The Diels–Alder Reactions of 1,2-Naphthaquinones with 2,3-Dimethylbutadiene

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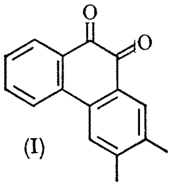
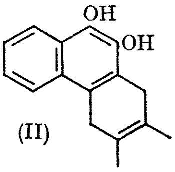
Summary 1,2-Naphthaquinones react with dimethylbutadiene to give either tetrahydro-9,10-phenanthraquinones or spirodihydropyrans.

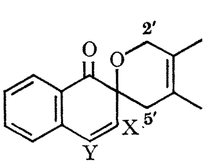
IT has been stated[1] that "1,2-naphthaquinone . . . is an extremely sensitive compound and gives with dienes reaction mixtures of a most unpromising nature." With the exception of a reported adduct formed with levopimaric acid, no Diels–Alder reactions involving 1,2-naphthaquinone have been reported. We now report that pure 1,2-naphthaquinone reacts readily with 2,3-dimethylbutadiene (used in excess) in boiling chloroform solution to give 2,3-dimethyl-9,10-phenanthraquinone (I). The reaction is considered to proceed *via* the primary adduct which then enolises to yield the aromatic compound (II). Such compounds have been observed[2] to dehydrogenate readily, thus producing the phenanthrene-9,10-diol which by aerial oxidation[3] yields the phenanthraquinone (I).

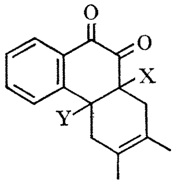
With the exception of 3,7-dimethyl-,[1] 4-benzyl-,[4] 4-diethoxycarbonylmethyl-,[4] and 4-cyanomethyl-1,2-naphthaquinones,[5] the only other naphthaquinones reported to undergo the Diels–Alder reaction are[6] the 3-bromo-, 3-chloro-, 4-chloro-, and 3,4-dichloro-1,2-naphthaquinones. We have previously confirmed[7] that the 3-chloroquinone does form the expected primary adduct but in contrast we now report that addition to the 3,4-double bond does not occur when either the 4-bromo-, 4-chloro-, or 3,4-dichloro-1,2-naphthaquinones react with dimethylbutadiene. In each case addition occurs to the 2-carbonyl group to yield the spirodihydropyrans (IIIa, b, c). The adduct from the 3,4-dichloroquinone shows only a single carbonyl absorption at 1700 cm.^{-1} and its n.m.r. spectrum shows in addition to the four aromatic protons (δ 8·0—7·2), the 2′-protons as an AB quartet [δ 4·89 and 4·20$|J|$16 Hz.], the 5′-protons as a broad singlet (δ 2·40) and the 3′- and 4′-methyl groups as a broad singlet (δ 1·63). The thermal conversion of (IIIc) into the naphthodioxan (IV) [no carbonyl absorption, n.m.r. δ 8·2—7·15 (m, 7, 8, 9, and 10-H), 5·1 and 4·95 (broad singlets, CH_2), 4·41 and 4·04 (AB q,$|J|$11·5 Hz. (3-H_2), 1·86 (pair of doublets, $|J|$3 and 1 Hz., vinyl-Me), 1·52 (s, 2-Me)] is confirmation of the structure.

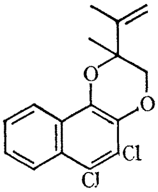
The crystalline adducts from 4-chloro- and 4-bromo-1,2-naphthaquinone have the spirodihydropyran structures (IIIa) and (IIIb), respectively. In both cases no other adduct could be detected spectroscopically in the crude reaction product. This is the first time that the formation of a spirodihydropyran has been reported from a monohalogenated quinone, and the result is in contrast to the report[6] that the 4-chloroquinone with dimethylbutadiene gives 2,3-dimethyl-9,10-phenanthraquinone in low yield. Both the adducts (IIIa) and (IIIb) had, with the exception of the chemical shift of the 3-proton, essentially the same n.m.r. spectra [δ 7·2—8·0 (m, 5, 6, 7, and 8-H), 6·28 (s, 3-H in chloro adduct), 6·52 (s, 3-H in bromo adduct), 4·89 and 4·20 (AB q, |J| 16 Hz., 2'-H_2), 2·40 (br s, 5'-H_2), and 1·62 (br s, 3'- and 4'-Me)].

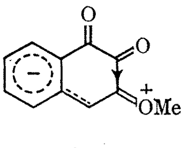

(I)


(II)


(III) a; X=H, Y=Cl
b; X=H, Y=Br
c; X=Y=Cl
d; X=OMe, Y=H,


(V) a; X=OMe, Y=H
b; X=H, Y=CN
c; X=CO_2Me, Y=H
d; X=NO_2, Y=H


(IV)


(VI)

The previous examples[8] of the non-photochemical additions of dienes to the carbonyl group of *o*-quinones have involved tetrahalogeno-*o*-benzoquinone and such reactions are considered to depend on the electron-withdrawing powers of the halogen atom. It is for this reason that we consider that the cycloaddition occurs at the 2-carbonyl group since only this carbonyl group is conjugated to the halogen atom in the 4-position.

The previously unreported reaction between 3-methoxy-1,2-naphthaquinone leads to the formation of a mixture (94% yield) of the adduct (Va) (75%) arising from addition to the 3,4-bond and the adduct (IIId) (25%) arising from addition to the 2-carbonyl group. This latter result is the first example of the non-photochemical addition of a diene to the carbonyl group of a non-halogenated quinone. We consider that in this case the known electron-withdrawing inductive effect of the methoxy-group is enhanced due to the contribution to the ground-state of canonical form (VI). The structure of the adduct follows from its spectroscopic properties [carbonyl absorption 1690 cm.$^{-1}$, n.m.r. δ 7·82 (d, |J| 8 Hz., 8-H), 7·6—6·9 (m 5, 6 and 7-H), 5·63 (s 4-H), 4·63 and 4·14 (AB q, |J| 15 Hz. 2'-H_2), 3·80 (s, OMe), 2·63 and 2·02 (AB q, |J| 17 Hz. 5'-H_2), 1·64 (br s 3'- and 4'-Me)].

In compounds derived from 1,2-naphthaquinones in which there is a carbonyl group at C-1 but no halogen at C-4 the peak due to the 8-proton is distinct from the other aromatic protons and occurs between δ 7·67 and 8·15 due to the deshielding of the 1-carbonyl group. An ether oxygen at the peri-position would not be expected to have a comparable deshielding effect. The observation that the peak due to the 8-proton is at δ 7·95 in the 3-methoxy-1,2-naphthaquinone and at δ 7·82 in the adduct (IIId) together with the observation that the 4-proton appears at lower field in the parent quinone than in the adduct (δ 6·42 and 5·63, respectively) supports the conclusion that the diene has added to the 2-carbonyl group as shown. The structure of adduct (IIIc) is similarly supported by the fact that the peak due to the 3-proton in the adduct (δ 6·28) is at higher field than that (δ 6·79) of the 3-proton in the parent quinone.[9]

The Diels–Alder reactions of 1,2-naphthaquinones having electron-withdrawing groups other than halogen directly attached to the quinonoid ring have not been previously reported. We now record that 4-cyano- and 3-methoxycarbonyl-1,2-naphthaquinone readily undergo addition to the 3,4-bond to give the adducts (Vb) and (Vc) whose spectroscopic properties are in accord with these structures. 3-Nitro-1,2-naphthaquinone also undergoes this reaction. This is novel for although the nitro-olefins are known dienophiles,[10] as far as we are aware no stable adduct containing angular nitro-groups have previously been prepared [carbonyl absorption 1750 and 1690 cm.$^{-1}$, n.m.r. δ 8·15 (pair of doublets, |J| 7·5 and 2 Hz., 8-H, 7·9—7·1 (m, 5, 6, and 7-H), 4·07 (pair of doublets, |J| 12 and 6 Hz., 4a-H), 3·5—1·8 (m, 1 and 4-H_2), 1·78 (br s, 2-Me), 1·61 (br s, 3-Me)].

The adduct (Vd) on heating in boiling mesitylene loses nitrous acid to give 2,3-dimethyl-9,10-phenanthraquinone.

Satisfactory analyses were obtained for all new compounds and all integrations in the reported n.m.r. spectra were consistent with the assignments made.

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