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THERMAL ADDITION REACTION OF CYCLOHEPTATRIENE WITH 1,4-NAPHTHOQUINONE: AN EXPERIMENTAL EVIDENCE ON THE MECHANISM OF vic-DITROPYLATION TO QUINONES

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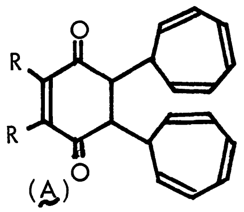
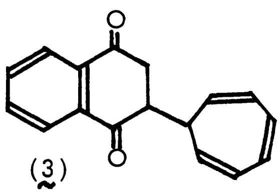
Thermal reaction of cycloheptatriene with 1,4-naphthoquinone produced 2-(7-tropyl)-2,3-dihydro-1,4-naphthoquinone and a dimeric 2:2-adduct in addition to the similar types of adducts with some p-benzoquinones. An experimental support for the previously suggested mechanism on the vic-ditropylation process was obtained by a further conversion of isolated intermediates.

Recently, we have reported the results on the thermal addition reaction of cycloheptatriene (1) with some p-benzoquinone derivatives.1) A novel feature of this reaction was the characteristic formation of vic-ditropylation products (A) in a step-wise manner. Although, the concerted machanism to the formation of A has been excluded, a direct evidence for the step-wise formation, for instance, isolation of the precursors, remained yet to be studied. We have now extended the study to the reaction of 1 with 1,4-naphthoquinone (2) which in fact afforded the desired mono-tropylation product (3). We will herein present the related findings on the precursor of A together with the characterizations of other products.



(A)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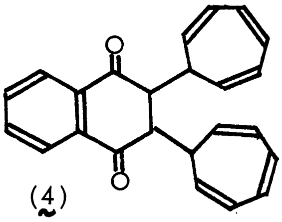
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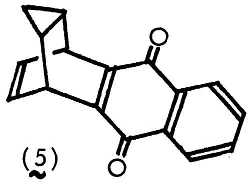
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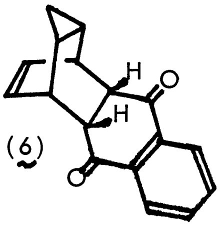

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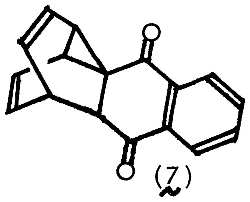
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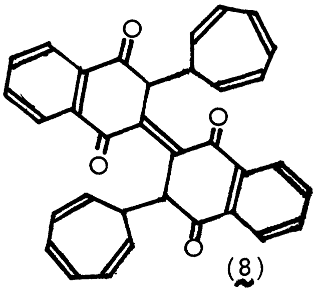
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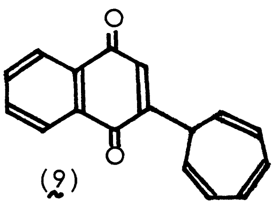
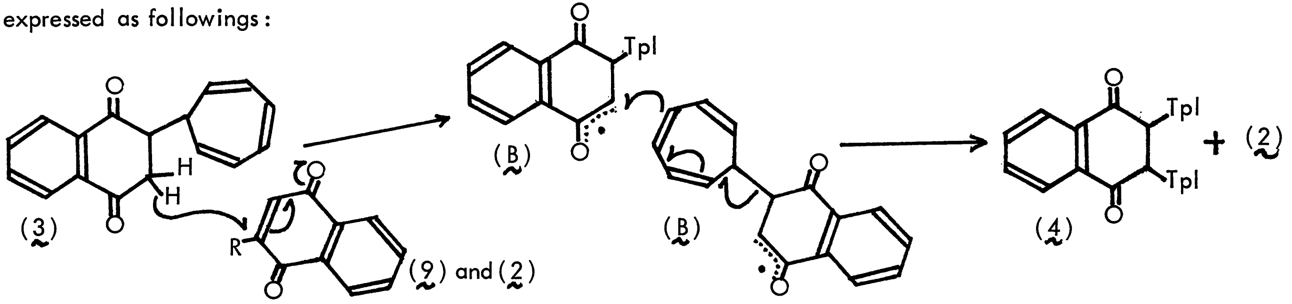

(9)

When a toluene solution of 1 and 2 were heated 110°C for 12 hr, a complex mixture as in cases of 1 and p-benzoquinones was obtained. After silica-gel column chromatography, the products characterized, besides 7,7'-ditropyl,2) were a colorless oil (4, 0.6 %) [δ3): 1.88(2H, dt, J=11, 6 Hz), 3.50(2H, d, J=11 Hz), 5.29(4H, m), 6.22(4H, m), 6.62(4H, t, J=2.5 Hz), 7.6-8.2(4H, m)], yellow needles, mp 188-189°C (5, 16 %) [δ: 0.70(1H, td, J=7, 6 Hz), 0.93(1H, dt, J=6, 3.5 Hz), 1.36(2H, ddm, J=7, 3.5 Hz), 4.58(2H, ddm, J=5, 3.5 Hz), 6.12(2H, dd, J=5, 3.5 Hz), and 7.6-8.1(4H, m)], colorless plates, mp 165-166.5°C(6, 22 %)[δ:0.0-0.2(2H, m), 1.20(2H, m), 3.23(2H, dm, J=1.5 Hz), 3.58(2H, dddm, J=5, 3.5, 1.5 Hz), 5.67(2H, dd, J=5, 3.5 Hz), and 7.6-8.1(4H, m)] and a colorless oil (3, 5.4 %)[δ:2.24(1H, dt, J=9, 6 Hz), 3.1-3.7(3H, m), 5.28(1H, dd, J=10, 6 Hz), 5.40(1H, dd, J=10, 6 Hz), 6.23(2H, m), 6.62(2H, t, J=3 Hz), and 7.7-8.1(4H, m)].

On the other hand, when the reaction was carried out without diluent, new products, yellow-orange needles, mp 131-132.5°C(7, 3.0 %)[δ:2.48(1H, dd, J=8.5, 6 Hz), 2.84(1H, d, J=3 Hz), 3.54(2H, m), 5.67(1H, ddm, J=9.5, 6 Hz), 5.80(1H, ddm, J=9.5, 6 Hz), 6.06(2H, ddm, J=9.5, 6 Hz), and 7.7-8.1(4H, m)] and a colorless oil (8, 1.3 %)[δ:2.26(2H, dtm, J=12, 6 Hz), 4.73(2H, d, J=12 Hz), 5.10(2H, dd, J=9, 6 Hz), 5.18(2H, dd, J=9, 6 Hz), 6.16(4H, m), 6.71(4H, t, J=2.5 Hz), and 7.6-8.1(8H, m)], were isolated together with 4(1.9 %), 5(10 %), 6(7.2 %), and 3(0.9 %). The structures depicted for these products relied on the PMR evidences and other physico-chemical determinations including the mass spectral fragmentations.[4]

Although DDQ-dehydrogenation of 3 has failed to give any isolable product, a dehydrogenation has smoothly occurred by contacts with basic alumina to give the quinone (9), an orange-yellow oil (47 %)[δ:3.64(1H, td, J=7, 1.5 Hz), 5.41(2H, dd, J=9.5, 7 Hz), 6.34(2H, dt, J=9.5, 4 Hz), 6.64(2H, t, J=4 Hz), 6.84(1H, d, J=1.5 Hz), and 7.5-8.1(4H, m)]. When 9 was heated together with 1 at 110°C for 7 hr, only 7 was isolated in 28 %, but none of 4 could be isolated from the mixture.[5] This was rather disappointing result but should be explained in terms of an easy intramolecular Diels-Alder process against an intermolecular ene-addition process. However, when an equimolecular mixture of 9 and 3 in 1 was heated 110°C for 6 hr, 4(19%) was obtained together with 7(27%) and some amounts of regenerated 2. Therefore, it would be conceivable that a radical (B) formed from 3, by an abstraction of hydrogen with 9, disproportionated into 4 and 2. This was verified by heating a mixture of 1, 2, and 3 for 11 hr under similar conditions to give 4(3.5 %) and 7(25 %). Therefore, the formation of 4 can be expressed as followings:



These findings have confirmed the mechanism of the step-wise formation of 4 and A in general, and further disclosed an oversighted precursor B to form A. It would be worthwhile to note that 7, an unsymmetrical barbaralane, showed no signal due to the valence isomer and was virtually fixed as expressed according to variable temperature measurements of both CMR[6] and PMR spectra.

References and Notes

1) H. Takeshita, A. Mori, and H, Mametsuka, Chemistry Lett., 1976, 445.

2) W. von E. Doering, and L. H. Knox, J. Amer. Chem. Soc., 79, 352(1957).

3) The PMR spectra were measured in $CDCl_3$ solutions at 100 M Hz.

4) Details of uncited data of physical measurements will be reported elsewhere.

5) The reaction mixture in fact showed an undistinguishable spot with 6 on a tlc plate, but any spectroscopic identification was unsuccessful due to a gradual decomposition to 2 and unidentifiable materials.

6) We thank Mr. K. Fujita, JEOL Co., Akishima, for the measurements.

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