Oxidation of Abel's Ketone and Similar Spiroketones with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Synthesis of Novel Tropone Derivatives

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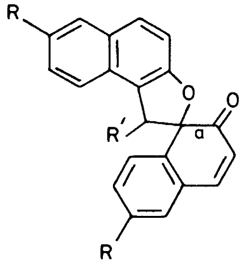
The structure of the novel product obtained from the oxidation of Abel's ketone **(1a)** and similar spiroketones **(1b—d)** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone has been determined on the basis of spectral data (i.r., n.m.r., and mass).

As part of our studies on the oxidation of naphthols with quinones,[1,2] the reaction of Abel's ketone {naphtho[2,1-*b*]-furan-2(1*H*)-spiro-1′(2′*H*)-naphthalen-2′(1′*H*)-one} (**1a**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was investigated. The structure of the novel product obtained from this reaction is reported here.

Oxidation of (**1a**) (1 mol) with DDQ (1 mol) in refluxing dry benzene for 8 h resulted in the formation of two yellow compounds (A and B†). On the basis of spectral data‡ (i.r., n.m.r., mass), the structure (**2a**) was assigned to compound A (M^+; 296). The low carbonyl i.r. absorption [ν_{max}(Nujol) 1628 cm^{-1}] of this compound is characteristic of tropones fused with aromatic systems. The two vinylic protons of the tropone skeleton are deshielded and appear with the other aromatic protons in the ^{1}H.n.m.r. spectrum. The two doublets at δ 8.68 and 9.58 are due to the highly deshielded protons at C-8 and C-1, probably deshielded by the furan oxygen atom and the carbonyl group, respectively. ^{13}C N.m.r. spectroscopy revealed the presence of one carbonyl carbon atom (δ 183.7) and two unsaturated carbon atoms attached to an oxygen atom (δ 156.4 and 152.8).



(1)

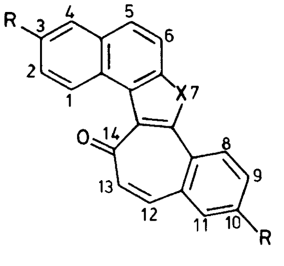
a; R = H, R′ = H

b; R = OMe, R′ = H

c; R = Br, R′ = H

d; R = $\mathrm{CMe_3}$, R′ = H

e; R = H, R′ = Ph



(2)

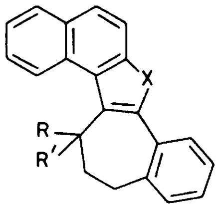
a; R = H, X = O

b; R = OMe, X = O

c; R = Br, X = O

d; R = $\mathrm{CMe_3}$, X = O

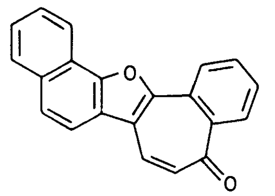
(5) R = H, X = NH



(3) R,R′ = O; X = O

(4) R,R′ = H, OH; X = O

(6) R,R′ = O; X = NH



(7)

To test the generality of this reaction, the oxidation of several spiroketones (**1b—d**) with DDQ was carried out and similar pairs of compounds (A and B) were formed (indicated by spectral data). However, oxidation of (**1e**) gave only a compound of type B. The compounds (A series) with ν_{max}(Nujol) 1628 cm^{-1} were therefore assigned the structures (**2b—d**).§

Hydrogenation of (**2a**) with 10% Pd–C gave a dihydroderivative (**3**), which on further treatment with sodium borohydride gave the alcohol (**4**). The spectral properties of compound (**2a**) and its dihydroderivative (**3**) are similar to those of the previously reported[4] compound (**5**)¶ and its dihydroderivative (**6**), respectively, thus further confirming structure (**2**) for compound A. Finally, an *X*-ray crystal structure analysis of (**2a**) proved the proposed structure beyond doubt.**

Mechanistically, the formation of compound (**2**) from (**1**) could occur by the initial abstraction of a hydride ion at a benzylic position by DDQ resulting in a carbonium ion, followed by migration of bond 'a' and subsequent loss of a proton.

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† The structure of compound B [M^+ 296; ν_{max}(Nujol) 1760 cm^{-1}], which seems to be complex, is still under investigation.

‡ All new compounds reported here have satisfactory elemental analyses. Spectroscopic data: (**2a**), ^{1}H n.m.r. δ (270 MHz; $\mathrm{CDCl_3}$) 7.03—7.97 (10H, m), 8.68 (1H, d, *J* 8 Hz), and 9.58 (1H, d, *J* 8 Hz); (**3**), M^+ 298; ν_{max}(Nujol) 1660 cm^{-1}; ^{1}H n.m.r. δ (270 MHz; $\mathrm{CDCl_3}$) 3.1—3.2 (4H, sym. m), 7.26—8.15 (9H, m), and 9.22 (1H, d); (**4**), M^+ 300; ν_{max}(Nujol) 3300—3400 cm^{-1}; ^{1}H n.m.r. δ [60 MHz, $\mathrm{(CD_3)_2SO}$] 1.8—2.6 (2H, m), 3.1 (2H, t), 5.5 (1H, OH), 5.65(1H, t), 7.2—8.3 (9H, m), and 8.8 (1H, d). The isomeric furanotropone (**7**) reported by Chatterjea and coworkers[3] has similar spectral properties.

§ Yield of compound A; (**2a**), 40; (**2b**), 50; (**2c**), 35; and (**2d**), 38%.

¶ Compound (**2a**) has been suggested[4] as an intermediate in the conversion of (**1a**) into (**5**) by reaction with hydroxylamine hydrochloride. However, when compound (**2a**) was treated with hydroxylamine hydrochloride under similar conditions no trace of compound (**5**) was detected.

** The *X*-ray crystal structure analysis was carried out by T. N. Guru row and K. R. Acharya; details will be published later.