A New Synthesis of Cyclobutadienequinones and Benzocyclobutadienequinone

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We wish to report a new approach to the synthesis of substituted cyclobutadienequinones and benzocyclobutadienequinone. It was found that under very mild conditions perbromide ion oxidizes the bis-silyl ether 1 to the cyclobutadienequinone 2.

Presumably after oxidative cleavage of the bis-silyl ethers 1 to a cyclobutenedione, bromination of the position 2 to a carbonyl group as well as the C==C double bond occurs to give the tribromodione 3. Spontaneous dehydrobromination of 3 at -78° gives the stable cyclobutadienequinone 2.

Upon treating 2 with a strongly basic amine such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), further dehydrobromination occurs to give high yields of benzocyclobutadienequinone (4).

Compared to previous syntheses of benzocyclobutadienequinone, the shorter procedure described here (diethyl 4-cyclohexene-1,2-dicarboxylate → 1 → 2 → 4) represents a several-fold improvement in overall yield from inexpensive non-aromatic starting materials.

3,4-Dibromo-7,8-dioxobicyclo[4.2.0]oct-6-ene (2):
To a solution of 7,8-bis-(trimethylsiloxy)-cis-bicyclo[4.2.0]octa-3,7-diene (1; 2.82 g, 10 mmol) in anhydrous tetrahydrofuran
(50 ml) maintained at -78° was added dropwise a solution of pyridinium hydrobromide perbromide (6.4 g, 20 mmol) in anhydrous tetrahydrofuran over a period of an hour. The solution was stirred for an additional hour. Upon warming to room temperature, the solid pyridine hydrobromide was filtered off and the solvent removed under reduced pressure at room temperature. The resultant red-brown oily crystals were triturated with ether and filtered. Recrystallization from dichloromethane/cyclohexane gave very light yellow crystals; yield: 0.8 g (27%), m.p. 161-164°.

C₇H₆Br₂O₂  calc. C 32.65  H 2.04  (293.9)  found  32.63  2.04

I.R. (CHCl₃):  ν_max = 3000 (C=H), 1795 (C=O), and 1615 cm⁻¹ (C=C).

¹H-N.M.R. (CDCl₃): δ = 4.74 (m, 2H, C-HBr), 3.67 (m, 4H, allylic) ppm.

Mass spectrum (70 eV): m/e = 134 (parent).

**Benzycyclobutadienequinone (4):**

To a solution of 3,4-dibromo-7,8-dioxobicyclo[4.2.0]oct-6-ene (2: 0.6 g) in dichloromethane (30 ml) was added dropwise, over a period of 1 hr, a solution of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN; 0.5 g, 4 mmol) in dichloromethane. The solution was then stirred at room temperature for 20 hr. The solution was washed well with water and saturated sodium chloride solution, then dried with magnesium sulfate, and the solvent removed; yield: 250 mg (92%); m.p. 129-132°.

I.R. (CHCl₃):  ν_max = 1808, 1777, 1760 cm⁻¹ (C=O).

¹H-N.M.R. (CDCl₃): δ = 8.00 ppm (AA'BB' pattern, aromatic).

Mass spectrum (70 eV): m/e = 132 (parent).

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