CHEMISTRY LETTERS, pp. 885-888, 1977. Published by the Chemical Society of Japan

SYNTHESIS OF PLEIADIENE-7,8-DIONE, o-PLEIADIENOQUINONE

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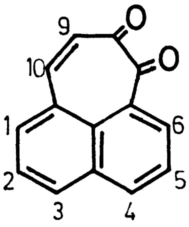
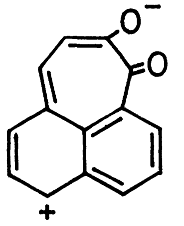
Pleiadiene-7,8-dione, o-pleiadienoquinone (I), was synthesized by hydrolysis of acenaphthylene-dichloroketene adduct (III). $E_{1/2}$ value is -0.23 V at pH 5.28. Spectral data suggest that I has the contribution from such canonical forms as 2,3- (Ia) and/or 4,5-benzotropolonate (Ib) structures.

Syntheses of pleiadene-7,12-dione and several of its derivatives were reported.[1] It was of interest to prepare and characterize the parent compound, a pleiadienoquinone, which is considered to belong to the class of nonbenzenoid quinones.[2]

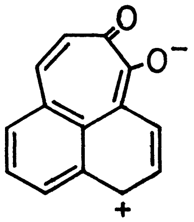
We wish to report the simple synthesis of pleiadiene-7,8-dione, o-pleiadienoquinone (I), which was proved to be appreciably diatropic, indicating the contribution of canonical forms such as (Ia) and/or (Ib). The compound I has a unique seven-membered quinone structure, which can be regarded as a kind of higher analog of acenaphthenequinone (II). Although II has been known for a long time and studied recently with respect to pyracyloquinone,[3] comparison of characteristics of I with those of II would reveal more essential features of these systems.



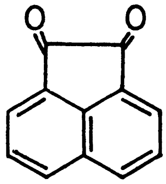
I



Ia



Ib



II

Addition of dichloroketene to acenaphthylene[4] resulted in the formation of the adduct (III)(10% yield): colorless cubes, mp 115-116°C; λ_{max}^{MeOH} 287 nm (log ε 4.18); ν_{max} 1796 cm^{-1}; δ (60 MHz) 4.93 (1H, d, J=7.0 Hz), 5.46 (1H, d, J=7.0 Hz), 6.67-8.33 (6H, m, aromatic). Hydrolysis of III either with sodium acetate in hot acetic acid at 85°C for 22 hr or with triethylamine in acetic acid at room temperature for 1 hr[5] afforded three products, namely, a hydroxyketone (IV)(9% yield): colorless needles, mp 153-154°C; $\nu_{max}^{CHCl_3}$ 3475, 1659, 1579 cm^{-1}; δ (100 MHz) 3.26(1H, d, J=13.1 Hz), 3.30 (1H, d, J=13.1 Hz), 4.41 (1H, s, OH), 7.10-8.50 (6H, m, aromatic); o-pleiadienoquinone (I)(52% yield): yellow needles, mp 115-116°C; m/e (75 ev), 208 (M^+), 180 (76%, M^+-CO), 152 (100%, M^+-2CO), 126 (10%, $M^+-2CO-C_2H_2$); $\nu_{max}^{CHCl_3}$ 1661, 1562 cm^{-1}, and a γ-lactone (V) (2% yield): pale yellow needles, mp 194-195°C; ν_{max} 1770 cm^{-1}; δ (60 MHz) 4.87 (1H, octet, J=10.5, 6.0, 1.0 Hz), 5.33 (1H, d, J=10.5 Hz), 6.43 (1H, d, J=6.0 Hz). Refluxing of IV in acetic anhydride gave an acetate (VI): red plates, mp 191-192°C; ν_{max} 1773, 1658 cm^{-1}; δ (60 MHz) 2.30 (3H, s), 3.29 (1H, d, J=9.9 Hz), 3.37 (1H, d, J=9.9 Hz).

The compound I can be obtained in 90 % yield from hydroxyketone(IV) by the same hydrolytic conditions as described above and therefore, IV is a precursor of I. The spectral data show that IV has a hydroxyketone structure but not a pleiadiene diol form (IV'), suggesting that in IV' the resonance energy obtained by taking the conjugated pleiadiene structure is smaller than the strain energy caused by the seven-membered ring skeletone.

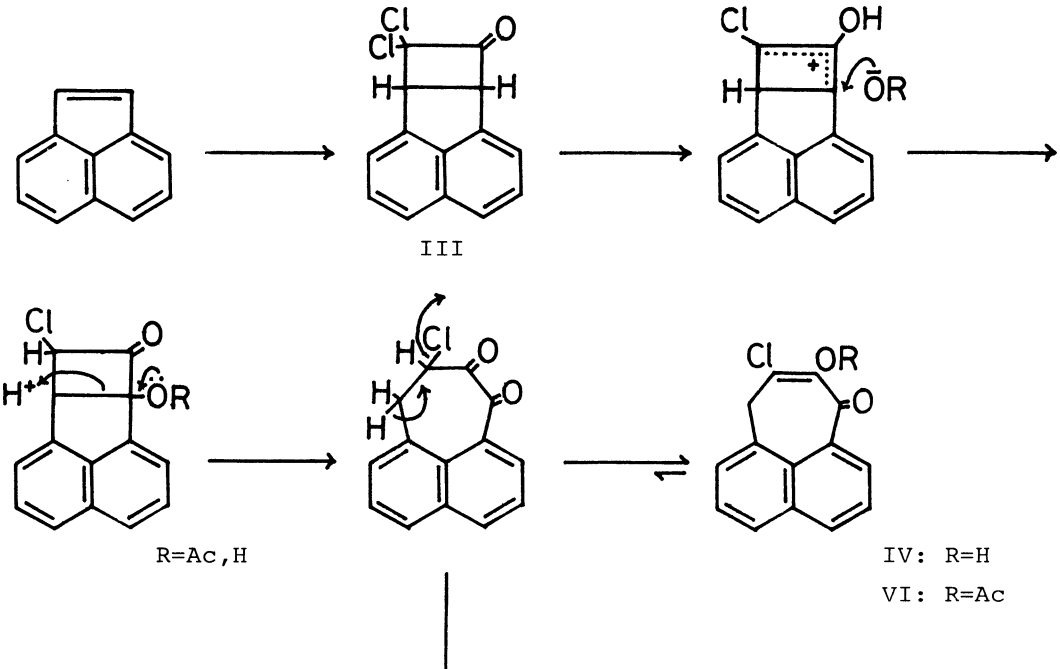
The mass spectra of I suggest that it is decomposed through phenalenone and acenaphthylene successively.

The reaction sequence of the formation of I can be considered as shown on the next page. It is interesting to note that Bartlett's reaction mechanism about the hydrolysis of the dichloroketene-cyclopentadiene adduct to tropolone can successfully be applied in this case also.[5)]

Upon refluxing IV with 2,3-dichloro-5,6-dicyanobenzoquinone for 22 hr in dry benzene, 9-chloropleiadiene-7,8-dione (VII) was obtained in 39 % yield; VII: yellow needles, mp 163-164°C; λ_{max} 300 nm (log ε 3.49), 315 (3.46), 360 (sh, 3.71), 405 (4.00); ν_{max} 1662, 1652, 1560 cm^{-1}; δ (60 MHz) 8.10 (1H, s), 7.55-8.59 (6H, m, aromatic). On refluxing with o-phenylenediamine in methanol, I and VII afforded the corresponding quinoxaline derivatives, VIII (98% yield) and IX (76% yield), respectively, VIII: orange yellow needles, mp 127-128°C; λ_{max}^{MeOH} 260 nm (log ε 4.69), 314 (4.41), 428 (4.61); ν_{max} 1654 cm^{-1}; δ (100 MHz) 6.15 (1H, d, J=12.7 Hz), 6.82 (1H, d, J=12.7 Hz), 7.08-8.10 (5H, m, aromatic), 8.55 (1H, dd, J=7.4, 1.7 Hz, aromatic); IX: yellow needles, mp 147-148°C.

Table. The ^{1}H NMR parameters of quinone (I) (δ values, internal standard TMS, J values in Hz.)

	H-1	H-2	H-3	H-4	H-5	H-6	H-9	H-10
δ_{CDCl_3}	7.84	7.60	8.09	8.23	7.73	8.43	6.56	7.59
	$J_{1,2}$=7.6, $J_{1,3}$=1.5, $J_{1,10}$=1.1, $J_{2,3}$=7.8, $J_{4,5}$=7.5, $J_{4,6}$=1.2, $J_{5,6}$=7.5, $J_{9,10}$=12.8							
δ_{CF_3COOH}	8.11	7.76	8.31	8.45	7.86	8.75	6.91	8.03
	$J_{1,2}$=7.5, $J_{1,3}$=1.0, $J_{2,3}$=7.5, $J_{4,5}$=8.0, $J_{4,6}$=1.2, $J_{5,6}$=8.0, $J_{9,10}$=12.5							
$\delta_{CDCl_3}-\delta_{CF_3COOH}$	-0.27	-0.16	-0.22	-0.22	-0.13	-0.32	-0.35	-0.44

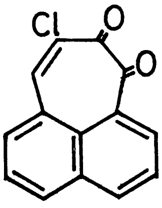


III

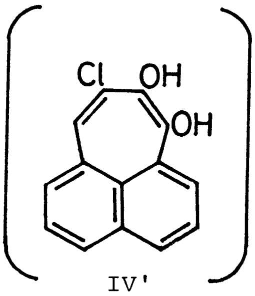
R=Ac,H

IV: R=H
VI: R=Ac

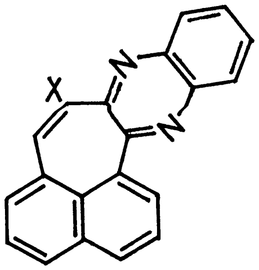
I



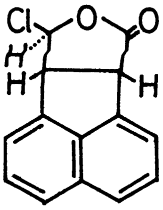
VII



IV'



VIII: X=H
IX: X=Cl



V

By comparing the PMR chemical shift difference (0.85~1.40 ppm) of the aromatic protons between pleiadiene ($CDCl_3$)[7] and I ($CDCl_3$) with that (0.45~0.56 ppm) between acenaphthylene (DMSO-d_6) and II (DMSO-d_6), it is evident that the ene-dione group attached to the peri position of naphthalene ring is significantly more electron attractive than the dione group. The diatropicity of I is increased appreciably in trifluoroacetic acid solution [δ(CF_3COOH) - δ($CDCl_3$) = -0.13~-0.32 ppm], while II showed little diatropicity [δ(CF_3COOH) - δ(DMSO-d_6) = -0.05~+0.1 ppm].[3] These facts suggest that I has some contribution from canonical structures like 2,3- (Ia) and/or 4,5-benzotropolonate (Ib) ions, 1,2- or 1,10-homophenalenium structures being discarded.8)

The half wave reduction potential of I [$E_{1/2}$(vs aq SCE), $E_1 = -0.23$ V (one electron), $E_2 = -0.40$ V (one electron), $E_3 = -1.14$ V (four electrons); c = 1.05mM in aqueous ethanol solution (28%); pH 5.28 (0.1M KNO_3), 0.05M citric acid, 0.1M Na_2HPO_4)] 6) is much higher than that of II 9) and is between that of β-naphthoquinone10) and anthraquinone.11)

^{13}C NMR data of carbonyl carbons of I, δ 191.6 and δ 192.6 (TMS, $CHCl_3$, 25 MHz), show the intermediate value of ordinary quinones12) and orthodicarbonyl carbons or conjugated carbonyl carbons. All these data seem to suggest that I has a considerable "quinone" character.

Further study of chemical reactions of I is in progress and will be reported elsewhere.

REFERENCES AND NOTES

1. A. Rieche and E. Frühwald, Chem. Ber., 64, 1603 (1931); A. Rieche, H. Sauthoff, and O. Müller, Chem. Ber., 65, 1371 (1931); W. Knapp, Monatsh. Chem., 60, 189 (1932); M. P. Cava and R. H. Schlessinger, Tetrahedron, 21, 3073 (1965).
2. T. A. Turney in "The Chemistry of the Quinonoid Compounds, Part 2," ed. by S. Patai, Wiley-interscience, New York, N. Y. (1974), P. 857.
3. B. M. Trost, J. Am. Chem. Soc., 88, 853 (1966); ibid., 91, 918 (1969).
4. All new compounds gave satisfactory elemental analyses. The spectral parameters refer to the following condition unless otherwise stated: ES, $CHCl_3$; IR, KBr disk; NMR, $CDCl_3$.
5. H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, J. Am. Chem. Soc., 87, 5257 (1965); P. D. Bartlett and T. Ando, ibid., 92, 7518 (1970); T. Asao, T. Machiguchi, and Y. Kitahara, Bull. Chem. Soc. Jpn., 43, 2662 (1970).
6. The authors wish to thank Dr. K. Takahashi and Prof. K. Takase of Tohoku University for running PMDR and ^{13}C NMR. They are also grateful to Nippon Electric Varian Co. for 100 MHz NMR and Prof. K. Morinaga of Saitama University for various supports on polarographic measurement.
7. J. E. Shields, D. Gavarilovic, J. Kopecky, W. Hartmann, and H. G. Heine, J. Org. Chem., 39, 515 (1974); I. Murata and K. Nakasuji, Tetrahedron Lett., 47 (1973).
8. R. C. Haddon, J. Am. Chem. Soc., 97, 3608 (1975); K. Nakasuji and I. Murata, Tetrahedron Lett., 2155 (1976).
9. K. Schwabe and H. Berg, Z. Electrochemie, 56, 952 (1952).
10. F. Poupe, Collection, 12, 225 (1947).
11. N. H. Furuman and K. G. Stone, J. Am. Chem. Soc., 70, 3055 (1948); D. Dobos, "Electrochemical Data," Akadèmiai Kiadò, Budapest, Hungary (1975).
12. J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York and London (1972), P. 294.

(Received May 10, 1977)