obtained. Data for new compounds or for ones which have not been well-defined in the literature are given below.

Nitromyrtane (10): IR 1545, 1385 cm^{-1}; ^1H NMR 4.40 (2 H, d, J = 8 Hz), 2.91 (1 H, m), 2.41 (1 H, m), 1.95 (5 H, m), 1.53 (1 H, m), 1.21 (3 H, s), 1.02 (3 H, s), 1.02 (1 H, d, J = 8 Hz); ^{13}C NMR 81.1 ppm. Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54, H, 9.28. Found: C, 65.62, H, 9.44.

1,3-Dinitroadamantane (13):[10] mp (subl) 211 °C; IR 1530, 1370 cm^{-1}; ^1H NMR 2.71 (2 H, s), 2.59 (2 H, m), 2.22 (8 H, m), 1.73 (2 H, m); ^{13}C NMR 84.8, 42.7, 39.3, 3.36, 30.2 ppm; MS m/z 180 [$(M - NO_2)^+$].

4,4'-Methylenebis(nitrocyclohexane) (14): mp 124 °C; IR 1550, 1540, 1385 cm^{-1}; ^1H NMR 4.50 (1 H, q, J = 4.5 Hz), 4.34 (1 H, tt, J_1 = 12 Hz, J_2 = 4 Hz); MS m/z 224 [$(M - NO_2)^+$], 178 [$(M - 2NO_2)^+$], 177 [$(M - 2NO_2 - H)^+$]. Anal. Calcd for $C_{13}H_{22}N_2O_4$: C, 57.76, H, 8.14. Found: C, 57.68, H, 8.10.

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Registry No. 1, 108-91-8; 2, 1122-60-7; 3, 124-22-1; 4, 100-46-9; 5, 768-94-5; 6, 16891-99-9; 7, 622-42-4; 8, 7575-82-8; 8-$N^{18}O_2$, 143957-73-7; 9, 74837-99-3; 10, 143957-74-8; 11, 10303-95-4; 12, 1761-71-3; 13, 55100-59-9; 14, 143957-75-9; HOF, 14034-79-8; CH_3CN, 75-05-8.

Halogen-Assisted Alkylation of Ester Enolates. Facile Synthesis of C_{10}-Functionalized Tricyclo[5.2.1.$0^{2,6}$]decenes

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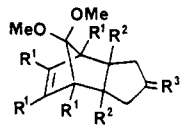
Tricyclo[5.2.1.$0^{2,6}$]decenes are valuable synthetic intermediates. However, utilization of these derivatives in the synthesis[1] of natural products is limited to the cyclopentanoid family due to lack of methods for preparation of various functionalized derivatives. Recently, we have demonstrated[2] that appropriately functionalized tricyclo[5.2.1.$0^{2,6}$]decenes may provide bridged eight-membered rings related to the A/B ring of taxanes. An extension of this route for the synthesis of taxane diterpenes required the synthesis of C_{10}-functionalized tricyclo[5.2.1.$0^{2,6}$]decenes **1** which could not be prepared by the commonly used[3] Diels-Alder reaction of 5,5-disubstituted cyclopentadiene derivatives. An alternative route[4] involving ring annelation via alkylation of the vicinal dianion generated from **2** with 1,3-dihalides also failed. Intrigued by the neighboring heteroatom influence[5] on the reactivity and facial selectivity during addition of electrophiles to nucleophilic double bonds, we investigated the behavior of the dienolate available in principle from the parent tetrachloro diester **3** toward electrophiles. We report here the results of this investigation and demonstrate a dramatic influence of the chlorine atoms on the reactivity of the dienolate of the tetrachloro diester **3** resulting in facile alkylation and annelation.

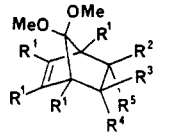
Results and Discussion

Treatment of the diester **2**[6] with LDA in THF followed by treatment of the resulting solution with 1 equiv of 3-chloro-2-(chloromethyl)propene or 2 equiv of MeI in the presence of HMPA failed to afford any alkylated product. Instead, simply a syn-anti isomerization of the ester moieties was observed,[7] giving rise to **4**. On the other hand, in a parallel experiment, the tetrachloro diester **3**,[8] under identical conditions, on reaction with 2 equiv of methyl iodide gave a solid in 93% isolated yield as a mixture of two chromatographically inseparable components in ca. a 1:1 ratio (t_R 2.20 and 2.47). Although theoretically three dimethylated products **5X**, **5N**, and **5T** may arise, the symmetrical nature of the ^1H and ^{13}C NMR spectra of the crude product suggested the presence of only *exo*-**5X** and *endo*-**5N** isomers. The assignment of the structure as exo to the component with t_R 2.20 in GLC, obtained by multiple fractional crystallization of the crude product, could be made by a single-crystal X-ray structure determination. Since the crude mixture and the crystallized product **5X** displayed indistinguishable ^1H and ^{13}C NMR spectra, the second component with t_R 2.47 in the mixture was assigned the endo structure **5N**, and the possibility of the presence of the trans dimethylated compound **5T** in the product mixture could thus be excluded. Successful achievement in alkylation of the diester **3** led us to investigate alkylation with other electrophiles.

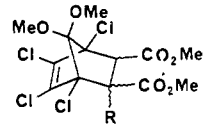


1

a, R^1=Cl, R^2=CO_2Me, R^3=H_2
b, R^1=Cl, R^2=CO_2Me, R^3=CH_2
c, R^1=H, R^2=CH_2OH, R^3=H_2
d, R^1=H, R^2=CH_2OH, R^3=CH_2



2, R^1=R^2=R^3=H, R^4=R^5=CO_2Me
3, R^1=Cl, R^2=R^3=H, R^4=R^5=CO_2Me
4, R^1=R^2=R^4=H, R^3=R^5=CO_2Me
5X, R^1=Cl, R^2=R^3=Me, R^4=R^5=CO_2Me
5N, R^1=Cl, R^2=R^3=CO_2Me, R^4=R^5=Me
5T, R^1=Cl, R^2=R^4=Me, R^3=R^5=CO_2Me



6, R=$CH_2CH=CH_2$
7, R=$CH_2C(=CH_2)CH_2Cl$

Thus, when the alkylation of **3** was carried out with 1 equiv of a bulkier electrophile (i.e., allyl bromide) again a 1:1 mixture of the monoallylated products **6** was obtained in 82% yield. Attempted addition of a second allyl group to **6** was not successful. Ring annelation on **3** was next examined using bifunctional electrophilic reagents. Treatment of the enolate of **3** with 1 equiv of 1,3-dibromopropane under the above conditions gave the ring

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(1) Applications of tricyclo[5.2.1.$0^{2,6}$]decenes in the synthesis of cyclopentanoid natural products: (a) Ito, T.; Tomiyoshi, N.; Nakamura, K.; Azuma, S.; Izawa, M.; Maruyama, F.; Yanagiya, M.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1982**, *23*, 1721. (b) Tsunoda, T.; Kodama, M.; Ito, S. *Tetrahedron Lett.* **1983**, *24*, 83. (c) Marchand, A. P.; Vidyasagar, V. *J. Org. Chem.* **1988**, *53*, 4412. (d) Takano, S.; Inomata, K.; Ogasawara, K. *J. Chem. Soc., Chem. Commun.* **1989**, 271. (e) Klunder, A. J. H.; Zwanenburg, B.; Liu, Z. Y. *Tetrahedron Lett.* **1991**, *32*, 3131.

(2) (a) Saha, G.; Bhattacharya, A.; Saha Roy, S.; Ghosh, S. *Tetrahedron Lett.* **1990**, *31*, 1483. (b) Ghosh, S.; Karpha, A.; Saha, G.; Patra, D. *Tetrahedron Lett.* **1992**, *33*, 2363.

(3) Camps, P.; Castane, J.; Feliz, M.; Figueredo, M. *Tetrahedron* **1984**, *40*, 5235.

(4) (a) Garratt, P. J.; Hollowood, F. *J. Org. Chem.* **1982**, *47*, 68. (b) Girard, C.; Bloch, R. *Tetrahedron Lett.* **1982**, *23*, 3683.

(5) Kahn, S. D.; Pau, C. F.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7396.

(6) Mehta, G.; Khan, F. A. *J. Am. Chem. Soc.* **1990**, *112*, 6140.

(7) Saha, G.; Karpha, A.; Saha Roy, S.; Ghosh, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1587.

(8) Newcomer, J. S.; McBee, E. T. *J. Am. Chem. Soc.* **1949**, *71*, 946.

0022-3263/92/1957-7344$03.00/0

annelated product **1a** in 81% isolated yield as an inseparable 1:1 mixture of exo and endo isomers. The formation of the annelated products in excellent yield with annelation occurring from both the exo and endo face is interesting in view of the investigation by Garratt et al.[4a] who demonstrated that the bulk of the alkoxy groups at C_7 in a bicyclo[2.2.1]heptane derivative lacking chlorine atoms directed annelation with 1,3-dibromopropane exclusively from the endo face, affording the endo-annelated product in poor yield. Attempted ring annelation of the tetrachloroester **3** with 1 equiv of 3-chloro-2-(chloromethyl)propene afforded the monoalkylated product **7** in 83% yield as a 1:1 mixture. Treatment of product **7** with LDA in the presence of a catalytic quantity of in situ generated LiI effected ring closure to give **1b**. However, **1b** could be obtained in 80% yield directly from **3** by carrying out the alkylation with 1 equiv of the dichloride in the presence of in situ generated LiI. The ease with which the tetrachloro diester **3** underwent alkylation and annelation, in contrast to the dechloro analogue **2**, clearly suggests an unprecedented assistance by the chlorine atoms, particularly by those at C_1 and C_4 which are allylic to the enolate double bonds at C_2 and C_3. The mechanism of action through which the chlorine atoms in the diester **3** influence the reaction outcome is difficult to understand. Qualitatively, it may be stated that an interaction of the nonbonded electrons on the chlorine atoms with the enolate π-systems possibly makes the enolate more nucleophilic[9] toward an electrophile, accounting for the enhanced reactivity and resulting in loss of exo–endo selectivity.

Thus, the presence of chlorine atoms in **3** has made it possible to overcome the steric hindrance posed by **2** toward enolate alkylation and annelation. Finally, removal of the chlorine atoms from **1a** and **1b** could be done conveniently by two consecutive reductions using $LiAlH_4$ and then Na in liquid NH_3 to afford C_{10}-functionalized tricyclo[5.2.1.$0^{2,6}$]decenes **1c** and **1d**.

Experimental Section

Compounds described are all racemates. Melting points were measured in open capillary tubes and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions with $SiMe_4$ as internal standard. IR spectra were recorded in KBr pellets. Gas chromatographic analyses were performed on a SE-30 (2-m × 3-mm) column using nitrogen as the carrier gas, and retention times (t_R) are reported in min. Column chromatography was performed on silica gel (60–120 mesh). *n*-BuLi in hexane solution (12% w/v) was purchased from E. Merck (Germany).

General Procedure for Alkylation and Annelation. The general procedure is illustrated by alkylation of the diester **2**. To a magnetically stirred solution of diisopropylamine (0.125 mL, 0.88 mmol) in anhydrous THF (2 mL) cooled to −78 °C under a N_2 atmosphere was added dropwise *n*-BuLi (0.47 mL, 0.88 mmol) by syringe. After complete addition, the reaction mixture was warmed to −10 °C and stirred for 15 min. The reaction mixture was cooled to −78 °C, to it was added dropwise a solution of the diester **2** (100 mg, 0.37 mmol) in THF (1 mL), and stirring was continued at −78 °C for 1 h and at −30 °C for another 1 h. The mixture was again cooled to −78 °C, and HMPA (0.10 mL, 0.57 mmol) was added followed by MeI (135 mg, 0.92 mmol). The reaction mixture was stirred at −78 °C for 1 h, at −10 °C for 1 h, at 0 °C for 2 h, and finally left at rt overnight. The reaction mixture, after acidification with cold 6 N HCl, was extracted with ether (3 × 20 mL). The ether extract was washed with brine and dried (Na_2SO_4). Removal of solvent afforded a liquid which on column chromatography [ether–petroleum ether (1:19)] afforded **4**[7] (63 mg, 63%); ^1H NMR (200 MHz) δ 2.76 (d, J = 4 Hz, 1 H), 3.16 (s, 3 H), 3.18 (s, 3 H), 3.25 (m, 1 H), 3.42 (m, 1 H), 3.64 (m, 1 H), 3.70 (s, 3 H), 3.76 (s, 3 H), 6.10 (dd, J = 6, 4 Hz, 1 H), 6.34 (dd, J = 6, 4 Hz, 1 H).

Alkylation of the Diester 3. (i) With MeI. Dimethyl 7,7-Dimethoxy-2,3-dimethyl-1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylates (5X) and (5N). Alkylation of **3** (408 mg, 1 mmol) using LDA [prepared from diisopropylamine (0.34 mL, 2.4 mmol) and *n*-BuLi (1.28 mL, 2.4 mmol)] with MeI (355 mg, 2.5 mmol) in the presence of HMPA (0.4 mL, 2.30 mmol) furnished ca. a 1:1 mixture of **5X** and **5N** (415 mg, 96%), mp 186 °C: t_R (250 °C) 2.20 and 2.47. The crude product was crystallized (ether-petroleum ether) to afford **5X**, mp 206 °C: t_R 2.20; IR 1745, 1615, 1130 cm^{-1}; ^1H NMR (270 MHz) δ 1.67 (s, 6 H), 3.50 (s, 3 H), 3.56 (s, 3 H), 3.60 (s, 6 H); ^{13}C [^1H] NMR (25 MHz) δ 18.55 (q), 51.78 (q), 52.25 (q), 52.60 (q), 61.02 (s), 79.74 (s), 113.3 (s), 131.3 (s), 171.65 (s). Anal. Calcd for $C_{15}H_{18}O_6Cl_4$: C, 41.31; H, 4.16. Found: C, 40.88; H, 4.12.

(ii) With Allyl Bromide. The alkylation of **3** (204 mg, 0.5 mmol) in THF (1.5 mL) using LDA [prepared from diisopropylamine (0.18 mL, 1.3 mmol) and *n*-BuLi (0.69 mL, 1.3 mmol)] with allyl bromide (75 mg, 0.6 mmol) in the presence of HMPA (0.2 mL, 1.14 mmol) afforded after column chromatography [ethyl acetate–petroleum ether (1:19)] the monoallylated diester **6** (180 mg, 82%) as a mixture of two components in a ratio of ca. 1:1: t_R (250 °C) 2.07 and 2.34; IR 1740, 1605, 1130 cm^{-1}; ^1H NMR (200 MHz) δ 2.94–3.08 (m, 2 H), 3.58 (s, 3 H), 3.64 (s, 4 H, OCH_3 and C_3-H), 3.66 (s, 3 H), 3.74 (s, 3 H), 5.10–5.26 (m, 2 H) and 5.92–6.10 (m, 1 H). Anal. Calcd for $C_{16}H_{18}O_6Cl_4$: C, 42.88; H, 4.05. Found: C, 43.14; H, 4.33.

(iii) With 3-Chloro-2-(chloromethyl)propene. The alkylation of **3** (500 mg, 1.20 mmol) in THF (4.5 mL) using LDA [prepared from diisopropylamine (0.42 mL, 3 mmol) in anhydrous THF (5 mL) and *n*-BuLi (1.60 mL, 3 mmol)] with 3-chloro-2-(chloromethyl)propene (188 mg, 1.5 mmol) in the presence of HMPA (0.5 mL, 2.87 mmol) furnished the monoalkylated product **7** (500 mg, 83%), mp 146–148 °C, as an inseparable mixture in a ratio of ca. 1:1: t_R (230 °C) 7.16 and 8.24; IR 1740, 1600, 1130 cm^{-1}; ^1H NMR (270 MHz) δ 3.09 (d, J = 13.9 Hz, 1 H), 3.27 (d, J = 14.2 Hz, 1 H), 3.56 (s, 3 H), 3.63 (s, 1 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 3.70 (s, 3 H), 3.96 (d, J = 12.3 Hz, 1 H), 4.20 (d, J = 12.6 Hz, 1 H), 5.10 (s, 1 H), and 5.34 (s, 1 H). The analytical sample melted at 166 °C. Anal. Calcd for $C_{17}H_{19}O_6Cl_5$: C, 41.12; H, 3.86. Found: C, 40.89; H, 4.10.

Annelation of the Diester 3. (i) With 1,3-Dibromopropane. Dimethyl 7,7-Dimethoxy-1,7,8,9-tetrachlorotricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2,6-dicarboxylate (1a). A solution of the diester **3** (204 mg, 0.5 mmol) in THF (1 mL) was alkylated using LDA [prepared from diisopropylamine (0.175 mL, 1.25 mmol) in anhydrous THF (2.0 mL) and *n*-BuLi (0.666 mL, 1.25 mmol)] with 1,3-dibromopropane (120 mg, 0.6 mmol) in the presence of HMPA (0.2 mL, 1.15 mmol) to afford the annelated product **1a** (180 mg, 81%), mp 206 °C, as a 1:1 mixture of two components: t_R (250 °C) 2.63 and 2.98; IR 1725, 1610, 1140cm^{-1}; ^1H NMR (270 MHz) δ 1.97–2.69 (m, 6 H), 3.52 (s, 3 H), 3.61 (s, 3 H), 3.63 (s, 6 H); ^{13}C [^1H] NMR (25 MHz) δ 28.38 (t), 34.0 (t), 51.43 (q), 52.25 (q), 52.60 (q), 72.72 (s), 78.40 (s), 113.85 (s), 132.22 (s), 171.18 (s). The analytical sample melted at 228 °C. Anal. Calcd for $C_{16}H_{18}O_6Cl_4$: C, 42.88; H, 4.05. Found: C, 43.10; H, 4.07.

(ii) With 3-Chloro-2-(chloromethyl)propene. Dimethyl 7,7-Dimethoxy-4-methylene-1,7,8,9-tetrachlorotricyclo[5.2.1.$0^{2,6}$]dec-8-ene-2,6-dicarboxylate (1b). (a) By Ring Closure of 7. To a magnetically stirred solution of LDA [prepared from diisopropylamine (0.19 mL, 1.35 mmol) in anhydrous THF (2 mL) and *n*-BuLi (0.72 mL, 1.35 mmol)], cooled to −78 °C, was added MeI (0.01 mL, 0.15 mmol), and the reaction mixture was warmed to −10 °C. A white precipitate appeared. A solution of the diester **7** (408 mg, 1 mmol) in THF (3 mL) followed by HMPA (0.4 mL, 2.20 mmol) was added to the reaction mixture on cooling to −78 °C. The reaction mixture was stirred at −78 °C for 1 h, at −10 °C for 1 h, at 0 °C for 1 h, and left at rt overnight. On acidification with 6 N HCl, the reaction mixture was worked up with ether to afford **1b** (380 mg, 86%), mp 172–174 °C, as a mixture of two compounds in a ratio of ca. 1:1: t_R (250 °C) 2.81 and 3.17; IR 1730, 1610, 1145 cm^{-1}; ^1H NMR (270 MHz) δ 3.16 (d, J = 18.4 Hz, 2 H), 3.39 (d, J = 18.40 Hz, 2 H), 3.53 (s, 3 H), 3.56 (s, 3 H), 3.64 (s, 6 H) and 4.83 (br s, 2 H); ^{13}C [^1H] NMR

(9) Enhancement of nucleophilicity by allylic chlorine atoms in dienes has been invoked in Diels–Alder reactions (Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 663).

(25 MHz) δ 41.37 (t), 51.6 (q), 52.54 (q), 52.78 (q), 71.20 (s), 79.40 (s), 104.84 (t), 113.40 (s), 131.90 (s), 150.12 (s), 171.0 (s). The analytical sample melted at 199 °C. Anal. Calcd for $C_{17}H_{18}O_6Cl_4$: C, 44.38; H, 3.94. Found: C, 44.82; H, 4.19.

(b) By Direct Alkylation of 3. Following the procedure described above, a solution of the diester **3** (204 mg, 0.5 mmol) in THF (1.5 mL) was treated with a suspension prepared by adding MeI to a cooled (−78 °C) solution of LDA [from diisopropylamine (0.18 mL, 1.28 mmol) and *n*-BuLi (0.68 mL, 1.28 mmol)] and 3-chloro-2-(chloromethyl)propene (75 mg, 0.6 mmol) in the presence of HMPA (0.2 mL, 1.15 mmol) to afford **7** (190 mg, 85%), mp and mixed mp with the sample prepared above 199 °C.

2,6-Bis(hydroxymethyl)-7,7-dimethoxytricyclo[5.2.1.0^{2,6}]-dec-8-ene (1c). A solution of the diester **1a** (200 mg, 0.44 mmol) in THF (10 mL) was treated with $LiAlH_4$ (150 mg, 3.9 mmol) with magnetic stirring at rt for 3.5 h. The reaction mixture, on cooling with ice, was quenched by dropwise addition of saturated aqueous Na_2SO_4 solution. The precipitated solid was filtered out, and the filtrate was dried (Na_2SO_4) and concentrated to afford the dihydroxy compound (160 mg, 91%). Without further purification this was subjected to the following reduction.

To magnetically stirred liquid NH_3 (40 mL) (distilled from sodium) was added sodium (150 mg, 6.5 mg atom) in small pieces. The blue solution was cooled to −78 °C, and a solution of the dihydroxy compound (200 mg, 0.51 mmol) obtained as above in anhydrous THF (1.5 mL) containing ethanol (60 mg, 1.3 mmol) was added dropwise. After being stirred at this temperature for 5 min, the reaction mixture was quenched by addition of powdered NH_4Cl. Ammonia was then allowed to evaporate. The residual mass was treated with water (5 mL). The organic mass was extracted with ether (3 × 15 mL) (NaCl) and dried (Na_2SO_4). Removal of solvent afforded a liquid (120 mg, 92%) which was purified by column chromatography [ether–petroleum ether (1:4)] to give pure **1c**, mp 125 °C; IR 3280, 1280, 1120 cm^{-1}; ^{1}H NMR (100 MHz) δ 1.52–2.36 (m, 6 H), 2.50 (br s, 2 H), 2.66 (t, J = 2 Hz, 2 H), 3.1 (s, 3 H), 3.2 (s, 3 H), 3.42 (s, 4 H) and 6.22 (t, J = 2 Hz, 2 H). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11, H, 8.72. Found: C, 66.36; H, 8.66.

2,6-Bis(hydroxymethyl)-7,7-dimethoxy-4-methylene-tricyclo[5.2.1.0^{2,6}]dec-8-ene (1d). A solution of the diester **1b** (180 mg, 0.4 mmol) in THF (10 mL) was reduced with $LiAlH_4$ (150 mg, 4 mmol) as above to produce the corresponding diol (150 mg, 95%) which without further purification was reduced with Na (200 mg, 8.7 mg atom) in liquid NH_3 (40 mL) as above to afford after column chromatography [ether–petroleum ether (1:4)] **1d** (70 mg, 71%), mp 89 °C: IR 3420, 1290, 1125 cm^{-1}; ^{1}H NMR (60 MHz) δ 2.73 (m, 6 H), 3.13 (s, 3 H), 3.21 (s, 3 H), 3.26 (br, partly under the singlet at 3.21, 2 H), 3.43 (s, 4 H), 4.70 (m, 2 H) and 6.20 (t, J = 2 Hz, 2 H). Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.16; H, 8.57.

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Registry No. *exo*-**1a**, 144270-78-0; *endo*-**1a**, 144270-83-7; *exo*-**1b**, 144270-84-8; *endo*-**1b**, 144270-85-9; *exo*-**1c**, 144270-86-0; *endo*-**1c**, 144270-87-1; *exo*-**1d**, 144270-88-2; *endo*-**1d**, 144270-89-3; *exo*-**1** (R^1 = Cl, R^2 = CH_2OH, R^3 = H_2), 144270-90-6; *endo*-**1** (R^1 = Cl, R^2 = CH_2OH, R^3 = H_2), 144270-91-7; *exo*-**1** (R^1 = Cl, R^2 = CH_2OH, R^3 = CH_2), 144270-92-8; *endo*-**1** (R^1 = Cl, R^2 = CH_2OH, R^3 = CH_2), 144270-93-9; **2**, 142743-08-6; **3**, 144270-79-1; **4**, 144370-44-5; **5X**, 144270-80-4; **5N**, 144270-94-0; **6**, 144270-81-5; **7**, 144270-82-6; allyl bromide, 106-95-6; 3-chloro-2-(chloromethyl)propene, 1871-57-4; 1,3-dibromopropane, 109-64-8.

Supplementary Material Available: Tables 1–5 listing positional and thermal parameters, bond lengths and bond angles, including estimated standard deviations, details of the X-ray analysis, and the ORTEP plot of **5X** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Dimerization of Substituted 1,3-Diarylallenes

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The regio- and stereoselectivity observed in thermal dimerization of allenes has usually been interpreted[3] on the basis of the bis-allyl diradical intermediate, **2**, but it has been shown that a concerted [$_\pi2_s$ + ($_\pi2_s$ + $_\pi2_s$)] mechanism can also explain the results in many instances.[4] Other calculations for allene indicate that a 1,1′-bis-allyl diradical intermediate corresponds to the smallest energy barrier for formation of 1,2-dimethylenecyclobutane.[5] Dehmlow[6] found that 1,3-diphenylallene, **1a**, gave **3a**, **4a**, and **5a** in approximately equal amounts. Optically active allene gave inactive dimers, and neither of the possible dimers having both phenyl groups inward on the exocyclic double bonds was formed. This result is in contrast to that with many other substituted allenes, which give dimers having the exocyclic substituents in the hindered inward positions as major products. We therefore dimerized 1,3-bis(*p*-chlorophenyl)allene and 1,3-bis(*p*-bromophenyl)allene to establish the generality of Dehmlow's results.

Dimerizations were carried out in refluxing benzene. Pure samples of the dimers **3b** and **3c** were obtained by precipitation from hexane and recrystallization from hexane–toluene. The other more soluble dimers were chromatographed on acidic alumina and recrystallized with difficulty from 95% ethanol. **1b** and **1c** gave similar products. **1b** gave only **3b**, **4b**, and **5b** in a ratio of 1.9:1.3:1 in 90–95% total yield. **1c** gave only **3c**, **4c**, and **5c** in a ratio of 2.1:1.4:1.

The identity of the products was determined principally by ^{1}H, 60-MHz NMR spectroscopy (see Table I) and is consistent with UV and IR data. Mass spectroscopy confirmed the dimeric nature of the compounds. X-ray crystallographic studies on **3b** confirmed the structure shown.

The cyclobutyl protons in **3b** are shifted to lower field than those in **4b** or **5b** by about 1 ppm. Models indicate that when the ring is trans substituted, the hydrogens are located in the shielding cone of the adjacent aryl group. When ring stereochemistry is cis, no such effect is operative and hydrogen resonance appears at lower field. Dimers **3b** and **5b** appear to have their aryl groups on the double bond directed outward since there is no mutual shielding as expected for aryl groups pushing against each other. The unsymmetrical structure of **4b** is revealed by its more complex NMR. Proton decoupling located the δ 7.22 signal within the aromatic multiplet. Similar reasoning was used in the assignment for **3c**, **4c**, and **5c** although aromatic

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(3) (a) Byrn, S. R.; Maverick, E.; Muscio, O. J., Jr.; Trueblood, K. N.; Jacobs, T. L. *J. Am. Chem. Soc.* **1971**, *93*, 6680 and references cited therein. (b) Dai, S.-H.; Dolbier, W. R., Jr. *Ibid.* **1972**, *94*, 3946. (c) Moore, W. R.; Mogolesko, P. D.; Traficante, D. D. *Ibid.* **1972**, *94*, 4753. (d) Gajewski, J. J.; Black, W. A. *Tetrahedron Lett.* **1970**, 899 and earlier papers. (e) Capdevielle, P.; Rigaudy, J. *Tetrahedron* **1979**, *35*, 2093. (f) For a review see: Hoff, H. In *The Chemistry of the Allenes*: Landor, S. R., Ed.; Academic Press; New York, 1982; pp 525–562.
(4) Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37.
(5) Lebedev, V. L.; Bagatur'yants, A. A.; Taber, A. M.; Kalechits, I. V. *Zh. Fiz. Khim.* **1979**, *53*, 2745; Engl. trans., 1572.
(6) Dehmlow, E. V.; Ezimora, G. C. *Tetrahedron Lett.* **1972**, 1265. Dehmlow, E. V. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 322.

0022-3263/92/1957-7346$03.00/0