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A NEW SYNTHESIS AND THERMAL REARRANGEMENT OF 3,4-BENZOBICYCLO[4.2.0]OCTA-3,7-DIENE-2,5-DIONE

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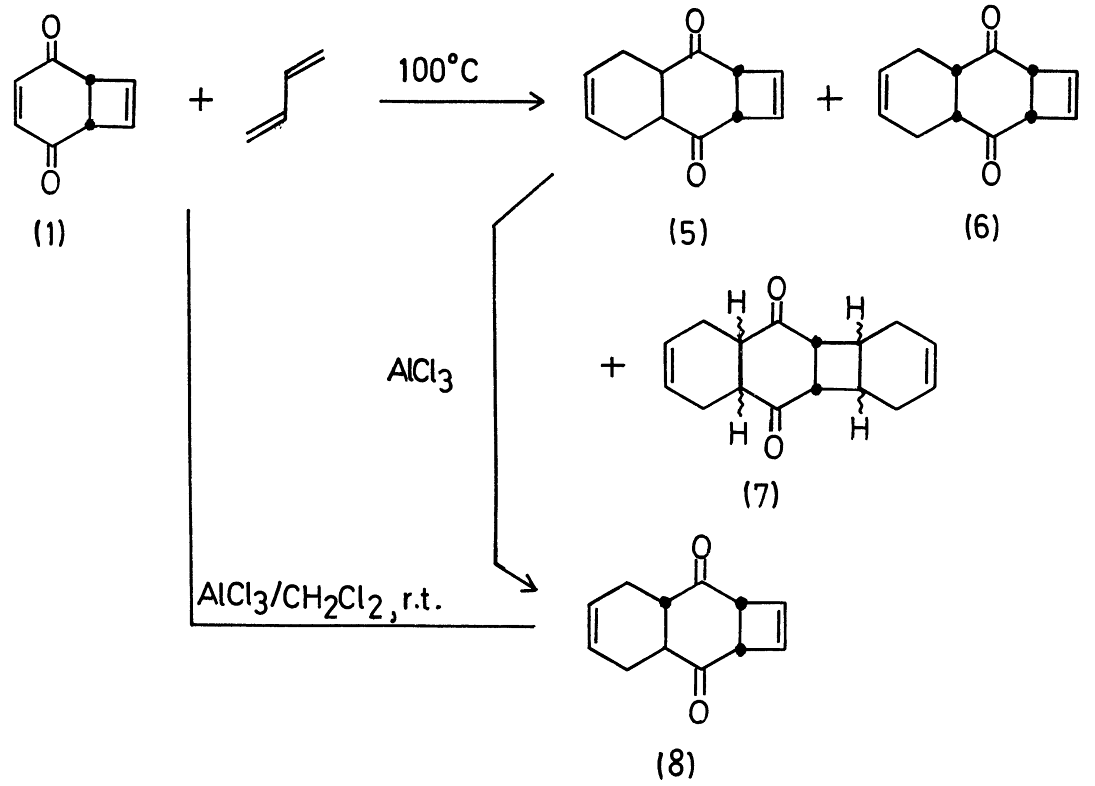
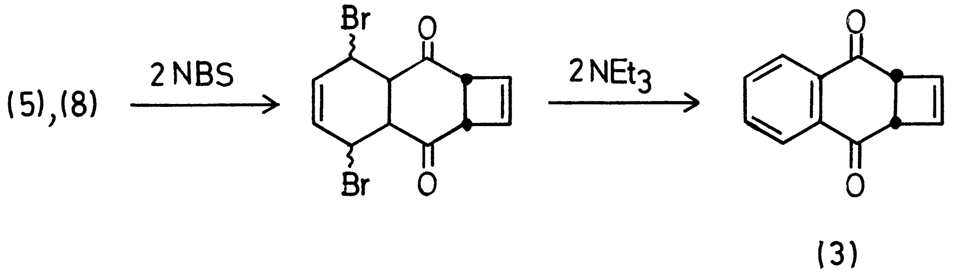
Title compound (3) was prepared by a new method from bicyclo-[4.2.0]octa-3,7-diene-2,5-dione through Diels-Alder reaction with butadiene, bromination with NBS, and then dehydrobromination with triethylamine. Thermolysis of (3) at 500°C gave, unexpectedly, 5-hydroxyacenaphthenone by a novel rearrangement. The intermediacy of 2,3-benzocyclooctatriene-1,4-dione is proposed.

We have recently reported the synthesis of bicyclo[4.2.0]octa-3,7-diene-2,5-dione (1) and its thermolysis which unexpectedly produced tropone (2) by extrusion of carbon monoxide.[1,2] As a plausible pathway for (2), we have suggested the intermediacy of *cis, cis, cis*- or *cis, cis, trans*-cycloocta-2,5,7-triene-1,4-dione.[2] According to the proposed pathway, 3,4-benzo-derivative of (1), title compound (3), should produce 2,3-benzocyclooctatriene-1,4-dione (4) on thermolysis. It was expected that there may be a good chance to isolate (4), since (4) may more resist to decarbonylation than (1) does by the stabilization effect of benzene ring, though the mechanism of decarbonylation is as yet uncertain. The preparation of (3) has been already reported from photo-addition of acetylene to naphthoquinone.[3,4] However, the yield is described only as poor. We wish here to report a new synthesis of (3) which starts from (1) and its thermal reaction which resulted, again unexpectedly, in a novel rearrangement.

Reaction of (1) with butadiene in xylene in a sealed tube at 100°C for 45 hrs gave two *cis* 1:1 Diels-Alder adducts, (5) and (6), and a 1:2 adduct (7) in 53%, 7%, and 3% yield, respectively [(5): mp 72-74°C; IR (KBr), ν_{max}=1698, 1560 cm^{-1}; ^{1}H-NMR (CDCl$_3$), δ=6.25 (2H, s), 5.55 (2H, s), 3.84 (2H, s), 3.1 (2H, m) 2.2 ppm (4H, m);

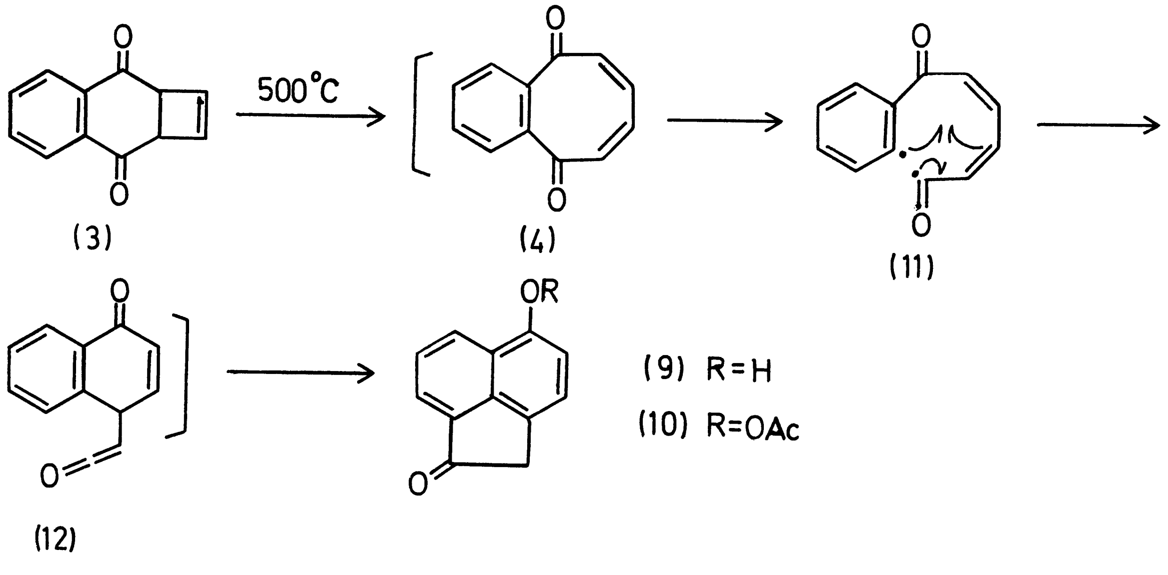
(6): mp 84.5-85.5°C; IR (KBr), ν_{max}=1700, 1560 cm^{-1}; ^{1}H-NMR (CDCl$_3$), δ=6.27 (2H, s), 5.59 (2H, t-like, J=1.3 Hz), 3.82 (2H, s), 3.03 (2H, m), 2.25 ppm (4H, m); (7): mp 113-115°C]. When the reaction was carried out at the presence of aluminum chloride (0.2 equiv) in methylene chloride at room temperature (one day), the *trans* 1:1 adduct (8) was obtained in 65% yield [mp 120.5-122°C; IR (KBr), ν_{max}=1705, 1690, 1560 cm^{-1}; ^{1}H-NMR (CDCl$_3$), δ=6.37 (2H, m), 6.21 (2H, narrow m), 3.88 (2H, m), 3.4-2.6 (2H, m), 2.6-2.0 ppm (4H, m)]. The adduct (8) may be the secondary product formed by acid catalyzed isomerization of (5), because the thermally obtained *cis*-adduct (5) gave (8) by treatment with aluminum chloride. The stereochemistry of (5) and (6) are tentatively assigned to *anti* and *syn*, respectively, from the steric viewpoint on accessibility of butadiene to (1); *anti*-side may be more accessible.





Bromination of (5) with N-bromosuccinimide (2.3 equiv) in refluxing carbon tetrachloride (1.5 hrs) and successive treatment with triethylamine gave (3) in 66% yield [pale yellow prisms, mp 169-170°C[6]; IR (KBr), ν_{max}=1670, 1595, 1580, 1286, 1213, 815, 775, 686 cm; ^{1}H-NMR ($CDCl_3$), δ=8.05 (2H, m), 7.73 (2H, m), 6.35 (2H, s), 4.12 ppm (2H, s); UV (EtOH), λ_{max}=227 (logε 4.47), 257 sh (3.89), 300 (3.17), 345 nm sh (2.27)].[7] The *trans*-adduct (8) gave similar result.

Thermal reaction of (3) at 400°C by a flow method[8] gave a yellow crystalline compound (9) (mp 214°C decomp) in ca 5% yield besides recovery of (3). At 500°C, (9) was obtained in 53% yield. The expected compound (4) was not detected. The compound (9) shows a hydroxy absorption at 3300 cm^{-1} and a carbonyl at 1690 cm^{-1} in the IR spectrum. The UV spectrum (EtOH) shows maxima at 242 (sh, logε 4.03), 265 (4.38), 307 (sh, 3.08), 322 (3.20), 336 (3.22), and 377 nm (3.47). The ^{1}H-NMR spectrum (acetone-d_6, 90 MHz) exhibits signals at δ 9.08 (br. s, OH), 8.30 (1H, dd, J=7.8 and 1.5 Hz, H-8), 7.81 (1H, dd, J=7.6, 1.5 Hz, H-6), 7.65 (1H, dd, J=7.8, 7.6 Hz, H-7), 7.27 (1H, slightly br. d, J=7.2 Hz, H-3), 6.97 (1H, d, J=7.2 Hz, H-4), and 3.67 ppm (2H, slightly br. s, H-2,2'). The compound (9) formed the acetate (10) [mp 125-126°C: IR, ν_{max}=1748, 1715 cm^{-1}; UV, λ_{max}=247 sh (logε 4.36), 255 (4.42), 304 (3.52), 321 (3.69), 328 (3.69), 342 nm (3.75); ^{1}H-NMR ($CDCl_3$, 90 MHz), δ=8.0-7.2 (5H, m), 3.78 (2H, s), 2.46 ppm (3H, s)]. These results indicate (9) to be 5-hydroxyacenaphthenone, and the ^{1}H-NMR signals can be reasonably assigned as indicated above.



The rearrangement probably proceeds via 2,3-benzocyclooctatriene-1,4-dione (4) which was expected to be formed, the diradical (11) and then the ketene (12). An attempt to trap (12) as an ester using methanol as the solvent in the thermolysis was, however, unsuccessful.[9]

Thus, thermal behaviors of (1) and (3) are markedly different; compound (1) undergoes decarbonylation, while (3) does not at all. Because thermolysis of bicyclo[4.2.0]oct-7-ene-2,5-dione affords 5,7-cyclooctadiene-1,4-dione in high yield,[10] it is apparent that the presence and nature of the double bond at C-3-C-4 in (1) and (3) plays decisive role on the reaction course. More resistance of (4) toward decarbonylation and higher stability of aryl radical over vinyl radical may be the reasons of the difference.

References and Footnotes

* To whom all correspondences should be addressed.

1) M. Oda, Y. Kayama, and Y. Kitahara, Tetrahedron Lett., 2019 (1974).
2) Y. Kayama, M. Oda, and Y. Kitahara, Tetrahedron Lett., 3293 (1974).
3) S. Farid, W. Kothe, and G. P. Pfundt, Tetrahedron Lett., 4147, 4151 (1968).
4) The yield of photo-adduct of naphthoquinone with 2-butyne is described as 6% in Lit. 5. Therefore, the yield with acetylene itself must be lower.
5) R. Breslow, D. R. Murayama, S. Murahashi, and R. Grubbs, J. Amer. Chem. Soc., 95, 6688 (1973).
6) The melting point is 15°C higher than the reported one (154-155°C[3]). We checked our data by a standard compound for melting point determination and hence the reported one may be that of impure compound.
7) The chemical shifts of protons on cyclobutene, the only reported data, are comparable with reported ones with a slight chemical shift difference.
8) The thermal reaction was carried out by passing a benzene solution of (3) under flow of nitrogen at normal pressure through a pre-heated column packed with pyrex glass tips.
9) Since intermolecular reaction may not be so favored against intramolecular reaction at the reaction condition, this result does not necessarily exclude the intermediacy of (12).
10) M. Oda, Y. Kayama, H. Miyazaki, and Y. Kitahara, Angew. Chem., in the press.

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