CHEMISTRY LETTERS, pp. 293-296, 1977. Published by the Chemical Society of Japan

SYNTHESES AND SOME CHARACTERIZATION OF 3,5,7-CYCLOOCTATRIENE-1,2-DIONE AND ITS 3-BROMO DERIVATIVE[1]

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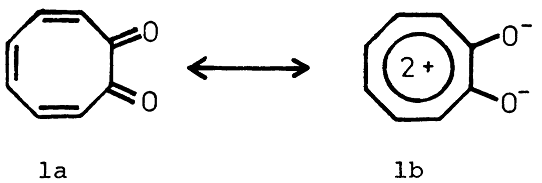
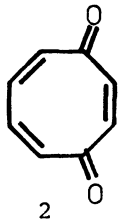
3,5,7-Cyclooctatriene-1,2-dione 1, a labile substance, is synthesized from 7-bromo-3,5-cyclooctadiene-1,2-dione by dehydrobromination and characterized by ^{1}H-NMR spectrum and some chemical reactions. The formation of 3-bromo derivative 3 is also demonstrated mainly by means of ^{1}H-NMR spectroscopy.

Among small to medium ring size non-benzenoid quinones, 3,5,7-cyclooctatriene-1,2-dione (cyclooctatetraeno-*o*-quinone) 1 is the most interesing compound remaining unknown, because 1 would show aromaticity if resonance contribution of the 6π canonical form 1b were significant enough. The other isomer of 1, cyclooctatetraeno-*p*-quinone 2, has been already synthesized in our laboratory;[2] however it was concluded 2 not to be aromatic. Although a few derivatives of 1 have been prepared[3] and attempts for synthesizing the parent compound 1 have been described,[4] 1 has escaped from the success. Very recently LeGoff et al. have suggested intermediary formation of 3-bromo-3,5,7-cyclooctatriene-1,2-dione 3 in the reaction of 3,7-dibromo-3,5-cyclooctadiene-1,2-dione 4 and triethylamine, which led to benzocyclobutenedione 5.[4b] We wish here to communicate the syntheses and some properties of 1 and 3.



1a 1b



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When a CDCl$_3$ solution of 7-bromo-3,5-cyclooctadiene-1,2-dione 6[5] was treated with one equivalent of triethylamine at -50°C in an NMR tube and a ^{1}H-NMR spectrum was taken at -48°C, a fairly clean and reasonable spectrum of 1 (Fig. 1) was obtained. The integrated area of the signals at olefinic region (δ 6.2-7.2) corresponds to approximately six protons by comparison with that of benzene added as an internal standard and of Et$_3$N$^+$HBr$^-$ concomitantly formed. The chemical shifts are comparable to those of *o*-benzoquinone.[6] The spectrum did not change appreciably on standing the solution at -20°C for one day, indicating either that 1 does not isomerize to the valence isomer 7 or that the equilibrium between 1 and 7 is at the side of 1, if any, beyond detection by ^{1}H-NMR spectroscopy.[7] When it was, however, brought up to room temperature, the observed signals disappeared in about ten minutes, and from this solution benzocyclobutenedione 5[8] and 4,6-cyclooctadiene-1,2-dione 8[9] were obtained although the yields were rather poor. This result indicates that at least at room temperature 1 valence-isomerized to 7 and there occurred an oxidation-reduction between 1 and 7. The valence isomer 7 was actually trapped as the Diels-Alder adduct 9 as follows; a crude solution of 1 was chromatographed on a short silica gel column in order to eliminate $Et_3N^+HBr^-$ using CH_2Cl_2-EtOAc (95:5) as the eluent at the temperature of Dry-Ice acetone and the yellow solution obtained was added to a CH_2Cl_2 solution of N-phenyltriazolinedione, wherefrom after standing at room temperature for a few hours 9 was obtained as solids by concentration in 13% yield [m.p. 220°C dec.; ν (C=O) 1810 sh, 1795 sh, 1770, 1705 cm^{-1}; δ ($CDCl_3$) 3.97 (2H, narrow m, four-membered ring protons), 5.47 (2H, m, bridgehead protons), 6.48 (2H, m, olefin protons), and 7.40 (5H, br. s, aromatic protons)]. The stereochemistry of 9 was tentatively assigned as depicted on the analogy of *anti-endo* configurations of Diels-Alder adducts of cyclooctatetraene.

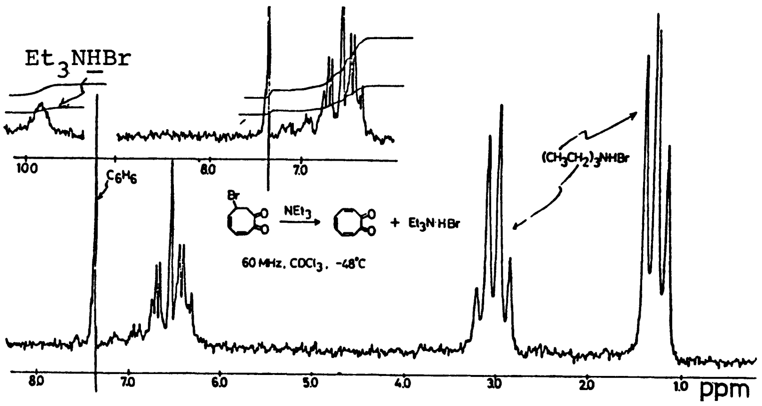
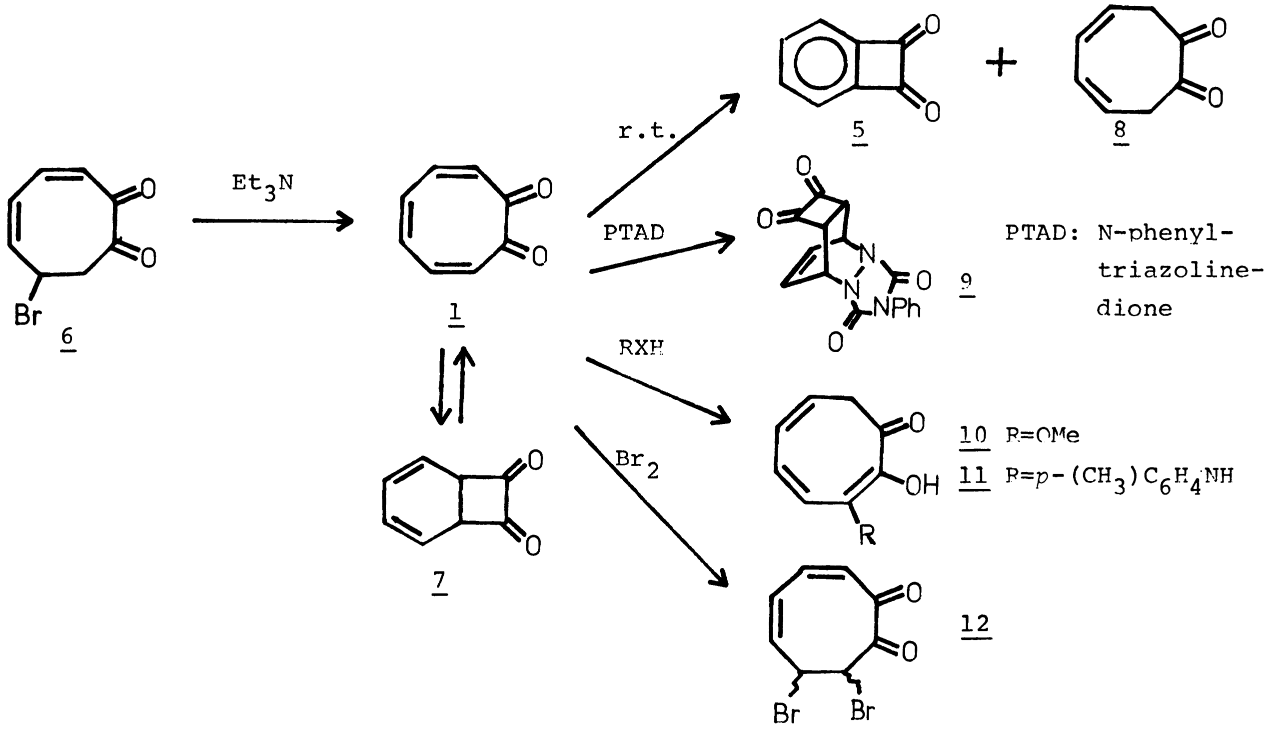


Fig. 1. ^{1}H-NMR spectrum (60 MHz) of 1 generated from 6 and Et_3N in $CDCl_3$, taken at -48°C.



The quinone 1 is susceptible to nucleophilic addition reactions. Addition of methanol to the solution of 1 at -30°C followed by warming the mixture to room temperature afforded 2-hydroxy-3-methoxy-2,4,6-cyclooctatrienone 10 in 56% yield [pale yellow liquid; ν (liquid) 2400-3500, 1645 cm^{-1}; λ (MeOH) 229 (logε 4.10) and 278 nm (3.77); δ (CCl_4) 2.67 (2H, d, J 6.7 Hz, methylene protons), 3.81 (3H, s, methoxy protons), 5.37 (1H, dt, J 9.5, 6.7 Hz, H-7), 6.1 (2H, m, H-5,6), 6.78 (1H, br. d, J 12 Hz, H-4), and 12.6 (1H, s, OH)]. With *p*-toluidine in a similar manner the corresponding addition product 11 (m.p. 148-149°C) was obtained in 25% yield. The mode of these additions is different from that in *o*-benzoquinone, in which nucleophilic additions usually occur at β-carbon to the carbonyl,[10] and rather resembles that in tropone.[11]

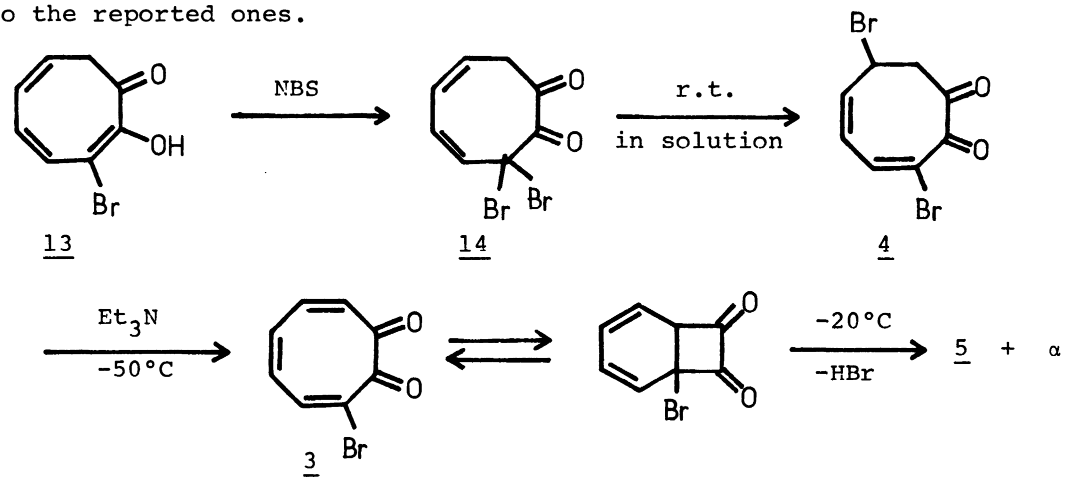
On action of bromine at -30°C, 1 afforded 7,8-dibromo-3,5-cyclooctadiene-1,2-dione 12 [δ ($CDCl_3$) 4.43 (1H, d, J 12.0 Hz), 4.93 (1H, dd, J 12.0, 7.0 Hz), 5.7-6.5 (3H, m), and 6.82 (1H, dd, J 12.0, 4.0 Hz] which is rather unstable and affords benzocyclobutenedione 5 on treatment with bases.

The IR spectrum of the $CHCl_3$ solution of 1 containing $Et_3N^+HBr^-$, when rapidly taken at room temperature, showed carbonyl and double bond absorptions assignable to those of 1 at 1644 (s) and 1568 (m) cm^{-1}, which decreased with time as new bands appeared at 1810 (m) and 1775 (s) cm^{-1}. The UV spectrum in CH_2Cl_2 showed maxima at 287 sh, 294, and 302 nm, which also decreased with a half-life of about fifteen minutes at 22°C. These spectral phenomena coincide with the result of ^{1}H-NMR and the chemical transformation.

All the attempts to isolate pure 1 by low temperature procedures have been so far unsuccessful.

Next we have attempted to synthesize the 3-bromo derivative 3. Although the precursor 4 was described by LeGoff, we prepared it in a different way as described below.

Treatment of 3-bromo-2-hydroxy-2,4,6-cyclooctatrienone 13[12] with N-bromosuccinimide in chloroform afforded, when rapidly worked up, the geminal dibromide 14 [m.p. 62.5-63°C; ν (KBr) 1725 and 1624 cm^{-1}; δ ($CDCl_3$) 3.54 (2H, d, J 7.6 Hz), 5.6-6.3 (3H, m), and 6.64 (1H, d, J 12.5 Hz)]. The dibromide 14 is, however, labile and rearranged on standing the reaction mixture at room temperature for one day to give 4 in 83% yield [m.p. 111-112°C, lit. 106-109°C[4b]], whose spectral data are identical to the reported ones.



Although LeGoff et al. could only obtain benzocyclobutenedione 5 by treatment of 4 with triethylamine and suggested the intermediacy of 3 for the formation of 5, we were able to observe 3 by means of low temperature ^{1}H-NMR spectroscopy in a similar way described for 1 (Fig. 2). The signals can be reasonably assigned as indicated in the chart. The rather small J_{Ha-Hb} and J_{Hc-Hd} (ca 4 Hz) are suggestive of non-planarity of the molecule.[13]

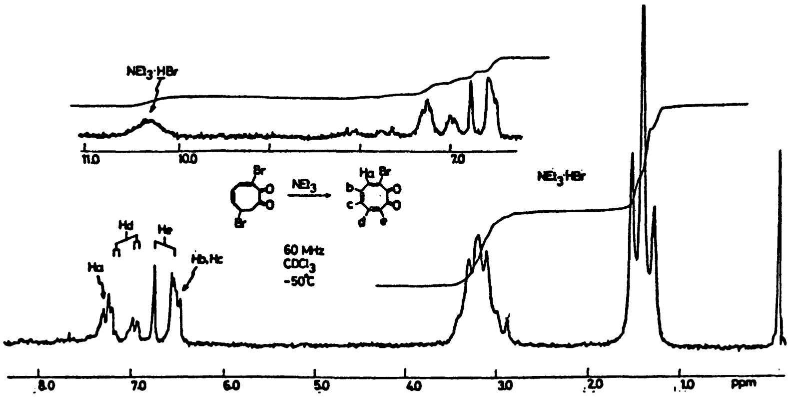


Fig. 2. ^{1}H-NMR spectrum (60 MHz) of 3 generated from 4 and Et_3N in $CDCl_3$, taken at -50°C.

The bromide 3 seems to be more labile than 1, for the signals assigned to the protons of 3 completely disappeared after four hours at -20°C, giving rise to benzocyclobutenedione and a compound not yet identified in ca 7:3 ratio in agreement with LeGoff's result.

In conclusion, 3,5,7-cyclooctatriene-1,2-diones, 1 and 3, do not show appreciable aromaticity, although some polar character is suggested by somewhat low chemical shifts of the protons and by the mode of methanol addition. The unusual instability of these compounds may be ascribed to the high reactivity of themselves and their valence isomers.

References and Notes

1) The contents of this paper were presented at "Ninth Symposium on Nonbenzenoid Aromatic Compounds" held in Sendai, December, 1976; text book, p. 67.
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6) St. Berger and A. Rieker, "The chemistry of the quinonoid compounds," Ed. S. Patai, Chapter 4, John Wiley & Sons, London, 1974.
7) The bridgehead protons of 7 are expected to appear at δ 4.0-4.5 as a doublet, because the corresponding proton of bicyclo[4.2.0]octa-2,4-diene-7-one is observed at δ 4.23; see M. Brookhart, G. O. Nelson, G. Scholes, and R. A. Watson, Chem. Commun., 195 (1976).
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9) Because of fairly ready enolization to 2-hydroxy-2,4,6-cyclooctatrienone, this compound has not been obtained in pure form. The structure was suggested by the spectra of a mixture with its enol and confirmed by isolation as the Diels-Alder adduct with N-phenyltriazolinedione [m.p. 240°C dec.; δ ($CDCl_3$) 3.01 (A_2B_2), 5.23 (2H, m), 6.60 (2H, m), and 7.5 (5H, m)].
10) Ref. 6, Chapter 17.
11) F. Pietra, "Seven-membered conjugated carbo- and hetrocyclic compounds," Chem. Rev., 73, 293 (1973).
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(Received January 17, 1977)