

XANTHYLIUM SALTS FROM THERMOLYSIS OF DIPHENYLCYCLOPROPANES FUSED WITH BROMO-SUBSTITUTED 1,4-BENZOQUINONES

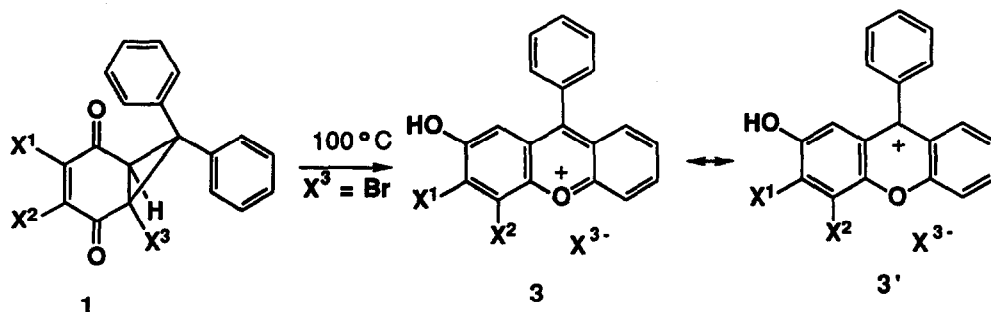
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Summary: Thermolysis of diphenylcyclopanes fused with bromo-substituted 1,4-benzoquinones resulted in the formation of xanthylum salts via ring opening accompanied by 6π electrocyclization.

Fusion of a functional component to cyclopropane ring is expected to endow a new structural and electronic feature as a candidate for the useful synthetic intermediate, because cyclopropane derivatives undergo a variety of ring-opening reactions¹. Recently, we have prepared quinone-fused diphenylcyclopanes in the dipolar addition of diphenyldiazomethane to variously chlorinated quinones². Cyclopanes bearing halogens like chlorine and bromine atoms are well known to cleave thermally to give olefins through a concerted process, with ring opening occurring simultaneously with the leaving group departure³. In view of the electrophilic property of quinones, it is of interest to investigate the effects of quinone-fusion on the thermolysis of cyclopanes.

We report here that the thermolysis of the title cyclopanes 1a-c gave xanthylum salts 3 in excellent yields⁴ (Scheme 1).



Scheme 1

Table Thermolysis of Quinone-fused Diphenylcyclopropanes(1a-d) at 100 °C in Benzene a)

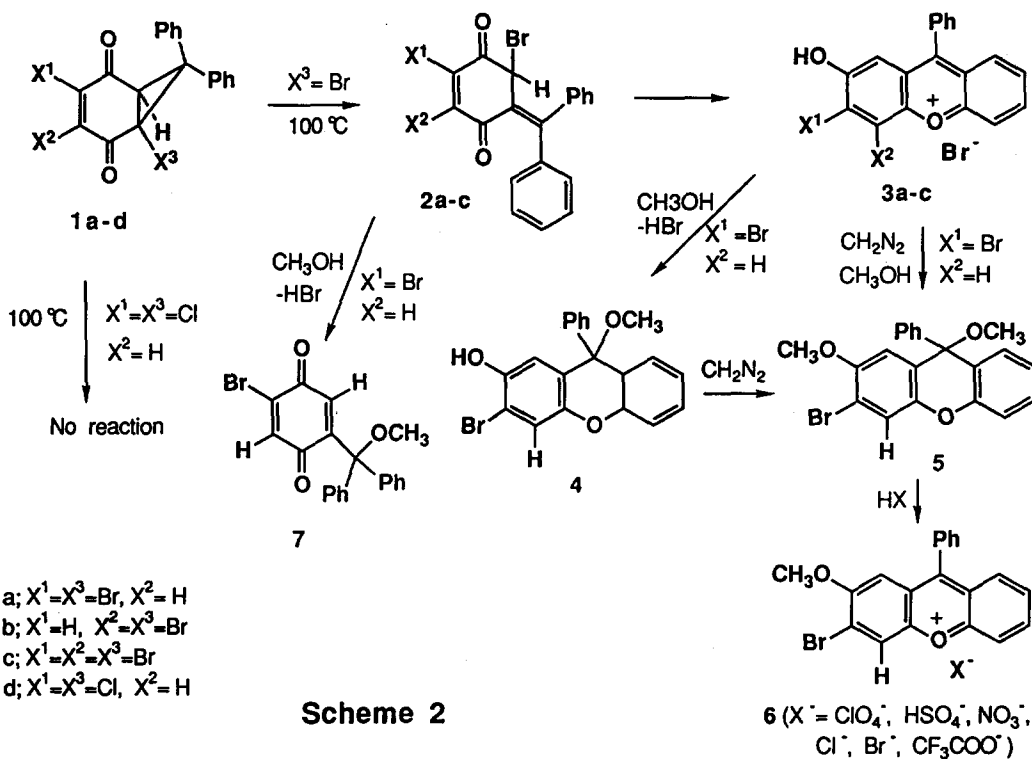
Entry	Cyclopropanes	Reaction time (day)	Yield(%) b)		
			2	3	7
1	1 a	2	--	97	--
2	1 a c)	1	--	--	89
3	1 b	1	35	58	--
4	1 b	3	--	95	--
5	1 c	3	--	96	--
6	1 d	2	No reaction		

a) Thermolysis was made on 4 to 5 x 10⁻¹ M solutions. b) Isolated yields. c) Reaction was carried out in the presence of methanol(20% by volume).

When a solution of cyclopropane 1a in benzene was heated in a sealed tube at 100 °C for 2 days, clear reddish-orange crystals were almost quantitatively deposited on the glass walls. The crystals were quite insoluble in nonpolar solvents, but slightly soluble in polar acetonitrile. The absorption spectrum recorded in acetonitrile was characterized by several strong absorptions with λ_{\max} = 227nm(log ϵ = 4.40), 249(4.36), 270(4.42), 408(4.53), and 491(3.82).⁵ Similarly, cyclopropanes 1b and 1c were converted into reddish precipitates on 2-3 day's heating (Table). These crystals did not melt, instead decomposed over 250 °C, and were found to have the same molecular formulas as the respective cyclopropanes. The IR spectra revealed no carbonyl absorption, but appreciable broad bands in the range of 2600 to 3050 cm⁻¹, indicating aromatization of quinone moiety. These compounds were easily dissolved in methanol with complete loss of the color to afford methanolysis product 4(75% yield on separation by HPLC). It was also noted that the addition of some excess of perchloric acid into an acetonitrile solution of the crystals from 1a brought about the anion exchange reaction to yield an analogous red compound involving perchlorate ion.

Based on both the chemical and spectral evidence, we tentatively assigned these salt-like pyrolysates to be xanthylum salts 3a-c. A confirmatory indication for xanthylum salts was provided by the treatment with methanolic diazomethane giving the colorless substance(83% yield) compatible with the xanthene derivative 5(scheme 2). The compound 5 was also derived from 4 by methylation of phenolic OH with ethereal diazomethane. Thus, the methoxy group at C-9 position of 5 is due to the nucleophilic attack of methanol, because the behavior of xanthylum ion is best

thought of in terms of the carbonium ion⁶ (here, stable triarylmethyl carbonium ion **3'** as illustrated in Scheme 1) rather than the oxonium ion.



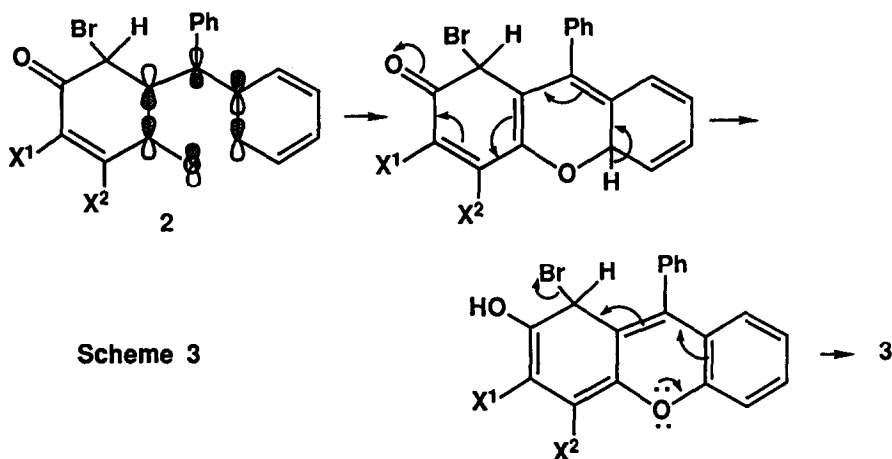
Scheme 2

As expected, xanthen derivative **5** can be reconverted into the xanthylium salt **6** by adding excess of strong acids(HX) like perchloric, sulfuric, nitric, hydrochloric, hydrobromic, and even trifluoroacetic acids; however acetic acid failed to cause such transformation because of the weak acidity. This reaction can be followed by changes in the visible spectrum; the spectra of **6** in acetonitrile solution were essentially counter anion independent and resembled that of **3a**, whereas the xanthen derivative **5** is colorless.

Mechanistically, formation of xanthylium salts is indicative of the participation of thermally ring-opened bromo-substituted 3-(diphenylmethylene)-2,3-dihydro-1,4-benzoquinone **2** as key intermediates. In fact, thermolysis of **1a** in the presence of additive methanol(20% by volume) provided 2-bromo-5-diphenyl(methoxy)methyl-1,4-benzoquinone **7** in 89% yield instead of the xanthylium salts(entry 2). Formation of this methanol adduct can be interpreted by considering that **1a** undergoes the thermal ring-cleavage to become 2,6-dibromo-3-diphenylmethylene-2,3-dihydro-1,4-benzoquinone **2a** as an initial product and the subsequent S_N' reaction with methanol takes place accompanying allylic rearrangement. Furthermore, we

succeeded in isolating the ring-opened intermediate 2b for the case of 1b by ceasing thermolysis before completion (entry 3), and confirmed transformation into the corresponding xanthylium salt 3b on further heating. Contrary to the bromo-substituted cyclopropanes, no such thermolysis was found in the case of chloro-substituted cyclopropane 1d, probably because of less liability of C-Cl bond toward thermal fission than C-Br one⁷ (entry 6).

From these findings, it is concluded that thermolysis of cyclopropanes 1a-c proceeds through a reaction sequence involving an initial ring cleavage of cyclopropanes, 6π electrocyclization of the resulting 2, and an electron reorganization associated with proton migration and bromide release (Scheme 3).



References

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4. Satisfactory analytical and spectroscopic data were obtained for all new compounds described here.
5. The absorption pattern is very similar to that of 9-phenylxanthylium; see R. A. McClelland *et al.*, *J. Am. Chem. Soc.*, **111**, 2929 (1989).
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