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DIELS-ALDER REACTIONS OF O-BENZOQUINONES

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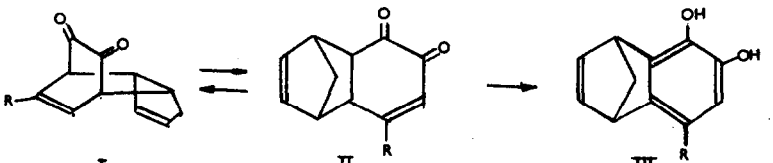
The Diels-Alder reactions of substituted o-benzoquinones with cyclopentadiene can lead to products of type (I) and type (II). It was pointed out in our previous communication[1] that these two structures might be interconvertible by a Cope rearrangement. Thus any evidence as to the structure of such an adduct based on aromatisation (II → III) must be cautiously interpreted.



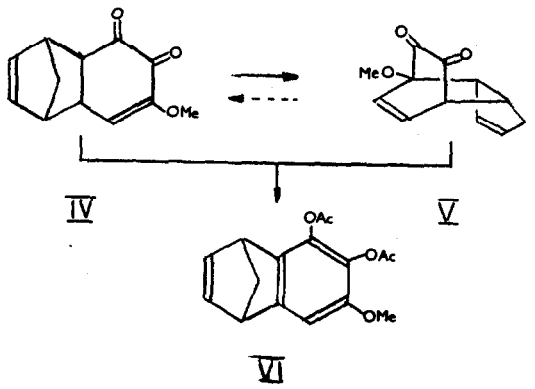
I II III

The structures of the adducts isolated from the reaction of cyclopentadiene with o-benzoquinone, 4-methyl- and 4-phenyl-o-benzoquinone were assigned[2] structures (II; R = Me or Ph) respectively. These observations have been confirmed by Tedder[3], Wilgus[4], and by our own observations. Tedder[3] has also reported the facile conversion of the adduct (II; R = H) in to the adduct (I; R = H). The latter has been previously reported[5] as the hydrolysis product of the adduct from cyclopentadiene and 2,2-diacetoxycyclohexa-2,5-dien-1-one.

We now report the results we have obtained (see table below) from the reactions of a number of substituted o-benzoquinones with cyclopentadiene.

Except in the case of 3-phenyl-, 3-methyl and 3,6-dimethyl-o-benzoquinone adducts of type (II) have been isolated, many of which (see table) have been thermally rearranged in boiling benzene to compounds of type (I). The latter type of compound has also been isolated directly from the reaction in the case of 3-methyl-, 3-methoxy-, 3-chloro-, 3-phenyl-, and 3,5-dimethyl-o-benzoquinone. The proportions of the two types of product in the crude reaction mixtures have been estimated by comparison of the n.m.r. spectra of

the crude products with those of the appropriate pure adducts, except in the reaction of 3-phenyl-, 3-methyl- and 3,6-dimethyl- o-benzoquinone, where use was made of the n.m.r. spectra of appropriate model compounds.



As stated above the products (IV) and (V) were isolated from the reaction of 3-methoxy-o-benzoquinone and cyclopentadiene. The adduct (IV) when boiled in benzene for 2 hours, was converted essentially quantitatively into the adduct (V), the rearrangement being followed by I.R. spectroscopy (of the carbonyl region). When this rearrangement was performed in the presence of two molar equivalents of maleic anhydride, no cyclopentadiene maleic anhydride adduct was detectable by n.m.r. examination of the material obtained on evaporation of the benzene solution. This result substantiates our view, expressed earlier, that such rearrangements are intramolecular and not retro-Diels-Alder reactions followed by recombination. The reversibility of the rearrangement is demonstrated by the observation that when the adduct (V) is heated with acetic anhydride and pyridine at 100° for 2 hours, it is converted, essentially quantitatively into the aromatised product (VI), presumably via the adduct (IV) which is also converted into the compound (VI) under the same conditions. The adduct (IV) is stable in ether solution at room temperature (the reaction conditions) for at least four days. This suggests that the product ratio in the initial Diels-Alder reaction is kinetically determined. In all cases so far examined, the adducts of type (I) are the thermodynamically stable products.

TABLE I

Reactions of o-Benzoquinone with Cyclopentadiene

Substituted o-Benzoquinone	Estimated Product Composition		Product(s) Isolated From Reaction*		Rearrangement Product (Type II→ Type I m.p.
	Type II	Type I	Type II	Type I	
o-Benzoquinone	-	-	32% (89-91°)	-	139-141°(a)
4-Methyl	95%(b)	5%	40% (79-80°)	-	91- 93°
4-Phenyl	85%	15%	60% (121-123°)	-	101.5-102.5°
4-Methoxy	100%	-	74%(102-103°)	-	-
4-t.Butyl	85%	15%	48% (77-78°)	-	98-99°
3-Methyl	65%	35%	-	20% (118-119°)	-
3-Methoxy	60%	40%	55% (95-96°)	18% (110-111°)	110-111°
3-Phenyl	40%	60%	-	55% (145-146°)	-
3-Chloro	50%	50%	45% (82-83°)(c)	15% (145-146°)	145-146°
3-Isopropyl	80%	20%	43% (82-83°)	-	125-127°
3,4-Dimethyl	85%	15%	35% (76-82°)	-	107-108°
3,5-Dimethyl	65%(d)	35%	17% (88-89°)	20% (117-118°)	117-119°
3,6-Dimethyl	15%	85%	-	38% (154-155°)	-

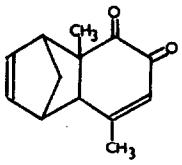
* Yields based on catechols - m.p. in parenthesis.

(a) m.p. 139-141° ref.[3].

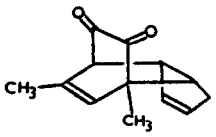
(b) reported[4] 85:15.

(c) solidifies after melting and remelts at 145-146°.

(d) addition to 3,4-double bond.



VII



VIII

When 3,5-dimethyl-o-benzoquinone acts as a dienophile towards cyclopentadiene, the adduct (VII) is formed by cyclo-addition to the 3,4- and not to the 5,6- double bond. This was determined by comparison of the n.m.r. spectrum of this product with those of other methyl-substituted adducts of type (II). The adduct (VII) obtained in this reaction may be thermally converted into the adduct (VIII). The latter compound and the adduct (I; R = Me) appear to be identical with those obtained by Wessely[5] directly from the appropriate reaction using a high-temperature work-up procedure.

These results clearly demonstrate the duality of behaviour of o-benzoquinones towards cyclopentadiene.

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