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ANOTHER LOOK AT THE PHOTODECHLORINATION OF BROMODAN

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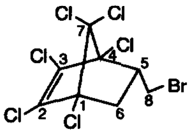
Abstract. Contrary to a previous report, there is no solvent-dependent selectivity to either of the double-bond-dechlorinated derivatives when Bromodan is irradiated in hexane or methanol. The 7-dechlorinated derivative formed on photolysis in triethyl amine is debrominated on further irradiation. ^{13}C chemical shifts and long-range C-H coupling constants indicate that the structural assignment of the double-bond-dechlorinated isomers must be reversed.

In a recent article the following claims were made about the photodechlorination of 5-*endo*-bromomethyl-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene (Bromodan, **1**).[1)]

a. Photolysis in hexane through quartz gave only **2** and **4**.
b. Photolysis in methanol through quartz gave only **3** and **4**.
c. Photolysis in triethyl amine gave only **5**, which was stable toward irradiation.
d. Photolysis in a mixture of hexane and acetone through quartz gave **2**, **3**, **4** and **6**.



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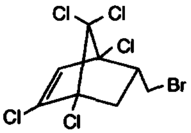

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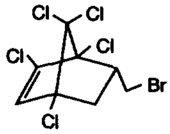

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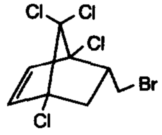

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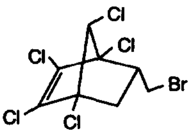

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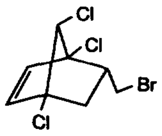

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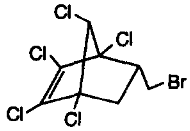
The mechanism of the photodechlorination has not been investigated in detail, but it is not likely to involve more than the cleavage of a C-Cl bond of an excited olefin. We were not aware of any previous indication of a solvent influence on the selectivity to isomers like **2** and **3**. Because such an effect would have important implications for the mechanism, we decided to repeat the photolysis of **1**.

The original report mentioned that a high-pressure mercury lamp had been used, but did not specify its make or the experimental configuration. The irradiation times were 48 h for the reactions in a and d, 24 h for that in c; no time was given for the reaction in b. We found that under our conditions the reactions proceeded much more rapidly than reported. Thus irradiation through quartz of 500 mL of a 1% solution of **1** in hexane gave 86.5% conversion to mostly **2** and **3** in 30 min; the reaction in methanol was similarly quick. The reactions in c and d were slower, but still faster than reported. These rate differences are not disturbing, since they are dependent on the lamps used and the fraction of the light reaching the solutions.

Disappointing, however, was our failure to find significant selectivity to **2** or **3** in hexane and methanol; in each case we observed that these isomers are formed in a ratio near 1:1. Compounds **2** and **3** were not separated at all on our 2-m SE-30 GC column and were only poorly separated by TLC and column chromatography; we purified small amounts of them by repeated column chromatography. We do not know what may have led to the original report of high selectivity. Because of the poor chromatographic separation we surmise that it arose through fortuitous NMR analysis of pure chromatography fractions that by TLC and GC looked like the others. We circumvented this difficulty by NMR analysis before separation. Since both **2** and **3** give **4** on further irradiation, we investigated the possibility of selective conversion in hexane and methanol, but the isomers disappeared at essentially the same rate. As expected, there was no reaction at all when **1** in hexane was irradiated through pyrex.

The original report made conflicting statements about whether the photolysis of **1** in triethyl amine was carried out with a quartz or a pyrex filter. We used a pyrex filter and confirmed that **5** is the initial product. Compound **5**, however, is less stable toward further irradiation than asserted; in a slow reaction it is reduced to **9**, which was identified by its mass and NMR spectra. Compound **9** can be prepared in high yield by stirring **5** with zinc powder in acetic acid. The Diels-Alder reaction of allyl bromide and 1,2,3,4,5-pentachlorocyclopentadiene gave a mixture of **5**, **7** and **8**. Compound **5** was separated by column chromatography, and **7** could be purified of **8** by recrystallization from petroleum ether. Compound **8** was identified from spectra of its mixture with **7**. The structures of **7** and **8** are readily assigned by long-range C-H coupling: C-7 of **7** is coupled with the single endo proton at C-6, while C-7 of **8** is coupled with the endo protons of both C-5 and C-6. Contrary to the report, the proton H-7 of **5** is a doublet (J = 1.7 Hz) at δ 4.15, not a singlet. The endo proton at C-6 is coupled with a syn proton at C-7.2) The anti protons in **7** and **8** are singlets.



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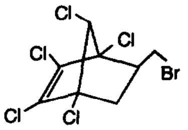

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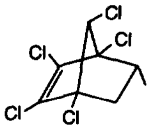

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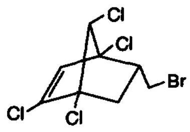

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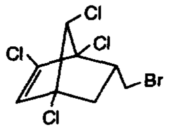

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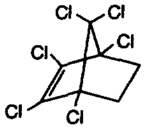

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The authors of the original report did not mention the concentration of acetone used for the sensitized photolyses; we used a 1% solution, as in a paper by another worker, which they cited.[3) GC analysis revealed, in addition to **2**, **3** and **4**, many products in small amounts. Two attempts were made to prepare **6** for comparison with the components of the mixture. Irradiation of **4** in triethyl amine gave no conversion at all. When **5** was irradiated in hexane it readily yielded the double-bond-monodechlorinated isomers **10** and **11**, which were slowly converted further. Prolonged photolysis of **5** did give a low yield of what we take to be **6**, although its spectra differ from those reported. Thus the bridge proton is a doublet (J = 1.7 Hz) at δ 4.05, not a singlet at δ 4.25, and the vinyl protons at δ 6.40 and 6.12 are a clear AB pattern (J = 6.4 Hz). The mixture resulting from the photolysis of **1** in 1% acetone in hexane was chromatographed, and fractions with R_f values similar to that of our compound **6** were examined by ^{1}H NMR. We found no evidence for the presence of **6**.

In the original report the assignment of structures to **2** and **3** was tentative and based on the chemical shifts of the vinyl protons; the isomer with the resonance at δ 6.28 was assigned structure **2** and the one with δ 5.98 (6.03 in our spectra) structure **3**. We have approached the problem with a bank of ^{13}C-NMR spectra and on the basis of both chemical shifts and long-range C-H coupling submit that the original assignment must be reversed.

The argument from chemical shifts depends on the β and γ effects of the bromomethyl and chlorine substituents on the shifts of the bridgehead carbons (Table 1). In the symmetrical compound 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-ene (**12**)[4) these are at δ 79.4. In **1** we see that the addition of the bromomethyl group has shifted the β bridgehead carbon C-4 2.5 ppm downfield and the γ carbon C-1 1.0 ppm upfield. These shifts are of appropriate magni-

Table 1: ^{13}C-NMR Spectra of Compounds **1-12**[a)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1	78.4	133.0	129.2	81.9	50.1	30.8	102.3	41.0
2	78.4	138.6	128.0	79.3	50.0	31.7	103.8	40.7
3	74.5	132.3	134.7	82.6	48.6	31.2	104.0	41.6
4	75.7	138.4	133.7	79.2	48.6	32.1	105.4	41.3
5	71.9	133.9	130.0	75.7	50.8	30.6	77.3	40.8
6	69.3	139.5	134.9	73.2	49.1	32.0	79.8	41.0
7	73.4	132.0	127.8	77.3	50.8	31.2	80.3	41.5
8	73.1	132.2	131.3	77.8	46.5	32.3	76.7	41.7
9	72.4	132.5	131.1	76.9	42.2	41.8	77.1	14.1
10	72.2*	139.0	129.4	72.7*	50.5	31.4	78.4	40.2
11	68.0	133.5	135.1	76.3	49.0	30.9	78.7	41.3
12	79.4	131.5	131.5	79.4	35.0	35.0	101.6	

[a) δ($CDCl_3$). Asterisks indicate uncertain assignments in **10**.

tude.[5] Having assigned these resonances in **1**, we turn to the effect of the vinyl chlorines. In the monodechlorinated isomer with its proton resonance at δ 6.28 the bridgehead carbons are at δ 74.5 and 82.6. The β effect (+3.9 ppm) and the small γ effect (-0.7 ppm) on going from this isomer to **1** show that these are C-1 and C-4, respectively.[6] The chlorine at C-2 was removed in forming this isomer, which is thus compound **3**. A β effect of +2.6 ppm and no significant γ effect identify the other isomer as **2**. Very similar effects are seen on going from **4** to **2** and **3**. One can quickly confirm that reversing the order of subtraction in these cases does not result in a consistent pattern.

Fully coupled ^{13}C-NMR spectra show that C-2 in these compounds is coupled with both protons at C-6, while C-3 is coupled with the proton at C-5. The coupling is complicated in **2**, **3** and **4** by the protons at C-2 and C-3 themselves, but in each case the carbon assigned to C-2 on the basis of the chemical shifts, as above, is more highly coupled than C-3.

Similar observations have been made about the spectra of a number of related compounds[7] and were used extensively in assigning the resonances in Table 1.

Experimental. All photolyses were carried out with Philips HPK 125W lamps in water-cooled quartz or pyrex wells surrounded by the reaction solution, which was stirred by a magnet. Hexane, acetone and methanol were of analytical grade (Merck, Darmstadt). Triethyl amine was dried and distilled before use. Column chromatography was performed on silica gel 60 (Merck) with petroleum ether (bp 50°) as eluent. ^{13}C-NMR spectra were made with a Varian CFT-20 spectrometer and ^{1}H spectra with this instrument modified for 80 MHz; the solvent was $CDCl_3$ and the standard TMS. Because of peak interference, some coupled spectra were made of acetone-d_6 solutions. GC-mass spectra were made at 70 eV on an LKB 9000S instrument fitted with a 2-m SE-30 column programmed from 70° to 240° at 10 deg/min. Bromodan (**1**) was prepared by the reaction of allyl bromide with hexachlorocyclopentadiene[8], chromatographed and recrystallized to a purity of more than 99%.

Photolysis of Bromodan (1): a. In hexane. A solution of 160 mg of **1** in 180 mL of hexane was irradiated through quartz for 10 min. Analysis by GC revealed less than 1% of **1**, 58% of **2** and **3** (as a single peak) and 24% of **4**, as well as small amounts of numerous other products. A ^{1}H-NMR spectrum showed the resonances at δ 6.03 (**2**) and 6.28 (**3**) in the ratio 54:46 (the true ratio of these resonances is nearer 50:50, because the resonances of **4** overlap unequally with those of **2** and **3**).

A second experiment, with 427 mg of **1** in 500 mL of hexane, gave 86.5% conversion in 30 min, to 82% of **2** plus **3** and 4% of **4**.

b. In methanol. A solution of 160 mg of **1** in 180 mL of methanol was irradiated through quartz for 10 min. Analysis by GC showed 2% of **1**, 67% of **2** plus **3** and 20% of **4**. The ratio of **2** to **3** was 53:47 (^{1}H NMR).

When an identical solution was irradiated for only 2 min, the conversion was 12% to a 1:1 mixture of **2** and **3**.

c. In triethyl amine. A solution of 500 mg of **1** in 64 mL of triethyl amine was irradiated through pyrex for 2 h 40 min. Analysis by GC revealed 51% of **1**, 39% of **5** and 8% of a product with shorter retention time. ^{1}H NMR showed that the major product was indeed **5** (the doublet at δ 4.15). The solvent was removed under vacuum and the residue partitioned between petroleum ether and water. The petroleum ether was washed free of triethyl amine with water, dried over Na_2SO_4 and stripped. A ^{13}C-NMR spectrum showed the resonances of **1** and **5** (see preparation of **5** below).

Isolation of ***2****,* ***3*** *and* ***4****.* The products from several photolyses of **1** in hexane and methanol were combined and subjected to repeated column chromatography. Small amounts of **2**, **3** and **4** could be isolated pure. As reported$^{1)}$, the less polar isomer of **2** and **3** is the one with the vinyl proton resonance at δ 6.28.

Preparation of Compounds ***5****,* ***7*** *and* ***8****.* A solution of 11.0 g of 1,2,3,4,5-pentachlorocyclopentadiene in 100 mL of allyl bromide was heated under reflux for 8 h. The allyl bromide was distilled out and the residue chromatographed on a large (2-L-solvent-volume) column. After elution of unreacted pentachlorocyclopentadiene, first **5**, then a mixture of **7** and **8** were obtained. Compound **5** was recrystallized from petroleum ether to give 5.4 g, 98% pure by GC analysis; it was shown by ^{1}H and ^{13}C NMR to be the product obtained on irradiation of **1** in triethyl amine. The mixture of **7** and **8** (8.6 g, 75% **7**) was recrystallized twice from petroleum ether to give **7** in ca. 95% purity. One fraction of the mother liquor contained ca. 40% **8** and 60% **7**; spectra of this were used to identify **8**.

7: GCMS m/e 356 (m^+, 4%), 321 (4), 277 (36), 241 (32), 236 (100), 215 (10), 201 (78); ^{1}H NMR δ 4.32 (s, H-7), 3.7 (m, 1H), 2.4-3.2 (m, 3H), 2.0 (m, 1H). **8**: GCMS m/e 356 (m^+, 11%), 321 (5), 277 (60), 241 (42), 236 (100), 215 (12), 201 (90); ^{1}H NMR δ 4.56 (s, H-7), other resonances under those of **7** in the mixture.

Photolysis of ***5****: a. In triethyl amine.* A solution of 200 mg of **5** in 64 mL of triethyl amine was irradiated through pyrex. After 6 h the solution was found by GC analysis to contain 32% of **5** and 40% of **9**. GCMS revealed the molecular ion of **9** at m/e 278 ($C_8H_7Cl_5$). A ^{13}C-NMR spectrum was made of the mixture, and the resonances of the product were identical with those of **9** formed in the reduction of **5** with zinc in acetic acid (see below).

b. In 1% acetone in hexane. A solution of 500 mg of **5** in 180 mL of 1% acetone in hexane was irradiated through quartz for 2.5 h. Analysis by GC revealed many products, among them ca. 12% of one with a short retention time that might be **6**. Similar mixtures with 9-12% of this component were obtained on irradiation through quartz of solutions of either **5** or the mixture of **10** and **11** in pure acetone. Several such product mixtures were combined and chromatographed to give **10** and **11** and, in a later fraction, ca. 100 mg of the compound we identify as **6**. This fraction was not pure, but all the impurities were present in low concentration, so that spectroscopic identification of **6** was possible. Separation of **10** and **11** required several column chromatography steps. Compound **11** was eluted first.

6: GCMS m/e 288 (m^+, 4%), 253 (4), 209 (11), 173 (55), 168 (100), 147 (66), 133 (58).

10: GCMS m/e 322 (m^+, 13%), 287 (12), 243 (24), 207 (64), 202 (100), 181 (62), 167 (79); ^{1}H NMR δ 6.13 (s, H-3), 4.11 (d, J = 1.7 Hz, H-7), 3.62 (m, one H of CH_2Br), 2.5-3.4 (m, 3H), 1.88 (ddd, J = 12.2, 3.5, 1.7 Hz, H-6-endo). **11**: GCMS m/e 322 (m^+, 3%), 287 (66), 207 (43), 202 (100), 181 (80), 167 (71); ^{1}H NMR δ 6.38 (s, H-2), otherwise just like **10**.

Photolysis of **4** *in triethyl amine.* A solution of 100 mg of **4** in 55 mL of triethyl amine was irradiated through pyrex for 1.5 h. Analysis by GC showed only unchanged starting material to be present.

Photolysis of **1** *in 1% acetone in hexane.* A solution of 64 mg of **1** in 70 mL of 1% acetone in hexane was irradiated through quartz. After 2 h 40 min analysis by GC revealed over 80% conversion, mostly to mono- and didechlorinated products, though two components with shorter retention times were present in small amounts and were considered possible candidates for **6**. The product mixture was chromatographed, and fractions with R_f values similar to that of **6** (as prepared above) were examined by ^1H NMR. None of the fractions contained any of the compound we had identified as **6**. The only vinyl protons observed were those of **4**.

Reduction of **5** *with Zinc in Acetic Acid.* To a stirred solution of 500 mg of **5** in 10 mL of acetic acid was added 1.00 g of fine zinc powder over 7 h. GC indicated ca. 95% conversion. After the mixture had been stirred overnight with another 200 mg of zinc, the conversion was 99.7% to a single product. The mixture was partitioned between petroleum ether and water. The petroleum ether was washed with water, then with a solution of Na_2CO_3. After drying over Na_2SO_4 the solvent was stripped out to yield a yellow oil, which was filtered through a few grams of silica gel with petroleum ether. Removal of the solvent gave 350 mg (90%) of **9** as a colorless oil.

9: GCMS m/e 278 (m^+, 23%), 236 (100), 215 (53), 201 (67); ^1H NMR δ 4.05 (d, J = 1.5 Hz, H-7), ca. 2.8 (m, H-5-exo), 2.59 (dd, J = 11.5, 9.0 Hz, H-6-exo), 1.54 (ddd, J = 11.5, 3.5, 1.6 Hz, H-6-endo), 1.01 (d, J = 6.7 Hz, CH_3).

Thin-Layer Chromatography. Aluminium-foil-backed silica-gel 60 F_{254} plates (0.2-mm layer thickness, 20 cm x 20 cm) (Merck) were developed with hexane. For visualization the plates were sprayed with diphenyl amine and irradiated with UV light. The following R_f values were determined on a single plate: **1**, 0.40; **2**, 0.30; **3**, 0.27; **4**, 0.17; **5**, 0.40; **6**, 0.21; **7**, 0.20; **8**, 0.19; **9**, 0.49; **10**, 0.38; **11**, 0.27.

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