Stable Quinotropones from Heptachlorotropylium Ion

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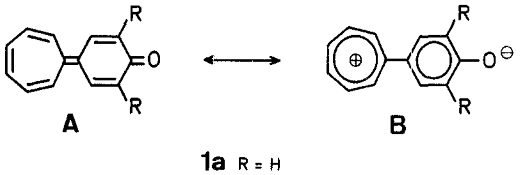
The possible existence of analogues of tropones in which the oxygen atoms are separated from the seven-membered ring have been discussed[1], and several workers have reported the synthesis of 4-cycloheptatrienlylidenecyclohexadienones. Bladon et al.[2], obtained a deeply colored material believed to be **1a** by treatment of *p*-hydroxyphenyltropylium perchlorate with base, and showed that on acidification their product was reconverted to the original perchlorate.

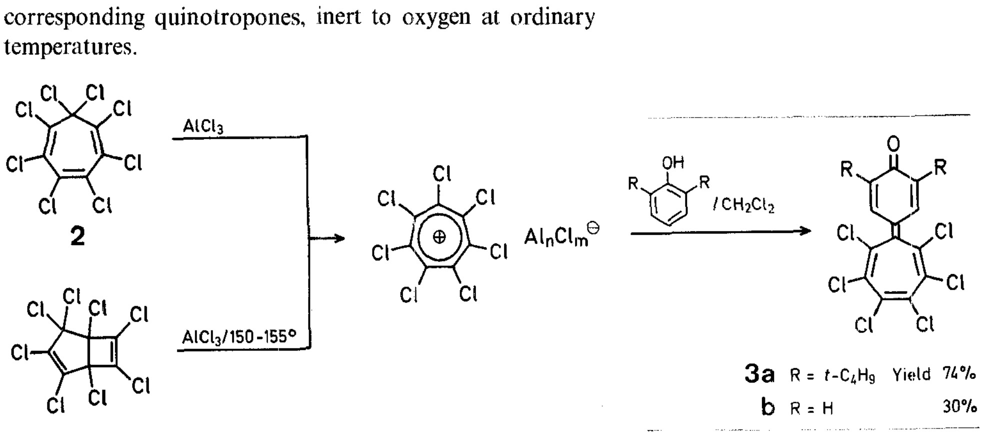
However, in this as in other earlier reports[3,4] of derivatives of **1a**, the product was highly air sensitive and no good analytical data could be obtained.



1a R = H
b R = Br

Convincing evidence for the existence of quinotropones has only recently been presented[5-8]. The methods of synthesis, in general, involve tropylation of a phenol to a mixture of tropylphenols and subsequent dehydration or dehydrohalogenation.

We find that heptachlorotropylium ion[9], as a chloroaluminate salt, prepared either from octachlorocycloheptatriene or octachlorobicyclo[3.2.0]hepta-2,6-diene and anhydrous aluminum chloride reacts with phenols in chloroform or dichloromethane to afford, after hydrolysis, the corresponding quinotropones, inert to oxygen at ordinary temperatures.



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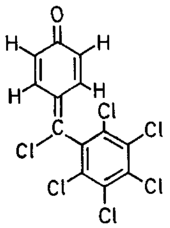
3a R = t-C_4H_9 Yield 74%
b R = H 30%

Whereas **1a** and **1b** are reported[6] to have no I.R. absorption between 1600 and 2850 cm^{-1}, the I.R. spectra of **3a** and **3b** showed absorptions in this region. Lack of absorption in this region has been attributed to contribution of the charge-separated form (**B**) to the ground state of the molecule. The presence of chlorines in the seven-membered ring of **3a** and **3b**, however, would tend to diminish the electron density on the oxygen atom, thereby favoring a larger contribution of the nonpolar form (**A**) to their ground state.

The ratio of **2** to aluminum chloride seems to play an important role in the formation of the quinotropone. Thus, a 1:2 complex of **2** and anhydrous aluminum chloride reacts with phenol to give **3b** whereas under the same conditions, a 1:1 complex affords 4-oxocyclohexadienylidenehexachlorotoluene (**4**).



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It is evident that the presence of chlorine atoms as substituents strongly stabilizes the quinotropone system towards oxidation. The reasons for this stabilization will be examined in our further experiments on 4-cycloheptatrienylidenecyclohexadienones.

3,5-Di-*t*-butyl-4-oxocyclohexadienylidene-hexachlorocycloheptatriene (3a):

In a 100 ml 3-neck round-bottom flask provided with a nitrogen inlet, dropping funnel, magnetic stirrer, and condenser, was placed a mixture of **2** (5.0 g, 13.6 mmol) and anhydrous aluminum chloride (2.0 g, 15.0 mmol) in dry dichloromethane (8 ml). The mixture was gently refluxed with stirring for 1 hr. The stirred slurry was then cooled to 4° and a solution of 2,6-di-*t*-butylphenol (3.12 g, 15.0 mmol) in dry chloroform (10 ml) was added slowly. The color of the slurry changed from yellow to amber. As soon as the color started to intensify, the remainder of the addition was done quickly and the slurry stirred at 4–6° for 1 hr. The dark violet reaction mixture was carefully decomposed with ice-cold water. The organic layer was diluted with chloroform (50 ml), separated from the aqueous layer, and dried with anhydrous magnesium sulfate. The drying agent was removed and the solvent evaporated under reduced pressure; yield: 7.2 g (74%); recrystallization from ethyl acetate, m.p. 225–227°.

$C_{21}H_{20}OCl_6$	calc.	C 50.33	H 4.02	Cl 42.45
	found	50.35	4.03	42.17

I. R. (mull): ν = 1648 (m), 1634 (s), 1582 (m), 1536 (w) cm^{-1}.

U.V.: λ_{max} (log ε) = 236 (4.21), 255 (4.04), 280 (3.82), 332 (4.54), ~380 (3.98) nm. The absorption at 380 nm is characteristic for the cycloheptatrienylidene system.

^{1}H-N.M.R. (CCl_4): τ = 2.92 (s, 2H), 8.72 (s, 18H)[10].

M.S.: m/e = 498 (M^+) for $C_{21}H_{20}O^{35}Cl_6$, with a cluster of peaks above the parent ion in the correct intensity ratios due to contribution from ^{37}Cl.

The N.Q.R. spectrum at room temperature showed absorptions at 35.6, 35.7, 36.7, 37.1 MHz in an approximate ratio of 1:1:1:3, the absorptions being consistent with the presence of only vinylic chlorine atoms[11].

4-Oxocyclohexadienylidene-hexachlorocycloheptatriene (3b):

To a stirred slurry of the heptachloroaluminate salt of **2** (19 mmol) in dry dichloromethane (15 ml) prepared as in the previous experiment was added, at room temperature, phenol (1.79 g, 19 mmol) in dry dichloromethane (15 ml) during 15–20 min. The slurry was stirred at room temperature for 6 hr. The complex was decomposed by pouring on cracked ice. The resulting brownish sticky solid was triturated with ethanol to give an orange yellow powder; yield: 2.2 g (30%); recrystallization from ethyl acetate, m.p. 152–153°.

$C_{13}H_4OCl_6$	calc.	C 40.15	H 1.24
	found	40.42	1.24

I.R. (mull): ν = 1645 (s), 1588 (w), 1545 (w) cm^{-1}.

U.V.: λ_{max} (log ε) = 238 (4.32), 260 (4.14), 317 (4.98), 385 (3.74) nm.

^{1}H-N.M.R. (CCl_4): τ = 2.62 (d, 2H), 3.57 (d, 2H).

4-Oxocyclohexadienylidene-hexachlorotoluene (4):

To a stirred suspension of heptachlorotropylium tetrachloroaluminate prepared from anhydrous aluminum chloride (0.70 g, 5.2 mmol) and compound **2** (1.9 g, 5.2 mmol) in chloroform (5 ml) was added a solution of phenol (0.5 g, 5.3 mmol) in chloroform (5 ml) at 4° under nitrogen. The color of the reaction mixture changed to dark red in 2–5 min after evolution of hydrogen chloride. The reaction mixture was maintained at this temperature for 1 hr. The complex was decomposed with ice water and worked up as before; yield: 0.8 g (40%). Recrystallization from ethyl acetate gave lemon yellow crystals, m.p. 205–207°.

$C_{13}H_4OCl_6$	calc.	C 40.15	H 1.04
	found	40.31	0.91

I.R. (mull): $\nu = 1638$ (m), 1555 (w) cm^{-1}.

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