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SO_2-Extrusion of an 8-Thiabicylo[3.2.1]octa-2,6-diene 8,8-dioxide and Rearrangement of the Resulting Cycloheptatriene

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ABSTRACT: *The reaction of 3,4-di-tert-butylthiophene 1-oxide (***8***) with tetrachlorocyclopropene provided 6,7-di-tert-butyl-2,3,4,4-tetrachloro-8-thiabicylo[3.2.1]octa-2,6-diene 8-oxide (***10***), which was oxidized to the corresponding 8,8-dioxide* **16** *by m-chloroperbenzoic acid. The thermolysis of* **16** *in refluxing chlorobenzene, xylene, or octane gave 5-tert-butyl-1,2-dichloro-3-[(1,1-dichloro-2,2-dimethyl)propyl]benzene (***18***) with extrusion of SO_2 and 2-tert-butyl-4,5,6-trichloro-9,9-dimethylbicyclo[5.2.0]nona-1,3,5-triene (***19***) with extrusion of SO_2 and HCl in 73–78% combined yields. On the other hand, the thermolysis of* **16** *in the presence of triethylamine gave* **19** *as the sole product in 98% yield. A mechanism that involves the initial formation of 4,5-di-tert-butyl-1,2,7,7-tetrachlorocycloheptatriene (***17***) is proposed to explain the observed products.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:132–137, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20079

INTRODUCTION

Reportedly, thiophene 1,1-dioxides (**1**) undergo Diels–Alder reactions with a series of cyclopropenes (**2**) to give the corresponding adducts (**3**), which extrude SO_2 spontaneously to furnish cycloheptatrienes (**4**) as the final product [1] (Scheme 1). We then examined the reaction of 3,4-di-*tert*-butylthiophene 1,1-dioxide (**5**) [2] with tetrachlorocyclopropene (**6**) with the expectation of obtaining a cycloheptatriene **7**, which would serve as the precursor that leads to a range of seven-membered nonbenzenoids possessing two *tert*-butyl groups at vicinal positions. Disappointingly, however, **5** failed to react with **6** probably due to the steric hindrance of **5**; under forcing conditions (190°C in a sealed tube), considerable decomposition of **6** took place. Recent studies uncovered that thiophene 1-oxides are a more reactive diene than thiophene 1,1-dioxides [3]. We therefore examined the Diels–Alder reaction of 3,4-di-*tert*-butylthiophene 1-oxide (**8**) [4] with **6**. This study led us to some new findings described below.

RESULTS AND DISCUSSION

Heating equimolar amounts of the 1-oxide **8** and the cyclopropene **6** in boiling toluene for 20 h provided the adduct **10** as the major product in 44% yield (Scheme 2). Thiophenes **13** (27%) and **14** (27%) were obtained as by-products. The use of two molar amounts of **6** did not improve the yield of **10**; **10** was obtained in a slightly decreased yield (36%) together with **13** (22%), **14** (36%), and (*Z*)-2,3-dichloropropenoic acid (**15**). The ^{1}H NMR spectrum

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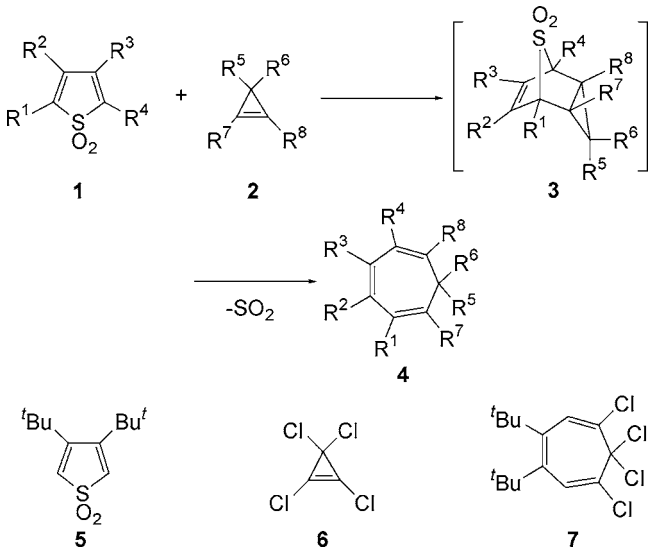
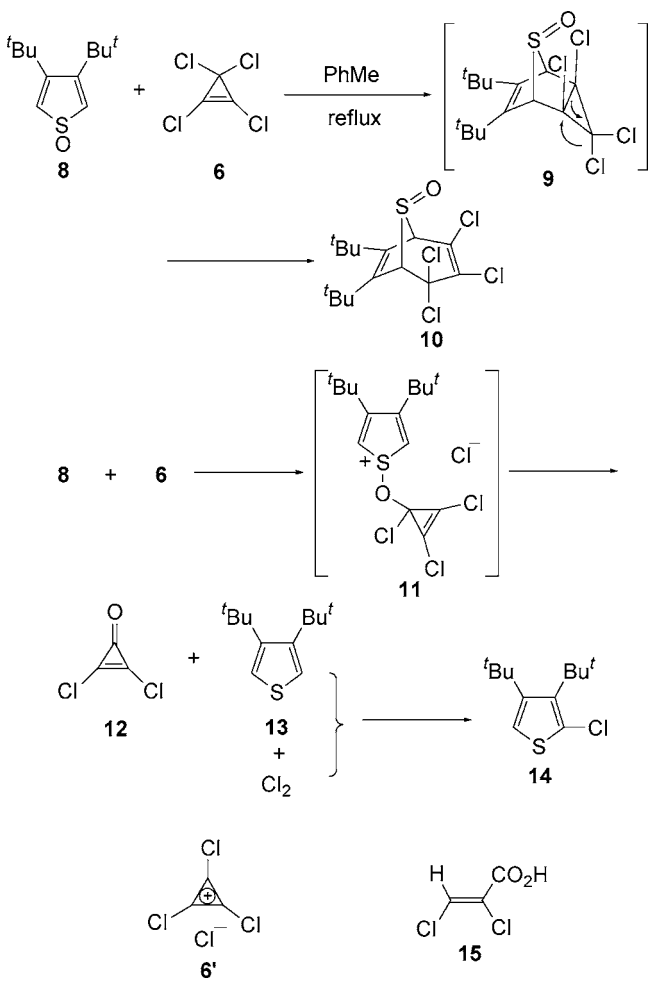


SCHEME 1

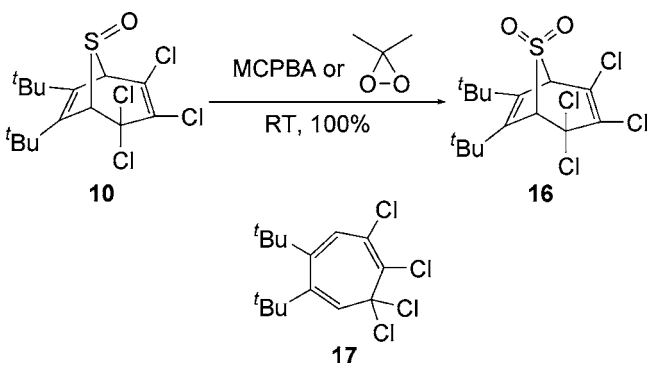


SCHEME 2

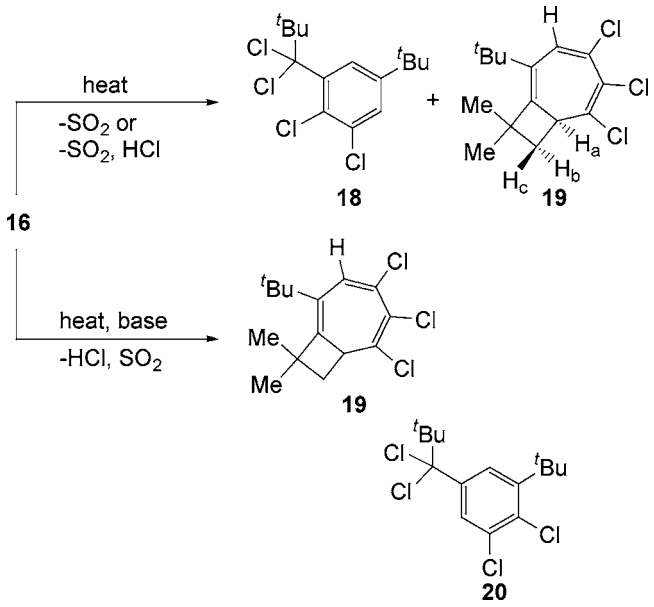
of **10** showed two singlets of the *tert*-butyl groups and two doublets of the bridgehead methine protons. The ^{13}C NMR spectrum showed 11 peaks including the 4 sp^2 carbon peaks. **10** would be formed by ring opening of the expected Diels–Alder adduct **9** [5] with a simultaneous chlorine migration. A similar rearrangement was observed for the adduct of 2,5-dimethoxyfuran with **6** [6]. The configuration of the S=O group in **10** was tentatively assigned on the basis of our recent results that Diels–Alder reactions of **8** with a variety of dienophiles take place exclusively at the *syn*-π-face with respect to the S=O group in an *endo*-mode [5]. The formation of **13** and **14** as by-products would be explained as follows. The reaction of **8** with **6** would produce a sulfonium ion **11**, which decomposes to cyclopropenone **12**, thiophene **13**, and molecular chlorine. Finally, chlorination of **13** would produce **14**. The cyclopropene **6** might dissociate slightly into the aromatic cyclopropenium ion **6′** under the conditions. Thus, the reaction of **8** with **6′**, and not the direct reaction of **8** with **6**, might be involved in the formation of **11**. Unfortunately, **12** could not be isolated probably because of the volatility. Hydrolysis of the unreacted **6**, and not of **12**, would produce the carboxylic acid **15**.

We then examined the oxidation of **10** with the intention of obtaining the sulfone **16** as the precursor of the cycloheptatriene **17** (Scheme 3). The oxidation of **10** with *m*-chloroperbenzoic acid (MCPBA) or dimethyldioxirane at room temperature furnished **16** quantitatively.

Thermolysis of **16** gave rather unexpected results. Thus heating **16** in boiling chlorobenzene gave aromatized compound **18** and bicyclic compound **19** in 23% and 55% yields, respectively (Scheme 4). Thermolysis of **16** in xylene or octane also gave **18** and **19** in good combined yields, whereas thermolysis in benzonitrile gave a complex mixture containing **18** and **19** (Table 1). The expected simple SO_2-extrusion product **17** was not obtained in any case.



SCHEME 3



SCHEME 4

The formation of **19** requires elimination of HCl in addition to SO_2. We therefore examined thermolysis of **16** in the presence of a base to promote elimination of HCl. Indeed, the thermolysis in the presence of triethylamine or *N*-ethyldiisopropylamine in refluxing chlorobenzene furnished **19** as the sole product in 98% or 85% yield, respectively.

The structure of **18** could not be determined unambiguously by ^{1}H and ^{13}C NMR analyses including NOE experiments; particularly the isomeric structure **20** was not ruled out. Therefore, the structure was determined by X-ray crystallographic analysis (Fig. 1). The structure of **19** was determined by NMR analyses; single crystals suitable for X-ray crystallographic analysis could not be obtained despite many efforts. The ^{1}H NMR spectrum (C_6D_6 as the solvent)

TABLE 1 Results of the Thermolysis of **16** in Varying Conditions[a]

			Yields (%)[b]	
Solvent	*Base*	*Reaction Time (h)*	**18**	**19**
PhCl		6	23	55
Xylene		8	22	55
Octane		16	49	24
PhCN[c]		6	+[d]	+[d]
PhCl	Et_3N	6	0	98
PhCl	*iso*-Pr_2NEt	6	0	85

[a]All the reactions were carried out at reflux unless otherwise stated.
[b]Yields based on the isolated products.
[c]At 130°C.
[d]Complex mixture containing **18** and **19**.

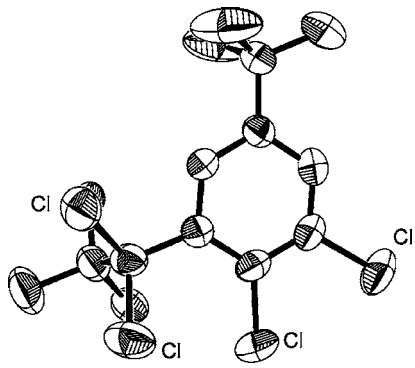
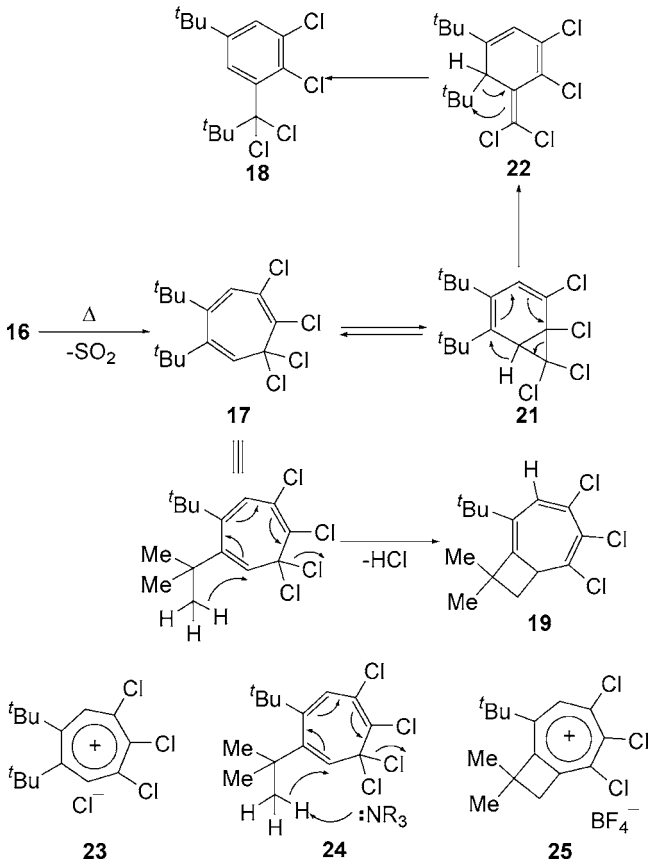


FIGURE 1 Molecular structure of **18**.

of **19** showed one singlet of the *tert*-butyl group and two singlets of the two methyl groups, indicating that one of the two *tert*-butyl groups of **16** incorporated in the construction of the four-membered ring. The vinyl proton appeared at δ 6.90 as singlet. Both methylene and methine protons appeared as multiplets; decoupling experiments revealed the chemical shifts of δ $H_a = 3.12$, H_b (or H_c) $= 1.65$, and H_c (or H_b) $= 1.69$, and the coupling constants of $J_{Ha-Hb} = 8.8$, $J_{Ha-Hc} = 3.8$, and $J_{Hb-Hc} = 14.3$ Hz. In addition, 15.7% NOE was observed between the *tert*-butyl and vinyl protons, and 16.6% and 17.5% NOEs were observed between the *tert*-butyl protons and the two methyl protons of the four-membered ring. The ^{13}C NMR spectrum showed 13 peaks, 6 of which appeared in the sp^2 carbon region. The methylene and methine peaks appeared at δ 42.4 and 54.2, respectively. The IR spectrum showed the C=C stretching vibrations at 1545 and 1576 cm^{-1}, and the UV-Vis spectrum showed an absorption maximum at 281 nm indicating the presence of the cycloheptatriene unit [7].

The formation of **18** and **19** is explained as follows (Scheme 5). It is well documented that SO_2-extrusion of 2,5-dihydrothiophene 1,1-dioxides takes place to give 1,3-butadienes in a thermally allowed disrotatory manner [8]. Thus the thermolysis of **16**, which possesses a dihydrothiophene dioxide ring, would produce the cycloheptatriene **17** initially. It is also known that an equilibrium exists between cycloheptatriene and norcaradiene structures and, in addition, the equilibrium lies to the norcaradiene side when electron-withdrawing substituents are attached at the 7-position [9]. Thus **17** tautomerizes to a norcaradiene **21**, which then rearranges to an exomethylene compound **22**. Finally **22** aromatizes to give **18** with a migration of the *tert*-butyl group. On the other hand, elimination of HCl from **17**, with simultaneous four-membered ring formation, would provide **19**. The elimination of HCl from



SCHEME 5

the cycloheptatrienyl (tropylium) cation **23** (ionized aromatic isomer of **17**) would be least probable because **19** is formed even for the thermolysis in octane, a typical nonpolar solvent, where the formation of **23** is least possible. Decreased yield of **19** (increased yield of **18**) in octane indicates that the four-membered ring formation takes place through a polarized transition state. The sole formation of **19** in the presence of the base suggests that the base promotes the elimination of HCl from **17** (see **24** in Scheme 5). Incidentally, attempted conversion of **19** to the cycloheptatrienyl salt **25** by treatment with trityl tetrafluoroborate was unsuccessful because of electronic and/or steric effects.

EXPERIMENTAL

*Reaction of 3,4-Di-tert-butylthiophene 1-oxide (**8**) with Tetrachlorocyclopropene(**6**); 6,7-Di-tert-butyl-2,3,4,4-tetrachloro-8-thiabicylo[3.2.1]octa-2,6-diene 8-oxide (**10**)*

A mixture of 212 mg (1 mmol) of **8** and 174 mg (1 mmol) of **6** [10] in 5 mL of toluene was heated at reflux for 20 h. The mixture was evaporated under reduced pressure. The residue was chromatographed on a column of silica gel. Elution of the column with hexane gave 116 mg of a 1:1 mixture of **13** and **14** (each 27% yield). ^{1}H and ^{13}C NMR spectra of **13** and **14** agreed with those of authentic samples [2a]. Further elution of the column with CH_2Cl_2 gave 172 mg (44%) of **10**: mp 146–147°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 9H), 1.40 (s, 9H), 4.34 (d, J = 2.2 Hz, 1H), 4.81 (d, J = 2.2 Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl3) δ 31.8, 33.0, 34.2, 36.2, 68.0, 72.0, 83.3, 129.1, 132.4, 142.5, 150.6; IR (KBr) 2977, 1613, 1484, 1469, 1397, 1367, 1187, 1108 (S=O), 1072, 1045, 1015, 965, 807, 725, 654, 640, 546 cm^{-1}; MS (EI, 70 eV) m/z 388 (M^+), 305, 263. Anal. Calcd for $C_{15}H_{20}Cl_4OS$: C, 46.17; H, 5.16. Found: C, 46.33; H, 5.04.

Heating a mixture of 100 mg (0.47 mmol) of **8** and 167 mg (0.94 mmol) of **6** in 5 mL of toluene for 20 h gave 59 mg of a mixture of **13** (22%) and **14** (36%), 65 mg (36%) of **10**, and 42 mg of (*Z*)-2,3-dichloropropenoic acid (**15**) [11].

*6,7-Di-tert-butyl-2,3,4,4-tetrachloro-8-thiabicylo[3.2.1]octa-2,6-diene 8,8-dioxide (**16**)*

Oxidation with MCPBA. A mixture of 100 mg (0.26 mmol) of **10** and 46 mg (0.27 mmol) of MCPBA in 5 mL of CH_2Cl_2 was stirred for 5.5 h at room temperature. The mixture was washed with aqueous $NaHSO_3$, aqueous $NaHCO_3$, and water successively, dried over $MgSO_4$, and evaporated to give 104 mg (100%) of practically pure **16**: mp 170–171°C (dec) (from hexane/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9H), 1.47 (s, 9H), 4.41 (d, J = 3.3 Hz, 1H), 4.99 (d, J = 3.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.3, 32.7, 35.0, 36.9, 71.7, 77.7, 85.3, 130.5, 131.6, 144.8, 152.5; IR (KBr) 3027, 1597, 1481, 1367, 1334 (SO_2), 1203, 1180, 1129 (SO_2), 1063, 1009, 954, 862, 814, 759, 639, 578, 458 cm^{-1}; MS (EI, 70 eV) m/z 404 (M^+), 305. Anal. Calcd for $C_{15}H_{20}Cl_4O_2S$: C, 46.17; H, 5.16. Found: C, 46.11; H, 4.97.

Oxidation with Dimethyldioxirane. Oxidation of 50 mg (0.13 mmol) of **10** dissolved in 1 mL of ether was carried out by adding a 0.54 mM solution of dimethyldioxirane in acetone at 0°C. The oxidation was sluggish and the oxidant was added several times at 10 h-intervals until **10** is completely consumed. A total of ca. 1 mmol of the oxidant was used for completion of the oxidation to provide 52 mg (100%) of practically pure **16**.

Thermolysis of **16**

Thermolysis in Refluxing Chlorobenzene. A solution of 50 mg (0.12 mmol) of **16** in 5 mL of chlorobenzene was heated at reflux for 6 h. The reaction

mixture was evaporated under reduced pressure, and the residue was chromatographed on a column of silica gel. Elution of the column with hexane gave 21 mg (55%) of **19** and 9.5 mg (23%) of **18** in this order.

5-*tert*-Butyl-1,2-dichloro-3-[(1,1-dichloro-2,2-dimethyl)propyl]benzene (**18**): mp 89–90°C (from MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 9H), 1.31 (s, 9H), 7.51 (d, $J = 2.3$ Hz, 1H), 8.02 (d, $J = 2.3$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.0, 30.9, 34.8, 47.8, 103.3, 128.5, 130.3, 135.4, 137.5, 148.4; IR (KBr) 2964, 1479, 1465, 1396, 1385, 1364, 1279, 1205, 1170, 1050, 877, 804, 692 cm^{-1}; MS (EI, 70 eV) m/z 340 (M^+), 283. Anal. Calcd for $C_{15}H_{20}Cl_4$: C, 52.66; H, 5.89. Found: C, 52.70; H, 5.90.

2-*tert*-Butyl-4,5,6-trichloro-9,9-dimethylbicyclo-[5.2.0]nona-1,3,5-triene (**19**): colorless oil; solidified when kept in a refrigerator for a long time of period; mp 106–107°C (from MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 9H), 1.13 (s, 3H), 1.41 (s, 3H), 2.01–2.10 (m, 2H), 3.31 (dd, $J = 7.8$, 4.7 Hz, 1H), 7.09 (s, 1H); ^{1}H NMR (400 MHz, C_6D_6) δ 0.78 (s, 3H), 0.84 (s, 9H), 1.07 (s, 3H), 1.63–1.73 (m, 2H), 3.13 (dd, $J = 8.8$, 3.8 Hz, 1H), 6.91 (s, 1H); ^{1}H NMR (400 MHz, CD_3CN) δ 0.95 (s, 9H), 1.12 (s, 3H), 1.42 (s, 3H), 2.04–2.12 (m, 2H), 3.33 (dd, $J = 7.0$, 5.6 Hz, 1H), 7.29 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.5, 29.7, 35.4, 36.9, 42.4, 43.5, 54.2, 122.6, 129.2, 131.4, 132.4, 142.7, 154.6; ^{13}C NMR (100.6 MHz, C_6D_6) δ 28.3, 29.8, 35.0, 36.8, 42.5, 43.4, 54.4, 122.9, 130.0, 132.0, 133.2, 143.0, 154.9; IR (neat) 2958, 2871, 1735, 1576, 1545, 1479, 1466, 1418, 1396, 1385, 1363, 1310, 1286, 1234, 1218, 1167, 1111, 868, 821, 765, 759, 701 cm^{-1}. Anal. Calcd for $C_{15}H_{19}Cl_3$: C, 58.94; H, 6.27. Found: C, 59.11; H, 6.28.

Thermolysis in Other Solvents. The thermolysis of 50 mg of **16** in refluxing xylene (5 mL) gave 9 mg (22%) of **18** and 21 mg (55%) of **19**, that in octane (2 mL) gave 21 mg (49%) of **18** and 9 mg (24%) of **19**, and that in benzonitrile at 130°C gave a complex mixture containing **18** and **19**.

Thermolysis of **16** *in the Presence of a Base*. A solution of 100 mg (0.25 mmol) of **16** and 51 mg (0.50 mmol) of triethylamine in 5 mL of chlorobenzene was heated at reflux for 6 h. The mixture was evaporated, the residue was chromatographed on a column of silica gel, and the column was eluted with hexane to give 74 mg (98%) of **19**. Similarly heating a solution of 100 mg (0.25 mmol) of **16** and 159 mg (1.2 mmol) of *N*-ethyldiisopropylamine in 5 mL of chlorobenzene gave 64 mg (85%) of **19**.

X-Ray Crystal Structure Determination of **18**

The crystal data for **18** were recorded on a Bruker SMART APEX CCD area detector by using 0.30°-wide ω scans and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Frame data (20 s, 0.30°-wide ω scans) were collected using the Bruker SMART software package [12]. Peak integration was performed by the Bruker SAINT-Plus software package [13]. Absorption correction was made by the software SADABS [14]. Space group determination was done by the software XPREP [15]. All calculations were performed by the Bruker SHELXTL 5.1 software package [16]. The structure was solved by direct methods and refined with full-matrix least squares by all independent reflections. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions.

X-Ray Crystallographic Data of **18**. $C_{15}H_{20}Cl_4$, $M_w = 342.13$, Monoclinic, $P2_1/c$, $a = 9.5912(6)$ Å, $b = 17.5121(10)$ Å, $c = 10.5039(6)$ Å, $\beta = 107.8340(10)°$, $V = 1679.48(17)$ Å^3, $Z = 4$, $D_c = 1.353$ g/cm^3, number of measured reflections 8453, number of independent reflections 3116, number of reflections with $I > 2\sigma(I)$ 1904, parameters 178, $R_1 = 0.0519(I > 2\sigma(I))$, $wR_2 = 0.1478$ (all), $S = 0.998$, $T = 298$ K.

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