phosphono esters. Although special precautions may be necessary to avoid aldol condensation during formation of aldehyde enolates, in two cases it was shown that the resulting enolates react readily with diethyl chlorophosphite. Finally, a set of five ethyl esters was converted to α-phosphono esters by this method. Yields of the α-phosphono esters are influenced by steric hindrance at the enolate carbon, but the average yield for this series was ca. 70%. Because this synthetic method relies upon an electrophilic phosphorus reagent for formation of the C–P bond, it is complementary to the traditional Arbuzov synthesis. On the basis of the 21 examples presented here, it appears to be more widely applicable.

β-Keto phosphonates are commonly employed as synthetic reagents, particularly in the Horner–Wadsworth–Emmons reaction.[1] While there are many sequences that can be used to prepare them,[2] the classical Arbuzov reaction,[3] in which an α-halo carbonyl compound is treated with a trialkyl phosphite (eq 1), is by far the predominant choice. This reaction has been studied extensively, and its limits are well understood. Of prime importance for

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