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THERMAL ADDITION REACTION OF CYCLOHEPTATRIENE TO SOME AROMATIC QUINONES: THE FORMATION OF vic-DITROPYLATION PRODUCTS

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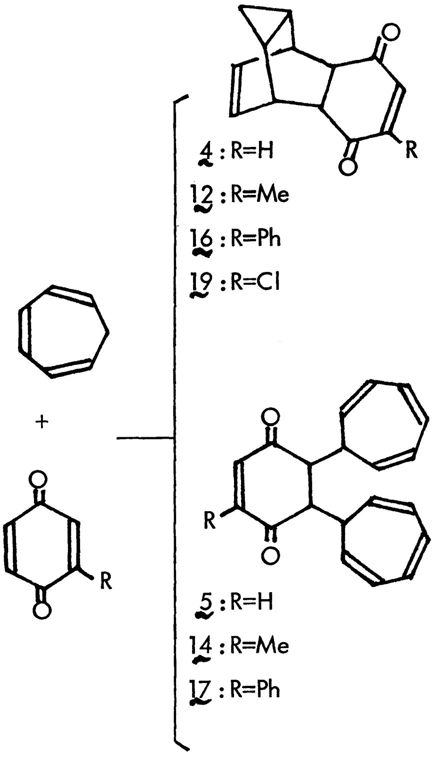
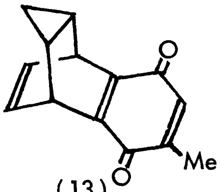
Thermal addition reaction of cycloheptatriene with some aromatic quinones was studied. In addition to ordinary Diels-Alder adducts, identified in the products were 2,3-ditropylcyclohex-5-ene-1,4-diones which were shown to be formed after series of tropylation, dehydrogenation, and further tropylation processes.

Recently, we have shown the formation of the characteristic $(6+2)\pi$ cycloadducts in the photo-reaction of p-benzoquinone(**1**) and 1,4-naphthoquinone(**2**) to cycloheptatriene(tropylidene, **3**).[1] As a part of studies on the cycloaddition reactions of **3**, it would be desirable to carried out the thermal reaction with these particular dienophiles in view of oxidation-reduction properties, although **3** is shown to form tricyclo[3,2,2,$0^{2,4}$]nonene derivatives in general.[2] The novel features disclosed along the line will be described in this paper.

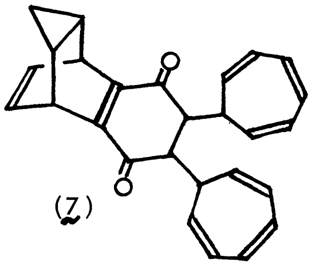
When **1** and **3** were heated in toluene solution at 110°C for 1 hour, two adducts(**4** and **5**) were isolated by silica-gel column chromatography together with some amounts of 7,7′-ditropyl (**6**), mp 63-64°C,[3] and reduced hydroquinone. The structure of **4** was assigned as an ordinary Diels-Alder adduct on the basis of the physical observations;[4] especially, the NMR spectrum exhibited the signals due to four hydrogens of cyclopropyl group[δ: 0.04(1H, dt, J=5.5, 4.0 Hz), 0.14(1H, dt, J=5.5, 7.0 Hz), and 1.12(2H, ddm, J=7.0, 4.0 Hz)] together with other signals[δ:3.02(2H, t, J=1.5 Hz), 3.48(2H, ddm, J=4.5, 1.5 Hz), 5.76(2H, dd, 4.5, 3.5 Hz), and 6.62(2H, s)]. The other product(**5**), a 1 : 2-adduct[m/e :290(M^+)], colorless crystals, mp 112-113°C, obtained in 32 % yield,[5] was shown to be a vic-ditropyl derivative by the NMR[δ:1.90(2H, dt, J=11.0, 6.0 Hz), 3.30(2H, d, J=11.0 Hz), 5.20(2H, dd, J=9.5, 6.0 Hz), 5.27(2H, dd, J=9.5, 6.0 Hz), 6.23(2H, dtm, J=9.5, 3.0 Hz), 6.32 (2H, dtm, J=9.5, 3.0 Hz), 6.59(2H, s), 6.70(2H, d, J=3.0 Hz), and 6.73(2H, d, J=3.0 Hz)] and IR[$\nu_{C=O}$: 1685 cm^{-1}] spectral analyses.

The reaction of **1** and **3** with no solvent gave more complex results. In addition to **4**(∼1 %), **5**(6.3 %) and **6**(8 %), newly isolated after repeated column chromatography were another vic-ditropyl derivative(**7**, 5.1 %), a 1:3-adduct[m/e :380(M^+)], colorless crystals, mp 161-162°C[δ: 0.57(1H, q, J=7 Hz), 0.80(1H, dm, J=7 Hz), 1.16(2H, dm, J=7 Hz), 1.72(2H, dtm, J=10.5, 7 Hz), 3.28(2H, ddd, J=10.5, 3, 1.5 Hz), 4.22(2H, m), 5.22(4H, dm, J=7 Hz), 5.97(2H, m), 6.2(4H, m), and 6.55(4H, m). $\nu_{C=O}$: 1665 cm^{-1}], a cage-compound(**8**, ∼1 %), colorless crystals, mp 198-201°C[δ: 2.21(1H, dt, J=10, 7 Hz), 2.38(1H, d, J=5.5 Hz), 2.79(1H, ddd, J=9. 5.5, 3 Hz), 3.1(5H, overlapped m), 5.22(1H, dd, J=9, 7 Hz), 5.66(2H, dm, J=9 Hz), 6.04(1H, t, J=9 Hz), 6.24(2H, m), 6.44(2H, dd, J=9, 7 Hz), and 6.64(2H, t, J=3 Hz). $\nu_{C=O}$: 1730 cm^{-1}], and a bis-Diels-Alder adduct(**9**, 2.5 %), colorless crystals, mp 177-178°C[δ: 0.00(4H, m), 0.92(4H, m), 2.80(4H, m), 3.25(4H, m), and 5.87(4H, dd, J=5.0, 3.0 Hz). $\nu_{C=O}$: 1690 cm^{-1}]. **8** was formed by an intramolecular Diels-Alder reaction of **5**, since, in presence of **3**, the isomerization occurred by heating at 110°C.

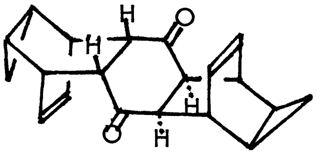




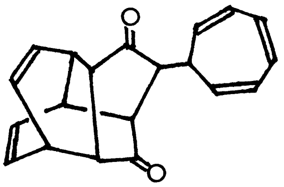
(**13**)



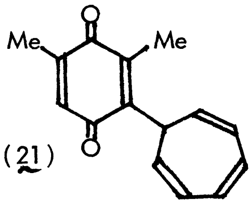
(**7**)



(**9**)



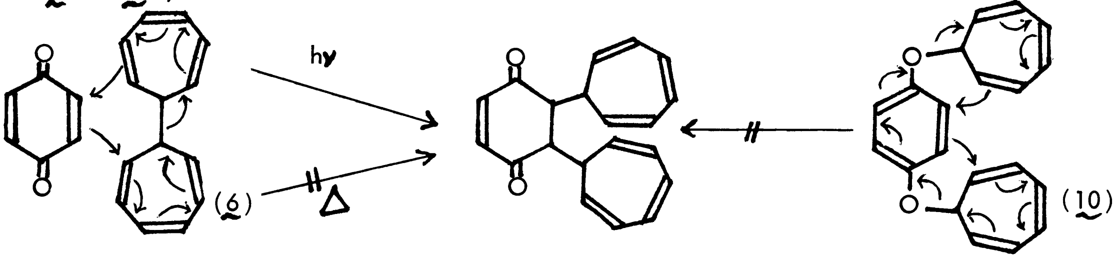
(**8**)



(**21**)

The formation of vic-ditropyl derivatives, ene-products in a sense,6) may need some explanations. We have consequently carried out some detailed experiments on this point. At first, an electrocyclic reaction between

1 and 6, i.e., the ($2n\pi + 2\sigma + 2n\pi + 2\pi$)-process should be an attractive hypothesis. However, heating the mixture of two under similar conditions as above yielded none of 5.[7)] On the other hand, when a chloroform solution of two was irradiated by means of a 450 W tungsten lamp, 5 was in fact produced as a main product. Therefore, at least in photochemically, such an electrocyclic reaction does occur. But in thermally, the reaction carefully performed in the dark with 1 and 3 showed no difference in distribution of products, including 5 and 7. Accordingly, there is another non-photochemical pathway to 5 and 7. In the next, we have examined a possibility of a double-Claisen type rearrangement of di-O-tropylhydroquinone (10) which can be formed by hydroquinone and tropylium ion or its equivalent species, though the formation under the conditions appears less likely. When a dioxane solution of 10 was heated to reflux, no isolable product was however obtained. The formation of 5 and 7 by a concerted fashion has been thus ruled out.[8)]

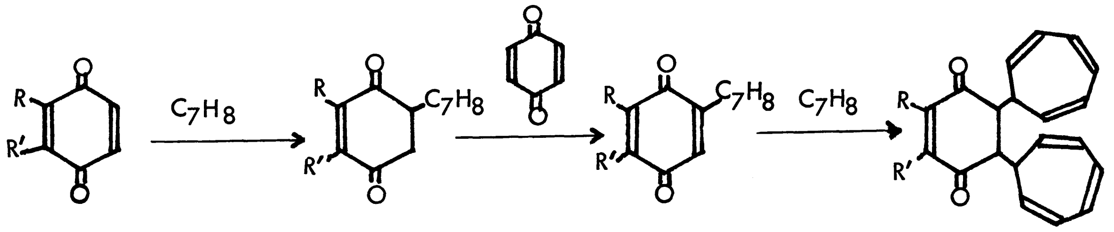


Hoping to isolate a precursor of the vic-ditropyl derivatives in experimentally, we have then extended the study to some other p-benzoquinone derivatives. The reaction with p-toluquinone (11) yielded a Diels-Alder adduct (12, 15.7 %), colorless crystals, mp 81-82°C [δ : 0.80(2H, m), 1.08(2H, m), 1.98(3H, d, J=2 Hz), 2.98 (2H, t, J=2 Hz), 3.40(2H, m), 5.68(2H, dd, J=5, 4 Hz), and 6.46(1H, q, J=2 Hz). $\nu_{C=O}$: 1660 cm^{-1}], its dehydro-derivative (13, 6.0 %), yellow liquid [δ : 0.66(1H, q, J=7 Hz), 0.87(1H, dt, J=7, 3 Hz), 1.24(2H, m), 2.06(3H, d, J=1.5 Hz), 4.36(2H, m), 6.05(2H, dd, J=5, 4 Hz), and 6.45(1H, q, J=1.5 Hz). $\nu_{C=O}$: 1635, 1650 cm^{-1}] and a vic-ditropyl derivative (14, 17.8 %), colorless crystals, mp 107-108°C [δ : 1.80(2H, m), 1.92(3H, d, J=1.5 Hz), 3.26(1H, dm, J=11.0 Hz), 3.32(1H, dm, J=11.0 Hz), 5.20(4H, m), 6.17(2H, dt, J=9.5, 3.0 Hz), 6.28(2H, dt, J=9.5, 3.0 Hz), 6.42(1H, q, J=1.5 Hz), and 6.67(4H, t, J=3.0 Hz). $\nu_{C=O}$: 1680 cm^{-1}], and with phenyl-p-benzoquinone (15) yielded a Diels-Alder adduct (16, 12.5 %), colorless crystals, mp 139-140.5°C [δ : 0.12(1H, tm, J=4 Hz), 0.24(1H, tm, J=6 Hz), 1.19(2H, ddm, J=6, 4 Hz), 3.17(2H, t, J=3 Hz), 3.52(2H, m), 5.82(2H, dd, J=5, 4 Hz), 6.73(1H, s), and 7.40(5H, m). $\nu_{C=O}$: 1665 cm^{-1}] and a ditropyl derivative (17, 18 %), colorless liquid [δ : 2.05(2H, dt, J=11.0, 6.0 Hz), 3.39(1H, d, J=11.0 Hz), 3.41(1H, d, J=11.0 Hz), 5.70(4H, dm, J=6.0 Hz), 6.27 (4H, m), 6.67(5H, m), and 7.39(5H, s). $\nu_{C=O}$: 1665, 1685 cm^{-1}]. But, chloro-p-benzoquinone (18) gave only a Diels-Alder adduct (19, 16.2 %), colorless crystals, mp 98-98.5°C [δ : 0.12(1H, tm, J=4 Hz), 0.21(1H, tm, J=6 Hz), 1.16(2H, ddm, J=6, 4 Hz), 3.04(2H, t, J=2 Hz), 3.49(2H, m), 5.80(2H, dd, J=4, 3.5 Hz), and 6.81(1H, s).

$\nu_{C=O}$: 1665 cm^{-1}]. Although, many of di-substituted quinones caused only hydrogen transfer reaction to result in formations of 6 and corresponding hydroquinones, 2,6-xyloquinone (20) has shown to give 2,6-dimethyl-3-tropyl-p-benzoquinone (21, 15.8 %), yellow crystals, mp 90-93°C [δ : 2.05(3H, s), 2.09(3H, d, J=2.0 Hz), 3.16(1H, t, J=6.0 Hz), 5.16(2H, dd, J=9.0, 6.0 Hz), 6.17(2H, dm, J=9.0 Hz), and 6.62(3H, m). $\nu_{C=O}$: 1640 cm^{-1}] as the sole product. This should be an indication of stepwise formation of the vic-ditropyl derivatives.

It will be interesting that the thermal reaction, to contrast to photo-reaction, were complicated due to consecutive reactions with 3, up to a formation of 1:3-adducts, facilitated by the electron transfer process between dihydroquinones, primary adducts, and the quinones in the mixture. Furthermore, intermediate products isolated (e.g., 15 and 21) were limited to the derivatives having a steric hindrance against the next process.

In conclusion, the formation of the vic-ditropyl derivatives can be expressed by the following scheme:



Currently, photochemical vic-ditropylation process is under investigations, and will be reported in future.

References and Notes

1) A. Mori, and H. Takeshita, Chemistry Lett., 1975, 599.
2) K. Alder, and G. Jacobs, Chem. Ber., 86, 1528 (1953).
3) W. von E. Doering, and L. H. Knox, J. Amer. Chem. Soc., 79, 352 (1957).
4) All the new compounds gave satisfactory elemental analyses. The NMR measurements were made in $CDCl_3$ solutions at 100 MHz. The IR spectra were obtained either by KBr disks or CCl_4 solutions.
5) The yields were calculated on the stoichiometry of the quinones.
6) Recently, H. Zander has reported the similar ene-reaction in the studies of 2 and β-vinylnaphthalene. Cf. Chem. Ber., 108, 367 (1975).
7) The reaction mixture was quite complex, but a formation of 3-tropylbicyclo[3,2,2,0^{2,4}]nonene derivative was predominant. This was also the case for that of 6 and maleic anhydride.
8) In the same time, the reaction of quinhydrone and 6 and 3 was attempted, but 5 was undetectable in the mixture

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