δ 1.27, 4.15 (CO_2Et), 1.7 (4 H, m, 8-, 9-CH_2), 2.33 (1 H, dt, J = 12.1, 6.7 Hz, 7-H), 2.77 (1 H, dt, J = 8.7, 5.9 Hz, 10-H), 3.09 (1 H, m, 2-H), 3.31 (1 H, t, J = 8.7 Hz, 11-H), 4.00 (1 H, t, J = 5.9 Hz, 1-H), 4.57 (1 H, bd, J = 12.1 Hz, 7-H′), 5.89 (1 H, d, J = 9.9 Hz, 4-H), 6.45 (1 H, dd, J = 9.9, 6.0 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ 14.1, 21.8, 23.4, 33.8, 37.8, 39.0, 47.5, 50.8, 60.7, 125.4, 137.7, 162.5, 172.8; mass spectrum m/z (relative intensity) 235 (M^+, 6), 96 (100). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.38, H, 7.23; N, 5.96. Found: C, 66.11; H, 7.02; N, 6.18.

Ethyl 8-Oxo-7-azatricyclo[5.4.1^{2,11}.0]dodec-9-ene-*endo*-12-carboxylate (16). A solution of 4 (822 mg, 3.0 mmol) and benzophenone (200 mg, 1.1 mmol) in acetonitrile (480 mL) was irradiated for 1.5 h, and the usual workup afforded 16 (221 mg, 27%) as a colorless oil: IR (neat) 1730, 1670 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.27, 4.17 (CO_2Et), 1.55 (1 H, q, J = 12.5 Hz, 3-H), 1.6 (4 H, m, 4-, 5-CH_2), 2.01 (1 H, m, 3-H′), 2.27 (1 H, m, 6-H), (1 H, t, J = 7.3 Hz, 12-H), 2.79 (1 H, m, 2-H), 3.49 (1 H, m, 11-H), 4.2 (1 H, t, J = 10.8 Hz, 1-H), 4.72 (1 H, bd, J = 13.6 Hz, 6-H′), 5.83 (1 H, d, J = 8.8 Hz, 9-H), 6.38 (1 H, dd, J = 8.8, 5.1 Hz, 10-H); ^{13}C NMR ($CDCl_3$) δ 14.3, 27.6, 27.7, 31.7, 32.2, 45.4, 48.8, 51.4, 54.5, 61.0, 123.4, 138.4, 162.0, 173.4; mass spectrum m/z (relative intensity) 249 (M^+, 21), 96 (100). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.50; H, 7.63; N, 5.62. Found: C, 67.33; H, 7.31; N, 5.83.

Ethyl 9-Oxo-8-azatricyclo[6.4.1^{2,12}.0]tridec-10-ene-*endo*-13-carboxylate (17). A solution of 5 (130 mg, 0.50 mmol) and benzophenone (30 mg, 0.16 mmol) in acetonitrile (70 mL) was irradiated for 4 h, and the usual workup gave 17 (10 mg, 8%) as a colorless oil: IR (neat) 1730, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 4.19 (CO_2Et), 1.62–1.83 (8 H, m, 3-, 4-, 5-, 6-CH_2), 2.44 (1 H, dt, J = 13.2, 4.4 Hz, 7-H), 2.52 (1 H, t, J = 3.7 Hz, 7-H), 2.68 (1 H, m, 2-H), 3.51 (1 H, m, 12-H), 4.27 (1 H, t, J = 9.2 Hz, 1-H), 4.48 (1 H, ddd, J = 13.2, 9.9, 4.4 Hz, 7-H′), 5.88 (1 H, dd, J = 9.9, 1.8 Hz, 10-H), 6.39 (1 H, dd, J = 9.9, 4.0 Hz, 11-H); mass spectrum m/z (relative intensity) 263 (M^+, 18), 96 (100). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.44; H, 7.98; N, 5.32. Found: C, 68.18; H, 8.20; N, 5.58.

Ethyl 4-[[5-(Ethoxycarbonyl)-*trans*-4-pentenyl]oxy]-5-oxo-6-azatricyclo[4.4.1^{2,10}.0]undec-3-ene-*endo*-11-carboxylate (18). A solution of 6 (2.59 g, 7.0 mmol) and benzophenone (0.40 g, 2.2 mmol) in acetonitrile (1200 mL) was irradiated for 1.5 h, and the usual workup gave 18 (0.67 g, 26%) as a colorless oil: IR (neat) 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 4.16 (CO_2Et), 1.69 (4 H, m, 8-, 9-CH_2), 1.94 (2 H, m, CH_2), 2.30 (1 H, m, 7-H), 2.38 (2 H, q, J = 6.6 Hz, CH_2), 3.12 (1 H, m, 2-H), 3.26 (1 H, t, J = 9.9 Hz, 11-H), 3.70 (2 H, t, J = 5.7 Hz, OCH_2), 3.98 (1 H, t, J = 5.6 Hz, 1-H), 4.57 (1 H, d, J = 10.9 Hz, 7-H′), 5.26 (1 H, d, J = 7.0 Hz, 3-H), 5.85 (1 H, d, J = 10.4 Hz, =CH), 6.96 (1 H, m, =CH); mass spectrum m/z (relative intensity) 391 (M^+, 27), 94 (100). Anal. Calcd for $C_{21}H_{29}NO_6$: C, 64.45; H, 7.42; N, 3.58. Found: C, 64.19; H, 7.31; N, 3.65.

2-[[5-(Ethoxycarbonyl)-*trans*-4-pentenyl]oxy]-2-azabicyclo[2.2.2]hex-5-en-3-one (19). A solution of 3 (395 mg, 1.7 mmol) in acetonitrile (240 mL) without benzophenone was irradiated for 10 h, and the usual workup gave 19 (380 mg, 96%) as a colorless oil: IR (neat) 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28, 4.15 (CO_2Et), 1.69, 2.24 (each 2 H, CH_2), 3.12, 3.26 (each 1 H, NCH_2), 4.10 (1 H, m, 4-H), 4.34 (1 H, m, 1-H), 5.84 (1 H, d, J = 15.4 Hz, =CH), 6.59 (2 H, m, 5-, 6-H), 6.92 (1 H, dt, J = 15.4, 7.2 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 14.2, 26.0, 29.5, 42.8, 54.0, 57.5, 60.3, 122.2, 140.5, 141.0, 147.3, 170.6; mass spectrum m/z (relative intensity) 235 (M^+, 2) 52 (100). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.38; H, 7.23; N, 5.96. Found: C, 66.09; H, 7.48; N, 6.31.

Extensive Chlorination of Methylnaphthalenes, Friedel–Crafts Alkylation of Pentachlorobenzene by Heptachloro(chloromethyl)naphthalenes, and Related Results

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The chlorination of 2-methylnaphthalene (1) and 1-methylnaphthalene (12) by means of Silberrad's reagent (initial components: SO_2Cl_2, S_2Cl_2, and $AlCl_3$) has been performed. From 1 or 12, the following compounds have been synthesized for first time: nonachloro-3-(chloromethyl)-1,4-dihydronaphthalene (3), nonachloro-7-(chloromethyl)-1,4-dihydronaphthalene (4), perchloro-3-vinylindene (2), perchloro-1-vinylindan, nonachloro-4-(chloromethyl)-1,4-dihydronaphthalene (11), heptachloro-7-(chloromethyl)naphthalene (6), heptachloro-8-(chloromethyl)naphthalene (10), heptachloro-7-methylnaphthalene, heptachloro-8-methylnaphthalene, 2-(bromochloromethyl)heptachloronaphthalene, 1-(bromochloromethyl)heptachloronaphthalene, heptachloro-7-formylnaphthalene (24), heptachloro-8-formylnaphthalene (26), (2-heptachloronaphthyl) (pentachlorophenyl)methane (17), and (1-heptachloronaphthyl) (pentachlorophenyl)methane (20). Silberrad's reagent interconverts dihydronaphthalenes 3 and 4. The $AlCl_3$-promoted Friedel–Crafts alkylation of pentachlorobenzene (16) by naphthalenes 6 and 10, giving diarylmethanes 17 and 20, respectively, takes place in mild conditions (refluxing CS_2) although the substrate and the alkylating agents are highly crowded polychloro compounds. By heating (100 °C) a mixture of 17, 16, and $AlCl_3$, 1*H*-heptachloronaphthalene (18) and bis(pentachlorophenyl)methane were obtained. Aldehyde 24, treated with $Rh(PPh_3)_3Cl$, gave 2*H*-heptachloronaphthalene, which was prepared in pure form for the first time. Under similar treatment, aldehyde 26 gave 18. The X-ray structures of indene 2 and dihydronaphthalene 11 are reported and discussed. Some probable mechanisms, as well as IR, UV, and ^1H NMR spectra data of the compounds synthesized, are presented.

Introduction

In the context of our investigations on highly chlorinated compounds, we reported the Friedel–Crafts condensation between polychlorobenzenes and highly chlorinated alkylating agents by means of $AlCl_3$.[1] This condensation leads to overcrowded polyphenylmethanes (which are the usual precursors of exceptionally stable radicals[2] and carbanions[2d,f,3]),[1a,c,2h,i] and the relevant method is high-

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[†] Departamento de Materiales Orgánicos Halogenados.

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(1) (a) Ballester, M.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *Synthesis* **1986**, *64*; Span. Patent 541.891, 1985; Span. Patent 541.892, 1985. (b) Riera, J.; Castañer, J.; Armet, O.; Rovira, C. *An. Quim.* **1986**, *82*, 268. (c) Armet, O.; Veciana, J.; Rovira, C.; Riera, J.; Castañer, J.; Molins, E.; Rius, J.; Miravitlles, C.; Olivella, S.; Brichfeus, J. *J. Phys. Chem.* **1987**, *91*, 5608.

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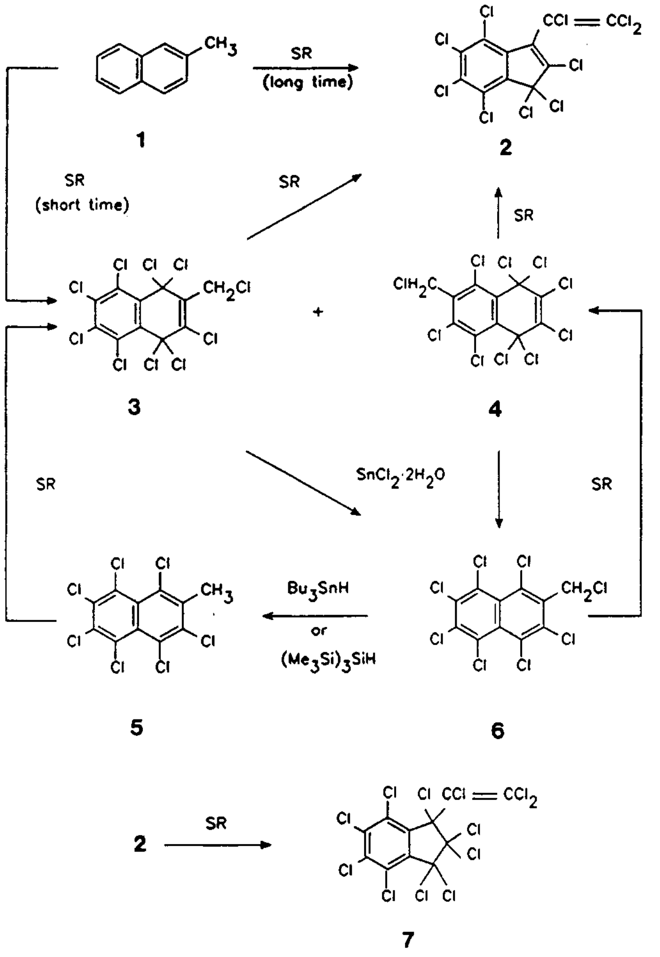
yielding, easy, and straightforward. However, the scope of such condensation was not extended to the synthesis of highly chlorinated arylmethanes containing a fused polycyclic aryl group. In this connection, we now describe our results concerning the synthesis of the two heptachloro(chloromethyl)naphthalenes (**6** and **10**) and the Friedel–Crafts alkylation of pentachlorobenzene (**16**) by **6** and **10**. A method by which to prepare the two heptachloronaphthalenes is also reported.

Results and Discussion

Chlorinations with Silberrad's Reagent (SR).[4] Chlorination of 2-methylnaphthalene (**1**) with SR (initial components: SO_2Cl_2, S_2Cl_2, and $AlCl_3$) gave a complex mixture (TLC) from which nonachloro-3-(chloromethyl)-1,4-dihydronaphthalene (**3**) and nonachloro-7-(chloromethyl)-1,4-dihydronaphthalene (**4**) were isolated. The yields of these compounds in the chlorination mixture were estimated (by ^{1}H NMR) to be around 20 and 40%, respectively. Longer reaction times permitted the isolation of perchloro-3-vinylidene (**2**) and a mixture of **3** and **4**.

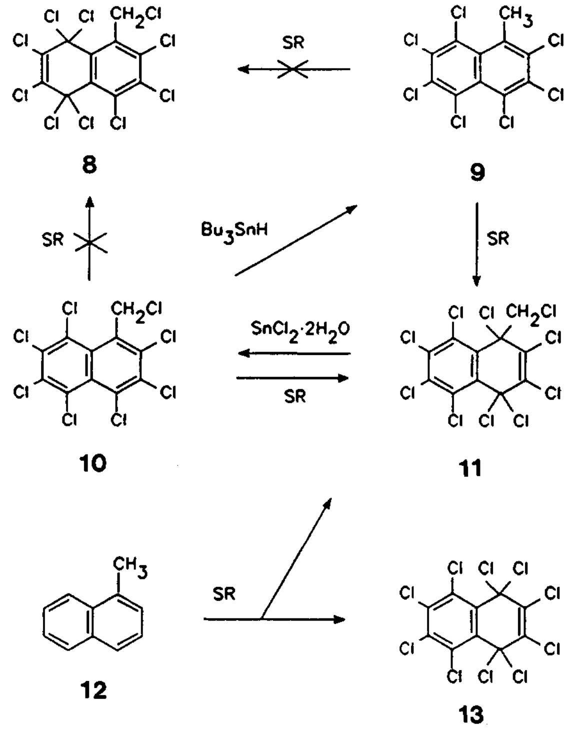


Treatment of 1-methylnaphthalene (**12**) with SR led to a complex mixture (TLC), as in the chlorination of **1**. From this mixture, nonachloro-4-(chloromethyl)-1,4-dihydronaphthalene (**11**) and perchloro-1,4-dihydronaphthalene (**13**) were isolated.

Formation of dihydronaphthalenes **3**, **4**, and **11** could proceed through the corresponding perchloroaromatic methylnaphthalenes since (i) related chlorination of toluene with SR gives 1,2,3,4,5-pentachlorotoluene,[4c] (ii) chlorination of methylnaphthalene **5**[5] with this reagent gave **3** and **4**, and (iii) chlorination of methylnaphthalene **9**[5] with the same reagent led to **11**.

We believe that the two preceding chlorinations occur via the processes shown in Scheme I for the following reasons: (i) formation of σ-complexes **14** and **15** is favored by the strain release of the peri interaction[6] and the carbocation stability due to the electronic effects of the methyl group; (ii) addition of Cl_2 to the ethylene double bond with mixtures of SO_2Cl_2, S_2Cl_2, and $AlCl_3$ has been observed in other cases;[8] and (iii) it has been confirmed that SR interconverts **3** and **4**.

In order to obtain information on this interconversion, chlorination of (chloromethyl)naphthalene **6**[5] with SR was carried out, giving a mixture of **3** and **4**. This result suggests that these compounds are interconverted through **6**. Supporting this possibility, it is known that $AlCl_3$ dechlorinates dihydronaphthalene **13** to perchloronaphthalene in CS_2.[9]



Formation of indene **2** is not a surprising result since a related ring contraction in triphenylene by the action of SO_2Cl_2–S_2Cl_2–$AlCl_3$ has been reported.[10] Compound **2**

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(2) (a) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215. (b) Ballester, M. *Acc. Chem. Res.* **1985**, *18*, 380. (c) Ballester, M. *Adv. Phys. Org. Chem.* **1989**, *25*, 267. (d) Ballester, M.; Pascual, I.; Torres, J. *J. Org. Chem.* **1990**, *55*, 3035. (e) Ballester, M.; Pascual, I. *J. Org. Chem.* **1991**, *56*, 841. (f) Ballester, M.; Pascual, I.; Riera, J.; Castañer, J. *J. Org. Chem.* **1991**, *56*, 217. (g) Juliá, L.; Riera, J.; Teixidó, R. *J. Chem. Soc., Perkin Trans. 1*, **1991**, 1101. (h) Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552. (i) Carilla, J.; Juliá, L.; Riera, J.; Brillas, E.; Garrido, J. A.; Labarta, A.; Alcalá, R. *J. Am. Chem. Soc.* **1991**, *113*, 8281.

(3) (a) Ballester, M.; de la Fuente, G. *Tetrahedron Lett.* **1970**, 4509. (b) Veciana, J.; Riera, J.; Castañer, J.; Ferrer, N. *J. Organomet. Chem.* **1985**, *297*, 131.

(4) (a) Silberrad, O. *J. Chem. Soc.* **1921**, *119*, 2029; (b) **1922**, *121*, 1015; (c) **1925**, *127*, 2677.

(5) The synthesis of this compound is described in the following text.

(6) The existence of strong steric repulsion between chlorines in peri position was observed by X-ray diffraction analysis in perchloronaphthalene.[7]

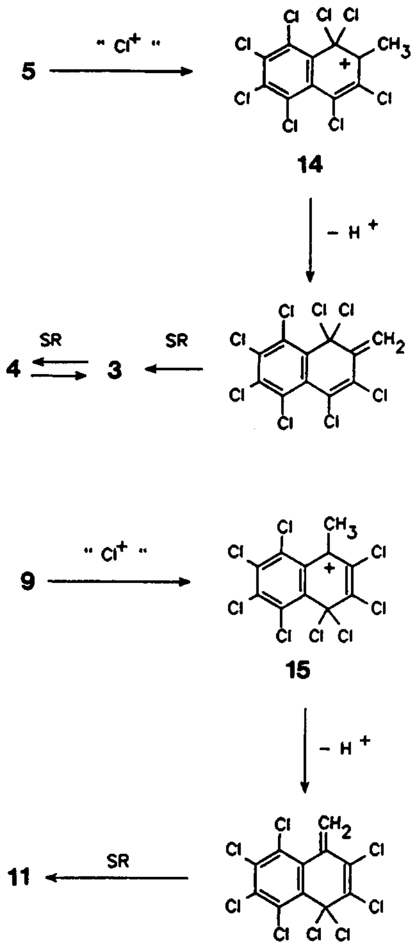
(7) Gafner, G.; Herbstein, F. H. *Acta Crystallogr.* **1960**, *13*, 702; *Nature* **1963**, *200*, 130.

(8) (a) Ballester, M.; Riera, J. *An. R. Soc. Esp. Fís. Quím.* **1960**, *56B*, 897. (b) Ballester, M.; Castañer, J. *An. R. Soc. Esp. Fís. Quím.* **1966**, *62B*, 397.

(9) García, R.; Riera, J.; Carilla, J.; Juliá, L. Unpublished results.

(10) (a) Gall, J. H.; MacNicol, D. D.; Mallinson, P. R.; Welsh, P. A. *Tetrahedron Lett.* **1985**, *26*, 4005. (b) Campbell, M. C.; Humphries, R. E.; Munn, N. M. *J. Org. Chem.* **1992**, *57*, 641.

Scheme I

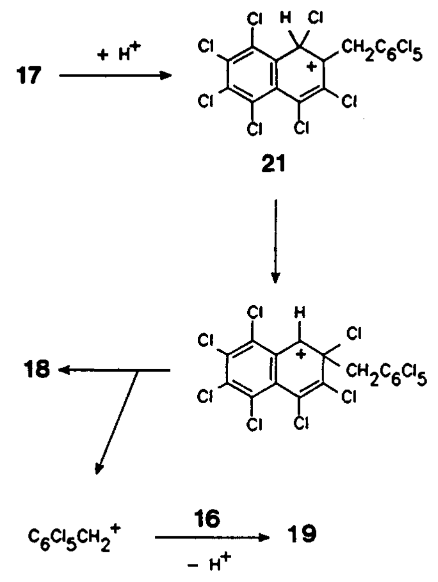


arises, at least partly, from dihydronaphthalenes **3** and **4**, since these gave **2** (and perchloro-1-vinylindan (**7**)) when treated with SR. In view of the fact that this reagent interconverts **3** and **4**, it is suggested that formation of **2** from **4** may occur through **3**. As expected, indan **7** arises, at least partly, from indene **2**, since treatment of the latter with SR gave the former.

One attempt to obtain dihydronaphthalene **8** by treating (chloromethyl)naphthalene **10**[5] with SR failed. Dihydronaphthalene **11** was obtained as the sole product and in a high yield.

Structural Assignments. Structures of isomeric dihydronaphthalenes **3** and **4** were assigned by UV, IR, and ^1H NMR spectroscopy. Their UV spectra are very similar in shape to that of dihydronaphthalene **13**,[11] indicating that both isomers are 1,4-dihydronaphthalenes. From the maximum absorptivity of the "smoothed" secondary band of **13** (ϵ 975)[11,12] and the migration moment of Cl (+14),[12] the migration moment of the constellation o-$CCl_2CCl{=}CClCCl_2$ (−16.6) was determined.[12] Then, from these moments and the migration moment of the constellations 1,3,2-$Cl_2(CH_2Cl)$ (−21.2)[12] and o-$CCl_2C(CH_2Cl){=}CClCCl_2$ (−16.6),[13] the smoothed maximum absorptivities (ϵ) for the secondary band of **3** and **4** were calculated.[12] Since the values obtained (974 for **3** and 1554 for **4**) agree excellently with the observed ones (1000 and 1635), the position of the CH_2Cl group in **3** and **4** has been determined and, in consequence, the structures of these isomers have been stablished. Structures of **3** and **4** were confirmed by IR and ^1H NMR spectroscopy: the position for the vinylene stretching peak of **4** (1645 cm^{-1}), unlike that of **3** (1670 cm^{-1}), is coincident with that of **13**;[11] the chemical shift of the singlet due to the CH_2Cl group is higher for **4** (δ 5.07) than for **3** (δ 4.68).

Scheme II



Indene **2** and dihydronaphthalene **11** have been characterized unambiguously by X-ray diffraction analysis (see below). The structure of indane **7** has been assigned considering that its UV spectrum is similar to that of perchloroindan and quite different from that of perchloroindene.[15]

Synthesis of Heptachloro(chloromethyl)naphthalenes and Heptachloromethylnaphthalenes. Heptachloro-7-(chloromethyl)naphthalene (**6**) was obtained in excellent yields by dechlorination of dihydronaphthalenes **3** or **4** with $SnCl_2{\cdot}2H_2O$.[16] However, it is recommended to prepare naphthalene **6** as follows: chlorination of hydrocarbon **1** with SR, purification of the crude material until a mixture containing only **3** and **4** is obtained, and treatment of this mixture with $SnCl_2{\cdot}2H_2O$. By means of this method, **6** was obtained in 34% yield from **1**. Heptachloro-8-(chloromethyl)naphthalene (**10**) was synthesized in excellent yield by dechlorination of dihydronaphthalene **11** with $SnCl_2{\cdot}2H_2O$. Heptachloro-7-methylnaphthalene (**5**) was synthesized by reduction of naphthalene **6** with $(n\text{-}Bu)_3SnH$ or the less toxic $(Me_3Si)_3SiH$.[17] Heptachloro-8-methylnaphthalene (**9**) was synthesized by reduction of naphthalene **10** with $(n\text{-}Bu)_3SnH$.

Friedel–Crafts Alkylations and Related Results. The $AlCl_3$-promoted Friedel–Crafts alkylation of pentachlorobenzene (**16**) by (chloromethyl)naphthalenes **6** and **10** in refluxing CS_2 afforded (2-heptachloronaphthyl)-

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(11) Ballester, M.; Castañer, J.; Riera, J.; Parés, J. *An. Quím.* **1980**, *76C*, 157.

(12) Ballester, M.; Riera, J.; Spialter, L. *J. Am. Chem. Soc.* **1964**, *86*, 4276.

(13) It was assumed that the constellations o-$CCl_2CCl{=}CClCCl_2$ and o-$CCl_2C(CH_2Cl){=}CClCCl_2$ have the same migration moment. This is a reasonable assumption since the migration moment is a measure of the migration into or out of the benzene ring caused by the resonance with the substituent.[14]

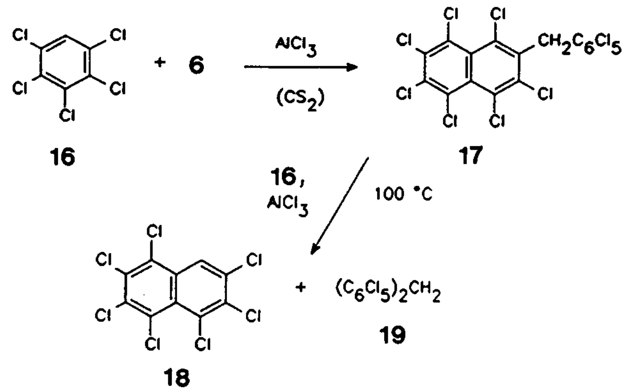
(14) (a) Sklar, A. L. *J. Chem. Phys.* **1942**, *10*, 135. (b) Ballester, M.; Riera, J. *Spectrochim. Acta* **1967**, *23A*, 1533.

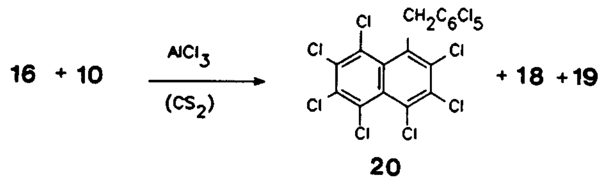
(15) Ballester, M.; Castañer, J. *An. R. Soc. Esp. Fís. Quím.* **1970**, *66B*, 487.

(16) Related dechlorinations were performed with anhyd $SnCl_2$.[11]

(17) Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1988**, *53*, 3641; **1989**, *54*, 2492.

(pentachlorophenyl)methane (**17**) in excellent yield and (1-heptachloronaphthyl)(pentachlorophenyl)methane (**20**) in moderate yield, respectively. It is emphasized that formation of diarylmethanes **17** and **20** takes place under mild conditions although the substrate and the alkylating agents are highly crowded polychloro compounds. In the latter alkylation, formation of small proportions of 1*H*-heptachloronaphthalene (**18**) and bis(pentachlorophenyl)methane (**19**) were detected, indicating that transalkylation between **20** (and/or **10**) and **16** occurs slowly.





In view of the preceding transalkylation, it was decided to heat a mixture of diarylmethane **17**, **16** and $AlCl_3$ for a long time to attempt to obtain 2*H*-heptachloronaphthalene (**23**) which had not been prepared in pure form.[18] The reaction did not give **23**, but heptachloronaphthalene **18**, along with diphenylmethane **19**. Even though **18** was isolated in almost pure form, it contained at least two impurities (detected by ^1H NMR spectroscopy and HPLC) which could not be removed by column chromatography, sublimation, and several crystallizations. A plausible mechanism to explain the reaction between **17** and **16** is outlined in Scheme II, in which formation of σ-complex **21** is assisted by strain release of peri interaction,[6] and the sequence which leads to **18** is similar to that reported previously to explain 1,2-shifts of Cl substituent in the $AlCl_3$-catalyzed isomerization of chlorofluorobenzenes and dichlorobenzenes.[20]

Heptachloronaphthalenes. Heptachloronaphthalene **23** was prepared in pure form from naphthalene **6** in three steps: photobromination with Br_2 of **6** to 2-(bromochloromethyl)heptachloronaphthalene (**22**); hydrolysis of this to heptachloro-7-formylnaphthalene (**24**) by treatment with oleum and then with water; and finally, decarbonylation of **24** by means of $Rh(PPh_3)_3Cl$.

Heptachloronaphthalene **18**, which had been obtained in different ways and at different purities (see above and previous papers[19,21]), was prepared in pure form by the above method, starting from naphthalene **10**, through 1-(bromochloromethyl)heptachloronaphthalene (**25**) and heptachloro-8-formylnaphthalene (**26**). The mp we report for **18** (183.5–4.5 °C) is significantly higher than that given for this compound elsewhere (160–2 °C).[21c]

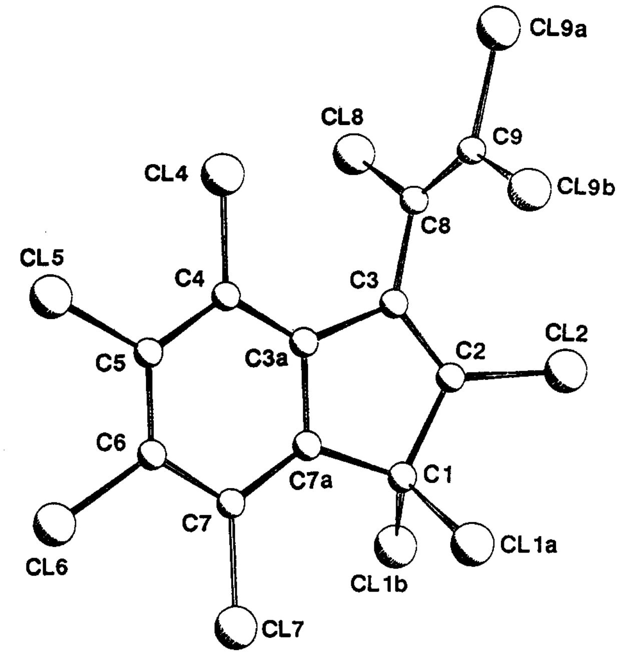
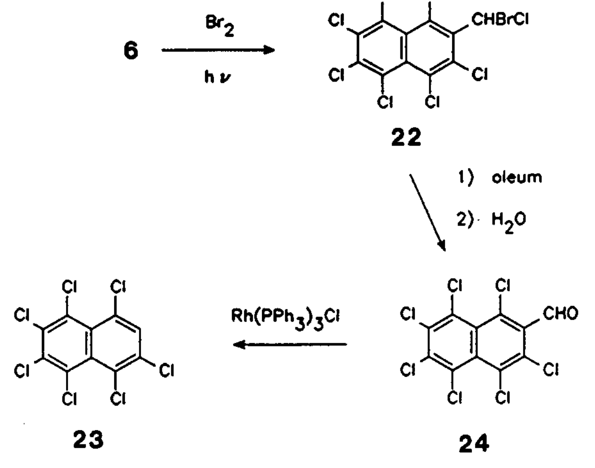
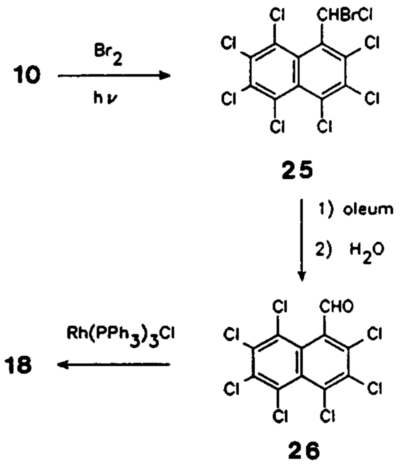


Figure 1. A perspective view of indene **2** with atom numbering.





X-ray Structure of Indene 2 and Dihydronaphthalene 11. X-ray crystallographic analysis of **2** and

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[18] It has been reported that impure samples of **23** can be obtained by fractional crystallization of Halowax 1051 (a commercial mixture of highly chlorinated naphthalenes).[19]

[19] Brinkman, U. A. Th.; De Kok, A. *J. Chromatogr.* **1976**, *129*, 451.

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[21] (a) Sundström, G. *Chemosphere* **1976**, *3*, 191. (b) Clark, J.; Maynard, R.; Wakefield, B. J. *J. Chem. Soc., Perkin Trans. 2*, **1976**, 73. (c) Brady, J. H.; Tahir, N.; Wakefield, B. J. *J. Chem. Soc. I* **1984**, 2425. (d) Haglund, E.; Bergman, A. *Chemosphere*, **1989**, *19*, 195.

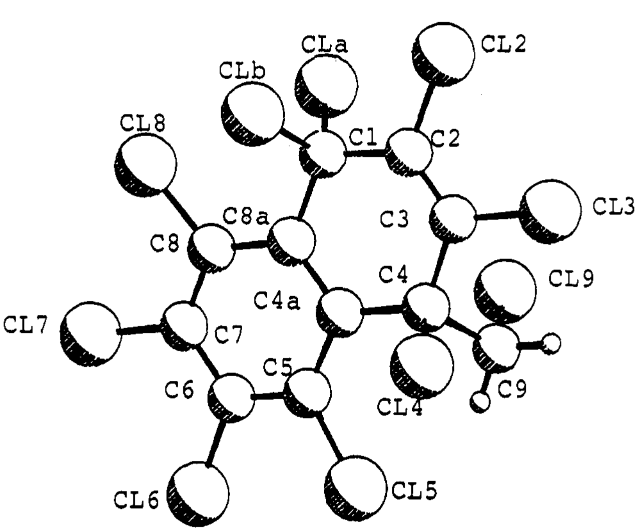

Figure 2. A perspective view of dihydronaphthalene **11A** with atom numbering.

Table I. Selected Torsion Angles for 11A and 11B[a]

tor angle	deg	tor angle	deg
C6–C7–C8–C8a	4.24 (0.6)	C6′–C7′–C8′–C8a′	0.84 (0.5)
C4a–C5–C6–C7	-6.06 (0.5)	C4a′–C5′–C6′–C7′	-3.41 (0.6)
C8a–C1–C2–C3	-1.32 (0.5)	C8a′–C1′–C2′–C3′	-4.77 (0.5)
C2–C3–C4–C4a	0.41 (0.5)	C2′–C3′–C4′–C4a′	4.40 (0.5)

[a] See ref 22.

11 was performed to establish the structure of these overcrowded compounds unambiguously.

A perspective view of the molecular structure of **2** is shown in Figure 1. The benzene ring, the five-membered ring and the trichlorovinyl group are planar within 0.019, 0.025, and 0.075 Å, respectively. The dihedral angle between the mean planes of the benzene ring and the five-membered ring is 176.8°. On account of the steric repulsions between the chlorine pairs Cl8/Cl4 (interatomic distance = 3.479 Å) and Cl9b/Cl2 (3.773 Å), the dihedral angle between the mean planes of the trichlorovinyl group and the five-membered ring is 76.5°. The two ethylene stretching peaks in the IR spectrum of **2** have been assigned on the basis of these angles. The peak located at 1630 cm^{-1} is attributed to the "almost isolated" vinylic double bond, while that at 1575 cm^{-1} is regarded as due to the conjugated endocyclic double bond. Accordingly, this peak is located nearer to that of perchloroindene (1587 cm^{-1}).[15]

In a single crystal of dihydronaphthalene **11**, two molecules (**11A** and **11B**) with slightly a different conformation were observed. A perspective view of one of them (**11A**) is shown in Figure 2. Bond lengths and bond angles for **11A** and **11B** are almost coincident. However, from the torsion angles listed in Table I, one can conclude that while the aromatic ring is bent along the C5–C8 axis in **11A**, a similar bending occurs along the C1′–C4′ axis in **11B**.[22] Accordingly, the analysis of least-squares mean planes shows that (i) the bent rings present higher rmsd's and (ii) the atoms of the bicyclic system which are more distant (~0.035 Å) from the corresponding ring mean plane are C5 and C8 in **11A** and C1′ and C4′ in **11B**. The chloromethyl group shows similar orientation in **11A** and **11B**, and the dihedral angle between the mean planes of the rings in both molecules is about 177°.

Experimental Section

General. Melting points are uncorrected. SO_2Cl_2 was purchased from Fluka and used without further purification. $AlCl_3$ and other reagents were also used as provided by commercial sources. TLC analyses were performed on plastic sheets precoated with Merck silica gel 60 F_{254}. Preparative column chromatography separations were accomplished on SDS silica gel of either 40–60 (flash) or 60–200 μm. Since the locations of the IR peaks of highly chlorinated compounds differ markedly from those of their nonchlorinated counterparts, they are included in this section, although weak peaks in the region 400–1300 cm^{-1} are not given.

Chlorinations with Silberrad's Reagent (SR).[4] **General Procedure.** From a dropping funnel, a solution of the substrate and S_2Cl_2 in SO_2Cl_2 was added slowly (addition time) to a boiling solution of anhyd $AlCl_3$ in SO_2Cl_2, and the resulting solution was refluxed for 0.15–10 h (reaction time), keeping the volume constant with occasional small additions of SO_2Cl_2. Most of the SO_2Cl_2 was then evaporated under reduced pressure at 40–50 °C, the rest of the solution was poured over cracked ice, and solid $NaHCO_3$ was added until gas evolution ceased. The mixture was then heated (50–60 °C, 30 min), and, when cold, strongly acidified with concd aqueous HCl and extracted with $CHCl_3$. The organic layer was washed with water, dried, and evaporated, yielding a crude material which was further worked up.

Nonachloro-3-(chloromethyl)-1,4-dihydronaphthalene (3) and Nonachloro-7-(chloromethyl)-1,4-dihydronaphthalene (4). 2-Methylnaphthalene (**1**) was chlorinated by means of SR according to the general procedure described above. Starting materials: **1** (5.01 g), S_2Cl_2 (2.50 g), SO_2Cl_2 (140 mL); $AlCl_3$ (1.32 g), SO_2Cl_2 (350 mL). Addition time: 45 min. Reaction time: 75 min. The resulting crude material (16.15 g) was passed through silica gel (hexane) and crystallized (same solvent). The crystalline fraction obtained (5.81 g) was flash chromatographed (silica gel, hexane) to give the following: (a) **3** (1.53 g, 9%), mp 186–9 °C [IR (KBr) 3025 (w), 2980 (w), 1670 (m), 1520 (m), 1440 (m), 1360 (s), 1340 (m), 1320 (w), 1290 (s), 1255 (m), 1240 (s), 1220 (m), 1190 (s), 1150 (m), 1125 (s), 1020 (m), 940 (s), 900 (m), 755 (s), 730 (s), 635 (s), 620 (m), 610 (m), 580 (m), 565 (s), 505 (s), 415 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 216 nm, 228 (sh), 254 (sh), 290 (sh), 300, 312 (ϵ 35 600, 33 100, 10 300, 560, 950, 1050); ^1H NMR ($CDCl_3$) δ 4.68 (s, CH_2Cl). Anal. Calcd for $C_{11}H_2Cl_{10}$: C, 27.0; H, 0.4; Cl, 72.6. Found: C, 27.1; H, 0.1; Cl, 72.6]; (b) a mixture of **3** and **4** (2.53 g, 15%) (both identified by TLC, IR and ^1H NMR), molar ratio **3**/**4**:[23] 0.39; and (c) **4** (1.60 g, 9%), mp 185–7 °C: IR (KBr) 3040 (w), 1645 (m), 1540 (w), 1525 (w), 1445 (m), 1375 (m), 1365 (s), 1270 (m), 1260 (m), 1155 (s), 1020 (m), 940 (m), 920 (m), 850 (m), 735 (s), 620 (s), 610 (s), 600 (m), 580 (m), 570 (m), 475 (m), 470 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 218 nm, 226 (sh), 255 (sh), 288 (sh), 303, 312 (ϵ 38 800, 37 300, 8400, 650, 1570, 1700); ^1H NMR ($CDCl_3$) δ 5.07 (s, CH_2Cl). Anal. Calcd for $C_{11}H_2Cl_{10}$: C, 27.0; H, 0.4; Cl, 72.6. Found: C, 27.1; H, 0.3; Cl, 72.6.

Perchloro-3-vinylindene (2). 2-Methylnaphthalene (**1**) was chlorinated as described in the preceding chlorination, but reaction time was increased. Starting materials: **1** (5.14 g), S_2Cl_2 (2.50 g), SO_2Cl_2 (150 mL); $AlCl_3$ (1.40 g), SO_2Cl_2 (350 mL). Addition time: 40 min. Reaction time: 9 h. The resulting crude material was subjected to flash chromatography (silica gel, hexane) yielding (a) a solid (2.09 g) which was purified by recrystallization (hexane) to give **2** (1.48 g, 8%) as prisms mp 143–5 °C [IR (KBr) 1630 (m), 1575 (m), 1540 (w), 1385 (w), 1365 (s), 1345 (w), 1330 (w), 1320 (w), 1290 (s), 1250 (m), 1185 (s), 1150 (m), 1020 (m), 1000 (m), 935 (s), 870 (s), 825 (m), 815 (m), 805 (s), 725 (m), 620 (s), 600 (s), 540 (s), 510 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 209 nm, 242 (sh), 249, 257, 294, 339 (ϵ 34 400, 23 800, 29 400, 29 600, 3140, 2840); MS 482 ($C_{11}{}^{35}Cl_{10}$, M^+), 447 ($M^+ - Cl$), 412 ($M^+ - 2Cl$), 377 ($M^+ - 3Cl$), 342 ($M^+ - 4Cl$), 307 ($M^+ - 5Cl$). Anal. Calcd for $C_{11}Cl_{10}$: C, 27.2; Cl, 72.8. Found: C, 27.2; Cl, 73.0] and (b) another solid (11.70 g) which was digested with pentane to give a mixture of dihydronaphthalenes **3** and **4** (5.75 g, 33%) (both identified by TLC, IR, and ^1H NMR), molar ratio **3**/**4**:[23] 0.08.

Nonachloro-4-(chloromethyl)-1,4-dihydronaphthalene (11). 1-Methylnaphthalene (**12**) was chlorinated as described in

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(22) Atoms of **11B** are numbered as in **11A** but with the symbol ′.

(23) The value of this ratio was determined by ^1H NMR.

the preceding chlorinations, but with a shorter reaction time (10 min).[24] Starting materials: **12** (5.09 g), S_2Cl_2 (2.50 g), SO_2Cl_2 (140 mL); $AlCl_3$ (1.27 g), SO_2Cl_2 (350 mL). Addition time: 20 min. The resulting crude material (18.03 g) was subjected to flash chromatography (silica gel, hexane) to give the following: (a) perchloro-1,4-dihydronaphthalene (**13**) (0.738 g, 4%), identified by TLC and its IR spectrum;[11] (b) a mixture (0.734 g) containing **13** (identified by TLC) and **11** (identified by ^{1}H NMR); (c) an impure fraction (4.66 g), which was recrystallized (hexane) to afford **11** (3.74 g, 21%) as prisms mp 151.5–3.5 °C [IR (KBr) 3040 (w), 1655 (m), 1525 (w), 1520 (w), 1445 (s), 1355 (s), 1335 (w), 1260 (s), 1145 (s), 960 (m), 950 (s), 900 (m), 885 (m), 785 (m), 765 (m), 720 (s), 680 (s), 655 (m), 580 (m), 560 (s), 500 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 210 nm, 229, 248 (sh), 286 (sh), 297, 307 (ϵ 34 900, 30 600, 12 500, 450, 640, 660); ^{1}H NMR ($CDCl_3$) δ 4.37 (d, 1 H, J = 12 Hz, H-C(CH_2Cl)), 5.27 (d, 1 H, J = 12 Hz, H-C(CH_2Cl)). Anal. Calcd for $C_{11}H_2Cl_{10}$: C, 27.0; H, 0.4; Cl, 72.6. Found: C, 27.3; H, 0.3; Cl, 72.6]; and (d) a complex mixture (0.467 g) containing some **11** which was identified by TLC and ^{1}H NMR.

Treatment of Dihydronaphthalenes 3 and 4 with SR. By treatment of the title compounds with SR according to the general procedure described above, the following transformations were observed: (1) **Conversion of 3 into 4.**[25] Starting materials: **3** (0.100 g), S_2Cl_2 (0.059 g), $AlCl_3$ (0.024 g), SO_2Cl_2 (11 mL). Reaction time: 1 h. The resulting crude material (0.094 g) consisted mainly of **3** and **4** (both identified by IR and ^{1}H NMR), molar ratio **3**/**4**:[23] 0.55.

(2) Conversion of 3 into Indene 2 and Perchloro-1-vinylindan (7). Starting materials: **3** (0.198 g), S_2Cl_2 (0.100 g), SO_2Cl_2 (8 mL); $AlCl_3$ (0.055 g), SO_2Cl_2 (14 mL). Addition time: 5 min. Reaction time: 7 h. The resulting crude material (0.196 g) was subjected to flash chromatography (silica gel, hexane) to give the following: (a) indene **2** (0.088 g, 45%), identified by TLC and its IR spectrum; (b) a mixture (0.029 g) of **2** and indan **7**, both identified by TLC and IR; and (c) another mixture which by crystallization (hexane) afforded indan **7** (0.050 g; 22%) as prisms, mp 187–8 °C: IR (KBr) 1560 (s), 1535 (w), 1380 (s), 1365 (w), 1345 (w), 1330 (w), 1255 (s), 1235 (s), 1180 (s), 1110 (m), 1025 (m), 1000 (m), 975 (m), 955 (m), 925 (s), 890 (s), 850 (m), 805 (m), 755 (s), 725 (s), 680 (s), 625 (s), 605 (m), 595 (m), 555 (s), 520 (m), 440 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 217 (sh) nm, 236, 257 (sh), 299, 310 (sh) (ϵ 22 500, 37 700, 10 200, 470, 350). Anal. Calcd for $C_{11}Cl_{12}$: C, 23.7; Cl, 76.3. Found: C, 23.7; Cl, 76.5.

(3) Conversion of 4 into Indene 2, Indan 7, and 3. Starting materials: **4** (0.207 g), S_2Cl_2 (0.100 g), SO_2Cl_2 (10 mL); $AlCl_3$ (0.059 g), SO_2Cl_2 (14 mL). Addition time: 5 min. Reaction time: 7 h. The resulting crude material (0.189 g) was purified by flash chromatography (silica gel, hexane) to give the following: (a) **2** (0.066 g, 32%), identified by TLC and its IR spectrum; (b) **7** (0.032 g, 13%), identified by TLC and its IR spectrum; and (c) an impure fraction (0.061 g) containing **3** and **4** (both identified by TLC and ^{1}H NMR), molar ratio **3**/**4**:[23] 0.59.

Heptachloro-7-(chloromethyl)naphthalene (6). (1) From Dihydronaphthalene 4. A solution of **4** (0.198 g, 0.4 mmol) and $SnCl_2 \cdot 2H_2O$ (0.093 g, 0.4 mmol) in dioxane (10 mL) was refluxed under argon for 22 h. The reaction mass was poured over 6 M aqueous HCl, the resulting mixture was extracted with $CHCl_3$, and the extract was washed with water, dried, and evaporated. The residue obtained was then passed through silica gel (hexane) and recrystallized (same solvent) to give **6** (0.155 g; 92%) as needles, mp 109–11 °C: IR (KBr) 3045 (w), 1550 (m), 1530 (s), 1440 (m), 1415 (m), 1365 (m), 1330 (w), 1290 (s), 1270 (s), 1240 (s), 1180 (m), 1075 (s), 995 (m), 915 (m), 870 (m), 830 (s), 775 (m), 760 (s), 730 (m), 655 (s), 630 (m), 615 (m), 600 (m), 550 (m), 470 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} 252 (sh) nm, 274, 331, 339 (sh), 375 (sh) (ϵ 25 700, 51 900, 7100, 6750, 1650); ^{1}H NMR ($CDCl_3$) δ 5.08 (s, CH_2Cl). Anal. Calcd for $C_{11}H_2Cl_8$: C, 31.6; H, 0.5; Cl, 67.9. Found: C, 31.5; H, 0.3; Cl, 67.8.

(2) From Dihydronaphthalene 3. A solution of **3** (0.107 g, 0.2 mmol) and $SnCl_2 \cdot 2H_2O$ (0.051 g, 0.2 mmol) in dioxane (6 mL) was treated as described in the preceding reaction, yielding **6** (0.082 g, 90%), mp 109–11 °C, identified by its mp and IR spectrum.

(3) From a Mixture of 3 and 4. Naphthalene **1** was chlorinated by means of SR according to the general procedure described above. Starting materials: **1** (1.047 g), S_2Cl_2 (0.50 g), SO_2Cl_2 (30 mL); $AlCl_3$ (0.26 g), SO_2Cl_2 (70 mL). Addition time: 15 min. Reaction time: 1.75 h. The resulting crude material (3.40 g) was then subjected to column chromatography (silica gel, hexane) and successive recrystallizations (same solvent) until a mixture containing only **3** and **4** (1.335 g, 37%) (both identified by IR and ^{1}H NMR) was obtained, molar ratio **3**/**4**:[23] 0.25. Finally, this mixture was treated with $SnCl_2 \cdot 2H_2O$ (0.637 g) in dioxane (66 mL), as in the preceding dechlorinations of **4** and **3**, to give **6** (1.037 g, 34% yield from **1**), mp 108–10 °C, identified by its mp and IR spectrum.

Heptachloro-8-(chloromethyl)naphthalene (10). This compound was synthesized from dihydronaphthalene **11** in a fashion analogous to that described for the synthesis of **6** from **4**. Starting materials: **11** (2.940 g, 6.0 mmol), $SnCl_2 \cdot 2H_2O$ (1.492 g, 6.6 mmol), dioxane (120 mL). Reaction time: 6 h. Naphthalene **10** (2.304 g, 92%) was obtained as needles, mp 115–116 °C: IR (KBr) 1520 (m), 1455 (m), 1420 (s), 1365 (w), 1345 (w), 1330 (w), 1300 (s), 1280 (s), 1260 (s), 1185 (s), 1095 (s), 965 (m), 925 (m), 775 (m), 720 (s), 670 (m), 625 (m), 610 (m), 570 (s), 490 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 236 (sh) nm, 254 (sh), 273, 306 (sh), 320 (sh), 332, 343 (sh), 376 (sh) (ϵ 16 600, 28 300, 49 800, 4630, 6850, 7860, 6260, 525); ^{1}H NMR ($CDCl_3$) δ 5.30 (broad, CH_2Cl). Anal. Calcd for $C_{11}H_2Cl_8$: C, 31.6; H, 0.5; Cl, 67.9. Found: C, 31.6; H, 0.5; Cl, 68.0.

Heptachloro-7-methylnaphthalene (5). This compound was synthesized by two different methods. **Method A.** Under an argon atmosphere, (n-Bu)$_3$SnH (0.9 mL, 3.4 mmol) was added slowly (15 min) to a refluxing solution of naphthalene **6** (1.419 g, 3.4 mmol) in benzene (15 mL), and the reflux was continued for 3 h. The solvent was then evaporated, 2 M aqueous solution of KF (100 mL) and then ether (200 mL) were added to the residue, the resulting mixture was shaken for 30 min, and the insoluble part was filtered off. The ethereal solution was then washed with water, dried, and evaporated to leave a residue, which was purified by flash chromatography (silica gel, hexane:CCl_4 = 3:1) and recrystallization (hexane) giving **5** (0.933 g, 72%) as needles, mp 186–8 °C: IR (KBr) 1530 (s), 1410 (m), 1380 (w), 1360 (w), 1330 (w), 1290 (s), 1285 (s), 1260 (m), 1245 (s), 1170 (m), 1075 (s), 980 (s), 825 (m), 750 (m), 680 (m), 665 (s), 655 (s), 600 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 243 (sh) nm, 272, 306 (sh), 318 (sh), 330, 374 (sh) (ϵ 24 100, 44 900, 4330, 6370, 7540, 1040); ^{1}H NMR ($CDCl_3$) δ 2.75 (s, CH_3). Anal. Calcd for $C_{11}H_3Cl_7$: C, 34.5; H, 0.8; Cl, 64.7. Found: C, 34.5; H, 0.7; Cl, 65.0.

Method B. Under an argon atmosphere, to a stirred solution of **6** (0.663 g, 1.6 mmol) in toluene (10 mL) at 90–95 °C was added slowly (20 min) a solution of ($Me_3Si)_3SiH$ (0.5 mL, 1.6 mmol) and AIBN (0.008 g) in the same solvent (5 mL), and the resulting solution was stirred at this temperature for 4.5 h. Distillation of the solvent gave a residue which was purified by flash chromatography (silica gel, hexane) and recrystallization (same solvent) to yield **5** (0.431 g, 71%), mp 185–8 °C, identified by its mp and IR and ^{1}H NMR spectra.

Heptachloro-8-methylnaphthalene (9). This synthesis was performed as in that of **5** (Method A), but from naphthalene **10**. Starting materials: **10** (0.474 g, 1.1 mmol), benzene (5 mL), (n-Bu)$_3$SnH (0.3 mL, 1.1 mmol). Reaction time: 6 h. Compound **9** (0.347 g, 80%) was obtained as needles, mp 186–8 °C: IR (KBr) 2995 (w), 1530 (m), 1510 (m), 1455 (w), 1440 (m), 1410 (w), 1375 (w), 1355 (w), 1295 (s), 1265 (s), 1160 (m), 1090 (m), 1010 (m), 940 (m), 695 (s), 560 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} 240 (sh) nm, 271, 317 (sh), 327, 337 (sh) (ϵ 21 100, 47 600, 6310, 7190, 680); ^{1}H NMR ($CDCl_3$) δ 2.90 (s, CH_3). Anal. Calcd for $C_{11}H_3Cl_7$: C, 34.5; H, 0.8; Cl, 64.7. Found: C, 34.8; H, 0.8; Cl, 64.7.

Chlorination of Heptachloromethylnaphthalenes (5 and 9), Heptachloro(chloromethyl)naphthalenes (6 and 10), and Indene 2 with SR. (1) Chlorination of 5.[25] Starting materials: **5** (0.092 g), S_2Cl_2 (0.042 g), $AlCl_3$ (0.035 g), SO_2Cl_2 (11 mL). Reaction time: 1 h. The crude material obtained (0.110 g) was a mixture containing dihydronaphthalenes **3** and **4** (both identified

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[24] This chlorination was carried out in a short reaction time to preserve the side chain from chlorinolysis, since in a preliminary experiment it was found that normal treatment of hydrocarbon **12** with SR for 4 h gives considerable amounts of perchloro-1,4-dihydronaphthalene (**13**) (yield of the isolated **13**: 34%).

[25] In this reaction, the substrate was added to a refluxing solution of S_2Cl_2 and $AlCl_3$ in SO_2Cl_2 in solid form and at one time.

by TLC and ^{1}H NMR), molar ratio 3/4:[23] 0.50.

(2) Chlorination of 9.[25] Starting materials: 9 (0.105 g), S_2Cl_2 (0.048 g), $AlCl_3$ (0.045 g), SO_2Cl_2 (10 mL). Reaction time: 20 min. The resulting crude material was identified (by ^{1}H NMR and IR) as dihydronaphthalene 11 (0.129 g, 96%), probably containing some perchloro-1,4-dihydronaphthalene (13) (TLC).

(3) Chlorination of 6. Starting materials: 6 (0.199 g), S_2Cl_2 (0.100 g), SO_2Cl_2 (6 mL); $AlCl_3$ (0.056 g), SO_2Cl_2 (14 mL). Addition time: 8 min. Reaction time: 30 min. The resulting crude material consisted of a mixture containing mainly 3 and 4 (0.214 g) (both identified by IR and ^{1}H NMR), molar ratio 3/4:[23] 0.55.

(4) Chlorination of 10. Starting materials: 10 (0.542 g), S_2Cl_2 (0.250 g), SO_2Cl_2 (15 mL); $AlCl_3$ (0.125 g), SO_2Cl_2 (35 mL). Addition time: 9 min. Reaction time: 30 min. The resulting crude material was passed through silica gel (hexane) yielding dihydronaphthalene 11 (0.606 g, 96%), identified by TLC and its IR spectrum.

(5) Chlorination of 2. Starting materials: 2 (0.212 g), S_2Cl_2 (0.100 g), SO_2Cl_2 (10 mL); $AlCl_3$ (0.064 g), SO_2Cl_2 (14 mL). Addition time: 5 min. Reaction time: 10 h. The resulting crude material (0.224 g) was flash chromatographed (silica gel, hexane) to give: (a) 2 (0.058 g, 27% recovery), identified by TLC and its IR spectrum; (b) a mixture (0.110 g) of 2 and indan 7, both identified by TLC and IR; and (c) 7 (0.040 g, 16%), mp 186–8 °C, identified by its mp and IR spectrum.

(2-Heptachloronaphthyl)(pentachlorophenyl)methane (17). Powdered $AlCl_3$ (0.972 g) was added to a solution of naphthalene 6 (1.031 g, 2.5 mmol) and pentachlorobenzene (16) (0.695 g, 2.8 mmol) in CS_2 (30 mL), and the resulting mixture was refluxed and stirred for 21 h, while additional amounts of fresh $AlCl_3$ were added (0.948 g, 4 h; 1.092 g, 6 h).[26] Distillation of the solvent gave a residue which was digested with 6 M aqueous HCl, with ether, and dried to afford diarylmethane 17 (1.490 g, 95%), mp 239–41 °C: IR (KBr) 2980 (w), 1520 (m), 1420 (m), 1410 (m), 1365 (m), 1350 (s), 1320 (w), 1270 (m), 1240 (s), 1230 (s), 1065 (m), 915 (s), 720 (m), 680 (m), 670 (s), 660 (m), 640 (m), 590 (m), 500 (m), 460 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 213 nm, 250, 276, 332, 373 (sh) (ϵ 74 000, 37 300, 57 100, 7430, 1410); ^{1}H NMR ($CDCl_3$) δ 5.00 (s, CH_2). Anal. Calcd for $C_{17}H_2Cl_{12}$: C, 32.3; H, 0.3; Cl, 67.4. Found: C, 32.5; H, 0.4; Cl, 67.3.

(1-Heptachloronaphthyl)(pentachlorophenyl)methane (20). The reaction was carried out as in the synthesis of diarylmethane 17, but from naphthalene 10. Starting materials: 10 (0.487 g, 1.2 mmol), 16 (0.724 g, 2.9 mmol), CS_2 (15 mL), $AlCl_3$ (0.534 g; 0.501 g, 3 h; 0.540 g, 10 h; 0.491 g, 21 h; 0.477 g, 26 h).[26] Reaction time: 31 h. Distillation of the solvent gave a residue which was digested with 6 M aqueous HCl and with ether and dried. The resulting solid was passed through silica gel ($CHCl_3$), and the eluate was evaporated to give a residue (0.461 g) which consisted of diarylmethane 20 and some bis(pentachlorophenyl)methane (19), both identified by ^{1}H NMR (see below). Recrystallization of this mixture ($CHCl_3$) afforded pure 20 (0.327 g, 44%) as prisms, mp 270.0–2.5 °C [IR (KBr) 3000 (w), 1530 (m), 1505 (m), 1410 (s), 1365 (m), 1355 (s), 1340 (w), 1325 (w), 1280 (s), 1240 (s), 1200 (m), 1150 (m), 1080 (s), 960 (s), 915 (m), 780 (m), 750 (m), 725 (s), 700 (m), 670 (s), 570 (s), 510 (m), 465 (m) cm^{-1}; UV ($CHCl_3$) λ_{max} 274 nm, 309 (sh), 325 (sh), 332 (ϵ 48 800, 5510, 7940, 8830); ^{1}H NMR ($CDCl_3$) δ 5.05 (s, CH_2). Anal. Calcd for $C_{17}H_2Cl_{12}$: C, 32.3; H, 0.3; Cl, 67.4. Found: C, 32.3; H, 0.3; Cl, 67.0]. The ethereal solution was washed with water, dried, and evaporated to give a residue (0.715 g), identified (by IR and ^{1}H NMR) as a mixture of heptachloronaphthalene 18 (see below) and 16 with a preponderance of the latter.

Transalkylation between Diarylmethane 17 **and Pentachlorobenzene (16) in the Presence of $AlCl_3$.** A mixture of 17 (1.000 g), 16 (5.706 g), and powdered $AlCl_3$ (1.295 g) was heated at 100 °C for 46 h. The reaction mixture was treated with ice-water, and the solid precipitate was separated by filtration, washed with 6M aqueous HCl and with water and dried. Most of the 16 in the resulting solid was sublimated off (80 °C (20 mmHg)), and the residue was digested with ether to give another residue consisting of bis(pentachlorophenyl)methane (19) (0.711 g, 87%), mp 304–6 °C, identified by its mp (lit.[2a] mp 299–302 °C) and IR spectrum.[2a] ^{1}H NMR ($CDCl_3$) δ 4.80 (s, CH_2). Evaporation of the ethereal solution left a residue which was purified by column chromatography (silica gel, hexane) and successive recrystallizations (same solvent) to give essentially pure 1*H*-heptachloronaphthalene (18) (0.464 g, 79%) as needles, mp 182–5 °C. Compound 18 was identified by ^{1}H NMR,[19] elemental analysis (Anal. Calcd for $C_{10}HCl_7$: C, 32.5; H, 0.3; Cl, 67.2. Found: C, 32.9; H, 0.3; Cl, 67.0) and comparison of its mp and IR spectrum with those of an authentic sample prepared by decarbonylation of 26 (see below).

2-(Bromochloromethyl)heptachloronaphthalene (22). A solution of naphthalene 6 (0.816 g) and Br_2 (1 mL) in CCl_4 (60 mL) was refluxed and illuminated (with a 500-W incandencent lamp located 20 cm from the reaction flask) until the disappearance (TLC) of 6 (100 h). The resulting solution was washed with an aqueous solution of $Na_2S_2O_3$ and with water, dried, and evaporated. The residue was flash chromatographed (silica gel, hexane) to give 22 (0.775 g, 80%) as needles, mp 101–3 °C (from hexane): IR (KBr) 3050 (w), 1540 (m), 1520 (s), 1415 (m), 1360 (w), 1325 (w), 1280 (s), 1240 (s), 1185 (m), 1075 (s), 995 (s), 870 (m), 830 (s), 785 (m), 765 (s), 750 (m), 720 (s), 655 (s), 645 (m), 630 (m), 620 (m), 600 (m), 540 (m), 480 (s), 450 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 252 (sh) nm, 278, 331, 340 (sh), 367 (sh), 381 (sh) (ϵ 19 900, 46 500, 6090, 5680, 2260, 1900); ^{1}H NMR ($CDCl_3$) δ 7.91 (broad, CHBrCl). Anal. Calcd for $C_{11}HBrCl_8$: C, 26.6; H, 0.2. Found: C, 26.6; H, 0.2.

1-(Bromochloromethyl)heptachloronaphthalene (25). This compound was synthesized in the same way as its isomer 22, but from naphthalene 10. Starting materials: 10 (1.014 g), Br_2 (1.2 mL), CCl_4 (100 mL). Reaction time: 75 h. The crude product was purified by flash chromatography (silica gel, hexane) and recrystallization (hexane) to give 25 (0.927 g, 77%) as prisms, mp 165.0–6.5 °C: IR (KBr) 3080 (w), 1525 (m), 1500 (s), 1410 (s), 1350 (w), 1325 (w), 1290 (s), 1270 (m), 1240 (m), 1230 (s), 1170 (m), 1150 (s), 1080 (s), 1015 (m), 950 (m), 900 (m), 775 (m), 720 (s), 620 (m), 600 (m), 560 (s), 480 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 260 (sh) nm, 281, 315 (sh), 340 (ϵ 24 200, 38 900, 4880, 7160); ^{1}H NMR ($CDCl_3$) δ 7.85 and 7.90 (s, CHBrCl). Anal. Calcd for $C_{11}HBrCl_8$: C, 26.6; H, 0.2. Found: C, 26.5; H, 0.2.

Heptachloro-7-formylnaphthalene (24). A mixture of naphthalene 22 (0.261 g) and 30% oleum (5 mL) was stirred for 5 h. The resulting violet solution was poured over cracked ice, and the mixture was extracted with ether. The ethereal layer was washed with water, dried, and evaporated. The residue obtained was chromatographed (silica gel, hexane:$CHCl_3$ = 4:1) to afford 24 (0.191 g, 91%) as yellow needles, mp 171–2 °C (from hexane): IR (KBr) 3420 (w), 2870 (w), 1725 (s), 1540 (m), 1525 (s), 1420 (w), 1390 (w), 1360 (m), 1320 (w), 1285 (s), 1245 (s), 1180 (s), 995 (m), 870 (m), 835 (s), 660 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} 223 (sh) nm, 248 (sh), 275, 320 (sh), 331, 340 (sh), 375 (sh) (ϵ 9740, 18 500, 38 500, 4990, 5980, 5610, 1840); ^{1}H NMR ($CDCl_3$) δ 10.40 (s, CHO). Anal. Calcd for $C_{11}HCl_7O$: C, 33.2; H, 0.2; Cl, 62.5. Found: C, 33.3; H, 0.3; Cl, 62.5.

Heptachloro-8-formylnaphthalene (26). This compound was synthesized as in the preceding reaction, but from naphthalene 25. Starting materials: 25 (0.255 g), 30% oleum (5 mL). Reaction time: 6 h. Aldehyde 26 (0.166 g, 81%) was obtained as a white solid, mp 148–90 °C dec: IR (KBr) 1860 (w), 1700 (s), 1535 (w), 1510 (m), 1425 (s), 1390 (w), 1355 (w), 1325 (w), 1295 (s), 1280 (s), 1265 (s), 1165 (s), 1090 (s), 985 (m), 890 (m), 680 (m), 570 (m), 515 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 222 (sh) nm, 237 (sh), 253 (sh), 261, 313 (sh), 324, 332 (sh) (ϵ 13 300, 24 800, 44 100, 53 800, 5830, 7020, 6430); ^{1}H NMR ($CDCl_3$) δ 10.70 (s, CHO). Anal. Calcd for $C_{11}HCl_7O$: C, 33.2; H, 0.2; Cl, 62.5. Found: C, 33.3; H, 0.2; Cl, 62.6.

2*H*-Heptachloronaphthalene (23). Under an argon atmosphere, a solution of formylnaphthalene 24 (2.134 g, 5.37 mmol) and $Rh(PPh_3)_3Cl$ (4.948 g, 5.34 mmol) in benzonitrile (100 mL) was heated at 160–70 °C and maintained at this temperature for 2 h. The benzonitrile was then distilled off (90 °C (0.5 mmHg)), the residue was digested with refluxing hexane (400 mL), and the insoluble part was filtered off. The filtrate was evaporated, and the residue was passed through silica gel (hexane) and sublimated (80–90 °C (0.05 mmHg)) to afford heptachloronaphthalene 23 (1.880 g, 95%), mp 105.0–6.0 °C (needles mp 110.0–10.5 °C from

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[26] The times quoted following the weight data are the times elapsed before the additions were performed.

Table II. Fractional Atomic Coordinates (×10^4) and Equivalent Temperature Factors for 2

atom	x/a	y/b	z/c	B_{eq} (Å^2)
Cl1a	8976 (2)	2654 (1)	6229 (2)	5.30
Cl1b	7885 (3)	2004 (1)	3840 (2)	5.51
Cl2	6328 (3)	3798 (2)	4196 (3)	7.00
Cl4	2301 (2)	1648 (1)	6085 (2)	5.43
Cl5	3566 (3)	−25 (1)	7077 (2)	5.50
Cl6	6843 (3)	−595 (1)	7023 (2)	5.94
Cl7	8961 (2)	548 (1)	6035 (2)	5.32
Cl8	1838 (3)	2703 (2)	3444 (2)	5.84
Cl9a	1152 (3)	4201 (2)	4806 (3)	7.17
Cl9b	4215 (3)	4042 (2)	6533 (2)	6.39
C1	7321 (8)	2261 (5)	5109 (7)	3.87
C2	6039 (9)	2893 (5)	4791 (7)	4.48
C3	4762 (8)	2646 (5)	5036 (7)	4.25
C3a	5030 (8)	1835 (4)	5550 (6)	3.52
C4	4110 (8)	1342 (5)	6025 (6)	3.74
C5	4688 (8)	589 (4)	6489 (6)	3.63
C6	6164 (8)	349 (5)	6479 (6)	4.10
C7	7108 (7)	840 (5)	6032 (6)	3.78
C7a	6537 (7)	1590 (4)	5570 (6)	3.54
C8	3233 (10)	3080 (5)	4706 (7)	4.93
C9	2941 (11)	3679 (6)	5269 (8)	5.97

ethanol): IR (KBr) 3070 (w), 1560 (m), 1530 (m), 1520 (w), 1430 (w), 1370 (w), 1310 (w), 1280 (s), 1250 (s), 1180 (m), 1150 (m), 1040 (m), 920 (m), 870 (m), 700 (m), 630 (m), 480 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 241 (sh) nm, 264, 328 (ϵ 26 200, 40 200, 8380); ^{1}H NMR ($CDCl_3$) 7.78 (s, Ar-H). Anal. Calcd for $C_{10}HCl_7$: C, 32.5; H, 0.3; Cl, 67.2. Found: C, 32.8; H, 0.3; Cl, 67.1.

1*H*-Heptachloronaphthalene (18). The reaction was performed as for **23**, but from formylnaphthalene **26**. Starting materials: **26** (0.197 g, 0.5 mmol), $Rh(PPh_3)_3Cl$ (0.464 g, 0.5 mmol), benzonitrile (10 mL). Reaction time: 7 h. The benzonitrile was distilled off (80 °C (1 mmHg)), the residue was digested with refluxing hexane (150 mL), and the insoluble part was filtered off. The filtrate was evaporated, and the residue was flash chromatographed (silica gel, hexane) to give the following: (a) heptachloronaphthalene **18** (0.085 g, 47%) as needles, mp 183.5–4.5 °C (from hexane) [IR (KBr) 3080 (w), 1745 (w), 1580 (w), 1540 (m), 1505 (w), 1480 (w), 1430 (s), 1350 (m), 1335 (w), 1330 (m), 1290 (s), 1275 (s), 1245 (s), 1165 (s), 970 (m), 960 (m), 870 (s), 820 (m), 740 (m), 555 (m) cm^{-1}; UV (C_6H_{12}) λ_{max} 232 (sh) nm, 249 (sh), 256, 294 (sh), 304, 316, 328 (sh) (ϵ 21 500, 51 300, 62 100, 4170, 6280, 7560, 5770); ^{1}H NMR ($CDCl_3$) 8.73 (s, Ar-H). Anal. Calcd for $C_{10}HCl_7$: C, 32.5; H, 0.3; Cl, 67.2 Found: C, 32.5; H, 0.2; Cl, 67.0] and (b) impure **18** (0.015 g), identified by its IR spectrum. Elution of the column with hexane:$CHCl_3$ = 70.30 gave slightly impurified starting material **26** (0.064 g), identified by IR and ^{1}H NMR spectra.

X-ray Analysis. Indene 2. Prismatic colorless crystal, monoclinic, space group $P2_1/n$, $a = 8.913$ (10) Å, $b = 16.536$ (11) Å, $c = 11.753$ (14) Å, $\beta = 106.76$ (5)°, $V = 1659$ (3) Å^3, $Z = 4$, $D_{calcd} = 1.949$ g/cm^3, μ(Mo Kα) = 16.81 cm^{-1}, $R = 7.3\%$ (over 1898 reflections with $F > 5\sigma(F)$).

Dihydronaphthalene 11. Prismatic colorless crystal, triclinic, space group P-1, $a = 9.173$ (3) Å, $b = 13.620$ (3) Å, $c = 14.608$ (4) Å, $\beta = 98.43$ (1)°, $V = 1623.16$ Å^3, $Z = 4$, $D_{calcd} = 2.098$ g/cm^3, μ(Mo Kα) = 17.2 cm^{-1}, $R = 4.2\%$ (over 3681 reflections with $F > 3\sigma(F)$).

The structures were solved using MULTAN 11/84,[27] the refinements were carried out with anisotropic full-matrix least-squares methods,[28] and scattering factors were taken from ref 29.

Table III. Fractional Atomic Coordinates (×10^4, Hydrogen Atoms ×10^3) and Equivalent Temperature Factors for 11A and 11B[a,b]

atom	x/a	y/b	z/c	B_{eq} (Å^2)
Cla	2449 (1)	3800.7 (8)	5736.2 (8)	4.40 (3)
Clb	1163 (1)	1682.2 (9)	3972.6 (8)	4.51 (3)
Cl2	0008 (2)	3743.4 (8)	3946.4 (7)	4.51 (3)
Cl3	−3115 (1)	3515.8 (8)	4485.3 (8)	4.79 (3)
Cl4	−3784 (1)	1306.8 (8)	4842.3 (8)	3.66 (2)
Cl5	−2950 (1)	1191.8 (9)	6977.8 (8)	4.34 (3)
Cl6	−0327 (2)	0651.9 (8)	8039.9 (7)	4.46 (3)
Cl7	2736 (1)	0810.4 (8)	7427.1 (9)	4.91 (3)
Cl8	3291 (1)	1694.5 (9)	5855.6 (9)	4.75 (3)
Cl9	−1264 (1)	4420.3 (8)	7259.8 (9)	4.47 (3)
C1	0824 (4)	2668 (3)	5096 (3)	2.56 (8)
C2	−0421 (5)	3105 (3)	4726 (3)	2.80 (9)
C3	−1735 (4)	3007 (3)	4961 (3)	2.87 (9)
C4	−2182 (4)	2456 (3)	5641 (3)	2.54 (8)
C4a	−0945 (4)	2017 (3)	6049 (2)	2.17 (8)
C5	−1203 (4)	1491 (3)	6705 (3)	2.68 (8)
C6	−0042 (5)	1165 (3)	7155 (3)	2.84 (9)
C7	1338 (5)	1260 (3)	6892 (3)	2.93 (9)
C8	1586 (4)	1692 (3)	6198 (3)	2.83 (9)
C8a	0462 (4)	2113 (3)	5797 (2)	2.32 (8)
C9	−2763 (4)	3261 (3)	6492 (3)	3.3 (1)
H1	−354 (4)	353 (3)	623 (3)	5 (1)*
H2	−306 (4)	294 (3)	691 (3)	4 (1)*
Cla′	7723 (1)	3478.6 (8)	1479.5 (7)	3.46 (2)
Clb′	6632 (1)	1347.3 (8)	0307.5 (8)	4.23 (3)
Cl2′	7064 (1)	1272.1 (8)	1834.3 (9)	4.89 (3)
Cl3′	4013 (1)	1144.3 (8)	2466.1 (7)	4.21 (3)
Cl4′	1486 (1)	1059.8 (8)	0700.0 (8)	4.09 (3)
Cl5′	0607 (1)	3058.4 (9)	0383.5 (9)	4.37 (3)
Cl6′	1236 (1)	3903.3 (8)	−1188.5 (9)	5.17 (3)
Cl7′	4384 (2)	4176.1 (8)	−1679.8 (7)	5.16 (3)
Cl8′	6889 (1)	3450.0 (9)	−0710.8 (7)	4.21 (3)
Cl9′	4369 (1)	4158.6 (8)	2933.2 (8)	4.05 (3)
C1′	6115 (4)	2347 (3)	0721 (3)	2.59 (8)
C2′	5692 (4)	1800 (3)	1391 (3)	2.83 (8)
C3′	4393 (4)	1752 (3)	1657 (3)	2.59 (8)
C4′	3148 (4)	2219 (3)	1317 (3)	2.41 (8)
C4a′	3481 (4)	2694 (3)	0550 (2)	2.27 (8)
C5′	2369 (4)	3086 (3)	0107 (3)	2.82 (9)
C6′	2643 (5)	3512 (3)	−0594 (3)	3.28 (9)
C7′	4039 (5)	3614 (3)	−0835 (3)	3.12 (9)
C8′	5168 (4)	3256 (3)	−0396 (3)	2.76 (9)
C8a′	4881 (4)	2775 (3)	0286 (2)	2.09 (8)
C9′	2777 (5)	3038 (3)	2254 (3)	3.3 (1)
H1′	192 (5)	337 (3)	208 (3)	6 (1)*
H2′	267 (4)	272 (3)	271 (3)	4.0 (9)*

[a] See ref 22. [b] Starred atoms were refined isotropically.

Fractional atomic coordinates are given in Tables II and III.

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Supplementary Material Available: Bond lengths, bond angles, torsion angles and anisotropic thermal parameters for **2** and **11** (Tables IV–IX) and molecular packing diagrams (Figures 3 and 4) (10 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.

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