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Unusual Chlorination of 2,4,4,6-Tetraaryl-4*H*-thiopyrans to give Carbocyclized Products

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The reactions of 2,4,4,6-tetraaryl-4*H*-thiopyrans **1** or **3** with chlorine at room temperature proceed rapidly to give the corresponding 3,5-dichloro derivatives **2** or **4** and then slowly to give 6,7-benzo-1,3,5-triaryl-4,8,8-trichloro-2-thiabicyclo [3.2.1]octa-3,6-dienes **5** or **6**; the structure of **6** has been determined by X-ray analysis.

Electrophilic 3,5-substitutions of 2,4,4,6-tetraaryl-4*H*-thiopyrans have recently been found to proceed very easily,[1] in accordance with the π-donor properties of the heterocycles.[2,3] We have found that the chlorodeprotonation can be accompanied by a slower unexpected and, at least for the sulfur heterocycles, as yet unobserved[2,4] intramolecular carbocyclization. Thus, 2,4,4,6-tetraphenyl-4*H*-thiopyran **1**, prepared[2,5] from 1,3,3,5-tetraphenylpentane-1,5-dione with P_4S_{10}, reacts with 2.4 mol chlorine in carbon disulfide at 0 °C for 1 min† to give the corresponding 3,5-dichloro derivative **2** $C_{29}H_{20}Cl_2S$ (m.p. 197 °C, 68% yield) which can be easily isolated and identified.[1] Analogous product **4** $C_{29}H_{18}Cl_2F_2S$ (m.p. 214–215 °C, 65% yield) is formed from 4*H*-thiopyran **3**. However, if **1**, **2**, **3** or **4** were allowed to react with 10 mol of the reagent to complete disappearance of the 3,5-dichloro intermediates **2** and **4** (5–10 h), new stable trichloro derivatives $C_{29}H_{19}Cl_3S$ [m.p. 240–241 °C, 89% yield, *m*/*z* 504 (M^+, 65%)] or $C_{29}H_{17}Cl_3F_2S$ [m.p. 258–260 °C, 71% yield, *m*/*z* 540 (M^+, 42%)] were exclusively obtained.

The ^1H NMR spectrum‡ of the trichlorodifluoro derivative exhibits signals of two AA′BB′X systems (4-FC_6H_4), one ABCD system (vicinal arrangement) and five additional aromatic signals. The ^{13}C NMR spectrum§ displays three peaks for quaternary sp^3 carbons, together with signals for two 4-FC_6H_4 moieties, nine aromatic methines and five quaternary sp^2 carbons.

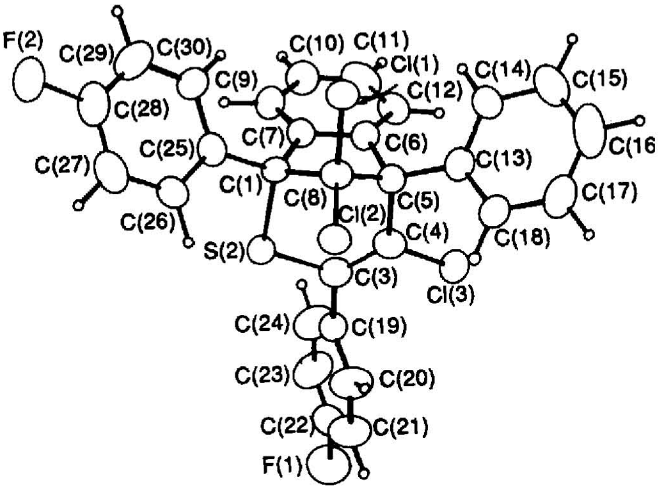

Fig. 1 Molecular structure of **6**. The thermal ellipsoids denote 50% probability

We concluded that neither of the molecular structures of the trichloro derivatives could be assigned with certainty from their NMR spectoscopic data and therefore the difluoro derivative was determined as 6,7-benzo-1,3-bis(4-fluorophenyl)-5-phenyl-4,8,8-trichloro-2-thiabicyclo[3.2.1]octa-3,6-diene **6** by X-ray structure analysis (Fig. 1).¶ Hence, considering similarities

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† All reactions were monitored by HPLC: Separon™ SGX C18 column (3 × 150 mm, 0.4 cm^3 min^{-1}), size of particles 5 μm (Tessek, Czechoslovakia) in the system MeOH–H_2O [9:1 (v/v)].

‡ *Spectroscopic data* for **6**: ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$, 298 K) δ_H 6.964 (2H, dd, 8.7, 8.6), 7.104 (2H, dd, 8.8, 8.5), 7.152 (2H, dd, 8.8, 8.5), 7.373–7.534 (6H, m), 7.613 (1H, ddd, 7.5, 7.3, 1.9), 7.641 (1H, dd, 7.8, 1.9), 7.849 (1H, 7.8, 1.9), 7.849 (1H, ddd, 7.8, 1.9, 1.1); 7.970 (2H, dd, 9.0, 5.1).

§ *Spectroscopic data for* **6**: ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$, 298 K, multiplicity caused by ^1H NMR only) δ_C 69.73s, 70.22s, 99.40s, 115.19d (2C, J_{CF} 21.5 Hz), 115.45d (2C, J_{CF} 21.8 Hz), 120.73s, 121.84d, 125.19d, 126.90d, 127.36d, 128.43d, 128.68d, 128.86s (J_{CF} 3.3 Hz), 129.02d, 130.46d, 131.21d (2C, J_{CF} 8.4 Hz), 131.96s, 131.96d (2C, J_{CF} 8.3 Hz), 132.26s (J_{CF} 3.4 Hz), 132.69s, 134.29s, 136.56s, 140.15s, 162.74s (J_{CF} 249.0 Hz), 163.37s (J_{CF} 250.1 Hz).

¶ *Crystal data* for **6**: $C_{29}H_{17}Cl_3F_2S$, triclinic, space group $P\bar{1}$, $a = 10.560(2)$ Å, $b = 11.023(2)$ Å, $c = 11.665(2)$ Å, $\alpha = 100.07(2)°$, $\beta = 98.33(2)°$, $\gamma = 110.97(2)°$, $V = 1216.2(5)$ Å^3, $D_c = 1.48$ g cm^{-3}, $F(000) = 552$, $Z = 2$, λ(Mo-Kα) = 0.71073 Å, $\mu = 4.9$ cm^{-1}. $R = 4.53\%$ ($R_w = 4.54\%$) for 3245 observed reflections ($F_0 \geqslant 3\sigma(F_0)$). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1992, Issue No. 1.

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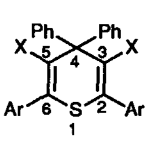
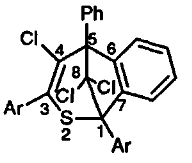
between the NMR spectra the final chlorination product of **1** may be regarded as 6,7-benzo-1,3,5-triphenyl-4,8,8-trichloro-2-thiabicyclo[3.2.1]octa-3,6-diene **5**.

These observations enable us to formulate the chlorodeprotonation processes in terms of sequences **1**→**2**→**5** and **3**→**4**→**6**, respectively.



1; Ar = Ph, X = H
2; Ar = Ph, X = Cl
3; Ar = 4-FC_6H_4, X = H
4; Ar = 4-FC_6H_4, X = Cl



5; Ar = Ph
6; Ar = 4-FC_6H_4

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