

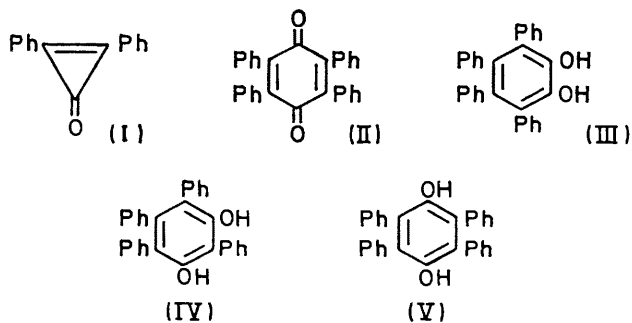
## The Dimerization and Rearrangement of Diphenylcyclopropenone: a Re-evaluation

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**Summary** The bimolecular reduction of diphenylcyclopropenone yields tetraphenylresorcinol rather than tetraphenylcatechol as previously reported: the reaction involves the rearrangement of a cyclopropene derivative to a *meta*-substituted benzene.

REARRANGEMENTS of appropriately substituted cyclopropenes to *ortho*- and *para*-substituted benzenes have



been described by several authors<sup>1,2</sup> in recent years. We report what we believe to be the first example of such a rearrangement to a *meta*-substituted benzene under mild conditions and, in the process, correct an earlier structural assignment.

The reduction of diphenylcyclopropenone (I) by various dissolving metals (*e.g.* Mg-MgI<sub>2</sub> in refluxing ether-benzene) has been reported<sup>3</sup> to yield small amounts of tetraphenylcyclopentadienone and tetraphenyl-*p*-benzoquinone (II) plus a major product which has been assigned structure (III). Evidence for the formation of (III) rested largely on "characteristic pyrocatechol tests" and oxidation of the product to tetraphenylcyclopentadienone. The deduction based on the latter reaction, and the structural assignment in general, seemed rather tenuous in view of the results reported by Güsten *et al.*<sup>4</sup>

We have carried out the reduction under similar conditions (Al-Hg in refluxing ethanol-benzene)<sup>5</sup> and obtained, along with (II), a product which was identical in physical properties (m.p., elemental analysis, i.r., u.v., and n.m.r. spectra) with the substance purported to be (III). Furthermore, the reduction product and its diacetate† derivative

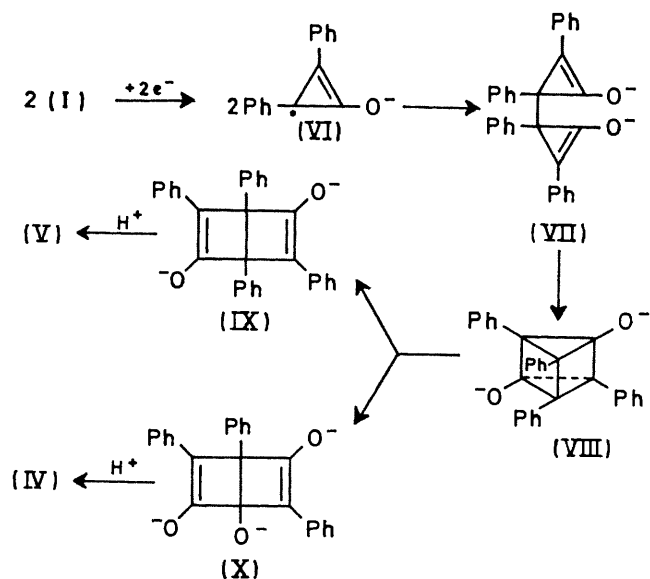
† Satisfactory elemental analysis was obtained for this new compound.

were also found to be identical in all respects (m.p., mixed m.p., i.r., and n.m.r. spectra) with authentic samples of tetraphenylresorcinol<sup>4</sup> (IV) and its diacetate. That the substance is indeed (IV) rather than (III) is amply confirmed by its n.m.r. spectrum (CDCl<sub>3</sub>) which exhibited singlets at  $\tau$  4.88 (2H, disappeared on addition of D<sub>2</sub>O), 3.15 (5H), and 2.83 (10H), as well as a multiplet at  $\tau$  2.48 (5H). Such a spectrum is consistent with structure (IV) which contains *three different sets of aromatic hydrogens* (ratio of 5:10:5), but not with structure (III) for which only *two resonance lines* (ratio of 10:10) in the aromatic region would be predicted.†

There are several possible mechanisms which can be formulated to rationalize the conversion of (I) into (II) and (IV). One of the more attractive of these (analogous to a mechanism suggested by Breslow *et al.*<sup>1</sup>) is presented in the Scheme. Electron transfer from the metal to (I) generates the radical anion (VI).<sup>6,7</sup> This species has available to it a number of options,<sup>8</sup> one of which is dimerization to the pinacolate anion (VII).§ Ring-closure to the prismane (VIII) followed by rearrangement to the "Dewar benzenes" (IX and X) and final ring-opening yields the products (IV) and (V),¶ after proton abstraction.

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SCHEME

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† Extension of this argument to the case of (V) leads to the prediction of a single aromatic absorption (20H) in the n.m.r. spectrum of this compound. In agreement with this, we have observed the following n.m.r. (CDCl<sub>3</sub>) absorptions for (V):  $\tau$  5.40 (s, OH, 2H) and 2.77 (s, aromatic, 20H).

§ Anion (VII) can have two stereoisomers, but only one isomer will lead to the *meta*- and *para*-substituted products isolated if the above mechanism is assumed. Such stereospecificity has been observed in other bimolecular reductions<sup>9</sup> and been implied in the case of certain cyclopropenyl rearrangements.<sup>1</sup>

¶ (V) is readily oxidized to (II) under the conditions of the reaction.

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<sup>3</sup> N. Toshima, I. Moritani, and S. Nishida, *Bull. Chem. Soc. Japan*, 1967, **40**, 1245.

<sup>4</sup> H. Güsten, G. Kirsch, and D. Schulte-Frohlinde, *Tetrahedron*, 1968, **24**, 4393.

<sup>5</sup> M. S. Newman, *J. Org. Chem.*, 1961, **26**, 582.

<sup>6</sup> H. O. House, "Modern Synthetic Reactions," Benjamin, New York, 1965, p. 61.

<sup>7</sup> R. C. Fuson, *Record Chem. Prog.*, 1951, **12**, 1.

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<sup>9</sup> W. E. Bachmann and R. V. Shankland, *J. Amer. Chem. Soc.*, 1929, **51**, 306.