

## 7,7-Dichloro-2,5-diphenylbenzocyclopropene

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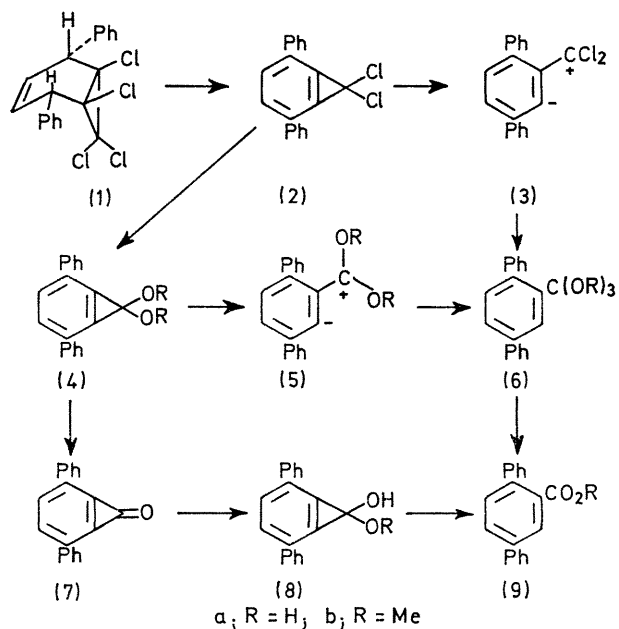
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**Summary** 7,7-Dichloro-2,5-diphenylbenzocyclopropene is formed by dehydrohalogenation of 1,6,7,7-tetrachloro-2,5-diphenylbicyclo[4,1,0]hept-3-ene in aprotic solvent whereas its solvolytic ring cleavage product, trialkyl 2,5-diphenylortho-benzoate, is formed in alcoholic media.

ALTHOUGH benzocyclopropene<sup>1</sup> and several of its derivatives<sup>2</sup> have been synthesised, the only hitherto known *gem*-dihalogeno-compound was 7,7-difluorobenzocyclopropene prepared by dehydrobromination of 1,6-dibromo-7,7-difluorobicyclo[4,1,0]hept-3-ene.<sup>3</sup> The *gem*-dichloro-compounds, having more labile carbon-halogen bonds, might be expected to undergo either easy solvolysis to benzocyclopropenones by analogy with 1,2-diaryl-3,3-dichlorocyclopropenes,<sup>4,5</sup> or solvolytic ring cleavage to acids or esters by analogy with tetrachloro- and 1-aryltrichloro-cyclopropenes.<sup>5-7</sup> We now report the preparation of 7,7-dichloro-2,5-diphenylbenzocyclopropene (2) and some of its solvolysis reactions.

Addition of tetrachlorocyclopropene<sup>6,8</sup> to *trans,trans*-1,4-diphenylbutadiene gave (1)† [ca. 85%; m.p. 174–175°] (see Scheme). Dehydrochlorination of (1) with a slight excess of potassium *t*-butoxide in tetrahydrofuran gave a single product identified as (2)‡ [ca. 80%; m.p. 134–136° (decomp.);  $\delta$  (CCl<sub>4</sub>) 7.30–7.50 (6H, m), 7.70–7.88 (4H, m), and 7.70 (2H, s),  $\lambda_{\max}$  (cyclohexane) 316 nm (log  $\epsilon$  4.67);  $\nu_{\max}$  (Nujol) 1685, 760, and 715 cm<sup>-1</sup>] from its spectral data and by analogy of its mode of preparation with that of 7,7-difluorobenzocyclopropene.<sup>3</sup> Treatment of (1) with an excess of potassium hydroxide in 30–70 v/v dry benzene-methanol afforded two products; the major component (ca. 90%) has been identified as the ortho ester (6b), m.p. 102–103°, and the minor component (ca. 5%) as the acid (9a).<sup>9</sup> The ortho ester was stable to base but underwent acid hydrolysis to give the benzoate (9b) which on base

hydrolysis gave (9a) (see Scheme). Reaction of (1) with sodium methoxide in the same solvent system gave (6b) in essentially the same yield but only traces of carboxylic acid



SCHEME

were obtained. The formation of these products can be rationalised as dehydrochlorination of (1) to give (2) which, under these conditions, undergoes solvolytic ring cleavage.

In methanol, (2) rapidly (< 5 min) gave the benzoate (9b) but with excess base (KOH, NaOMe, or Et<sub>3</sub>N) the

† Satisfactory microanalytical and spectral data were obtained for all new compounds reported.

‡ A mass value accurate to 2.5 p.p.m. was obtained for C<sub>19</sub>H<sub>12</sub><sup>35</sup>Cl<sub>2</sub> (MS 902).

ortho ester (**6b**) was formed in quantitative yields. It is significant that reaction of (**2**), and dehydrochlorination of (**1**), with HO<sup>-</sup>-MeOH yield only ortho ester. The ketone (**7**), formed by solvolysis of (**2**) by hydroxide ion, is unlikely to be involved since benzocyclopropenone is known<sup>10</sup> to undergo ring opening to methyl benzoate in methanol. However, addition of solvent to the *gem*-dichloro-compound (**2**), or to the species (**3**) produced by ring cleavage,<sup>10</sup> would be followed by simple solvolysis of the benzylic chlorine atoms and formation of the ortho ester (**6b**). An equally valid and alternative mechanism involves the solvolysis of

(**2**) to give the acetal (**4b**) which would afford (**6b**), either *via* (**5b**) or by direct solvent addition. In the absence of base the acid generated in the solvolysis of (**2**) is available to catalyse decomposition of the ortho ester to benzoate by moisture.‡

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‡ In one n.m.r. experiment a little methanol was added to a solution of (**2**) in CDCl<sub>3</sub> and the initial formation of the ortho ester was confirmed by the appearance of the characteristic methoxy-resonance at  $\delta$  3.07.

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