

## The Reaction of *o*-Benzoquinone with Cyclopentadiene

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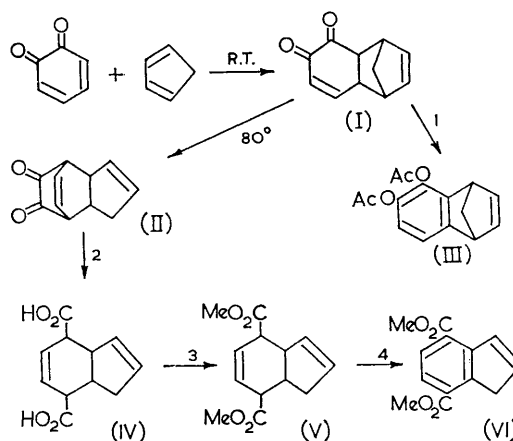
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EVANS, WILGUS, and GATES report<sup>1</sup> the reaction of *o*-benzoquinone and cyclopentadiene to form an adduct to which they assign structure (I). In support of this structure they describe the conversion of 4-substituted analogues of (I) into the aromatic compounds analogous to (III) by treatment with acetic anhydride and pyridine. Ansell and Gosden<sup>2</sup> have questioned this structure and suggested instead that the adduct has structure (II) and that the formation of (III) is due to a Cope rearrangement prior to aromatisation.

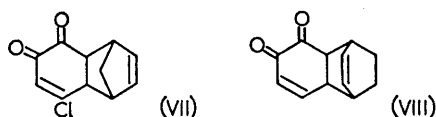
The reaction of cyclopentadiene with *o*-benzoquinone in benzene solution at room temperature yields (I) (m.p. 89–91°). The n.m.r. spectrum (CDCl<sub>3</sub>) alone [singlet (2)  $\tau$  8.37; complex multiplet (4)  $\tau$  6.35–6.90; multiplet (2)  $\tau$  3.93; doublet (1)  $\tau$  3.66 ( $J = 10$  c./sec.); double doublet (1)  $\tau$  2.82, 2.76 ( $J = 10$  c./sec.)] is sufficient to confirm the structure proposed by Evans *et al.* (I) forms the expected quinoxaline derivative (m.p. 147–149°) with *o*-phenylenediamine and the spectra characteristics of this compound give further support to the structure of (I). The aromatisation to form (III) proceeds readily as reported for analogous compounds by Evans.<sup>1</sup> When (I) is heated in benzene solution it is converted into the more stable (II) (m.p. 139–141°). This may involve a dissociation followed by re-addition or a rearrangement. Evidence for the structure we assign to (II) comes from its n.m.r. spectrum (CDCl<sub>3</sub>) [broad multiplet (6),  $\tau$  6.3–8.0; multiplet (2)  $\tau$  4.1–4.55; multiplet (2)  $\tau$  3.70] particularly, the chemical shift of the olefinic protons. Comparison of the ultraviolet spectra of (I) and (II) [ $\lambda_{\max}$  (EtOH) 238  $\mu\mu$ ,  $\epsilon = 4906$ ;  $\lambda_{\max}$  435  $\mu\mu$ ,  $\epsilon = 8.13$  for (I);  $\lambda_{\max}$  (EtOH) 214  $\mu\mu$ ,  $\epsilon = 1428$ ;  $\lambda$  453  $\mu\mu$ ,  $\epsilon = 44.75$  for (II)] further supports our structural assignments. (II) forms the expected quinoxaline derivative (m.p. 159–160°) and on oxidation with hydrogen peroxide yields acid (IV) (m.p. 192–200°). The acid was converted into its methyl ester (V) [b.p. 186–188°/20 mm., n.m.r. (CDCl<sub>3</sub>) broad multiplet (4)  $\tau$  7.0–8.0, singlet with upfield shoulder (8),  $\tau$  6.30, singlet (2)  $\tau$  4.25, singlet (2)  $\tau$  4.01] which was brominated with *N*-bromosuccinimide. The brominated product was dehydrobrominated by treatment with triethylamine to yield the indene derivative (VI) {m.p. 104–106°; n.m.r. (CCl<sub>4</sub>) multiplet (2)

$\tau$  6.29, singlet (6)  $\tau$  6.09, multiplet (1)  $\tau$  3.22, multiplet (1)  $\tau$  2.34, doublet (1)  $\tau$  2.26 [ $J = 9$  c./sec.], doublet (1)  $\tau$  2.06 [ $J = 9$  c./sec.]}.

(II) treated with acetic anhydride and pyridine, under the conditions which converted (I) into (III), was recovered unchanged. Ansell and Gosden questioned the structure of (I) on the basis of experiments with 4-substituted *ortho*-quinones. 4-Chloro-*o*-benzoquinone reacts with cyclopentadiene in benzene solution at room temperature to yield (VII) (m.p. 56–57°) exactly analogous to (I). Similarly, *o*-benzoquinone reacts with cyclohexa-1,3-diene to yield (VIII) (m.p. 125–127°). The structures of these two compounds are authenticated by comparison of the properties and spectra with those of (I).



R.T. = Room temperature; 1, Ac<sub>2</sub>O—C<sub>5</sub>H<sub>5</sub>N; 2, H<sub>2</sub>O<sub>2</sub>; 3, CH<sub>2</sub>N<sub>2</sub>; 4, *N*-Bromosuccinimide—Et<sub>3</sub>N.



Differences between this work and that of previous workers may be attributable to the fact that all these experiments were performed using freshly prepared, recrystallised *o*-benzoquinone<sup>3</sup> and not *o*-benzoquinone prepared *in situ* by silver oxide oxidation.

In a private communication, Dr. M. F. Ansell informs us that he and his colleagues have isolated

compounds of type (I) from the reaction of 4-alkylbenzoquinones with cyclopentadiene.

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<sup>1</sup> F. J. Evans, H. S. Wilgus, and J. W. Gates, *J. Org. Chem.*, 1965, **30**, 1655.

<sup>2</sup> M. F. Ansell and A. F. Gosden, *Chem. Comm.*, 1965, 520.

<sup>3</sup> L. Horner and W. Duerckheimer, G.P. 1,126,852 (*Chem. Abs.*, 1962, **57**, 8504).