# Novel Structures of a *trans*-Cyclooctene and *trans*-Fused Cyclopropane Generated *via* Photoisomerization of a *gem*-Dichlorocyclopropyl-benzocycloheptenone

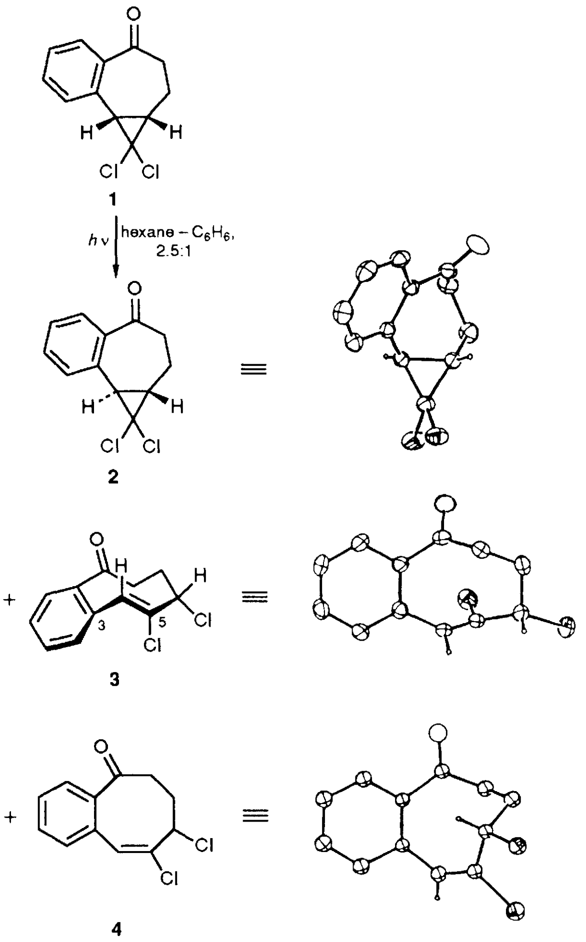
**John L. Wood, Patrick J. Carroll and Amos B. Smith, III***

*Department of Chemistry, the Monell Chemical Senses Center, and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA*

Photoisomerization of the *gem*-dichlorobenzobicyclo[5.1.0]octenone **1** (6 h, Pyrex) furnished the *trans*-fused cyclopropane **2** and the *trans*- and *cis*-cyclooctenes **3** and **4**; single-crystal X-ray analyses defined the novel photoproduct structures.

Recently we reported an efficient preparation of a *trans*-benzobicyclo[5.1.0]octene derivative *via* photoisomerization of the corresponding *cis*-fused cyclopropane.[1] In an effort to elucidate the scope of this transformation, we have explored the photochemical reactivity of the *gem*-dichloro substrate **1**.† Upon brief irradiation (1 h; 0.5 mol dm$^{-3}$ in degassed hexane–benzene, 2.5:1),‡ **1** provided predominantly the *trans*-fused cyclopropane **2**† (28% yield, 77% based on recovered **1**). In contrast, prolonged photolysis (6 h) led to a complex mixture from which **1** (21% recovery), *trans*-cyclooctene **3**† (16%), and a mixture of **2** and *cis*-cyclooctene **4** (21%) were isolated *via* flash column chromatography (FCC) on silica gel. The mixture of **2** and **4** proved inseparable by normal-phase HPLC; analytically pure **4**† was secured *via* photoisomerization of the *trans*-isomer **3** (0.016 mol dm$^{-3}$ in 1:1 benzene–hexane, 2 h, 30% yield) followed by FCC. Irradiation of **2** likewise furnished **1** as well as **3** and **4**, but the cyclooctenes, although interconvertible, did not revert to either cyclopropane progenitor upon photolysis. Surprisingly, none of the reactions produced more than a trace of the diastereoisomeric *trans*-cyclooctene **5** (<1% yield).§ In a previous study, photoisomerization of a dichlorocyclopropane fused to a six-membered ring afforded the *cis*-cycloheptene exclusively.[2]

The stability of **3** towards chromatographic purification contrasts markedly with the behaviour of the *trans*-compound **6**; the latter, prepared *via* isomerization of the *cis*-alkene, undergoes rapid hydration to diol **7** upon exposure to silica gel.[3] This striking result was attributed to transannular interaction of the alkene and carbonyl moieties, as revealed by the significantly lower IR carbonyl absorption frequency for **6** *vis-à-vis* the *cis*-isomer (1657 *vs.* 1696 and 1671 cm$^{-1}$, respectively). The carbonyls in both **3** and **4** absorb at 1680



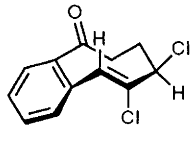
---

† The structure assigned to each new compound is in accord with its IR and high-field $^1$H (500 MHz) and $^{13}$C (125 MHz) NMR spectra, as well as appropriate parent ion identification by high-resolution mass spectrometry; *cis* and *trans* refer to the carbon skeleton. The numbering used is that of the cyclooctene unit.

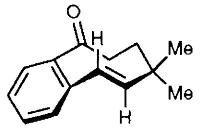
‡ Photolyses were carried out with a Hanovia 450-watt medium-pressure Hg vapour lamp suspended in a Pyrex immersion well.

§ The stereoselective formation of **3** will be discussed further in the full account of this work.

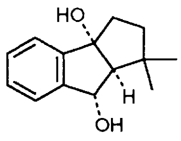
$cm^{-1}$; hence, the C(5) chlorine substituent appears to inhibit transannular interaction and diminish the reactivity of **3**.



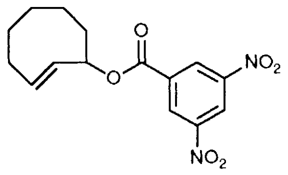
**5**



**6**



**7**



**8**

The crystalline photoproducts **2**–**4** proved suitable for single-crystal X-ray analyses.¶ Remarkably, the ring-fusion cyclopropane bond in **2** is slightly shorter than the average of the corresponding bond lengths for 79 *gem*-dichlorocyclopropanes in the Cambridge Crystallographic Data Base (1.508 *vs.* 1.524 Å), even though all the latter structures appear to be less strained than **2**. Of further interest was the structure of the *trans*-cyclooctene **3**. In the sole previous crystallographic study of a non-metallocomplexed *trans*-cyclooctene, Ermer elegantly demonstrated the importance of the out-of-plane bending contribution to the overall torsion about the *trans*-double bond in **8**.[4] Despite the strain induced by the three additional $sp^2$ centres, the C(3)–C(4)–C(5)–C(6) torsion angle in **3** is only 47°, with a C(5) out-of-plane bending contribution of 22°;‖ the corresponding values for **8** are 43 and 24°, respectively.

We thank the National Institutes of Health (grant CA-22807) for support.

*Received, 22nd June 1992; Com. 2/03272D*

## References

1 J. L. Wood, N. J. Liverton, M. Visnick and A. B. Smith, III, *J. Am. Chem. Soc.*, 1989, **111**, 4530.

2 H. Hart and M. Weiner, *Tetrahedron Lett.*, 1981, **22**, 3115.

3 M. Suzuki, H. Hart, E. Dunkelblum and W. Li, *J. Am. Chem. Soc.*, 1977, **99**, 5083.

4 (a) O. Ermer, S. A. Mason *Acta Crystallogr., Sect. B*, 1982, **38**, 2200. (b) O. Ermer, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 604.

---

¶ Compound **2**, $C_{12}H_{10}Cl_2O$, crystallized in the triclinic space group $P\bar{1}$ with $a = 5.859(1)$, $b = 8.516(1)$, $c = 11.377(2)$ Å, $\alpha = 91.6(2)$, $\beta = 84.05(2)$, $\gamma = 77.41(1)°$, $V = 550.3(3)$ Å$^3$, $Z = 2$, and $D_c = 1.455$ g $cm^{-3}$. The cell constants were determined from a least-squares fit of the setting angles for 25 accurately centred reflections. X-Ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) and the $\omega$–$2\theta$ scan technique. A total of 1926 reflections were measured over the ranges: $4 \leqslant 2\theta \leqslant 50°$, $0 \leqslant h \leqslant 6$, $-10 \leqslant k \leqslant 10$, $-13 \leqslant l \leqslant 13$. Three standard reflections measured after every 3500 s of X-ray exposure showed no intensity decay over the course of data collection. The intensity data were corrected for Lorentz and polarization effects but not for absorption. A total of 1602 unique reflections with $F^2 > 3\sigma(F^2)$ were used during subsequent structure refinement. The structure was solved by direct methods (MULTAN11/82). Refinement was by full-matrix least-squares techniques based on $F$ to minimize the quantity $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to $R = 0.038$ and $R_w = 0.057$.

Compound **3**, $C_{12}H_{10}Cl_2O$, crystallized in the monoclinic space group $P2_1/n$ (systematic absences $0k0$: $k$ = odd and $h0l$: $h + l$ = odd) with $a = 5.719(1)$, $b = 18.229(3)$, $c = 10.853(2)$ Å, $\beta = 101.01(1)°$, $V = 1110.6(6)$ Å$^3$, $Z = 4$, and $D_c = 1.442$ g $cm^{-3}$. A total of 1945 reflections were measured over the ranges: $4 \leqslant 2\theta \leqslant 50°$, $-6 \leqslant h \leqslant 6$, $0 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 12$. A total of 1005 unique reflections with $F^2 > 3\sigma(F^2)$ were used during subsequent structure refinement. Refinement converged to $R = 0.055$ and $R_w = 0.065$.

Compound **4**, $C_{12}H_{10}Cl_2O$, crystallized in the monoclinic space group $P2_1/n$ (systematic absences $0k0$: $k$ = odd and $h0l$: $h + l$ = odd) with $a = 6.241(1)$, $b = 21.534(2)$, $c = 8.483(1)$ Å, $\beta = 110.79(1)°$, $V = 1065.8(5)$ Å$^3$, $Z = 4$, and $D_c = 1.503$ g $cm^{-3}$. X-Ray intensity data were collected employing graphite-monochromated Cu-K$\alpha$ radiation ($\lambda = 1.54184$ Å) and the $\omega$–$2\theta$ scan technique. A total of 1814 reflections were measured over the ranges: $4 \leqslant 2\theta \leqslant 130°$, $0 \leqslant h \leqslant 7$, $0 \leqslant k \leqslant 25$, $-9 \leqslant l \leqslant 9$. A total of 1677 unique reflections with $F^2 > 3\sigma(F^2)$ were used during subsequent structure refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically with fixed $B$'s of 6.0 Å$^2$. Refinement converged to $R_0 = 0.056$ and $R_w = 0.073$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‖ The C(4) hydrogen atom was not refined in the X-ray structure of **3**; accordingly the C(4) out-of-plane bending, although presumably substantial, could not be quantified.