Tetrahedron Vol. 27, pp. 4883 to 4887. Pergamon Press 1971. Printed in Great Britain

PHOTOCHEMICAL ADDITION OF TETRAMETHYLALLENE TO 1,4-QUINONES

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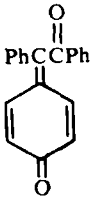
(*Received in Japan* 17 *June* 1971; *Received in the UK* 30 *June* 1971)

Abstract—The photochemical reaction of tetramethylallene with 1,4-benzoquinone and 1,4-naphthoquinone forms 1:1 adducts whose structures were assigned as 1,1,3,3-tetramethyl-5-hydroxyindan-2-one and 1,1,3,3-tetramethyl-5-hydroxy-1*H*-benz[e]inden-2-one, respectively. Methylenoxetane 3, would be an intermediate, which rearranges to phenol derivatives as in case of dienone-phenol rearrangement.

The photochemistry of mixtures of 1,4-quinones and olefinic or acetylenic compounds has shown that two major reaction pathways are available.[1] The first involves cycloaddition of the carbonyl function to the unsaturated C–C bond to give the oxetanes[2] or their rearranged products,[3] and the second involves cycloaddition of the ring double bond of 1,4-quinones to a C—C double or triple bond.[4] Recently, Arnold *et al.*[5] and Hammond *et al.*[6] have found that allenes undergo photochemical cycloaddition to aldehydes and ketones to form oxetanes. In some cases the latter in turn reacts with the carbonyl compounds giving 1:2 adducts, dioxaspiro[3.3]heptane derivatives. However, there is no report on the photochemical cycloaddition of 1,4-quinones to allenes. It is known that the photochemical addition of diphenylacetylene to 1,4-benzoquinone yielded a 1:1 adduct of structure **1**.[3a] The oxetane adduct **2** was postulated as an intermediate in this process. The photoaddition of allenes to the carbonyl group of 1,4-quinones might afford the valence isomer of **2** involving an exocyclic double bond, which might yield a rearranged product. For these reasons the photoaddition of tetramethylallene to 1,4-benzoquinone and 1,4-naphthoquinone was considered to be an attractive subject.



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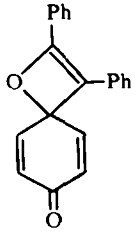

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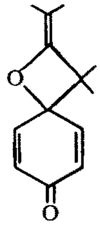
RESULTS AND DISCUSSION

Photoaddition of tetramethylallene to 1,4-benzoquinone and 1,4-naphthoquinone was carried out in benzene or dioxane solution with a medium pressure mercury arc filtered through a Pyrex reaction vessel. In each case, only one product was isolated in significant quantity which was shown to be a 1:1 adduct of 1,4-quinone and tetramethylallene on the basis of elemental analysis and molecular weight determination.

The adducts exhibited a single strong CO absorption at 1735–1745 cm^{-1}, suggestive of the 5-membered ring ketone[7] and exhibited a broad OH absorption at 3300–3400 cm^{-1}. The UV spectrum of the adduct from 1,4-benzoquinone exhibited maximum at 286 nm suggesting the presence of alkyl phenol moiety.[8] The UV spectrum of the adduct from 1.4-naphthoquinone exhibited maxima at 233 (log ε 3·49), 305 (2·78), 320 (2·72), 334 nm (2·70), a pattern which indicates the presence of 1-naphthol moiety.[9] The presence of the OH group in the adduct was confirmed by formation of acetate with acetic anhydride, whose IR spectrum did not show the OH absorption band. The NMR spectrum of the adduct with 1,4-benzoquinone exhibited the benzene ring proton at δ 6·75 (2H) and 7·15 (1H) correspondent with the ABX system. The adduct showed a strong singlet resonance of the Me proton at δ 1·24 (12H), indicating the Me group adjacent to a saturated C atom. The resonance of OH proton at δ 8·25 disappeared in the acetate of this adduct, which showed the Me resonance of the acetyl group at δ 2·20. The NMR spectrum of the adduct with 1,4-naphthoquinone showed a multiplet at δ 7·5–8·5 (5H), a singlet at 6·77 (1H), and two singlets at 1·65 and 1·37 due to the Me proton. These results indicate clearly that the photochemical adducts of tetramethylallene with 1.4-quinones do not have both the methyleneoxetane structures **3** or **4** as the photoadduct of allenes with ketones[5,6] and the cyclobutene moiety **5** as the photoadduct of alkynes with methoxy-1,4-benzoquinone.[4] Refluxing the photoadduct under acidic condition resulted in the recovery of the photoadduct, indicating that there is no oxetane moiety in 1:1 adduct since hydrolytic cleavage of the adduct of allenes with ketones gives the original ketone and the ketone that is formally derived by addition of the elements of water to the allene.[5,6] From the presence of the phenol or 1-naphthol function and the cyclopentanone moiety in the adducts, the structures of the adducts were assigned as 1,1,3,3-tetramethyl-5-hydroxy-indan-2-one, **6** and 1,1,3,3-tetramethyl-5-hydroxy-1*H*-benz[e] inden-2-one, **7**. To confirm the presence of indanone structure in the photoadduct, 1,1,3,3-tetramethyl-indan-2-one, **8*** was synthesized according to Bruson's method.[10] The IR spectrum of **8** ($\nu_{C=O}$ 1730 cm^{-1}) is consistent with that of **6** except for the absorption bands due to the presence of the OH group (ν_{OH} and $_{C-O}$). The NMR spectrum of **8** exhibited a singlet Me resonance at δ 1·32. These results support the contention that the photo-



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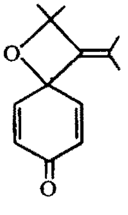

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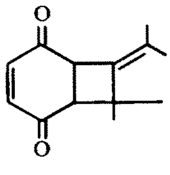

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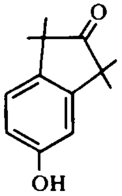
* An attempt to prepare **6** or methoxy analog of **6** failed using phenol or anisole in place of benzene as a starting reagent.

products of tetramethylallene with 1,4-benzoquinone and 1,4-naphthoquinone are 6 and 7·



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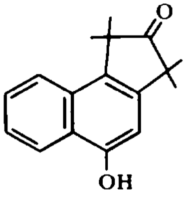

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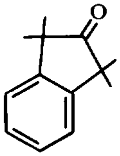

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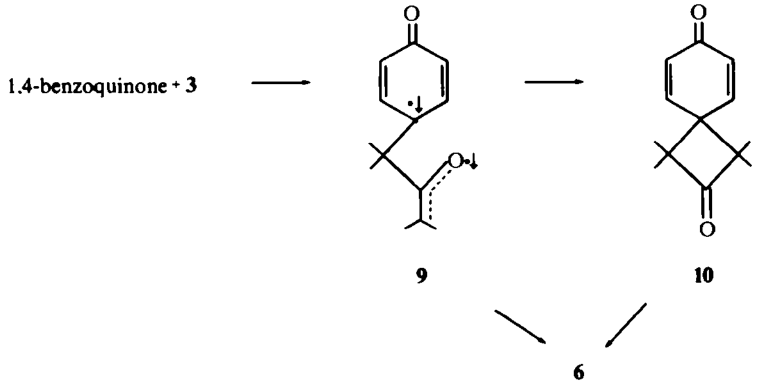
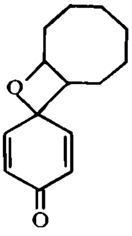
The OH proton resonance of 7 in NMR spectrum was not observed clearly. However, addition of deuterium oxide showed a decrease of proton integration in the phenyl proton region from 5*H* to 4*H*, indicating that the OH proton is superimposed in the naphthalene ring proton. The proton resonance of 7 at δ 7·5–8·5 would be assigned to the protons at C-6, C-7, C-8, and C-9 of the naphthalene ring and that at δ 6·77 to the proton at C-4. The Me proton of 6 was observed as a singlet, while the Me proton of 7 was detected as two singlets. We believe that in 7 the resonance at δ 1·65 can be attributed to the Me proton at C-1, since the deshielding effect in 1-Me proton in naphthalene derivative is known,[11] the Me protons of 7 at C-1 would resonate downfield from the Me protons at C-3.

The lowest triplet energies of 1,4-benzoquinone and 1,4-naphthoquinone in n–π* configuration are 50[12] and 57 kcal/mole.[13] Hammond *et al.* pointed out that the triplet





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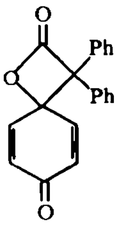

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excitation energy of allene is significantly greater than 74 kcal/mole.[6] In the photochemical cycloaddition reactions of CO compounds and alkenes, it is well established that only CO compounds having the n–π* configuration in their lowest triplet states show high reactivity and cycloaddition occurs only if transfer of triplet excitation from the CO compounds to olefinic compounds is inefficient because of the higher excitation energy of alkene.[1,14] Consequently, the addition of CO triplet of 1,4-quinones to tetramethylallene would occur to form **3**, which was never isolated from the reaction mixture. This adduct would be expected to have a triplet excitation energy similar to that of 2,5-cyclohexadienone derivatives (67–71 kcal/mole)[15] whereas the triplet energy of 1,4-quinones used is 50–57 kcal/mole. The difference in the excitation energies of about 15 kcal/mole causes the difficulty of energy transfer to be competitive with cycloaddition to the allene. 1,4-Quinones serve as the sensitizers forming **9** which would rearrange to **6** directly and/or *via* **10**. The formation of cyclobutanone derivatives is reported in the photochemical addition of allenes to fluronone.[6] Since the photochemical rearrangement of 2,5-cyclohexadienones to the phenol derivatives is well known[16] and the formation of phenol derivative from **11**[3(b)] and **12**[17] is documented, the intermediate **10** would rearrange to phenol derivative **6**[*].

It should be noted that while many steps are required to the synthesis of indan-2-one derivatives,[10] the photochemical reaction of allenes with 1,4-quinones affords directly to 5-hydroxyindan-2-ones in fairly good yield. This photochemical addition-rearrangement reaction is quite useful, to prepare the indan-2-ones and benzinden-2-ones.

EXPERIMENTAL

Commercially available 1,4-benzoquinone and 1,4-naphthoquinone were purified by recrystallization. Tetramethylallene, Aldrich Chemical Co., was used without further purification. Benzene and dioxane were distilled before use. IR spectra were taken with a JASCO spectrophotometer, Model 402G. UV spectra were run with a Hitachi 124 spectrophotometer. NMR spectra were determined using a JEOLCO PS-100 spectrometer. Mass spectra were run with Hitachi RMU-6 spectrometer. The m.ps are not corrected.

Photoreaction of 1,4-*benzoquinone with tetramethylallene.* A soln of tetramethylallene (2·0 g, 21 mmole) and 1,4-benzoquinone (0·7 g, 5·9 mmol) in benzene (150 ml) was irradiated under N_2 with a 100W medium pressure Hg lamp through the Pyrex filter for 50 hr. The ppt was filtered off and recrystallized from EtOAc to give a colorless crystal **6**, mp 243–244°, in 78% yield (based on 1,4-benzoquinone): IR (KBr), 3300 (ν_{OH}), 1735 cm^{-1} ($\nu_{C=O}$); UV (MeOH), λ_{max} 286 nm (log ε 3·46); NMR (acetone-d_6), δ 1·24 (s, 12 H), 6·75 (m, 2 H), 7·15 (d, 1H), and 8·25 (s, 1H); mass spectrum *m/e* (parent) 204. (Found; C, 76·25; H, 7·89; O, 15·91. Calc for $C_{13}H_{16}O_2$: C, 76·44; H, 7·89; O, 15·91).

Irradiation of the mixture of tetramethylallene (2·0 g, 21 mmol) and 1,4-benzoquinone (1·1 g, 11 mmol) in dioxane (150 ml) was carried out under the same condition as above. After evaporation of the solvent and removal of tetramethylallene under vacuum, the residue was chromatographed on a Florosil column with light petroleum—benzene (2:1) to yield **6** in 55% (based on 1,4-benzoquinone).

Photoreaction of 1,4-*naphthoquinone with tetramethylallene.* The soln of tetramethylallene (2·1 g, 21 mmol) and 1,4-naphthoquinone (1·3 g, 8 mmol) in benzene (150 ml) was irradiated under N_2 with a 100 W medium pressure Hg arc through a Pyrex filter for 50 hr. Chromatography of the residual oil, after removal of solvent, on Florosil and elution with light petroleum benzene (2:1) gave colorless solid which was recrystallized from cyclohexane to give **7** in 40% yield (based on 1,4-naphthoquinone): m.p. 191–192°; IR (KBr), 3300 (ν_{OH}) and 1745 cm^{-1} ($\nu_{C=O}$); UV (MeOH), λ_{max} 233 (log ε 3·49), 305 (2·78), 320 (2·72), and 344 nm (2·70); NMR ($CDCl_3$), δ 1·37 (s, 6H), 1·65 (s, H), 6·77 (s, 1H), and 7·50–8·50 (m, 5H); mass s'ectrum *m/e* (parent) 260. (Found: C, 80·42; H, 7·33; O, 12·68. Calcd. for $C_{17}H_{18}O_2$: C, 80·28; H, 7·34; O, 12·58.).

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[*] A possibility that **9** and/or **10** rearrange thermochemically to **6** cannot be ruled out, since the acid-catalyzed rearrangement of 2,5-cyclohexadienones is well known.[16]

Acetylation of the photoproduct **6**. 53 mg of **6** in a mixture of 5 g of Ac_2O and 20 g of pyridine was refluxed for 3 hr. After removal of Ac_2O and pyridine, the residual solid was recrystallized from benzene to give a white crystal of 1,1,3,3-tetramethylindan-2-one-5-acetate in 61% yield: mp 129–130°; IR (KBr), 1750 cm^{-1} ($\nu_{C=O}$); NMR (CCl_4), δ 1·28 (s, 12H); 2·20 (s, 3H), 6·80–6·95 (m, 2H), and 7·15 (d, 1H). (Found: C, 72·80; H, 7·51; O, 19·69. Cald for $C_{15}H_{18}O_3$: C, 73·10; H, 7·41; O, 19·49.)

Acknowledgement—The authors wish to express their thanks to Professor K. Teramura for his interest in this work.

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