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SYNTHESES OF 1,2,3,6-TETRAHYDROBENZOCYCLOBUTENE-3,6-DIONES

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Parent 1,2,3,6-tetrahydrobenzocyclobutene-3,6-dione and its simple derivatives were first synthesized by oxidation of bicyclo-[4.2.0]octane-2,5-diones in either one-step or stepwise manner.

Recently benzocyclobutenes have proved to be useful intermediates in organic syntheses, especially in syntheses of natural products and molecules of novel structure,[1] owing to their thermal ring opening to highly reactive *o*-xyxlylenes. In similar respect, the title compounds 1, new strained *p*-benzoquinones, would be interesting compounds as they could also undergo thermal ring opening of the four-membered ring. However, the parent quinone 1a (and even simple derivatives) has remained unknown, though the preparations of a naphtho analogue[2] and a tricyclic derivative[3] were described. We here report the first syntheses of the parent quinone 1a and its derivatives.

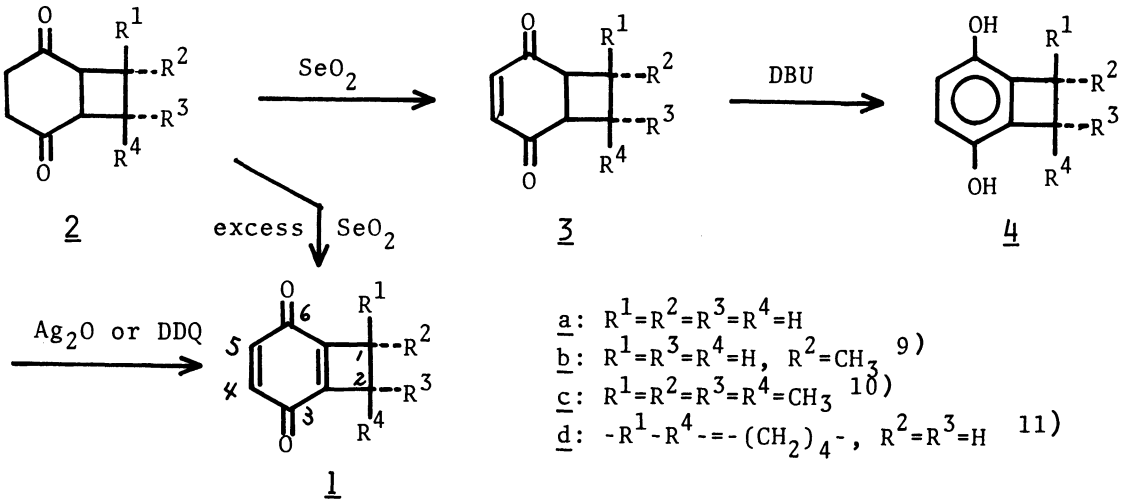
Having previously reported a simple synthesis of bicyclo[4.2.0]octane-2,5-diones (2),[4] we projected the transformation of the diketones 2 to the quinones 1.

When the diketone 2a was oxidized using two molar equiv. of selenium dioxide in refluxing dioxane (45-60 min) or ethyl acetate (10 hr), the quinone 1a was obtained in one step after chromatography on silica gel followed by sublimation *in vacuo* below 80°C in 25-35% yield.[5] The quinone 1a was also obtained in a stepwise manner as follows. Oxidation of the diketone 2a with one equiv. of selenium dioxide in ethyl acetate (3 hr reflux) gave the enedione 3a[6] in 50% yield,[7] which was then enolized to the hydroquinone 4a in 84% yield by treatment with 1,5-diazabicyclo[5.4.0]undecene-5 (1 equiv.) in tetrahydrofuran at room temperature. Oxidation of the hydroquinone 4a with either silver oxide in ether or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in acetonitrile gave the quinone 1a in 72-84% yield.

The physical and spectral properties of the quinone 1a and the hydroquinone 4a are following: 1a: yellow prisms; mp 71-72°C; MS, m/e 134 (M^+, 100%), 106 (38%), 78 (71%); IR, ν_{max}(KBr) 3050w, 1654vs, 1575m, 1343s, 1197m, 1083s, 1027s, 854s, 775m cm^{-1}; UV, λ_{max}(cyclohexane) 249 (log ε 4.25), 256 (sh, 4.19), 327 (2.72), 437 (1.34), 462 (1.36), 485 nm (1.22); ^1H NMR, δ (CCl_4) 3.03 (4H, s), 6.51 (2H, s); ^{13}C NMR, δ ($CDCl_3$-TMS) 28.6 (C-1,2; J_{CH}=145 Hz), 137.0 (C-4,5; J_{CH}=168.5 Hz), 152.1 (C-2a,6a), 181.9 (C-3,6). 4a: colorless crystals; mp 154-155°C; IR, ν_{max}(KBr) 3300 br, 1462s, 1240s; UV, λ_{max}(ethanol) 219 (3.81), 225 (sh, 3.78), 285 nm (3.39); ^1H NMR, δ ($CDCl_3$-CD_3OD) 3.08 (4H, s), 6.54 (2H, s).

The above transformations are applicable to the preparation of the derivatives bearing substituents on the four-membered ring. For instance, the derivatives

1b-1d were obtained from the corresponding diketones 2b-2d by the stepwise procedure in comparable or better total yield.[8]



a: $R^1=R^2=R^3=R^4=H$
b: $R^1=R^3=R^4=H$, $R^2=CH_3$ [9]
c: $R^1=R^2=R^3=R^4=CH_3$ [10]
d: $-R^1-R^4-=-(CH_2)_4-$, $R^2=R^3=H$ [11]

The chemistry of 1,2,3,6-tetrahydrobenzocyclobutene-3,6-diones (1) is under active investigation.

References and Notes

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2) (a) M.P. Cava and R.I. Shirley, J. Org. Chem., 26, 2212 (1961).
(b) P.J. Garratt and R. Zahler, Tetrahedron Lett., 1979, 73.

3) V. von Gizycki, Liebigs Ann. Chem., 753, 1 (1971).

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5) A small amount of a red, crystalline orgenoselenium compound (mp 113°C, $C_8H_6O_2Se_3$) was obtained as a by-product. Structural elucidation of this substance is under way.

6) Pale yellow liquid; bp 72°C/0.3 Torr; IR, ν_{max} 1675 cm^{-1} (C=O); ^1H NMR, δ (CCl_4) 2.05-2.75 (4H, m), 3.34 (2H, m), 6.62 (2H, s).

7) In addition to 3a, 1a (3%) and 4a (5%) were obtained as the minor products.

8) The yield of the quinones by the one-step procedure varied from poor to moderate depending on the substrates and the conditions employed, whereas the stepwise procedure seems to have better applicability.

9) 4b: mp 145°C; ^1H NMR, δ (CD_3OD) 1.43 (3H, d, J=7 Hz), 2.57 (1H, dd, 13, 2), 3.30 (1H, dd, 13, 5), 3.53 (1H, m), 6.52 (2H, s); 1b: oil; ^1H NMR, δ (CCl_4) 1.43 (3H, d, 7), 2.52 (1H, dd, 15, 1.8), 3.23 (1H, dd, 15, 4), 3.47 (1H, m), 6.52 (2H, s).

10) 4c: mp 213°C; ^1H NMR, δ (CD_3OD) 1.33 (12H, s), 6.47 (2H, s); 1c: mp 70°C; ^1H NMR, δ (CCl_4) 1.32 (12H, s), 6.46 (2H, s).

11) 4d: mp 179°C; ^1H NMR, δ (CD_3OD) 1.2-2.1 (8H, m), 3.50 (2H, m), 6.50 (2H, s); 1d: mp 47°C; ^1H NMR, δ (CCl_4) 1.3-2.2 (8H, m), 6.53 (2H, s).

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