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Synthetic Photochemistry. VII.[1] The Addition Reaction of Acenaphthenequinone and 1,2-Naphthoquinone to Cycloheptatriene

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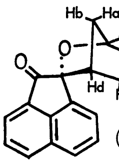
Synopsis. The photoaddition reaction of acenaphthenequinone and 1,2-naphthoquinone to cycloheptatriene was investigated. In contrast to acyclic α-diketones, various cycloadducts were formed from both quinones; the former giving the $(2+2)\pi$-, and $(2+6)\pi$-cycloadducts together with the ene-product, and the latter the $(2+6)\pi$-, $(4+2)\pi$-, and $(4+4)\pi$-cycloadducts.

A report was given on the results of the photoaddition reaction of cycloheptatriene (tropylidene, **1**) to some acyclic α-diketones.[2] The adduct solely isolated was found to be 7-tropyl-α-ketol derivative, an ene–product in every case. The absence of any cycloadducts is of interest. For comparison, we have examined the reaction of **1** to another type of 1,2-diketo derivatives, cyclic α-diketones.

Irradiation of a dioxane solution of acenaphthenequinone (**2**) and **1** by means of a 500 W tungsten lamp gave three products (**3**, **4**, and **5**) which were isolated by silica gel column chromatography. The first product (**3**, 18% yield) was shown to be a $(6+2)$ π-adduct from the NMR[3] [δ: 2.69 (Ha, d, J=12.0 Hz), 2.96 (Hd, dd, J=7.6, 6.0 Hz), 3.61 (Hb, ddd, J=12.0, 8.0, 6.0 Hz), 4.90 (Hc, ddm, J=8.0, 6.0 Hz), 5.48 (He, dm, J=7.6 Hz), 6.00 (3H, m), and 7.85 (6H, m)] spectral analysis; the coupling patterns of the protons Ha, Hb, Hc and Hd ruled out other possibilitits. Furthermore, the appearance of an isolated signal due to He from the rest of the olefinic proton signals provided an evidence for its stereochemistry.[4]

The second product (**4**, 37%), colorless crystals, was a $(2+2)$ π-adduct since the NMR [δ: 2.73 (Ha, ddm, J= 11.5, 4.5 Hz), 3.18 (Hb, tdm, J=11.5, 2.5 Hz), 4.14 (Hd, dt, J=8.0, 2.0 Hz), 5.31 (He, dd, J=11.5, 2.0 Hz), 5.57 (Hc, ddd, J=11.5, 8.0, 4.5 Hz), 5.6—6.1 (3H, m), and 7.6—8.1 (6H, m)] spectrum showed a signal ascribable to the proton of ethereal carbon (Hc), being spin–coupled to methylene protons (Ha and Hb) and also to Hd. The signal for He appearing in a higher field than for the rest of the protons is utilized to deduce the stereochemistry.



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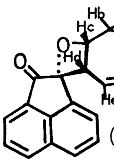

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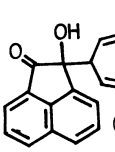

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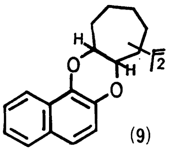

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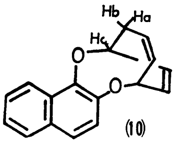

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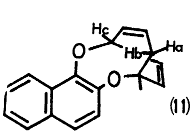

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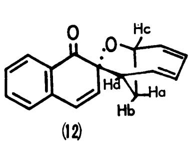

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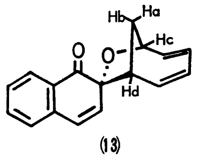

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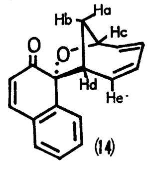

(14)

The third product (**5**, 38%), yellow crystals, was found to be the ene-product by the NMR [δ: 2.26 (1H, t, J=6.0 Hz), 5.01 (1H, dd, J=9.5, 6.0 Hz), 5.57 (1H, dd, J=9.5, 6.0 Hz), 6.17 (2H, m), 6.62 (2H, t, J=3.0 Hz), and 7.4—8.3 (6H, m)] spectrum.

When irradiation was carried out under aerial conditions, the products were formed in nearly the same ratio as above, although the main product in this case was 1,8-naphthalenedicarboxylic anhydride (31.3%).

These products must be formed independently, since **3** and **4** were quite stable for further irradiation, but **5** gradually decomposed into 7,7′-bitropyl (**6**),[5] 2-hydroxyacenaphthenenone (**7**),[6] and the starting material (**2**). A similar transformation has been observed in the irradiation of the ene-products derived from **1** and some benzil derivatives.[2] No interconversion of the products (**3**, **4**, and **5**) occurred.

1,2-Naphthoquinone (**8**) and **1** were similarly irradiated in benzene by use of a 500 W tungsten lamp, the products isolated after the column chromatography being a $(4+2)$ π-adduct (**9**, colorless crystals), a pair of $(4+4)$ π-isomers (**10** and **11**, pale yellow oils), a pair of $(6+2)$ π-adducts (**12** and **13** yellow oils) and another $(6+2)$ π-adduct (**14**, a yellow oil). No ene-product was detectable.

9, **10**, and **11** showed neither ν_{OH} nor $\nu_{C=O}$ in their IR spectra, indicating them to be cyclic ethers. The splitting patterns of the proton signals of sp^3-carbon in the NMR of **9** [δ: 2.74 (2H, m), 4.24 (1H, td, J=8.0, 4.6 Hz), 4.66 (1H, d, J=8.0 Hz), 5.95 (4H, m), 7.03 (1H, dd, J=8.0, 3.8 Hz), 7.28 (3H, m), 7.64 (1H, dd, J=8.0, 2.5 Hz), and 8.01 (1H, dd, J=8.0, 2.5 Hz)] was compatible to a $(4+2)$ π-structure. **10** and **11** were stereoisomers which could be separated by high–pressure liquid chromatography. By catalytic reduction, they were converted into the same tetrahydro derivative (**15**) which differs from the tetrahydro derivative (**16**) of **9**. Thus, **10** and **11** were deduced to be the $(4+4)$ π-adducts. Although the NMR spectra of **10** [δ: 2.55 (Ha, dm, J=16.0 Hz), 2.92 (Hb, dddd, J=16.0, 9.0, 3.0, 1.5 Hz), 4.63 (Hc, dt, J=9.0, 3.0 Hz), 4.81 (1H, br. s), 5.93 (4H, m), 6.94 (1H, d, J=9.5 Hz), 7.32 (3H, m), and 7.5—8.0 (2H, m)] and **11** [δ: 2.48 (Ha, dm, J=16.0 Hz), 2.83 (Hb, ddm, J=16.0, 8.0 Hz), 4.51 (Hc, dt, J=8.0, 3.0 Hz), 4.85 (1H, br. s), 5.88 (4H, m), 6.97 (1H, d, J=9.5 Hz), 7.28 (3H, m), and 7.5—8.1 (2H, m)] closely resembled each other, locations of the methylene group were tentatively assigned as depicted from the difference in chemical shifts of Ha, Hb, and Hc.

The NMR spectra of **12** and **13** were considerably different: **12** [δ: 2.53 (Ha, d, J=11.5 Hz), 2.71 (Hb, dt, J=11.5, 6.0 Hz), 2.88 (Hd, td, J=6.0, 1.5 Hz), 4.78 (Hc, tm, J=6.0 Hz), 5.40 (He, m), 5.84 (3H, m), 6.32 (2H, s), and 7.42 (4H, m)] revealed a high field shift for one of the olefinic protons (He); in contrast, **13** [δ: 2.35 (Ha, dt, J=12.0, 3.0 Hz), 2.96 (Hb and Hd, overlapped m), 4.86 (Hc, ddm, J=7.0, 6.5 Hz), 5.90 (4H, m), 6.50 (2H, s), and 7.40 (4H, m)] revealed combined signals for olefinic protons. The absence of α,β-unsaturated carbonyl group was also clear from the chemical shifts of the vinylic protons. Furthermore, the difference in chemical shift between each proton of methylene groups, $\delta_{\text{Ha}}-\delta_{\text{Hb}}$: 0.18 for **12**, and 0.61 for **13**, was interpreted in terms of the magnetic anisotropy of the carbonyl group on Hb. Thus, the stereochemistry for **12** and **13** was determined as depicted.

The structure of another type of (6+2) π-adduct (**14**) was also clarified from the NMR [δ: 2.41 (1H, d, J=12.0 Hz), 2.86 (1H, dt, J=12.0, 5.8 Hz), 3.24 (1H, dd, J=8.0, 5.8 Hz), 4.88 (1H, tm, J=6.0 Hz), 4.98 (He, tm, J=8.0 Hz), 5.7—6.2 (3H, m), 6.01 (1H, d, 10.0 Hz), 7.36 (1H, d, J=10.0 Hz), and 7.0—8.4 (4H, m)] spectrum. The presence of α,β-unsaturated carbonyl group in **14** is clear from the signals appearing at δ: 6.01 and 7.36. The isolated signal for He, revealing a high field shift, suggests the stereochemistry as depicted.

Formation of the (6+2) π-adducts resembles the mode of reaction of **1** with *p*-quinones. However, no cycloaddition took place at the C=C part of the quinones in contrast to the case with *p*-quinones. It is of interest that conjugated olefins, generally regarded to be good triplet quenchers, afforded various types of cycloadducts by irradiations with visible light.[1]

Experimental

Photoaddition Reaction of Cycloheptatriene (1) with Acenaphthenequinone (2): Formation of the Cycloadducts (3, and 4) and the Ene-Product (5). A dioxane solution (30 ml) of **1** (2 ml) and **2** (220 mg) was externally irradiated by means of a 500 W tungsten lamp under nitrogen atmosphere for 18 h. After evaporation of the solvent, the residue was fractionated by silica gel column chromatography; **6** was obtained as colorless crystals from the least polar fractions, mp 61—63 °C (lit,[5] 61—62 °C), 17 mg. With the use of benzene as an eluent, three products were obtained consecutively. First, pale yellow crystals (**3**) were eluted, mp 123—125 °C (from ethanol), 23.2 mg [Found: C, 83.12; H, 5.17%. Calcd for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15%. $\lambda_{\max}^{\text{MeOH}}$: 225 nm ($\varepsilon$: 55600), 255.5 (sh., 13800), 308 (6600), 348 (4700)]. Then, colorless crystals (**4**), mp 163—164 °C (from methanol), 47.6 mg [Found: C, 82.91; H, 5.15%. $\lambda_{\max}^{\text{MeOH}}$: 227 nm ($\varepsilon$: 29000), 285 (2700), 319 (2500), 347 (2200)], and pale yellow crystals (**5**), mp 146—147 °C (from methanol), 48.6 mg [Found: C, 83.29; H, 5.10%. $\lambda_{\max}^{\text{MeOH}}$: 223 nm ($\varepsilon$: 47500), 256 (14700), 321 (5100), 345 (4700). ν: 3570, 1735 cm^{-1}] were obtained along with recovered **2** (134 mg).

Photoaddition Reaction of 1 with 2 in the Presence of Oxygen. A dioxane solution (16 ml) of **1** (0.5 ml) and **2** (464 mg) was irradiated with a tungsten lamp as above but under aerial conditions for 18.5 h. After evaporation of the solvent, the mixture was washed with a small amount of cold chloroform to recover unreacted **2** (278 mg) from the less soluble portion. Silica gel column chromatography of the soluble portion afforded **3** (38.2 mg), **4** (74.0 mg), colorless crystals, mp 274—275 °C (identified as 1,8-naphthalenedicarboxylic anhydride, 64.5 mg), and **5** (50.1 mg).

Further Irradiation of 3 and 4. **3** (25 mg/3 ml of dioxane) and **4** (33 mg/4 ml of dioxane) were separately irradiated with a tungsten lamp for 9 h. No reaction took place according to the NMR analysis.

Further Irradiation of 5. **5** (15 mg) was dissolved in benzene (10 ml) and irradiated with a tungsten lamp for 17 h. By preparative thin layer chromatography, regenerated **2** (≈1 mg) and **7** (≈1 mg, mp 236—238 °C (lit,[6] 238—239 °C)) were isolated together with **6** which was characterized by gas-liquid chromatographic analysis.

Photoaddition Reaction of 1 and 1,2-Naphthoquinone (8): Formation of Cycloadducts (9, 10, 11, 12, 13, and 14). A benzene solution (25 ml) of **1** (1 ml) and **8** (780 mg) was irradiated by means of a 500 W tungsten lamp for 70 h. The product mixture was then separated by silica gel column chromatography. After elution of **6** (9 mg), **9** (colorless crystals, mp 93—94 °C from methanol, 113 mg) [Found: C, 81.29; H, 5.74%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%. $\lambda_{\max}^{\text{MeOH}}$: 242 nm ($\varepsilon$: 38200)], an oily mixture of **10** and **11** (233 mg), **12** (a colorless oil, bp 120 °C/0.5 Torr (bath temp), 14 mg) [Found: *m/e*: 250.09509 (M$^+$). Calcd for $C_{17}H_{14}O_2$: *m/e*: 250.09938. $\lambda_{\max}^{\text{MeOH}}$: 238 nm ($\varepsilon$: 24200), 275 (sh., 7100)]. **13** (a colorless oil, bp 120 °C/0.5 Torr (bath temp), 72.2 mg) [Found: *m/e*: 250.09987. $\lambda_{\max}^{\text{MeOH}}$: 240 nm ($\varepsilon$: 40800), 275 (7290)], and **14** (a colorless oil, bp 120 °C/0.5 Torr (bath temp), 47.5 mg) [Found: *m/e*: 250.10205. $\lambda_{\max}^{\text{MeOH}}$: 238 nm ($\varepsilon$: 14000)] were obtained by elution with benzene.

Preparative Liquid Chromatographic Separation of a Mixture of 10 and 11. The mixture was fractionated by Micropolasil column (2 m) with chloroform: hexane (5:95) using ALC 202/401 Model of Waters Co., from less polar fractions, a colorless oil (**10**) [Found: *m/e*: 250.09433. $\lambda_{\max}^{\text{MeOH}}$: 220.5 nm ($\varepsilon$: 24600), 241.5 (38400)] was obtained and from more polar fractions a colorless oil (**11**) [Found: *m/e*: 250.10009. $\lambda_{\max}^{\text{MeOH}}$: 219.5 nm ($\varepsilon$: 25500), 241.7 (43000)].

Catalytic Reduction of 10. **10** (12 mg) was dissolved in ethyl acetate (2 ml) and reduced by palladium carbon (5%, 4 mg). After the usual work-up, a tetrahydro-derivative (**15**, 8 mg) was obtained as a colorless oil [Found: *m/e*=254.13292. Calcd for $C_{17}H_{18}O_2$: 254.13068.], whose homogeneity was confirmed by liquid chromatographic analysis.

Catalytic Reduction of 11. Similarly, **11** (25.8 mg) was reduced to give a colorless oil (26 mg) which was identical with **15** in IR and liquid chromatographic comparison.

Catalytic Reduction of 9. **9** (25.6 mg) was dissolved in ethanol (4 ml) and dioxane (1 ml) and reduced by palladium carbon (5%, 7.5 mg). Isolation by the usual work-up afforded colorless crystals, mp 120—121 °C (from methanol) (**16**), 17 mg [Found: C, 79.79; H, 7.18%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%].

References

1) Part VI of this series: H. Takeshita, A. Mori, and Y. Toyonaga, *Bull. Chem. Soc. Jpn.*, **48**, 307 (1915).

2) A. Mori, T. Fujita, N. Yamamoto, and H. Takeshita, Abstract Papers of 7th Symposium on the Chemistry of Non-Benzenoid Aromatic Compounds, (Oct. 1974, Tokyo) p. 183.

3) The NMR spectra were taken in $CDCl_3$ solution.

4) A. Mori, and H. Takeshita, *Chem. Lett.*, **1975**, 599.

5) W. von E. Doering, and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

6) Unpublished results of Prof. O. Tsuge, Kyushu Univ.