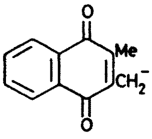
Cage Formation: a New Reaction of Quinones with Carbanions

By FRANCIS M. DEAN, LEONARD E. HOUGHTON, RASSOUL NAYYIR-MAZHIR, and CHACHANAT THEBTARANONTH
(*The Robert Robinson Laboratories, The University of Liverpool, Liverpool* L69 3BX)

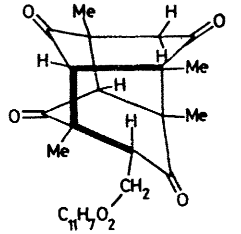
Summary Generated in methanol under controlled basicity, carbanions react with 2,5- or 2,6-dimethyl-1,4-benzoquinone to give cage tetraketones related to 1,4,7-[1]-ethyl[2]ylidenenaphthalene or to benz[1,2-*a*; 3,4-*g*]-azulene.

THE carbanion (**1**), which is generated from the requisite indazole derivative[1] (0·04 M) by treatment with sodium acetate trihydrate (0·2 M) in the presence of a four-fold excess of 2,5-dimethyl-1,4-benzoquinone (0·16 M) in methanol, adds 2 mol of the quinone to give the cage product (**2**) (20%) and 3 mol to give a more complex compound (50%) not considered here. The cage product (**2**) contains no hydroxy group, is yellow, and exhibits i.r. and ^{1}H n.m.r. characteristics that define the presence of the 2-methyl-1,4-naphthoquinone residue.[1] Otherwise the carbonyl groups absorb at 1735 and 1720 cm^{-1} (KBr) and the methyl protons all resonate as singlets at fields above δ 1·4 ($CDCl_3$). It follows that all the ethylenic links of the benzoquinone residues have vanished and consequently that a cage structure must have been formed. The carbonyl i.r. bands are at somewhat high frequencies consistent with their incorporation in six-membered rings subject to strain,[2] but still below those typical of five-membered rings. Only the electron shifts indicated in (**3**) lead to a cage devoid of five-membered rings as shown in structure (**2**). The substituents can be placed easily because the n.m.r. spectrum includes an AB quartet (δ 2·92 and 2·46, *J* 19 Hz) and an ABX spin system [δ 2·71, 2·76 (AB), and 3·68 (X); J_{AX} 7, J_{BX} 9 Hz] in which the X part is at a rather low field because of deshielding by the quinone grouping as in a model system.[1]

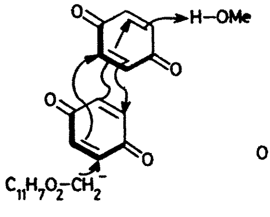
Under similar conditions the carbanion (**1**) reacts with an excess of 2,6-dimethyl-1,4-benzoquinone to give a bridged quinone product (aldol), not a cage.[3] In very dilute sodium hydroxide, however, the reaction does produce a cage product which has structure (**4**) and spectroscopic properties very similar to those of the isomer (**2**). A major difference is a carbonyl band at 1760 cm^{-1} with relative intensity 1 (compared with 3 for bands at 1740 and 1725 cm^{-1} combined). Thus the new product contains at least one cyclopentanone residue. Of the two possible cages limited to one such residue, only that shown in (**4**) affords a structure that can also satisfactorily explain the n.m.r. spectrum. Again a methylene quartet (δ 2·70 and 2·32, *J* 19 Hz) and an ABX spin system define the positions for the substituents, but the X part is at a much higher field (δ 2·98) than in isomer (**2**) and a shielding of *ca.* 0·7 p.p.m. must be accounted for. Structure (**4**) places the X proton immediately below a carbonyl group and at a distance (2 Å) from it that would produce such a shift.[4] The only possible cage structure containing two cyclopentanone rings fails to explain this shift and requires others not found. Hence we reject it notwithstanding the i.r. absorption at 1740 cm^{-1} approaches that (1750 cm^{-1}) observed in some related cage cyclopentanones.[3,5]


($C_{11}H_7O_2$-CH_2^-)

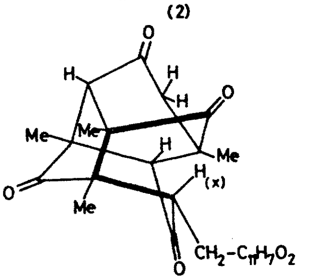
(1)



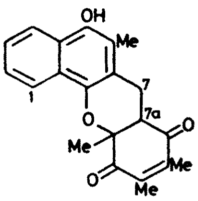
(2)



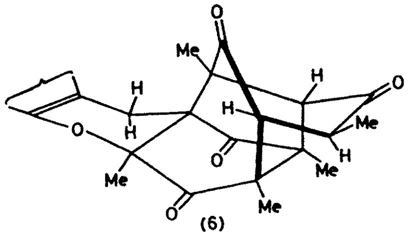
(3)



(4)



(5)



(6)

We have been unable to obtain a cage product from the reaction between the carbanion (**1**) and trimethylbenzoquinone alone. This reaction gives the xanthen derivative (**5**) readily, however, and removal of a proton from position 7a now leaves a carbanion[6] that does afford a cage with 2,5-dimethylbenzoquinone though not with the 2,6-dimethyl isomer. The product (**6**) has the spectroscopic properties of the 6-hydroxychroman species; in particular, its aromatic, methyl, and ring methylene protons all give signals that are (reversibly) greatly broadened by trifluoroacetic acid.[7] Carbonyl absorption bands appear at 1760, 1730, and 1720 cm^{-1} ($CHCl_3$), but decisions as to ring sizes are complicated since one carbonyl group has an adjacent phenoxy substituent that could raise its frequency.[8] Models show that the phenoxy group must lie at a considerable angle (*ca.* 45°) to the carbonyl plane; hence any rise in frequency will be small and we conclude that the cage product does contain one cyclopentanone ring. The skeleton in structure (**6**) best explains the n.m.r. details satisfactorily. There is now an Me·CH group evidenced by a methyl doublet (*J* 7 Hz) and a (broadened) methine quartet. One methine singlet appears at δ 2·8 as do similar protons in the other cage products, but a second resonates at higher field (2·19); moreover, decoupled spectra show that this signal is a doublet (*J* 2 Hz) because of interaction with the Me·CH methine proton (torsional angle *ca.* 60°). The high field is due to the location above, but not precisely over, a carbonyl group. The orientation of the secondary methyl group is assumed to avoid crowding with methyl groups on the ring below.

Though many reactions between carbanions and quinones have been described,[9] cage products have not been observed previously. The main reason, we think, is that the conditions have generally been alkaline enough to decompose them, or (in some cases) not alkaline enough to reverse the aldol condensations that are preferred kinetically. The nature and orientation of the cage products appears to be determined by the methyl substituents, possibly in charge-transfer complexes that act as intermediates; thus collisions prevent cage formation from two trimethylbenzoquinone rings, while two 2,5-dimethylbenzoquinone rings can fit together readily, other cases being intermediate.

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