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Thermolysis and Photolysis of Hexachloro-tris-σ-homotropone and Related Compounds

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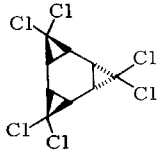
Thermolyse und Photolyse von Hexachlor-tris-σ-homotropon und verwandten Verbindungen

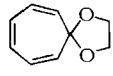
Troponethylenacetal (**2**) reagiert mit überschüssigem CCl_2 zu den Mono-, Bis- und Tris-Addukten **3**, **4a**, **b** und **5**. Thermolyse von **5** führt nicht zum Hexachlor-tris-σ-homobenzol (**1**), ebensowenig wie die Photolyse des Ketons **6a**, bei der unter Öffnung einer Cyclopropan-Brückenbindung das sterisch mehr gehinderte Isomere **6b** erhalten wird. Die Photolyse von **8** verläuft ebenfalls nicht unter Decarbonylierung (→ **7**) sondern unter Cyclopropanring-Öffnung zu **9** bzw. **10**, wobei hier die von der Carbonylgruppe am weitesten entfernten Bindungen geöffnet werden.

Contrary to a publication of *Greibrokk*[2] we reported that the synthesis of hexachloro-tris-σ-homobenzene (**1**) via CCl_2 addition to any suitable precursor seems to be impossible[3], and we stated that presumably **1** can never exist, because the spatial interaction of the two *endo*-chloro atoms is prohibitive.

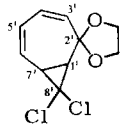
However, both a thermolytic and a photolytic approach to synthesize **1** should be interesting with respect to two publications. Thus thermolysis of tropone ethylene acetal (**2**) yielded benzene, CO_2 and ethylene[4], and photolysis of several spiroketones gave under elimination of CO highly strained spirocyclopropanes[5].



1



2



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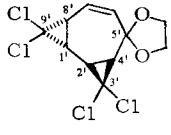
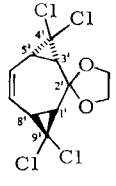
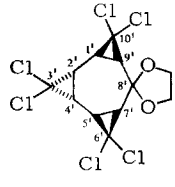


4a



4b



5

Chem. Ber. **118**, 840 – 844 (1985)

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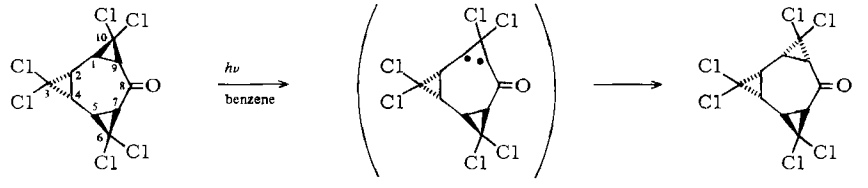
Therefore, we reacted **2** with excess CCl_2 and we obtained a mixture of the mono (**3**), bis (**4a, b**), and tris adducts (**5**). **4a** and **5** were described previously[6], but not **3** (unstable at room temperature) and **4b**. The very low yield of **5** (1%) in the one-pot reaction from **2** can be improved to 33% by reaction of isolated **4a** with CCl_2.

The *anti*-assignment for **4a** and the *anti,anti* for **5** are evident, because these structures are favored for sterical reasons. In addition both ^1H and ^{13}C NMR spectra prove the symmetrical structure **5**. The *anti*-assignment for **4b** is not predictable, because the two dichlorocyclopropane rings at these positions may also be *syn* (see **5**). But the shielding effect of the cyclopropane rings gives an upfield shift of about 3 ppm for these *syn*-oriented C-atoms in the ^{13}C NMR spectrum of **5**. The respective C-atoms of **4b** are not shifted.

For the thermolysis we heated **5** to about 150°C, where decomposition started with evolution of chlorine and HCl. Besides starting material only an inseparable mixture of olefinic compounds could be isolated.

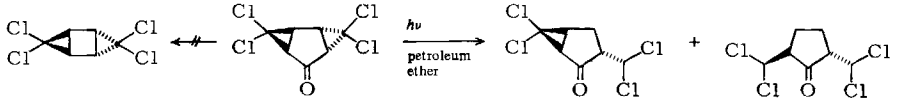
Starting material for the photolysis reaction was the ketone **6a**, readily accessible[7] from the CCl_2 tris adduct to cycloheptatriene. Irradiation of **6a** in benzene with a mercury lamp gave in low yield only one product, the isomer **6b**. The unsymmetrical structure of **6b** can be deduced from both the ^1H and ^{13}C NMR spectra. A complete ^1H NMR assignment was possible by spin decoupling.



6a **A** **6b**

Obviously, the C-1 – C-9 bond β to the carbonyl group is the weakest one under these conditions, and the diradical **A** is formed. After rotation of **A** the C – C bond is closed again. Similar isomerizations of simple phenyl cyclopropyl ketones via a comparable diradical are known[8]. However, the formation of **6b** is unexpected because this compound represents the first example of two vicinal dichlorocyclopropane rings *syn*-condensed to a seven-membered ring. Probably this ring size might be the lowest for such a sterical position.

In lit.[7] we described also the simple preparation of **8**, the lower homologue of **6a**. Irradiation under CO-elimination should lead to tetrachloro-bis-σ-homocyclobutadiene (**7**). However, photolysis of **8** in petroleum ether resulted in formation of the products **9** (14%) and the very labile **10** (27%), derived by onefold (→ **9**) or twofold (→ **10**) cleavage of the cyclopropane bonds γ to the carbonyl group, and a subsequent addition of hydrogen from the solvent.



7 **8** **9** **10**

Structure elucidation of **9** is based on the spectral data including spin decoupling and CI-MS. For the compound **10** with C_2-symmetry both the ^1H and ^{13}C NMR spectra are very characteristic. The ^{13}C NMR data for the carbonyl group of **8** (194.5), **9** (203.4), and **10** (212.0) show the additivity of the influence of a cyclopropane ring in α,β-position to the carbonyl group.

Besides these two compounds **9** and **10** about 40% of an unpolar mixture of unseparable decomposition products and about 15% polymeric residue could be isolated.

Since we can rule out the formation of considerable amounts of other primary photolysis products, this photo reaction seems to be highly selective. This peculiar result will motivate us to investigate the photochemistry of dichloro cyclopropyl ketones systematically.

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Experimental Part

^{1}H NMR ($CDCl_3$, int. TMS): Bruker WH-400. – ^{13}C NMR ($CDCl_3$, int. TMS): Varian CFT-20. – IR: Perkin-Elmer 225 (KBr) and 257 (CCl_4). – MS: Varian-MAT 711, 70 eV; CI with isobutane. All compounds and fragments show the isotope pattern according to the total number of their chlorine atoms. In all cases only the respective peak for ^{35}Cl is given. – All b.ps and m.ps are uncorrected. – Column chromatography (CC) on silica gel (PE = petroleum ether). – Flash chromatography (FC) on silica gel 60, Merck, particle size 0.040 – 0.063 mm.

1,4-Dioxaspiro[4.6]undeca-6,8,10-triene (*tropone ethylene acetal,* **2**): Preparation according to lit.[9], b.p. 76 – 80°C/3 torr (lit.[9] 62 – 65°C/0.7 torr). – ^{1}H NMR: δ = 4.00 (s; 2-, 3-H), 5.83 (dd, *J* = 10 and 2.5 Hz; 6-, 11-H), 6.46 (ddd, *J* = 10; 4 and 2.5 Hz; 7-, 10-H), 6.67 (dd, *J* = 4 and 2.5 Hz; 8-, 9-H). – ^{13}C NMR: δ = 64.3 (t; C-2, -3), 104.2 (s; C-5), 126.5, 127.7, 129.9 (3 d; C=C).

Reaction of **2** *with* CCl_2: To a stirred solution of 10.0 g (67 mmol) of **2** and 0.4 g of benzyltriethylammonium chloride (BTEAC) in 200 ml of $CHCl_3$ at room temp. 50 ml of 50% aqueous NaOH was added dropwise (1 h). After 24 h refluxing the mixture was stirred overnight, diluted with 400 ml of water and separated. The aqueous layer was extracted several times with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$ and evaporated to give 10.1 g of crude product. Repeated CC with PE/ether (4:1) afforded pure fractions.

8',8'-Dichlorospiro[1,3-dioxolane-2,2'-bicyclo[5.1.0]octa-3',5'-diene] (**3**), 1. fraction, 0.35 g (2%), m.p. 50 – 52°C, unstable at room temperature. – ^{1}H NMR: δ = 2.52 (dd, *J* = 12 and 7 Hz; 7'-H), 2.69 (dd, *J* = 12 and 1.5 Hz [W-coupling with 3'-H]; 1'-H), 3.95, 4.05, 4.20 (3 mc; 4-, 5-H), 5.63 (dd, *J* = 12 and 1.5 Hz; 3'-H), 5.77 (dd, *J* = 12 and 7 Hz; 4'-H), 5.90 (dd, *J* = 11.5 and 7 Hz; 6'-H), 6.06 (dd, *J* = 11.5 and 7 Hz; 5'-H). – MS: *m/e* = 232 (M^+, 12%), 197 (M – Cl, 20), 162 (M – 2 Cl, 10), 125 (100).

$C_{10}H_{10}Cl_2O_2$ (233.1) Ber. C 51.53 H 4.32 Gef. C 51.21 H 4.18

(1'α,2'β,4'β,5'α,7'α,9'α)-3',3',6',6',10',10'-Hexachlorospiro[1,3-dioxolane-2,8'-tetracyclo-[7.1.0.0^{2,4}.0^{5,7}]decane] (**5**), 2. fraction, 0.30 g (1%), m.p. 160 – 165°C (MeOH) [lit.[6] 176 to 181°C]. – ^{1}H NMR: δ = 1.85 (ddd, *J* = 11; 1.5 and 1.5 Hz; 1'-, 5'-H), 1.98 (dd, *J* = 1.5 and 1.5 Hz; 2',4'-H), 2.20 (d, *J* = 11 Hz; 7'-, 9'-H), 3.85, 4.05 (2 t, *J* = 6 Hz; 4-, 5-H). – ^{13}C NMR: δ = 25.1 (d; C-1', -5'), 28.9 (d; C-2', -4'), 38.9 (d; C-7', -9'), 60.6 (s; C-6', -10'), 64.4 (s; C-3'), 64.8, 66.3 (2 t; C-4, -5), 103.4 (s; C-2). – MS: *m/e* = 396 (M^+, 0.5%), 361 (M – Cl, 15), 325 (M – Cl, – HCl, 10), 289 (M – Cl, – 2 HCl, 12), 253 (M – Cl, – 3 HCl, 15), 219 (M – 3 Cl, – 2 HCl, 12), 183 (M – 3 Cl, – 3 HCl, 12), 107 (100).

(1'α,2'β,4'β,8'α)-3',3',9',9'-Tetrachlorospiro[1,3-dioxolane-2,5'-tricyclo[6.1.0.0^{2,4}]non-6'-ene] (**4a**), 3. fraction, 2.4 g (12%), m.p. 94 – 96°C (PE/ether) [lit.[6] 105 – 108°C]. – ^{1}H NMR: δ = 1.91 (dd, *J* = 11.5 and 2.5 Hz; 8'-H), 2.12 (d, *J* = 11.5 Hz; 1'-H), 2.22 (dd, *J* = 10 and 2 Hz [W-coupling with 6'-H]; 4'-H), 2.30 (dd, *J* = 11 and 2 Hz; 6'-H), 6.08 (dd, *J* = 11 and 2.5 Hz;

7'-H). – ^{13}C NMR: δ = 26.1 (d; C-2'), 29.7 (d; C-1'), 32.2 (d; C-8'), 40.0 (d; C-4'), 64.0 (s; C-3'), 64.7, 65.8 (2 t; C-4, -5), 65.8 (s; C-9'), 103.9 (s; C-2), 124.5 (d; C-7'), 138.7 (d; C-6'). – MS: *m/e* = 314 (M^+, 1%), 279 (M – Cl, 32), 243 (M – Cl, – HCl, 24), 208 (M – 2 Cl, – HCl, 30), 171 (M – Cl, – 3 HCl, 42), 136 (68), 73 (100).

(1'α,3'β,5'β,8'α)-4',4',9',9'-Tetrachlorospiro[1,3-dioxolane-2,2'-tricyclo[6.1.0.0^{3,5}]non-6'-ene] (**4b**), 4. fraction, 0.3 g (1%), m.p. 107–110°C (MeOH). – ^{1}H NMR: δ = 2.22, 2.93, 5.93 (AA'BB'XX'-system, $J_{XX'}$ = 9; J_{BX} = $J_{B'X'}$ = 3; $J_{BX'}$ = $J_{B'X}$ = 1.5; $J_{AA'}$ = $J_{BB'}$ = $J_{AB'}$ = $J_{A'B}$ = J_{AX} = $J_{A'X}$ = $J_{AX'}$ = 0 Hz; 1'-, 3'-, 5'-, 6'-, 7'-, 8'-H), 4.15 (AA'BB'-system; 4-, 5-H). – ^{13}C NMR: δ = 33.9 (d; C-5', -8'), 43.1 (d; C-1', -3'), 63.3 (s; C-4', -9'), 65.1 (t; C-4, -5), 106.1 (s; C-2), 126.1 (d; C-6', -7'). – MS: *m/e* = 314 (M^+, 0.5%), 279 (M – Cl, 32), 243 (M – Cl, – HCl, 18), 208 (M – 2 Cl, – HCl, 20), 136 (75), 73 (100).

$C_{11}H_{10}Cl_4O_2$ (316.0) Ber. C 41.81 H 3.19 Gef. C 41.70 H 3.12

Reaction of **4a** *with* CCl_2: 3.1 g (10 mmol) of **4a** was refluxed for 7 h with 50 ml of $CHCl_3$, 0.2 g of BTEAC and 20 ml of 50% aq. NaOH as described above. CC of 3.0 g of crude product with PE/ether (4:1) yielded 0.29 g (33%, on converted **4a**) of **5** as 1. fraction and 2.4 g of **4a** as 2. fraction.

Thermolysis of **5**: 0.35 g (0.9 mmol) of **5** was heated under N_2 to 140–150°C for 3 h. The volatiles had the typical odor of Cl_2 and HCl. CC of the residue with PE/ether (85:15) afforded 0.27 g of **5** and 18 mg of a complex mixture (tlc; ^{1}H NMR showed olefinic signals δ = 6.0–6.6).

Photolysis of (1α,2β,4β,5α,7α,9α)-3,3,6,6,10,10-Hexachlorotetracyclo[7.1.0.0^{2,4}.0^{5,7}]decan-8-one (**6a**): A degassed solution of 0.80 g (2.3 mmol) of **6a**[7] in 170 ml of benzene in an usual photolysis apparatus was irradiated with a 450 W Hanovia Hg lamp for 3 d. After removal of the solvent CC of the crude product with PE/ether (4:1) yielded 0.75 g of **6a** (2. fraction) and 0.04 g (5%) of *(1α,2β,4β,5β,7β,9α)-3,3,6,6,10,10-Hexachlorotetracyclo[7.1.0.0^{2,4}.0^{5,7}]decan-8-one* (**6b**), m.p. 134–137°C. – IR (KBr): 1720 cm^{-1} (CO). – ^{1}H NMR: δ = 1.37 (dd, *J* = 10 and 7 Hz; 5-H), 2.17 (d, *J* = 10 Hz; 7-H), 2.30 (d, *J* = 10 and 1 Hz; 2-H), 2.35 (dd, *J* = 10 and 7 Hz; 4-H), 2.39 (dd, *J* = 10 and 1 Hz; 1-H), 2.62 (d, *J* = 10 Hz; 9-H). Spin decoupling: ↯ 1.37 → 2.17 (s), 2.35 (d, *J* = 10 Hz); ↯ 2.39 → 2.30 (d, *J* = 10 Hz); ↯ 2.62 → 2.39 (s, br.). – ^{13}C NMR: δ = 27.4 (d; C-4), 32.5, 33.3, 34.0 (3 d; C-1, -2, -5), 43.8 (d; C-7, -9), 61.8 (s; C-3), 64.4 (s; C-6), 67.2 (s; C-10), 189.3 (s; C-8). – MS: *m/e* = no mol peak, 317 (M – Cl, 1%), 281 (M – Cl, – HCl, 3), 253 (M – Cl, – HCl, – CO, 6), 219 (M – 3 Cl, – CO, 30), 183 (M – 3 Cl, – HCl, – CO, 45), 149 (M – 5 Cl, – CO, 70), 136 (78), 73 (100).

$C_{10}H_6Cl_6O$ (354.9) Ber. C 33.85 H 1.70 Gef. C 33.72 H 1.66

Photolysis of anti-3,3,7,7-tetrachlorotricyclo[4.1.0.0^{2,4}]heptan-5-one (**8**): A solution of 2.40 g (9.75 mmol) of **8**[7] in 1000 ml of PE was irradiated as described above for 28 h at 30°C. After removal of the solvent FC of the crude product with pentane/ether (85:15) yielded three fractions: 1. fraction, 0.98 g, unseparable mixture (tlc, ^{1}H NMR) of unpolar compounds. – 2. fraction, 0.35 g (14%) of *anti-6,6-dichloro-3-(dichloromethyl)bicyclo[3.1.0]hexan-2-one* (**9**), b.p. 105–110°C/5 torr (kugelrohr). – IR (CCl_4): 1740 cm^{-1} (CO). – ^{1}H NMR: δ = 2.45 (ddd, *J* = 20; 3.5 and 1 Hz; *anti*-4-H), 2.58 (dd, *J* = 20 and 8.5 Hz; *syn*-4-H; assignment by NOED), 2.80 (dd, *J* = 6.5 and 1 Hz; 5-H), 2.86 (d, *J* = 6.5 Hz; 1-H), 3.27 (ddd, *J* = 8.5; 3.5 and 3.5 Hz; 3-H), 6.00 (d, *J* = 3.5 Hz; $CHCl_2$). Spin decoupling: ↯ 2.45 → 3.27 (dd, *J* = 8.5 and 3.5 Hz), ↯ 2.58 → 3.27 (dd, *J* = 3.5 and 3.5 Hz), ↯ 3.27 → 2.45 (d, br., *J* = 20 Hz), 2.58 (d, *J* = 20 Hz). – ^{13}C NMR: δ = 40.2 (t; C-4), 40.7 (d; C-5), 44.7, 45.7 (2 d; C-1, -3), 60.5 (s; C-6), 75.1 (d; $CHCl_2$), 203.4 (s; C-2). – MS: *m/e* = 246 (M^+, 1%), 211 (M – Cl, 6), 204 (pattern for 4 Cl, 15), 169 (204 – Cl, 100). – MS (CI): *m/e* = 247 (M + 1, 100%).

$C_7H_6Cl_4O$ (247.9) Ber. C 33.91 H 2.44 Gef. C 33.79 H 2.35

3. Fraction, 0.65 g (27%) of *trans-2,5-bis(dichloromethyl)-1-cyclopentanone* (**10**), unstable oil. – IR (CCl_4): 1760 cm^{-1} (CO). – ^1H NMR: δ = 2.55, 2.75 (AB-system, A as dd, *J* = 7 and 1 Hz, B as dd, *J* = 9 and 1.5 Hz; 3-, 4-H), 3.20 (mc; 2-, 5-H), 6.04 (d, *J* = 3 Hz; $CHCl_2$). – ^{13}C NMR: δ = 40.6 (t; C-3, -4), 48.4 (d; C-2, -5), 75.4 (d; $CHCl_2$), 212.0 (s; C-1). – MS: *m/e* = 248 (M^+, 5%), 165 (M – $CHCl_2$, 58), 137 (M – $CHCl_2$, – CO, 12), 75 (100). – The compound was too unstable for an elementary analysis.

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[122/84]