Photolysis of Cycloalkanones with Dichlorocyclopropanes in α,α'-Position

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Die Photolyse der Cycloalkanone **1** und **2** verläuft unter Öffnung der Cyclopropanringe zu den Dichlormethyl-Derivaten **3**, **5** und **4**, **6**. Die Strukturen von **3** und **4** wurden durch $NaBH_4$-Reduktion zu **7** und **8** bewiesen. Die früher angegebenen Strukturen[2] für **3** und **5** müssen revidiert werden.

Irradiation of the dichlorocyclopropane-fused cyclopentanone **1** should lead to CO elimination with formation of tetrachloro-bis-σ-homocyclobutadiene (**A**). However, photolysis of **1** yielded two products, and in accordance with the spectral data including spin decoupling and NOE difference spectra we assigned the structures **B** and **C**[2]. This peculiar result prompted us to investigate the photolysis of the higher homologue **2**.

2[3] was irradiated in pentane under the conditions described previously[2], and two products **4** and **6** were isolated. The main product **4** showed another substitution pattern than we believed in the case of **B**. To give final support for structure **4** we reduced the ketone with $NaBH_4$ to yield alcohol **7** (hydride attack from the less hindered side). Spin decoupling showed that the proton (δ = 2.46) vicinal to the $CHCl_2$ group (δ = 5.61) is not vicinal to the CHOH group (δ = 4.43), but separated by a CH_2 group (δ = 1.66, 2.12). Such a sequence can only be in agreement with structure **7** and consecutively with **4**.

Therefore, we reinvestigated the photolysis product **B** of **1**. Assignment to structure **B** had been based mainly on the chemical shift of δ = 3.27 for the proton supposed to be vicinal to the $CHCl_2$ *and* to the carbonyl group. Spin decoupling of the ketone can not give a decision for the structure of either **B** or **3**, but reduction to the alcohol **8** can. Spin decoupling of **8** showed unambiguously the same sequence as in the case of **7**. The relatively strong downfield shift for 4-H (δ = 3.12) is also maintained in **8**.

Accordingly, structure **C** for the twofold ring opening product is to be revised. Thus, the C_2 symmetry given by both ^1H- and ^{13}C-NMR spectra[2] is only consistent with formula **5**.

Hence, on irradiation of **1** or **2** one cyclopropane bond β to the carbonyl group is opened to give a diradical and subsequent addition of hydrogen from the solvent yields **3** and **5** or **4** and **6**, respectively.

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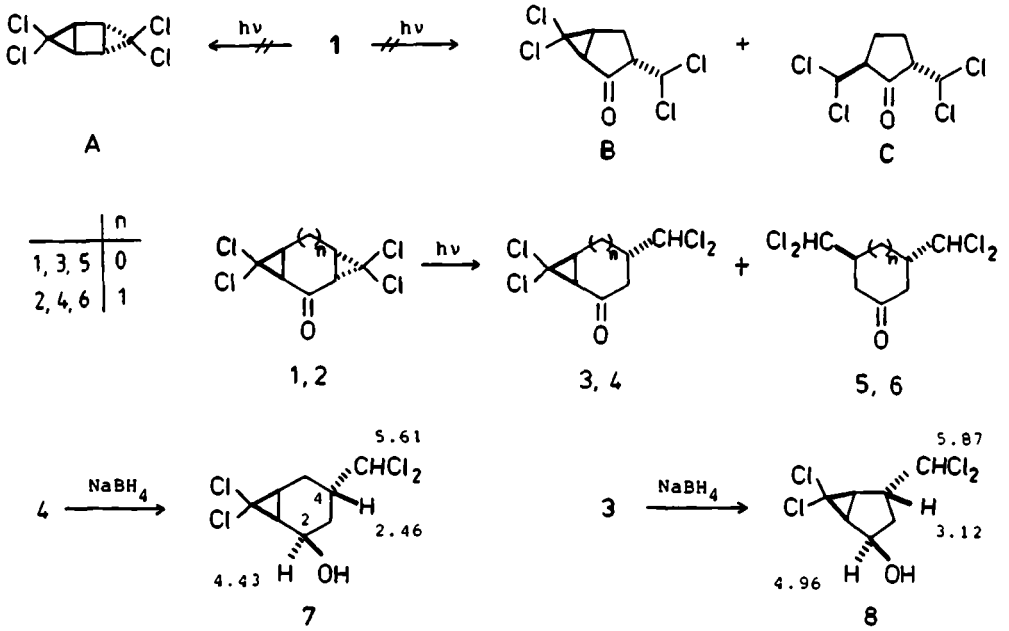
Experimental

^1H NMR (with spin decoupling; int. TMS): Bruker WH-400. – ^{13}C NMR ($CDCl_3$, int. TMS; DEPT): Bruker AM-270. – IR: Beckman IR-9. – MS: Varian-MAT 711, 70 eV. In all cases only the molecular peak for ^{35}Cl is given. – Flash chromatography (FC): silica gel 60, Merck. – PE = petroleum ether (b.p. 30–60°C). – C,H analyses: Hewlett-Packard C,H,N Analyzer.

Photolysis of anti-4,4,8,8-Tetrachlorotricyclo[5.1.0.0^{3,5}]octan-2-one (**2**): A degassed solution of 0.45 g (1.75 mmol) of **2**[3] in 400 ml of pentane in a usual photolysis apparatus was irradiated with a 450 W Hanovia Hg lamp for 30 h. After removal of the solvent the crude product was purified by FC with PE and increasing amounts of ether.



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1. Fraction: 0.17 g of recovered **2**.

2. Fraction: 0.14 g (50%) of *7,7-dichloro-4-(dichloromethyl)bicyclo[4.1.0]heptan-2-one* (**4**), oily. – IR (CCl_4): 1720 cm^{-1} (CO). – ^1H NMR (C_6D_6): δ = 1.45 (ddd, *J* = 10; 7; 2 Hz; 6-H), 1.55 (ddd, *J* = 15; 8; 7 Hz; 5-H), 1.70 (ddd, *J* = 15; 5.5; 2 Hz; 5-H), 1.80 (dd, *J* = 16; 9.5 Hz; 3-H), 2.02 (dd, *J* = 16; 4.5 Hz; 3-H), 2.02 (d, *J* = 10 Hz; 1-H), 2.17 (ddddd, *J* = 9.5; 8; 5.5; 4.5; 4.5 Hz; 4-H), 4.85 (d, *J* = 4.5 Hz; $CHCl_2$); in $CDCl_3$: 2.37 (dd, *J* = 16; 9.5 Hz; 3-H), 2.34–2.48 (m; 3-H), 2.54 (d, *J* = 10 Hz; 1-H), 2.57 (dd, *J* = 16; 4.5 Hz; 3-H), 2.87 (ddddd, *J* = 9.5; 8; 5.5; 4.5; 4.5 Hz; 4-H), 5.72 (d, *J* = 4.5 Hz; $CHCl_2$). – ^{13}C NMR: δ = 20.8 (t; C-5), 31.0 (d; C-6), 37.8 (d; C-1), 40.3 (t; C-3), 42.9 (d; C-4), 62.1 (s; C-7), 75.9 (d; $CHCl_2$), 198.5 (s; C-2). – MS: *m/z* (%) = 260 (M^+, 3), 224 (8), 189 (6), 161 (10), 122 (100), 87 (35), 83 (35), 51 (44).

$C_8H_8Cl_4O$ (262.0) Calcd. C 36.68 H 3.09
Found C 36.35 H 3.00

3. Fraction: 24 mg (8%) of *trans-3,5-bis(dichloromethyl)cyclohexanone* (**6**), m.p. 58–60°C. – IR (CCl_4): 1720 cm^{-1} (CO). – ^1H NMR ($CDCl_3$): δ = 2.23 (t, *J* = 6.5 Hz; 4-H_2), 2.57, 2.66 (AB, *J* = 16 Hz, A part as d, *J* = 9, B part as d, *J* = 5 Hz; 2-, 6-H_2), 2.85 (dtdd, *J* = 9; 7; 5; 5 Hz; 3-, 5-H), 5.75 (d, *J* = 5 Hz; $CHCl_2$). – ^{13}C NMR: δ = 27.7 (t; C-4), 41.6 (t; C-2, -6), 43.2 (d; C-3, -5), 75.9 (d; $CHCl_2$), 206.5 (s; C-1). – MS: *m/z* (%) = 262 (M^+, 2), 181 (20), 179 (30), 143 (12), 115 (20), 79 (34), 68 (100).

$C_8H_{10}Cl_4O$ (264.0) Calcd. C 36.40 H 3.82
Found C 36.08 H 3.71

$NaBH_4$ Reduction of **3** *and* **4**: 0.30 mmol of **3** or **4** in 3 ml of ethanol was treated with 20 mg of $NaBH_4$ at 0°C. After 1 h it was worked up as usual and purified by FC (PE/8% ether).

7,7-Dichloro-exo-4-(dichloromethyl)bicyclo[4.1.0]heptan-endo-2-ol (**7**): 78 mg of **4** yielded 62 mg (79%) of **7**, m.p. 56–58°C. – IR (KBr): 3400 cm^{-1} (br., OH). – ^1H NMR (C_6D_6/[$CDCl_3$]): δ = 1.22 [1.66] (ddd, *J* = 14; 9; 3.5 Hz; 3-H), 1.25 [1.98] (ddd, *J* = 10.5; 9; 4 Hz; 6-H), 1.30 (d, *J* = 7.5 Hz; OH), 1.44 [1.98] (ddd, *J* = 15; 5; 4 Hz; 5-H), 1.45 [2.14] (dddd, *J* = 15; 9; 4; 2 Hz; 5-H), 1.94 [2.46] (ddddd, *J* = 8.5; 5; 5; 4; 3.5 Hz; 4-H), 3.82 (dddd, *J* = 9; 8; 7.5; 7 Hz; 2-H) [4.43 (ddd, *J* = 9; 8; 7 Hz; 2-H)], 4.96 [5.61] (d, *J* = 8.5 Hz; $CHCl_2$). – ^{13}C NMR: δ = 21.1 (t; C-5), 28.2 (d; C-6), 30.7 (d; C-1), 32.3 (t; C-3), 43.3 (d; C-4), 62.6 (d; C-2), 65.0 (s; C-7); 76.0 (d; $CHCl_2$).

$C_8H_{10}Cl_4O$ (264.0) Calcd. C 36.40 H 3.82
Found C 36.45 H 3.68

6,6-Dichloro-exo-4-(dichloromethyl)bicyclo[3.1.0]hexan-endo-2-ol (**8**): 65 mg of **3**[2] yielded 60 mg (91%) of **8**, m.p. 72–74°C. – IR (CCl_4): 3600 cm^{-1} (OH). – ^1H NMR ($CDCl_3$): δ = 1.93 (ddd, *J* = 15; 9; 7 Hz; 3-H), 2.29 (d, *J* = 7 Hz; 5-H), 2.36 (ddd, *J* = 15; 9.5; 2 Hz; 3-H), 2.49 (dd, *J* = 7; 6 Hz; 1-H), 3.12 (ddd, *J* = 9; 3; 2 Hz; 4-H), 4.96 (ddd, *J* = 9.5; 7; 6 Hz; 2-H), 5.86 (d, *J* = 3 Hz; $CHCl_2$). – ^{13}C NMR: δ = 36.7 (t; C-3), 39.1, 41.2 (2 d; C-1, -5), 51.6 (d; C-4), 64.0 (s; C-6), 75.5, 75.7, (2 d; C-2, $CHCl_2$). – MS: *m/z* (%) = 249 (M^+, 1), 213 (40), 171 (90), 169 (100), 113 (66), 109 (70), 77 (82), 75 (92).

$C_7H_8Cl_4O$ (250.0) Calcd. C 33.63 H 3.23
Found C 33.39 H 3.14

CAS Registry Numbers

1: 95722-00-2 / **2**: 105929-84-8 / **3**: 105883-35-0 / **4**: 105883-36-1 / **5**: 105883-37-2 / **6**: 105883-38-3 / 7: 105883-39-4 / **8**: 105900-53-6 / B: 95639-35-3 / C: 95639-36-4

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