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THERMOLYSES OF 1,8-*CIS* AND *TRANS*-TRICYCLO[6.4.0.0^{3,6}]DODECA-4,10-DIENE-2,7-DIONE. A SEQUENTIAL RING OPENING AND INTRAMOLECULAR DIELS-ALDER REACTION LEADING TO A CAGE MOLECULE AND MARKED DEPENDENCE OF THE REACTION ON CONFIGURATION AND SUBSTITUENT

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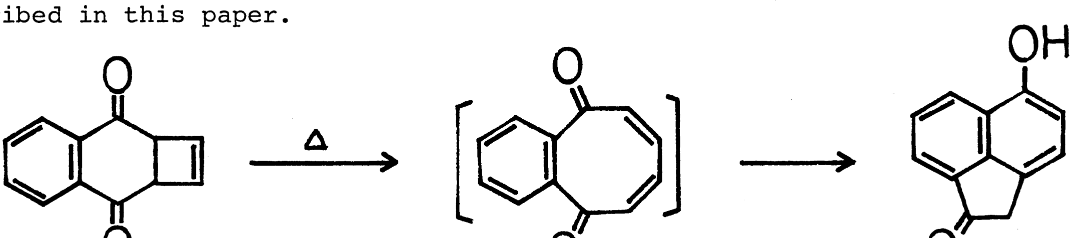
Thermolysis of the *cis* title compound 4 yields a cage molecule 6 by a sequential ring opening of the cyclobutene and intramolecular Diels-Alder reaction. On the other hand, the *trans* isomer 8 gives 2,3-benzo-2,5-cyclooctadiene-1,4-dione 10 by a ring opening followed by hydrogen shifts and an oxidation. While the former reaction shows a marked substituent effect, the latter does not. An unusual conformation of 10 is suggested.

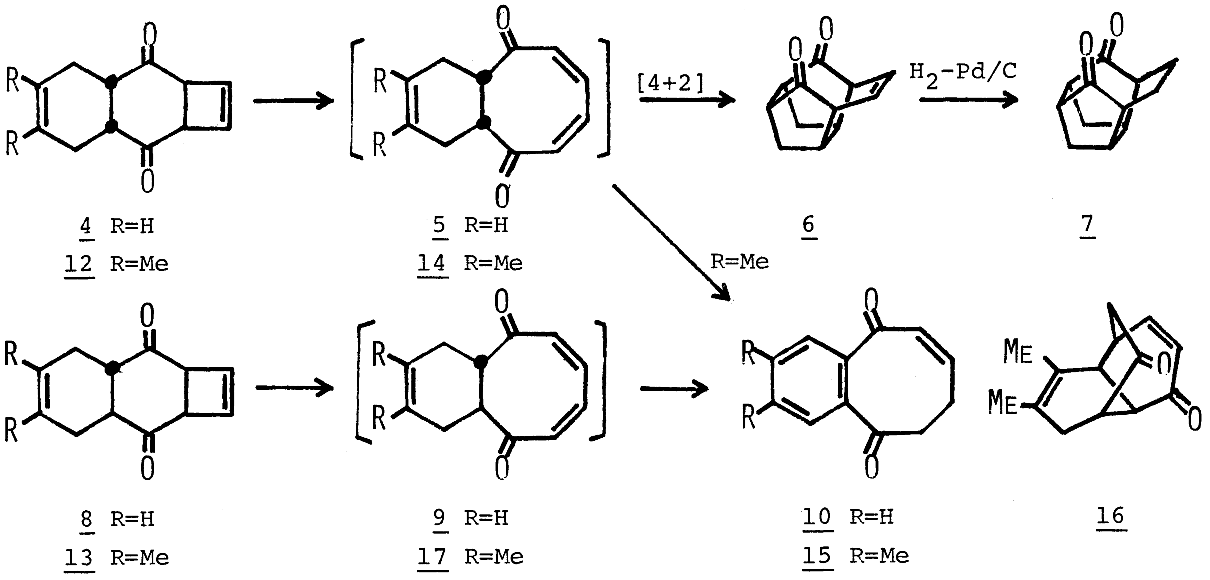
As a part of our project on the synthesis and chemistry of cyclooctatrienediones,[1] we are making efforts at the synthesis of 2,3-benzo-2,5,7-cyclooctatriene-1,4-dione 1. Our attempts to obtain 1 by thermal ring opening of 3,4-benzobicyclo[4.2.0]octa-3,7-diene-2,5-dione 2 were unsuccessful, giving 5-hydroxyacenaphthenone 3 by a rearrangement. For this rearrangement, however, we have suggested the intermediacy of 1, which may undergo thermal homolytic cleavage of the phenyl-carbonyl single bond in the first step of the rearrangement. In order to obtain insights into the reaction-mechanism and in addition to find a route to 1, we examined the title reactions and obtained some interesting results which are described in this paper.



2 1 3

Thermolysis of 1,8-*cis*-tricyclo[6.4.0.0^{3,6}]dodeca-4,10-diene-2,7-dione 4[2] at 480°C by a flow method[3] afforded the new cage molecule, tetracyclo[6.4.0.0^{3,11}.0^{6,10}]dodeca-4-ene-2,7-dione 6 (mp 244.5-246°C), in 43% yield.[4] The structure was elucidated from the following spectral data: MS, m/e=188 (M^+, 24%), 132 (37%), 78 (78%), 54 (100%); IR (KBr), ν=1738, 1625 cm^{-1} (five-membered ketone); UV (EtOH), λ=307 nm (ε 560)(β,γ-unsaturated ketone); PMR (100 MHz, $CDCl_3$), δ=6.19 (2H, dd, J=6.0, 3.0 Hz), 3.00 (2H, m), 2.76 (2H, br. s), 2.58 (2H, m), 2.38 (2H, d, J=13.0 Hz), 1.45 (2H, br. d, J=13.0 Hz). Hydrogenation of 6 over Pd-C yielded the dihydrocompound 7 [mp 249-250°C; m/e=190 (M^+, 63%), 112 (100%), 80 (93%); ν (KBr)=1740, 1721 cm^{-1}; λ (EtOH)=301 (38), 317 nm (sh, 27); δ (60 MHz, $CDCl_3$)=2.76 (4H, br.s), 2.55 (2H, d, J=13.0 Hz), 2.3-1.6 (6H, m), 1.36 (2H, br. d, J=13.0 Hz)]. The formation of 6 can be reasonably explained by ring opening of the cyclobutene producing *cis*-bicyclo[6.4.0]dodeca-3,5,10-triene-2,7-dione 5 and its successive intramolecular Diels-Alder reaction. In view of the participation of the relatively electron-rich olefin and the electron-poor diene, the cycloaddition may be a sort of *Diels-Alder reaction with inverse electron demand.*[5]

On the other hand, the *trans* isomer 8,[2] under the same condition, did not afford 6 at all and gave 2,3-benzo-2,5-cyclooctadiene-1,4-dione 10 in 65% yield [pale yellow liquid; m/e=186 (M^+, 28%), 86 (43%), 84 (66%), 49 (100%); ν (liquid film)=1705, 1640 cm^{-1}; λ (EtOH)=245 nm (8900); δ (100 MHz, CCl_4)=8.0-7.2 (4H, m), 6.45 (1H, dt, J=12.5, 7.0 Hz), 6.15 (1H, d, J=12.5 Hz), 2.8 (2H, m), 2.5 (2H, m)]. Hydrogenation of 10 yielded 2,3-benzocyclooctene-1,4-dione 11.[6] The reaction apparently involves ring opening to *trans*-bicyclo[6.4.0]dodeca-3,5,10-triene-2,7-dione 9, hydrogen shifts, and an oxidation, although the precise mechanism is obscure. The reason for this differnt result may be ascribed to the *trans* configuration of 9 which disfavors the intramolecular Diels-Alder reaction.



In order to examine generality of and substituent effects on these reactions, 10,11-dimethyl derivatives of 4 and 8, 12 and 13,respectively, were prepared by a similar way for 4 and 8: the reaction of bicyclo[4.2.0]octa-3,7-diene-2,5-dione[7] with 2,3-dimethylbutadiene in the presence of aluminum trichloride as a catalyst in methylene chloride at room temperature for one day afforded 12 and 13 in 19 and 48% yield, respectively [12: mp 76-77°C; ν (KBr)=1705, 1690, 1560 cm^{-1}; δ (60 MHz, $CDCl_3$)=6.31 (2H, s), 3.83 (2H, s), 3.19 (2H, m), 2.4-1.9 (4H, m), 1.63 (6H, s); 13: mp 116-117°C; ν (KBr)=1705, 16881, 1560 cm^{-1}; δ (60 MHz, $CDCl_3$)=6.3 (2H, m), 3.8 (2H, m), 3.3-2.6 (2H, m), 2.5-1.9 (4H, m), 1.65 (6H, s)].[8]

Against our expectation, thermolysis of 12 did not yield the dimethyl derivative of 6, but it afforded 2,3-(4,5-dimethylbenzo)-2,5-cyclooctadiene-1,4-dione 15 and a new diketone 16 in 27 and 22% yield, respectively [15: mp 97-98°C; ν (KBr)= 1705, 1639 cm^{-1}; λ (EtOH)=234 (10000), 272 nm (5900); PMR, Fig. 1; 16: mp 88.5-89.5 °C; ν (KBr)=1705, 1665, 1610 cm^{-1}; λ (EtOH)=244 nm (8600); δ (90 MHz, CCl$_4$)=7.16 (1H, dd, J=10.0, 6.3 Hz), 6.01 (1H, d, J=10.0 Hz), 3.0 (1H, m), 2.75 (4H, m), 2.53 (1H, d, J=6.0 Hz), 2.32 (1H, br. s), 2.13 (1H, m), 1.81 (3H, br. s), 1.75 (3H, s)]. From the spectroscopic data and mechanistic considerations, we tentatively assign the structure of 16 to 10,11-dimethyl tricyclo[6.4.0.0^{4,9}]dodeca-3,10-diene-2,7-dione which is formed by the bonding between C-4 and C-9 of the intermediate 14, probably via a diradical. Thus, the introduction of the dimethyl groups at the reaction center in the intramolecular Diels-Alder reaction caused a marked change in the fate of 5. Steric interactions between the methyl groups and carbon-6,7 of 14 in the transition state of the Diels-Alder reaction may be the reason.

The *trans* isomer 13 afforded only 15, as expected, in 67% yield.

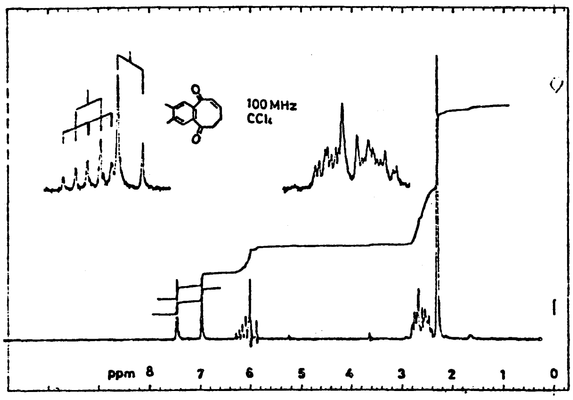


Fig. 1. PMR spectrum of 15 at 100 MHz

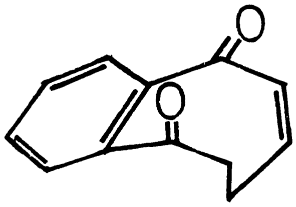


Fig. 2. Conformation of 10

Interestingly, 10 and 15 seem to take an unusual conformation when judged from the spectroscopic data. The carbonyl absorption of these compounds at 1705 cm^{-1} is 40 cm^{-1} higher than that of 11, although the partial structure is formally identical. The frequency corresponds to saturated eight-membered cyclic ketone. The two aromatic protons of 15 are seen at δ 7.48 and 6.98 in the PMR spectrum (Fig. 1). While the former chemical shift is comparable to those of aromatic protons of 11 (δ 7.61), the latter is substantially high. A molecular model of 10, when its enone group was set to be nearly coplanar with the benzene ring, indicates that the C-1 carbonyl group is almost perpendicular to the benzene ring (Fig. 2). This conformation reasonably explains the spectroscopic data, impeding conjugation between the carbonyl group and the benzene ring. Thus it seems that the strain energy of the eight-membered ring of 10 and 15 is greater than the stabilization energy gained by conjugation of the carbonyl group with the benzene ring.

REFERENCES AND NOTES

* To whom all correspondences should be addressed.

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2) M. Oda, H. Miyazaki, Y. Kayama, and Y. Kitahara, Chem. Lett., 627 (1975).

3) The thermolyses were performed by passing a benzene solution of substrates through a pre-heated column packed with pyrex chips at normal pressure under the flow of nitrogen.

4) Satisfactory elemental analyses were obtained for all the new compounds described in this paper.

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8) The ratio of 12 and 13 in this reaction depended on the reaction time. While short reaction time favors 12, prolonged reaction gave exclusively 13 by acid catalyzed isomerization of 12.

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