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SYNTHESIS OF CYCLOHEPTA-4,6-DIENE-1,2,3-TRIONE, o-TROPOQUINONE

Masahiro Hirama and Shô Itô*

Department of Chemistry, Tohoku University

Sendai 980, Japan

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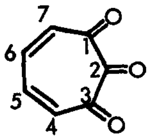
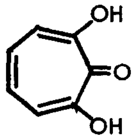
In the preceeding paper, we have described successful synthesis of p-tropoquinone, cyclohepta-3,6-diene-1,2,5-trione (1). The success encouraged us to prepare hitherto unknown o-tropoquinone **1**, a seven-membered vic-triketone analogous to o-benzoquinone. In this paper, we report the synthesis of its simple derivatives and the evidences for the presence of such a quinone itself

In analogous way to synthesizing p-tropoquinone, 3-hydroxytropolone **2** was submitted to a 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) oxidation. When DDQ (solid) was added under stirring to the colorless methanol solution of **2**, the solution immediately became yellow. The reaction mixture, after evaporation below 40° and short silica-gel column chromatography (CH_2Cl_2 soln.), afforded o-tropoquinone-2-methylhemiketal **3**, yellow crystals, m.p. ca 90°, with the following properties in 92% yield $\lambda_{max}^{CH_2Cl_2}$ 324 nm (log ϵ 3.70); $\nu^{CH_2Cl_2}$ 3430, 1699, 1670, 1527, 1358, 1115, 1070, 950 cm^{-1} ; MS (m/e) 168 (M^+), 138 (base peak), 136, 110, 92, 82, 81, 64; δ 3.33 (3H, s, Me), 5.7 (1H, br.m, OH), 6.33 and 6.68 (centers of AA'BB'); positive KI-starch test (2,3). **3** is very unstable to light. Catalytic reduction (Pd-C) of **3** afforded **2** quantitatively. However, all attempts to liberate methanol from **3** were unsuccessful contrary to the case of p-tropoquinone (1). The foregoing result disclosed that, although **2** can be oxidized to **1** by DDQ, the latter stabilizes as hemiketal in the presence of nucleophilic alcohol. This electrophilicity of **1** can be rationalized by the dipole-dipole interaction of three carbonyl groups in raw especially when the bond angle on seven-membered ring is taken into consideration, thus by forming hemiketal at the central carbonyl group the interaction should practically disappear (4).

The oxidation in the other solvents was next examined In dry acetone or acetonitrile the solution



1



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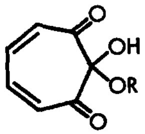
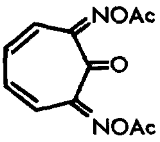


3 · R=Me

4 R=i-Pr

5 R=H



6

became deep red immediately on addition of DDQ. Although neither the isolation of the product nor the recovery of 2 was successful (5), the reaction mixture became orange yellow on addition of water and precipitated out in 81% yield the yellow prisms of o-tropoquinone-2-hydrate 5, m.p. 132° (dec.), λmax 307 (log ε 3.78), ν 3382, 3307, 1688, 1654, 1626 (sh), 1582, 1419, 1365, 1250, 1128, 1025, 943, 925, 836, 709 cm^{-1}; MS (m/e) 154 (M^+), 138, 110, 108, 92, 80, 64, 52 (base peak), 44, δ (acetone-d_6) 6.15 (1H, br.m, OH), 6.24 and 6.74 (centers of AA'BB', Table); positive KI-starch test. 5 is stable in the dark but decomposes under irradiation of light. 5 forms the corresponding dioxime, reddish purple crystals, m.p. ca 190° (dec.), whose diacetate, yellow needles, m.p. 132-134°, ν 1790, 1707, 1180, 1155, 944, 919, 893 cm^{-1}, has the anhydrous structure 6. Again, all efforts to dehydrate 5 were unsuccessful (6).

Thus, although not isolated, it is likely that o-tropoquinone exists in the red solution. This was verified spectroscopically. The IR spectrum of the reaction mixture (CH_3CN) clearly exhibits complex carbonyl bands at 1718 (sh), 1670 (sh), 1660 and 1655 (sh) cm^{-1} together with that due to DDQ (ν 1695 cm^{-1}). None of these bands corresponds either 2 or 5. The NMR spectrum of the reaction mixture in acetone-d_6 shows a clear AA'BB' pattern which is clearly different from those of 2 and 5 (Figure). Analysed parameters for these compounds are listed in the Table (7) Simulated spectrum of 1 using parameters in the Table is also shown in the Figure. The above observation disclosed beyond any doubt that the chemical species present in the red solution is different from any of 2 and 5 (8), and that the species is o-tropoquinone itself (9)

The oxidation was also attempted in CH_2Cl_2 and $CHCl_3$. When DDQ was added to the colorless solution of 2, the solution immediately turned to dark green at room temperature and no further change was observed for more than 5 hrs. IR spectrum of the solution is composed of the bands due to the starting materials, 2 and DDQ, while NMR spectrum is identical with that of 2 Upon addition of a few drops

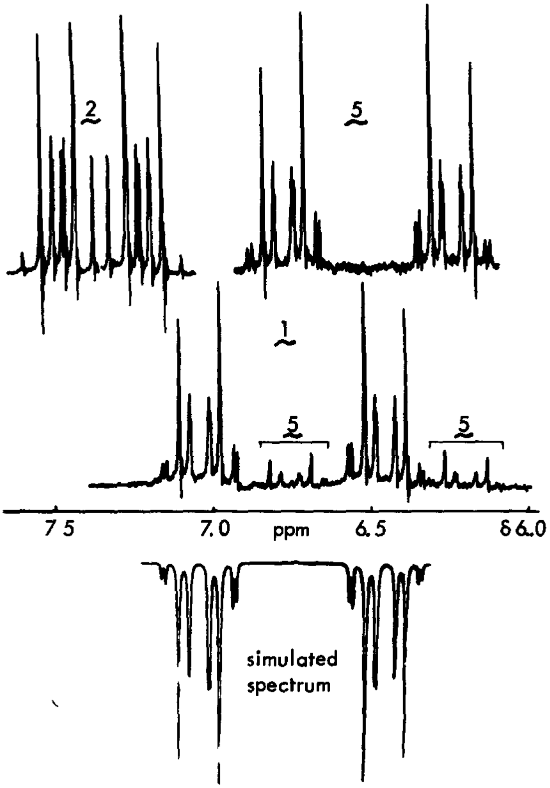


Figure. NMR spectra of 1, 2 and 5 (100 MHz, acetone-d_6) and simulated spectrum for 1 .

Table. NMR parameters for 1, 2 and 5

	2	1	5
δ_4, δ_7	7.228	6.460	6 238
δ_5, δ_6	7.490	7.038	6.749
$J_{4,5}$, $J_{6,7}$	10.24	12.45	12.65
$J_{5,6}$	10.38	8.27	7.96
$J_{4,6}$, $J_{5,7}$	0.93	0.47	0.68
$J_{4,7}$	0.28	0.84	0.92

of methanol, however, the green color immediately changed to yellow and afforded 3 in 80% yield. Furthermore, in UV spectrum of the green solution a broad charge-transfer band (λ 540-800 nm, ε 7-10 assuming 100% complexation) was clearly observed.

From these observations one could summarize the oxidation process proceeding through either one of the following sequences i) The initial formation of charge-transfer complex followed by the hydrogen transfer, subsequent dissociation to 1 and, if nucleophile is present, final hydrate (or hemiketal) formation. ii) The direct hydrogen abstraction without forming charge-transfer complex We prefer the former process because even in acetone transient green color was observed on the surface of DDQ (10).

Isolation of 1 as well as the reaction of 1 and 5 are in progress and will be reported elsewhere.

We thank Dr. Yoshimasa Fukazawa, Tohoku University, for his analysis of NMR spectra.

References and Footnotes

1) S. Itô, Y. Shoji, H. Takeshita, M. Hirama and K. Takahashi, *Tetrahedron Letters,* (1975).

2) All new compounds gave satisfactory elemental analyses. The spectral parameters refer to the following condition unless otherwise stated· UV, $CHCl_3$, IR, KBr disk; NMR, $CDCl_3$.

3) Similar oxidation in isopropanol yielded the corresponding hemiketal **4**, yellow oil, δ 1.16 (6H, d, J=6.1), 3.97 (1H, sep. J=6.1), 5.25 (1H, br.m, OH), 6.32 and 6.64 (centers of AA'BB') in 86% yield However in t-butanol, no hemiketal was formed although the oxidation proceeded.

4) The same tendency is observed for indantrione and cyclopentenetriones. Cf. indantrione T. Matsuura, R. Sugae, R. Nakashima and K. Omura, *Tetrahedron*, **24**, 6149 (1968), cyclopentenetriones T. Yamazaki, T. Oohama, T Doiuchi and T. Takizawa, *Chem. Pharm. Bull. Japan,* **20**, 238 (1972).

5) Evaporation of the solvent at -20° left dark violet resin which yielded nothing but 2,3-dichloro-5,6-dicyanohydroquinone on extraction with CH_2Cl_2 or $CHCl_3$. Direct chromatography (SiO_2 or Al_2O_3) of the reaction mixture eluted no product

6) All methods known to dehydrate ninhydrin have been tried. In most cases, **5** was recovered.

7) Analysis was carried out using Swalen's program. J D Swalen and C A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

8) That the coexistence of DDQ or the corresponding hydroquinone has little effect on the spectra was acertained also spectroscopically.

9) The decreasing order of chemical shift **2**→ **1**→ **5** is in parallel with the series 5-hydroxytropolone→ p-tropoquinone → p-tropoquinone methylhemiketal.

10) The formation of charge-transfer complexes was postulated for quinone dehydrogenation of hydroaromatic compounds. L M. Jackman, *Advan. Org. Chem.*, **2**, 329 (1960).