Anal. Calcd for C_5H_7NO: C, 61.83; H, 7.27. Found: C, 62.02; H, 7.38.

Registry No.—**3a**, 13369-23-8; **3b**, 13369-24-9; **3c**, 13369-25-0; **3d**, 13369-26-1; **4a**, 13369-27-2; **4b**, 13369-28-3; **4c**, 13369-29-4; **5b**, 4941-92-8; **5c**, 13369-31-8; **5d**, 13369-32-9; **6**, 13369-33-0; **7**, 6052-73-9.

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4-Cycloheptatrienylidene-2,6-dibromocyclohexa-2,5-dienone. A Stable Quinocycloheptatriene

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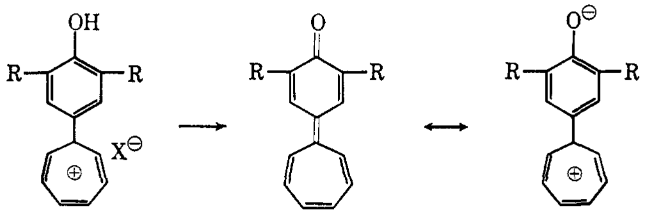
Interest in quinone methides of type **1** has centered around the question as to whether the charge-separated form contributes significantly to the structure.[1-3] This can presumably be determined by examination of the infrared carbonyl absorption. Several attempts have been made, therefore, to prepare compounds of type **1** by removal of HX from the appropriate tropylium ion **4** with base or thermally.[1-3] Compounds **1a** and **1b** have been reported to be air-sensitive, unstable, purple solids for which no satisfactory elemental analyses could be obtained. Their structural assignment[2] was supported[3] by the reaction of **1a** with acid to give the tropylium ion **4a** or with sodium borohydride to give the cycloheptatriene **3a**. Lack of absorption between 1600 and 2850 cm^{-1} was offered as evidence for the charge-separated form.[3] A recent patent[4] also reports several quinone methides of type **1**.



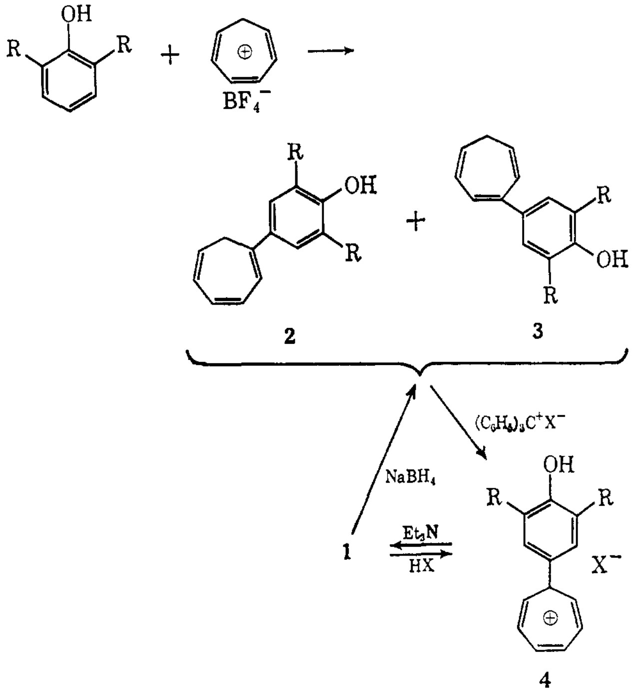
4 **1**

a, R = H; **b**, R = CH_3; **c**, R = Br

We wish to report the preparation and some reactions of a stable quinone methide, **1c**. The presence of bromine atoms has been found to increase the stability of analogous quinone methides in the cyclopropene series,[5,6] and it was hoped that the effect would be operative in the cycloheptatriene series.

Alkylation of 2,6-dibromophenol with tropylium fluoroborate in pyridine gave, upon distillation, a 46% yield of a mixture of **2c** and **3c** from which the 3 isomer **3c** was separated by fractional crystallization. The mixture was converted to the tropylium salt **4c** with the appropriate triphenylmethyl salt. When the tropylium salt **4c** was treated with triethylamine in acetonitrile, the crystalline quinone methide **1c** precipitated. It could also be obtained by treating an aqueous solution of **4c** with base (see Scheme I).

SCHEME I



a, R = H; **b**, R = CH_3; **c**, R = Br

The quinone methide **1c** is stable at room temperature in air and in acetonitrile solution. Addition of hydroxylic solvents or triethylamine to the solution destroys the characteristic purple color. The proposed structure is supported by chemical evidence. The compound is converted to the tropylium ion **4c** by perchloric or fluoroboric acid, and is reduced to a mixture of **2c** (45%) and **3c** (55%) by sodium borohydride.

A satisfactory nmr spectrum was not obtained for lack of a suitable solvent. The material is not sufficiently soluble in deuteriochloroform, deuteriobenzene, dueteriopyridine, acetone, acetonitrile, or methylene chloride; it reacts with dimethyl sulfoxide. Visible absorption occurs at 552 mμ. The infrared spectrum (KBr) shows no bands between 1580 and 3000 cm^{-1}, which suggests that the compound exists as the charge-separated form.

Since the dibromoquinone methide **1c** had been isolated as a stable solid from triethylamine in acetonitrile, the preparation of the dimethyl compound **1b** was reinvestigated under these conditions. Tropylation of 2,6-dimethylphenol in pyridine, followed by distillation, gave a 70% yield of a mixture of **2b** and **3b**. This yield compares favorably to the one previously reported from the alkylation in acetic acid[1] (9.1%). The 3 isomer **3b** could be separated by crystallization. The mixture was readily converted to the desired tropylium

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[1] R. VanHelden, A. P. terBorg, and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 599 (1962).

[2] C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29 (1964).

[3] P. Bladon, P. L. Pauson, G. R. Proctor, and W. J. Rodger, *J. Chem. Soc., Sect. C*, 926 (1966).

[4] T. Nozoe, Japanese Patent 17674 (1964); see *Chem. Abstr.*, **62**, 5234 (1965).

[5] B. Föhlisch and P. Burgle, *Tetrahedron Letters*, 2661 (1965).

[6] A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963).

salt **4b** (perchlorate or fluoroborate) with the appropriate triphenylmethyl salt. Treatment of salt **4b** with triethylamine in acetonitrile, however, gave only a purple solution from which no solid was isolated.

Experimental Section

Melting points and boiling points are uncorrected. The nmr spectra were measured in deuteriochloroform with a Varian A-60 instrument. Ultraviolet and visible spectra were measured in acetonitrile on a Perkin-Elmer Model 202 instrument.

Tropylation of 2,6-Dibromophenol.—A mixture of 20 g (0.12 mole) of 2,6-dibromophenol, 18 g (0.10 mole) of tropylium fluoroborate, and 100 ml of pyridine was heated at reflux for 2 hr and concentrated. The residue was extracted into methylene chloride, washed with acid followed by water, dried, and concentrated. Distillation of the residue gave some starting phenol, bp 80–150° (0.05 mm), followed by 15.8 g (46%) of the tropylphenols, bp 164° (0.05 mm), which solidified on standing, mp 87–97°.

Anal. Calcd for $C_{13}H_{10}Br_2O$: C, 45.8; H, 3.0; Br, 46.8. Found: C, 45.8; H, 3.1; Br, 46.5.

The nmr spectrum showed two types of allylic seven-membered ring protons; a triplet at τ 7.70 ($J = 7.0$ Hz), and a doublet at τ 7.39 ($J = 7.0$ Hz) of total area 2 H. The doublet is assignable to 1-(3,5-dibromo-4-hydroxyphenyl)-1,3,5-cycloheptatriene (**2c**) (42%) and the triplet to the 3 isomer **3c**. The 2 isomer would also show the triplet, but it is formed at a much slower rate.[7] The 3 isomer was isolated by fractional crystallization from ligroin, 2.7 g, mp 109–110°, and its nmr spectrum has peaks at τ 2.5, singlet (2 H, aromatic), 3.29, doublet ($J = 3.0$ Hz, 1 H, 4-vinyl), 3.6–3.9, multiplet (2 H, 2- and 5-vinyl), 4.20, singlet (1 H, hydroxyl), 4.3–4.7, multiplet (2 H, 1- and 6-vinyl), and 7.70, triplet ($J = 7.0$ Hz, 2 H, allyl).

Anal. Calcd for $C_{13}H_{10}Br_2O$: C, 45.8; H, 3.0; Br, 46.8. Found: C, 45.7; H, 3.2; Br, 46.8.

3,5-Dibromo-4-hydroxyphenyltropylium Perchlorate and Fluoroborate (**4c**).—When the mixture of isomers **2c** and **3c** was treated with an equivalent amount of triphenylmethyl fluoroborate in acetonitrile, the salt **4c**, mp 192–194° (94%), was obtained upon addition of ether.

Anal. Calcd for $C_{13}H_9Br_2OBF_4$: C, 36.4; H, 2.1; Br, 37.3. Found: C, 36.8; H, 2.4; Br, 37.6.

The perchlorate was prepared in a similar manner from triphenylmethyl perchlorate (62%), mp 213–214°.

Quinone Methide 1c.—A solution of 2.4 g (0.24 mole) of triethylamine in 10 ml of acetonitrile was added in portions to a solution of 10.0 g (0.0234 mole) of ion **4c** (fluoroborate) in 150 ml of acetonitrile. After the purple mixture had been stirred for 30 min, the solid was collected, washed with solvent, and dried; 7.0 g (88%), mp 167° dec. Microscopic examination revealed that the solid was crystalline.

Anal. Calcd for $C_{13}H_8Br_2O$: C, 46.0; H, 2.4; Br, 47.0. Found: C, 45.7; H, 2.7; Br, 46.9.

Visible absorption occurred at 552 mμ (log ϵ 4.25) and ultraviolet absorption at 224 mμ (log ϵ 4.35) and 285 mμ (log ϵ 3.96), with a shoulder at 315 mμ (log ϵ 3.81).

A 0.50-g (0.0015 mole) portion of compound **1c** in 5 ml of acetonitrile was treated with 48% fluoroboric acid until the purple color disappeared. Ether was added and the yellow solid collected to give 0.58 g (93%) of 3,5-dibromo-4-hydroxyphenyltropylium fluoroborate (**4c**), mp 192–194°, mmp 192–194°, which was identified by its infrared spectrum.

Reduction of Compound 1c.—A 0.50-g (0.0015 mole) portion of compound **1c** was added to a suspension of 0.25 g (0.0066 mole) of sodium borohydride in 10 ml of 1,2-dimethoxyethane. The purple color was discharged immediately. After the mixture had been standing for 15 min, the solvent was removed and cold dilute hydrochloric acid was added. The product was extracted into ether, washed with water, dried, and concentrated to give 0.48 g (96%) of oil. All operations were conducted below 30°. The nmr spectrum showed the oil to be a mixture of **2c** (45%) and **3c** (55%). See the Experimental Section of the tropylation of 2,6-dibromophenol for a discussion of the nmr data.

Tropylation of 2,6-Dimethylphenol.—The procedure described for the tropylation of 2,6-dibromophenol was used with 15 g (0.084 mole) of tropylium fluoroborate and 15 g (0.12 mole) of 2,6-dimethylphenol, and gave 12.5 g (70%) of the 4-tropylphenols, bp 135–140° (0.10 mm), which solidified on standing, mp 73–83°.

Anal. Calcd for $C_{15}H_{16}O$: C, 85.0; H, 7.6. Found: C, 85.3; H, 7.5.

The nmr spectrum showed that the product was a mixture of **2b** (25%) and **3b** (75%) by integration of the allylic methylene proton peaks. The 1 isomer has a doublet for the allylic proton (τ 7.30, $J = 7.0$ Hz) and the 3 isomer a triplet (τ 7.70, $J = 7.0$ Hz). The amount of 1 isomer, presumably formed by thermal isomerization of the 3 isomer, is reduced by decreasing the time of heating during distillation.

The 3 isomer was readily separated by crystallization from ligroin, 2.2 g, mp 85–86°. Its nmr spectrum has peaks at τ 2.91, singlet (2 H, aromatic), 3.15, doublet ($J = 3.0$ Hz, 1 H, 4-vinyl), 3.6–3.9, multiplet (2 H, 2- and 5-vinyl), 4.3–4.8, multiplet (2 H, 1- and 6-vinyl), 5.39, singlet (1 H, hydroxyl), 7.70 triplet ($J = 7.0$ Hz, 2 H, allyl), and 7.76, singlet (6 H, methyl).

Anal. Calcd for $C_{15}H_{16}O$: C, 85.0; H, 7.6. Found: C, 84.8; H, 7.8.

3,5-Dimethyl-4-hydroxyphenyltropylium Perchlorate and Fluoroborate (**4b**).—A solution of 4.25 g (0.020 mole) of the mixture of isomers, obtained as described, in acetonitrile was added to a suspension of 6.0 g (0.018 mole) of triphenylmethyl fluoroborate in acetonitrile. After 1 hr, excess ether was added and the solid was collected, 4.8 g (81%), mp 214–215°. The melting point was lowered (210–212°) upon recrystallization from acetonitrile.

Anal. Calcd for $C_{15}H_{15}BF_4O$: C, 60.6; H, 5.1. Found: C, 60.7; H, 5.4.

The perchlorate was obtained in a similar manner (97%), mp 222–223°.

Registry No.—**1c**, 13270-36-5; **2b**, 13250-34-5; **2c**, 13270-37-6; **3b**, 13250-32-3; **3c**, 13250-33-4.

Acknowledgment.—The author is grateful to Dr. T. H. Regan for the nmr spectra and for discussions concerning their interpretation.

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[7] A. P. terBorg and H. Kloosterziel, *Rec. Trav. Chim.*, **82**, 741 (1963).