Tetrahedron. Vol. 29, pp 2699 to 2702 Pergamon Press 1973. Printed in Great Britain

THE STRUCTURES AND ULTRAVIOLET SPECTRA OF THE BROMINATION PRODUCTS OF 6,6-DIPHENYLFULVENE

P.-T. CHENG, P. A. GWINNER, S. C. NYBURG, R. R. STANFORTH and P. YATES*
Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario, Canada,
and Heidelberg College, Tiffin, Ohio, U.S.A.

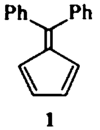
(*Received in the USA* 27 *November* 1972; *Received in the UK for publication* 30 *April* 1973)

Abstract – Bromination of 6,6-diphenylfulvene **1** gives *trans-trans-trans*-1,2,3,4-tetrabromo-1,2,3,4-tetrahydro-6,6-diphenylfulvene **3** via *trans*-1,2-dibromo-1,2-dihydro-6,6-diphenylfulvene **2**. Compound **3** in cyclohexane or carbon tetrachloride is converted by heating or exposure to sunlight to its *trans-cis-trans* stereoisomer **4**. The structures of **3** and **4** have been established by X-ray crystallography. Compound **3** is converted to a third stereoisomer **5** on standing in chloroform or dichloromethane solution. Anomalies in the ultraviolet spectra of **3**–**5** can be interpreted in terms of an interaction of the π system with the bromine atoms at C(1) and C(4). The formation of addition products from **1** is indicative of its olefinic rather than aromatic character.

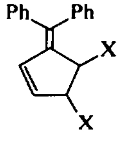
Bromination of 6,6-diphenylfulvene **1** has been reported to lead to both addition and substitution products.[1] We have reinvestigated this reaction because of interest in the question of the aromaticity of fulvenes.[2]

Treatment of **1** with 1 molar equivalent of bromine in carbon tetrachloride or cyclohexane gave the dibromo addition product **2**. Similar treatment of **1** or **2** with 2 or 1 molar equivalents of bromine, respectively, gave as the major product a tetrabromo addition product **3**. Compound **3** was converted in carbon tetrachloride or cyclohexane by exposure to sunlight or by heating under reflux to an isomer **4**. On standing in chloroform or dichloromethane solution, product **3** was converted to an isomer **5**. Compounds **4** and **5** accompanied **3** as minor products in the bromination of **1** and **2**. The gross structures of **2**–**5** were assigned on the basis of their NMR spectra (Table 1) and the observation that they regenerated **1** on treatment with sodium iodide in acetone. The stereochemistry of **3** and **4** have been determined by X-ray crystallography.

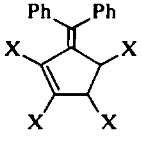
Compound **3** has clearly the *trans-trans-trans* structure and **4** the *trans-cis-trans* structure. The twist of the phenyl groups from the ethylenic plane are, for **3**, 60° each for **4**, 40° and 60°. The central C=C bonds are 1·37(2) and 1·39(2) A and the ethylenic systems are both closely planar, the biggest atomic deviations being 0·03 and 0·09 A. The five-membered ring in **3** is only slightly twisted from planar, but **4** is markedly non-planar.



1



2, X = Br
6, X = H



3–**5**, X = Br
7, X = H

Establishment of the *trans-trans-trans* structure for the initially formed tetrabromo product, **3**, is in accord with assignment of the anticipated *trans* stereochemistry to the dibromo product **2**. The NMR spectra of compound **5** show that the mole-

Table 1. PMR and CMR spectra of bromination products of 6,6-diphenylfulvene[a]

Compound	NMR Spectra	
2	$\delta_H^{CCl_4}$	5·18 (m, 2 H), 6·17 (ddd, J = 5·5, 2·5, 1 Hz, 1 H) 6·53 (dd, J = 5·5, 1 Hz, 1 H), 7·1–7·4 (m, 10H)
	$\delta_C^{CDCl_3}$	53·7 (d), 58·4 (d)
3	$\delta_H^{CCl_4}$	4·98 (t, $J_{12}+J_{13}$ = 2 Hz, 2 H), 5·63 (t, $J_{12}+J_{13}$ = 2 Hz, 2 H), 7·1–7·6 (m, 10 H)
	$\delta_C^{CDCl_3}$	51·9 (d), 54·9 (d)
4	$\delta_H^{CCl_4}$	4·98 (s, 4 H), 7·33 (s, 10 H)
	$\delta_H^{C_6H_6}$	4·68 (m), 5·03 (m)
	$\delta_C^{CDCl_3}$	52·3 (d), 58·4 (d)
5	$\delta_H^{CDCl_3}$	4·16 (dd, J = 10·5, 4·5 Hz, 1 H), 4·83 (dd, J = 10·5, 5·5 Hz, 1 H), 4·92 (dd, J = 4·5, 2·5 Hz, 1 H), 5·10 (dd, J = 5·5, 2·5 Hz, 1 H), 7·0–7·5 (m, 10 H)
	$\delta_C^{CDCl_3}$	50·1 (d), 55·8 (d), 56·0 (d), 59·1 (d)

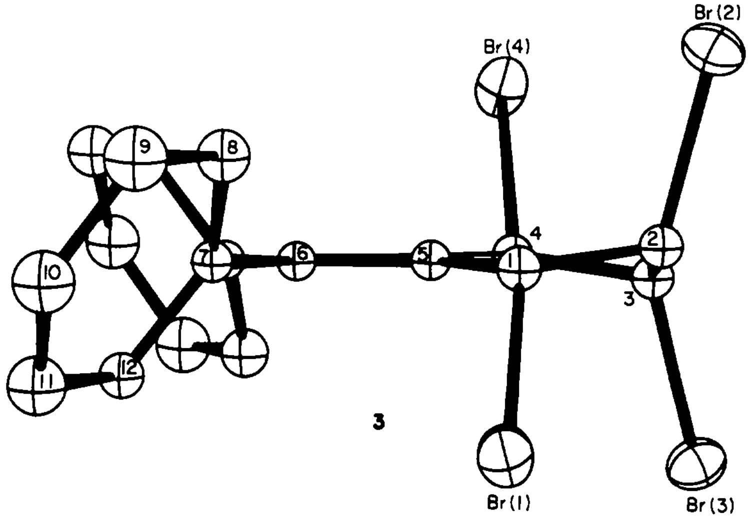
[a] PMR Spectra were recorded with Varian T-60 and HA-100 spectrometers and chemical shifts (δ_H) are reported in ppm downfield from TMS as internal standard. CMR spectra were recorded at 25·16 MHz with a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode. Chemical shifts (δ_C), which are reported in ppm downfield from TMS as internal standard, are given for the sp^3 carbons only; the multiplicities represent coupling (^{1}J) with directly bonded protons only.

cule lacks a plane or twofold axis of symmetry and it must be, therefore, one of the two unsymmetrical isomers, *trans-trans-cis* or *trans-cis-cis*.

The ultraviolet spectrum of **2** (Table 2) resembles that reported for the unbrominated analog **6** [$\lambda_{max}^{C_8H_{18}}$ 250 (ϵ 7,100), 290 nm (ϵ 19,500)[3]], but **3–5** show high intensity maxima in their ultraviolet spectra (Table 2) at considerably longer wavelength than the maximum in the spectrum of their unbrominated analog **7** [$\lambda_{max}^{C_8H_{18}}$ 250 nm (ϵ 14,500)[3]]. These bathochromic shifts are unexpected in that the divergence of the phenyl rings from coplanarity with the ethylenic double bond might be expected to be smaller for **7** than for **3–5**. This spectroscopic anomaly may have its origin in an interaction of the π-electron system with the bromine atoms at C(1)

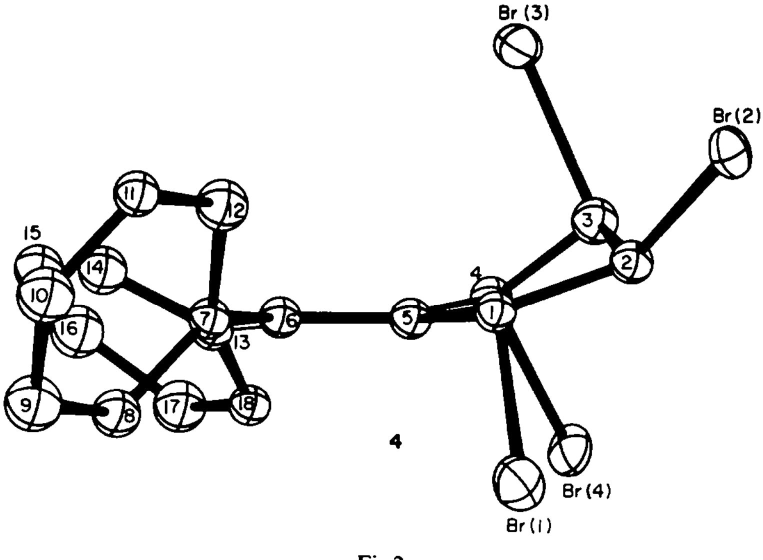
Table 2. Ultraviolet spectra of bromination products of 6,6-diphenylfulvene

Compound	$\lambda_{max}^{C_6H_{12}}$, nm ($\epsilon$)
2	245 (15,500), 305 (20,500)
3	232 (16,000), 305 (9,000)
4	226 (16,500), 292 (12,000)
5	227 (16,000), 294 (13,000)



3

Fig 1.



4

Fig 2.

and C(4) analogous to the interaction previously observed between the halogen atom and the carbonyl π-system in certain α-halocyclohexanones[4] that leads to a bathochromic shift of their $n \rightarrow \pi^*$ bands. This latter effect has been found to be dependent on an axial relationship between the carbon-halogen bond and the ring;[4] differences in the orientations of the carbon-bromine bonds at C(1) and C(4) in **3**–**5** together with variations in the orientations of the phenyl rings could account for the differences among their spectra.

The ready formation of addition products from **1** is indicative of olefinic rather than aromatic character, in accord with the conclusion reached on other grounds[2] that fulvenes are non-aromatic. The courses of the interconversions of the three tetrabromo products are under further investigation.

EXPERIMENTAL

M.ps are uncorrected. Spectroscopic data are given in Tables 1 and 2.

trans-1,2-*Dibromo*-1,2-*dihydro*-6,6-*diphenylfulvene* (**2**). Bromine (0·707 g, 0·00442 mole) in CCl_4 (15 ml) was added with stirring in 60 min to 6,6-diphenylfulvene[3] (1·02 g, 0·00442 mole) dissolved in CCl_4 (20 ml). After bromine addition was complete, most of the solvent was evaporated under vacuum to yield brown-yellow crystals (67%). Recrystallization twice from hexane-petroleum ether (b.p. 30–60°) gave pale yellow crystals of **2**, m.p. 104·5–106° (dec). (Calc. for $C_{18}H_{14}Br_2$: C, 55·38; H, 3·58; Br, 41·04. Found: C, 55·57; H, 3·68; Br, 41·01%).

trans-trans-trans-1,2,3,4-*Tetrabromo*-1,2,3,4-*tetrahydro*-6,6-*diphenylfulvene* (**3**). Bromine (2·82 g, 0·0176 mole) in CCl_4 (35 ml) was added with stirring in 7 min to 6,6-diphenylfulvene (2·00 g, 0·00868 mole) dissolved in CCl_4 (30 ml). After bromine addition was complete, the reaction mixture was stirred for 15 min. Most of the CCl_4 was removed under vacuum to yield small yellow crystals (69%). Recrystallization from petroleum ether (b.p. 60–70°) gave pale yellow plates of **3**, m.p. 120–121·5° (dec). (Calc. for $C_{18}H_{14}Br_4$: C, 39·27; H, 2·55; Br, 58·15. Found: C, 39·44; H, 2·64; Br, 57·94%). Analysis of the CCl_4 filtrate by PMR showed the product distribution to be 75% **3**, 6% **4**, and 7% **5**. Similar results were obtained in either the presence or absence of room light. Compound **3** was also formed as the major product when the dibromo compound **2** was treated with one molar equivalent of bromine under similar conditions.

trans-cis-trans-1,2,3,4-*Tetrabromo*-1,2,3,4-*tetrahydro*-6,6-*diphenylfulvene* (**4**). (a) A solution of **3** (0·99 g) in cyclohexane (50 ml) was stirred in the absence of light for 1 h at 72–76°. Removal of most of the cyclohexane under vacuum led to yellow crystals (84% **4** and 16% **3** as determined by PMR spectroscopy). Recrystallization from petroleum ether (b.p. 60–70°) yielded yellow crystals of **4**, m.p. 141·5–143° (dec). (Calc. for $C_{18}H_{14}Br_4$: C, 39·27; H, 2·55; Br, 58·15. Found: C, 39·37; H, 2·62; Br, 58·15%). Analysis of the cyclohexane filtrate by PMR spectroscopy showed the product distribution to be 66% **4**, 16% **3**, and 5% **2**.

(b) A solution of **3** (0·85 g) in CCl_4 (40 ml) was stirred in the absence of light for 3 h at 73–75°. Concentration of the reaction mixture and analysis by PMR showed 62% **4**, 28% **5**, and 10% **3**. Compound **2** was not detected as in (a) above.

Unsymmetrical 1,2,3,4-*tetrabromo*-1,2,3,4-*tetrahydro*-6,6-*diphenylfulvene* (**5**). (a) A solution of 1·00 g of **3** in 15 ml of $CHCl_3$ (0·75% EtOH) was stirred for 3 hr. HBr fumes were detected as the reaction proceeded. Removal of the solvent under vacuum led to a viscous, brown-orange residue. Treatment with petroleum ether (b.p. 60–70°) caused the formation of small brown crystals of **5** (24%). Recrystallization twice from petroleum ether (b.p. 60–70°) yielded orange-yellow crystals of **5**, m.p. 134·5–135·5° (dec). (Calc. for $C_{18}H_{14}Br_4$: C, 39·27; H, 2·55; Br, 58·15. Found: C, 39·37; H, 2·64; Br, 58·09%). Further work-up of the petroleum ether filtrates yielded only tarry material.

(b) A solution of **3** (0·90 g) in CH_2Cl_2 (15 ml) was stirred for 5·5 h. During the course of the reaction, HBr fumes were detected. Evaporation of most of the CH_2Cl_2 under vacuum yielded a clear orange oil. Addition of a small portion of petroleum ether (b.p. 60–70°) caused the formation of orange crystals of **5** (49%). Recrystallization from petroleum ether (b.p. 60–70°) gave orange-yellow crystals of **5**, m.p. 134·5–136° (dec). Work-up of the petroleum ether filtrate yielded only tarry material.

Isomerizations carried out in presence of sunlight. A nearly saturated CCl_4 solution of **3** was exposed to sunlight for approximately 5 h. PMR of the reaction mixture showed 67% **4** and 33% **5**. After 5 h exposure to sunlight, a nearly saturated solution of **3** in cyclohexane was observed to undergo complete conversion to **4** as indicated by PMR. A CCl_4 solution of **3** remained unchanged after 14 days storage in the dark.

Regeneration of 6,6-*diphenylfulvene from its bromination products.* Treatment of the four brominated fulvene products **2**–**5** with NaI/acetone solution (one I^- per Br atom) readily led to the deposition of a yellowish solid in each case. This was filtered and washed with CCl_4; a red filtrate was obtained, and analysis by PMR demonstrated the presence of only 6,6-diphenylfulvene.

Crystallography. Data were collected with filtered Cu-Kα radiation by a Canberra-automated Picker diffractometer (θ-2θ scan, $\sin\theta \leq 0{\cdot}89$). The number of observed reflections with $F \geq \sigma(F)$ were 1345 (**3**) and 1464 (**4**). Both structures were solved by direct methods using TANFOR (TANgent FORmula Refinement Program),[5] and refined (anisotropically for bromine atoms only) by full matrix least squares. The final residuals were 9·6 (**3**) and 8·7% (**4**). Crystal data: **3**, Monoclinic, a = 12·93(2), b = 8·64(1), c = 17·89(2) Å, β = 112·59(1)°, Z = 4; space group, Cc or C2/c (latter confirmed); molecular symmetry: diad. **4**, Orthorhombic, a = 9·13(1), b = 22·14(3), c = 9·03(1) Å, Z = 4; space group, Pnam or Pna2_1 (latter confirmed); molecular symmetry: none.

Acknowledgements—We thank the National Research Council of Canada for support of part of this work. One of us (P.A.G.) expresses his appreciation to Messrs. L. Silbert and E. Voightman, students at The Summer Organic Chemistry Institute, The Choate School, Wallingford, Conn., U.S.A., for their early participation in this work.

REFERENCES

[1] J. Thiele, *Ber.* **33**, 666 (1900); J. Thiele and H. Balhorn, *Ann.* **348**, 1 (1906); E. Bergmann and A. F. v. Christiani, *Ber.* **63**, 2559 (1930); J. H. Day and C. Pidwerbesky, *J. Org. Chem.* **20**, 89 (1955)

[2] Cf. P. Yates, *Adv. Alicyclic Chem.* **2**, 59 (1968)

[3] J. L. Kice and F. M. Parham, *J. Amer. Chem. Soc.* **80**, 3792 (1958)

[4] H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962, p. 181

[5] M. Drew, unpublished