Tetrahedron Letters No. 13, pp 1075 - 1078, 1975. Pergamon Press. Printed in Great Britain.

SYNTHESES OF CYCLOHEPTA-3,6-DIENE-1,2,5-TRIONE, p-TROPOQUINONE

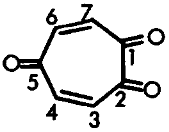
Shô Itô*, Yoshikazu Shoji, Hitoshi Takeshita, Masahiro Hirama and Kiyoshi Takahashi

Department of Chemistry, Tohoku University

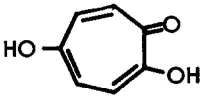
Sendai 980, Japan

(Received in Japan 28 January 1975; received in UK for publication 18 February 1975)

Cyclohepta-3,6-diene-1,2,5-trione, **1**, has a unique 7-membered quinone structure corresponding to 5-hydroxytropolone **2** and has been designated by Nozoe (1) as "p-tropoquinone" in analogy with p-benzoquinone. Although some of the derivatives, such as dibenzo-p-tropoquinone (2) and 4-hydroxy-3,6,7-triphenyl compound (3) have been synthesized and some of the 5-substituted tropolones behave as quinonoid derivatives (4), all attempts to synthesize the parent quinone **1** have been unsuccessful. We have succeeded in synthesizing **1**, both by photosensitized oxydation of **2** and tropolone, and by rather usual dichlorodicyano-p-benzoquinone (DDQ) oxidation of **2**.

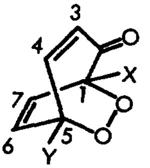


1

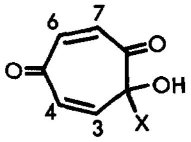


2

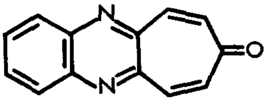
Photosensitized oxidation (600W tungsten lamp, hematoporphyrin, acetone, -60°) of 2-chloro-5-ethoxy tropone, m.p. 92-94°, (5) and 2,5-dimethoxytropone (7) resulted in the formation of the corresponding epidioxides **3** and **4** in 95% and 85% yields, respectively; **3**: pale yellow liquid, λmax 213 (log ϵ 3.79), 245 (3.44 sh), 270 (3.22 sh), 343 nm (2.92); ν 1710, 1660 cm^{-1} , δ 1.30 (3H, t), 3.90 (2H, q), 6.08 (H_3, d, J=12), 6.38 (H_7, d, J=10), 7.00 (H_4, dd, J=12, 1), 7.03 (H_6, dd, J=10, 1) (8), and **4** colorless crystals, m.p. 62.5-63 5°, λmax 214 (log ϵ 3.90), 250 (3.32 sh), 290 (2.52 sh), 360 nm (2.16 sh); ν 1698, 1640 cm^{-1} , δ 3.55, 3.58 (Me each 3H, s), 5.88 (H_3, d, J=12), 6.16 (H_7, d, J=10), 6.78 (H_4, dd, J=12, 1), 6.96 (H_6, dd, J=10, 1). Both **3** and **4** exhibit positive KI-starch test. Structure of these epi-



3 X=Cl, Y=OEt
4 X=Y=OMe
5 X=OMe, Y=H
6 · X=Y=H
7 X=Y=OH



8 X=OOH
10 X=OMe

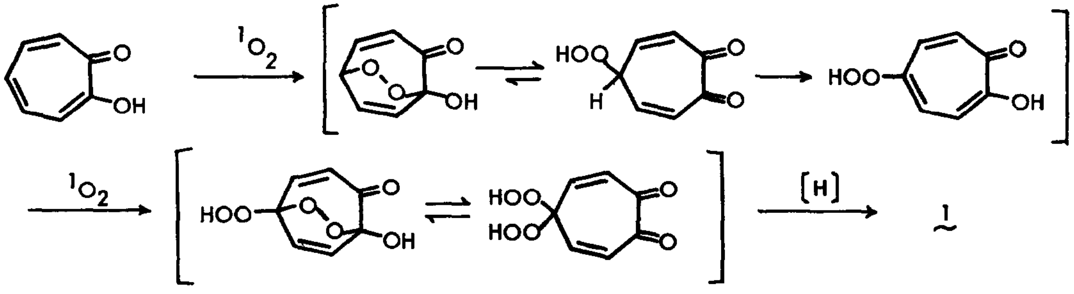


9

dioxides are evident from the comparison of the spectra with the known epidioxides 5 and 6 (9).

5-Hydroxytropolone 2 underwent the similar oxydation (hematoporphyrin, acetone, 0°, 2 hrs) (80% yield) but the product was not the epidioxide 7 but the hydroperoxide 8 with the tautomeric structure, pale yellow crystals, m.p. 80-83°, λmax 230 (log ε 3 89), 337 (2.88), 390 nm (2.68 sh); ν 3350, 1716, 1656, 1631, 1613, 1130, 860 cm^{-1} ; δ (acetone) 6 36 (H_4), 6 42 (H_3), 6.66 (H_6), 6.69 (H_7), J_{34}=11 6, J_{67}=12.6, J_{46}=1.2, J_{47}=0.6 The structure was determined from these spectra taking advantage of their similarity with those (vide infra) of p-tropoquinone methylhemiketal 10. 8 also exhibits a positive KI-starch coloration.

Although 3 and 4 hardly react with excess o-phenylenediamine, 8 forms quinoxalotropone 9 (4a) in quantitative yield. Apparently, o-phenylenediamine reacted as a reducing agent as well as the condensation reagent. Although H_2S, bisulfite, thiourea and triphenylphosphine are not effective to the reduction of 8, dimethylsulfide (MeOH, room temperature, 4 hrs) induced smooth reduction to give, after short SiO_2 column chromatography, p-tropoquinone 1 as pale yellow needles, m p. 62.5-63.5° (from CCl_4) in 80% yield (10, 11).



1 was also obtained in 10% yield directly from tropolone *via* similar exhaustive photooxydation (hematoporphyrin, acetone, -70°, negative $FeCl_3$ coloration, positive KI-starch test) and subsequent reduction with Me_2S. The entire reaction sequence is considered as shown above (12).

The third and more convenient synthesis of **1** was achieved by the chemical oxidation. Oxidation of **2** with p-chloranil (abs. MeOH, room temperature, 30 min.) or DDQ (abs. MeOH, room temperature, 5 min. or acetone, room temperature, 15 min.) afforded **1** after quick SiO_2 column chromatography in quantitative yield.

Structure of **1** was established from the following physical data as well as the correct elemental analyses. MS (m/e) 136 (M^+), 108, 82, 80, 54 (base peak), 52, 26; $\lambda_{max}^{CHCl_3}$ 253 (log ε 4.37), 342 (2.22), 410-500 nm (1 50), ν 1672, 1650, 1613, 1395, 1385, 1318, 1174, 1071, 868, 668 cm^{-1}; $\delta_{^1H}$ 6.88 (s), $\delta_{^{13}C}$ 134.6 (C_3, C_7), 138 8 (C_4, H_6), 186.0 (C_1, C_2), 187 4 (C_5), $J_{C_3H_3}$=$J_{C_4H_4}$=168, $J_{C_3H_4}$= $J_{C_4H_3}$=2, $J_{C_4H_6}$=4. $E_{1/2}$ (*vs.* aq. SCE) E_1=-0 28v, E_2=-0.92v for 1.05 mM CH_3CN solution at 25° (supporting electrolyte Et_4NClO_4 0.05 M). **1** gradually decomposes at room temperature under N_2. Although stable in nonpolar solvent, (*e g.* benzene 80°, 2 hrs) it decomposes gradually in acids and DMSO and rapidly in pyridine at room temperature.

1 forms hydrate and hemiketals reversibly at room temperature in water and primary alcohols, respectively, as detected spectroscopically, *e.g.* methylhemiketal **10**· λmax 230 (log ε 4.07), 286 (3 35 sh), 366 nm (2.46), δ (CD_3OD) 6 24 (H_4), 6 55 (H_3), 6 57 (H_6), 6.62 (H_7'), J_{34}=12.0, J_{67}=13.5, J_{46}=1.3, J_{47}=0.6. However, **10** easily reverts to **1** by evaporation of the solvent or on addition of nonpolar solvents.

Chemical reactions of **1** as well as the more detailed structure investigation are in progress and will be reported elsewhere

References and Footnotes

1) T. Nozoe, Yakugaku (Japanese), **3**, 174 (1949), Nature, **167**, 1055 (1951). The name "tropoloquinone" has been proposed for the same compound [M.J S. Dewar, Nature, **155**, 479 (1945)].

2) J. Rigaudy and L. Nédélec, Bull. soc chim. France, 655 (1959)

3) H. Wittmann, V. Illi, H. Rathmayer, H. Sterk and E. Ziegler, Naturforsch., **27B**, 524, 528 (1972).

4) a. For 5-nitrosotropolone· T. Nozoe, M. Sato and T. Matsuda, Sci. Repts. Tohoku Univ., Ser. I, **37**, 407 (1953), S. Itô, ibid., **42**, 236, 247 (1958), **43**, 216 (1959). b. For 5-arylazotropolones: T. Nozoe,

S. Itô, S. Suzuki and K. Hiraga, Proc. Japan Acad., **32**, 344 (1956), S. Itô, Sci. Repts. Tohoku Univ., Ser. I, **42**, 247 (1958).

5) Prepared by acid ethanolysis of 2,5-dichlorotropone (6).

6) T. Sato, J. Chem. Soc. Japan, **80**, 1171 (1959)

7) T. Nozoe, S. Seto, S. Itô, M. Sato and T. Katono, Proc. Japan Acad., **28**, 488 (1952).

8) All new compounds described gave correct elemental analyses. Spectral data refer to the following conditions unless otherwise stated UV, MeOH solution, IR; KBr disk for solid, film for liquid, NMR; CDCl$_3$ solution.

9) E.J. Forbes and J. Griffiths, J. Chem. Soc. (C), 575 (1968), M. Oda and Y. Kitahara, Tetrahedron Letters, 3295 (1969).

10) In normal manipulation, **8** was reduced without isolation and overall yield of **1** was 80% from **2**.

11) Although the reduction of **3** with dimethylsulfide (MeOH, room temperature) afforded **1** (in 30% yield isolated as **9**), a similar reduction of **4** yielded only dimethyl 4-keto-hepta-2,5-diendioate (30% yield).

12) That singlet oxygen is the actual reacting species was ascertained by radical quenching experiments: In the presence of excess of 2,6-ditertiarybutylphenol (DBP), the yield of peroxide (isolated as **9**) dropped to 1/4 after 2 hrs. However, addition of DBP after the oxidation also caused the decrease of the yield to the same extent.