

## Studies in the Cyclopropane Series: Acid-catalysed and Thermal Decompositions of 1,1-Dichloro-2,5-diphenylcyclopropabenzene

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1,1-Dichloro-2,5-diphenylcyclopropabenzene (1) readily decomposes in solution in halogenomethanes giving the isomeric tropones (4) and (5), and (*E*)-2,2'3,3'-tetrachloro-4,4',7,7'-tetraphenyl-1,1'-bicycloheptatrienyliene (8). On mild thermolysis in solution, compound (1) affords a mixture of two dimers, the 1,1'-bicycloheptatrienyliene (8) and an unidentified isomer.

THE reactivity associated with 1,1-dichloro-2,5-diphenylcyclopropabenzene (1)<sup>1</sup> has been utilised in the production of other *gem*-disubstituted derivatives by replacement reactions.<sup>2,3</sup> These processes are best rationalised as involving ionisation to give the corresponding cyclopropabenzonium ion which has been independently characterised.<sup>4</sup> Despite the facility with which these substitution reactions can be effected, the chemistry of the cyclopropabenzene (1) is complicated by its ready decomposition under a variety of conditions. We have reported previously on the rapid formation of orthoesters and carboxylate esters from compound (1) in alcoholic media,<sup>1</sup> and we present here the results of studies on the decomposition of 1,1-dichloro-2,5-diphenylcyclopropabenzene (1) induced by acid and by heat.

The <sup>1</sup>H n.m.r. spectrum obtained from compound (1) in deuteriochloroform (or dichlorodideuteriomethane) is

<sup>1</sup> B. Halton and P. J. Milsom, *Chem. Comm.*, 1971, 814; B. Halton, P. J. Milsom, and A. D. Woolhouse, *J.C.S. Perkin I*, 1977, 731.

<sup>2</sup> B. Halton, A. D. Woolhouse, and P. J. Milsom, *J.C.S. Perkin I*, 1977, 735.

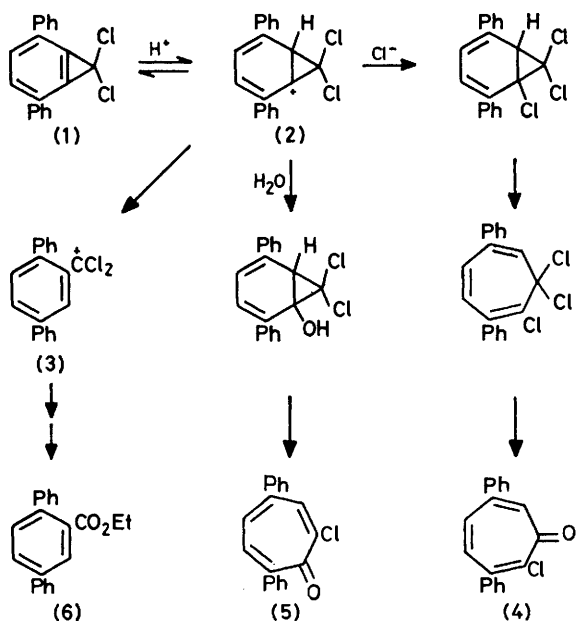
very dependent on the age of the solution. When run immediately, the spectrum is fully consistent with the cyclopropabenzene structure.<sup>1</sup> However, after as short a time as 5 min, changes are apparent and new signals appear in the range  $\delta$  6.2–7.2; the decomposition is essentially complete in 2 days. Repetition on a preparative scale (in freshly distilled chloroform) has led to the isolation of three new compounds, two of which have been identified as C<sub>19</sub>H<sub>13</sub>ClO species, and the third as a pale yellow dimer of compound (1) [dimer (A), C<sub>38</sub>H<sub>24</sub>Cl<sub>4</sub>, 33%] by high resolution mass spectrometry. The two isomeric species, formally derived from the cyclopropabenzene (1) by loss of hydrogen chloride and gain of water, are considered to be 2-chloro-3,6-diphenyltropone (4) (29%) and 2-chloro-4,7-diphenyltropone (5) (3%), principally on the basis of spectroscopic data. In particular, both compounds show high energy carbonyl

<sup>3</sup> P. Müller, *Helv. Chim. Acta*, 1974, **57**, 704; *J.C.S. Chem. Comm.*, 1973, 895.

<sup>4</sup> B. Halton, H. M. Hügel, D. P. Kelly, P. Müller, and U. Burger, *J.C.S. Perkin II*, 1976, 258.

stretching bands at *ca.* 1 620  $\text{cm}^{-1}$  (*cf.* ref. 5), and their u.v. spectra are similar to that for 4-bromo-2,7-diphenyl-tropone.<sup>6</sup> The  $^1\text{H}$  n.m.r. spectrum of the tropone (4) shows the AB component of an ABX system centred at  $\delta$  7.2 with the outer two downfield lines obscured by the phenyl proton signal ( $\delta$  7.3–7.6); the  $\text{H}_\text{X}$  resonance also lies under the phenyl proton envelope. In the spectrum of the tropone (5), however, only the  $\text{H}_\text{X}$  signal is visible ( $\delta$  7.19), and coupling to only one proton ( $J$  *ca.* 1.5 Hz) is apparent.

The formation of the tropones (4) and (5) from compound (1) is readily explained by the presence of traces of acid in the solvents. Electrophilic addition ( $\text{H}^+$ ) to the strained bridge-bond of the cyclopropabenzene (1) would afford the carbocation (2), which is capable of capture by chloride ion or water to give the observed products.<sup>7-9</sup> Furthermore, the product ratio



SCHEME 1

of the tropones (4) and (5) is unaltered when carefully dried solvents are employed. These observations lend further support to the assignment of the major tropone product as the isomer (4) generated by chloride ion incorporation (Scheme 1).

When compound (1) was treated with chloroform saturated with dry hydrogen chloride an immediate deep yellow colour was generated. Work-up afforded a mixture of the tropones (4) and (5) (30%), analogous to that described above, and ethyl 2,5-diphenylbenzoate (6) (20%); no dimeric material was isolated. Although the ester (6) could arise by ionisation of compound (1)

and capture of the cyclopropabenzenylium ion thus generated by the ethanol stabiliser in the solvent,<sup>1,4</sup> the failure to detect terphenic acid or the ester (6) in the product mixture from work-up of the decomposition of (1) in ethanol-free chloroform argues strongly in favour of the intervention of the benzylic ion (3) (Scheme 1). Nucleophilic capture of the cation (3) by chloride ion or, less likely, ethanol, and subsequent solvolysis readily accounts for the formation of compound (6). Thus, under these latter conditions, the behaviour of compound (1) closely parallels that for *gem*-difluorocyclopropabenzene (8).<sup>8</sup>

On mild heating in solution (benzene or acetone), compound (1) affords two sparingly soluble crystalline products, each of which has been identified as a dimer of the *gem*-dichlorocyclopropabenzene (1) by high resolution mass spectrometry; a mixture of the same compounds is produced when solutions of (1) are kept at ambient temperatures for periods in excess of 30 days. Dimer (A) (52%) is pale yellow, whereas dimer (B) (32%) is deep yellow; because of their extremely limited solubility in organic solvents the only efficient method of obtaining pure samples involves separation of the crystals by hand. Dimer (A) is identical with the dimeric compound obtained from the decomposition of the cyclopropabenzene (1) in chloroform.

Crystallographic data have now shown<sup>10</sup> dimer (A) to be (*E*)-2,2',3,3'-tetrachloro-4,4',7,7'-tetraphenyl-1,1'-bicycloheptatrienyldiene (8) in which the two seven-membered rings are bent up from the plane of the exocyclic double bond and face one another at an angle of *ca.* 100°. This novel conformation, in which conjugation across the exocyclic double bond is interrupted, explains the lack of colour and accounts for the unexpected mass

## Spectroscopic data of the dimers (A) and (B)

	Pale yellow dimer (A), the bicyclohepta- trienyldiene (8)	Bright yellow dimer (B)
<i>m/e</i>	620/622/624/626/628 ( $M^+$ ), 550 [( $M - \text{Cl}_2$ ) <sup>+</sup> , 100%], 310 (11%)	620/622/624/626/628 ( $M^+$ ), 550 [( $M - \text{Cl}_2$ ) <sup>+</sup> , 100%], 310 (11%)
$\lambda_{\text{max.}}/\text{nm}^a$	238 (log $\epsilon$ 4.61), 310 (4.46), 345sh (4.36)	243 (log $\epsilon$ 4.47), 297 (4.22), 343 (4.25)
$\nu_{\text{max.}}/\text{cm}^{-1}^b$	1 585, 1 485, 1 022, 830, 764, 750, 695, 685	1 595, 1 500, 1 030, 775, 750, 695, 685
$\delta_\text{H}$ ( $\text{CD}_2\text{Cl}_2$ )	6.16 (2 H, d, $J$ 6.5 Hz), 6.76 (2 H, d, $J$ 6.5 Hz), 7.05 (10 H, m), 7.44 (6 H, m), 7.85 (4 H, m)	6.16 (2 H, d, $J$ 6.5 Hz), 6.54 (2 H, d, $J$ 6.5 Hz), 7.08 (10 H, m), 7.42 (10 H, m)
$\delta_\text{C}$ ( $\text{CS}_2$ )	121.7, 128.3, 128.6, 129.0, 129.7, 130.0, 138.1, 140.2, 140.4, 141.2	121.7, 127.9, 128.8, 129.5, 138.6, 140.1, 140.4, 141.0

<sup>a</sup> In tetrahydrofuran. <sup>b</sup> KBr disc.

spectral fragmentation pattern (Table);<sup>11</sup> the base peak ( $m/e$  550) corresponds to the loss of two chlorine atoms rather than a symmetrical cleavage ( $m/e$  310). The

<sup>10</sup> J. A. Fahey, personal communication.

<sup>11</sup> W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, 1969, **91**, 6391; R. C. Joines, A. B. Turner, and W. M. Jones, *ibid.*, p. 7754; J. A. Meyers, R. C. Joines, and W. M. Joines, *ibid.*, 1970, **92**, 4740.

<sup>5</sup> L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' 3rd edn., Chapman and Hall, London, 1975, p. 172.

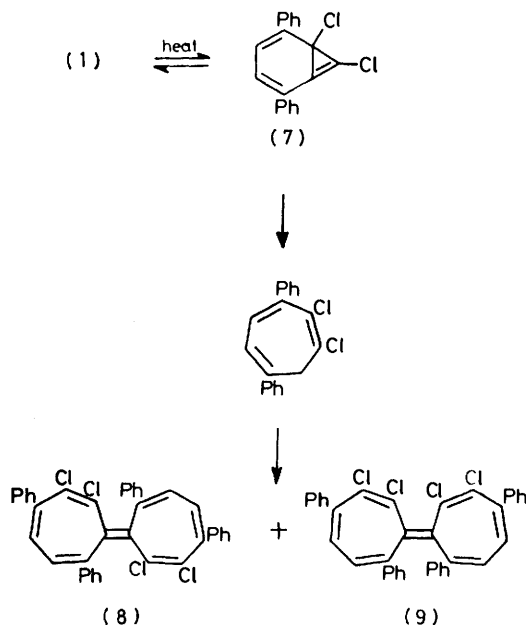
<sup>6</sup> T. Mukai, *Bull. Chem. Soc. Japan*, 1958, **31**, 852.

<sup>7</sup> E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Letters*, 1965, 3625.

<sup>8</sup> E. Vogel, personal communication.

<sup>9</sup> S. Korte, Ph.D. Thesis, University of Köln, 1965.

formation of the bicycloheptatrienyliene (8) can be rationalised by invoking a 1,2-chloride ion shift to give the bicyclo[4.1.0]hepta-2,4,6(7)-triene (7) and subsequent carbene formation (Scheme 2). The structure of dimer (B) remains unknown since the spectroscopic data (Table) do not allow for differentiation between a conformational isomer of the bicycloheptatrienyliene (8), a distorted conformation of bicycloheptatrienyliene (9), or a tricyclo[7.5.0.0<sup>2,8</sup>]tetradecahexaene formed *via* the cyclic allene<sup>12</sup> derived from compound (7).



SCHEME 2

## EXPERIMENTAL

Microanalyses were performed by Professor A. D. Campbell and his associates, Otago University, Dunedin, and high resolution mass measurements were obtained with an A.E.I. MS902 instrument by Dr. G. J. Wright, Canterbury University. I.r. spectra were recorded for KBr discs with a Unicam SP 200 or SP 1000 spectrophotometer unless otherwise stated, and u.v. spectra with a Shimadzu UV200 instrument. N.m.r. spectra were recorded on a hybrid HA-60 Digilab-PDP-15 spectrometer<sup>13</sup> operating in the F.t. mode at 60 MHz for <sup>1</sup>H and 15.08 MHz for <sup>13</sup>C. For the latter nucleus a spectral width of 5 kHz, a pulse angle of 40°, and a recycle time of 5 s were employed. Field stabilisation was provided by a concentric capillary of [<sup>2</sup>H<sub>6</sub>]acetone. <sup>13</sup>C Chemical shifts are quoted to within  $\pm 0.2$  p.p.m. from internal tetramethylsilane. Merck Kieselgel GF254 was used for t.l.c. and preparative plates (1 m  $\times$  20 cm) were made to a thickness of 0.75 mm.

**Decomposition of 1,1-Dichloro-2,5-diphenylcyclopropabenzene (1) in Chloroform.**—(a) A solution of the cyclopropabenzene (1)<sup>1</sup> (0.71 g, 2.3 mmol) in freshly distilled chloroform (10 cm<sup>3</sup>) was kept in the dark for 60 h. Concentration under vacuum afforded a yellow solid, which was subjected to preparative t.l.c. (benzene–light petroleum,

2:1). Band A (*R<sub>F</sub>* 0.9) [extracted with chloroform–benzene (1:1; 200 cm<sup>3</sup>)] gave (*E*)-2,2',3,3'-tetrachloro-4,4',7,7'-tetraphenyl-1,1'-bicycloheptatrienyliene (8) [dimer (A)] (0.23 g, 32%), m.p. 328–330° (Found: C, 73.0; H, 4.05; Cl, 22.7; *M*<sup>+</sup>, 620.063 081. C<sub>38</sub>H<sub>24</sub>Cl<sub>4</sub> requires C, 73.3; H, 3.9; Cl, 22.8%; *M*, 320.063 188) (for spectroscopic data see Table). Band B (*R<sub>F</sub>* 0.3) [extracted with chloroform–benzene (1:1; 200 cm<sup>3</sup>)] gave a yellow oil which solidified at –20 °C. Two recrystallisations from ethyl acetate gave 2-chloro-3,6-diphenylcyclohepta-2,4,6-trienone (4) (0.190 g, 29%) as pale yellow needles, m.p. 133–134° (Found: *M*<sup>+</sup>, 292.066 088. C<sub>18</sub>H<sub>13</sub><sup>35</sup>ClO requires *M*, 292.065 488);  $\nu_{\text{max}}$ , 1 620, 1 600, 765, 750, and 700 cm<sup>–1</sup>;  $\lambda_{\text{max}}$  (cyclohexane) 242sh (log  $\epsilon$  3.91), 272 (4.08), and 328 nm (3.46);  $\delta$  (CD<sub>2</sub>Cl<sub>2</sub>) 7.2 (2 H, AB of ABX) and 7.4–7.5 (11 H, m). Concentration of the mother liquors from band B (above) to dryness and recrystallisation of the residue from ethanol afforded 2-chloro-4,7-diphenylcyclohepta-2,4,6-trienone (5) (0.025 g, 3%) as yellow needles, m.p. 82–83° (Found: *M*<sup>+</sup>, 292.066 364. C<sub>19</sub>H<sub>13</sub><sup>35</sup>ClO requires *M*, 292.065 488);  $\nu_{\text{max}}$  (Nujol) 1 615, 780, 760, and 690 cm<sup>–1</sup>;  $\lambda_{\text{max}}$  (cyclohexane) 226sh (log  $\epsilon$  4.11), 284 (4.21), and 335 nm (3.80);  $\delta$  (CD<sub>2</sub>Cl<sub>2</sub>) 7.19 (1 H, X of ABX) and 7.42 (12 H, m).

(b) To chloroform (5 cm<sup>3</sup>) saturated with dry hydrogen chloride was added compound (1) (0.10 g, 3.23 mmol). The deep yellow solution was kept at ambient temperature for 4 h, washed successively with water (2  $\times$  10 cm<sup>3</sup>), sodium hydroxide (2M; 2  $\times$  10 cm<sup>3</sup>), and water (10 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), and concentrated in vacuum to give a yellow oily solid. Preparative t.l.c. (benzene–light petroleum, 2:1) gave three bands (A–C) which were extracted with chloroform (100 cm<sup>3</sup>). Band A (*R<sub>F</sub>* 0.9) gave 5 mg of unidentified material. Band B (*R<sub>F</sub>* 0.6) gave an oil identified as ethyl 2,5-diphenylbenzoate (6) (19 mg, 20%) by comparison with a sample prepared from (1).<sup>1</sup> Band C (*R<sub>F</sub>* 0.2–0.3) afforded a pale yellow solid (28 mg, 30%) identical with the material from band B in (a).

**Thermal Decomposition of 1,1-Dichloro-2,5-diphenylcyclopropabenzene (1).**—A solution of 1,1-dichloro-2,5-diphenylcyclopropabenzene (1) (0.50 g, 1.61 mmol) in benzene (10 cm<sup>3</sup>) was heated under reflux for 6 h. The cooled solution was kept at room temperature for 2 days, after which two distinct crystalline species had been deposited. Filtration, followed by separation of the crystalline species by hand, gave the bicycloheptatrienyliene (8) [dimer (A)] (0.13 g, 52%) as large pale yellow prisms, m.p. and mixed m.p. 328–330°, and dimer (B) (0.08 g, 32%) as deep yellow prisms, m.p. 327–330° (Found: C, 73.2; H, 4.05; Cl, 22.5; *M*<sup>+</sup>, 620.062 074. C<sub>38</sub>H<sub>24</sub>Cl<sub>4</sub> requires C, 73.3; H, 3.9; Cl, 22.8%; *M*, 620.063 188) (for spectroscopic data see Table).

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<sup>12</sup> P. W. Dillon and G. R. Underwood, *J. Amer. Chem. Soc.*, 1974, **96**, 779; W. R. Dolbier, O. T. Garza, and B. H. Al-Sader, *ibid.*, 1975, **97**, 5038; *Tetrahedron Letters*, 1976, 887.

<sup>13</sup> M. K. Dewar, R. B. Johns, D. P. Kelly, and J. F. Yates, *Austral. J. Chem.*, 1975, **28**, 917.