

THE CHEMISTRY OF SMALL RING COMPOUNDS. PART 18<sup>1</sup>

INDIRECT EVIDENCE FOR 2-CYCLOPROPYLIDENECYCLOHEXADIENONE AS AN INTERMEDIATE\*

by

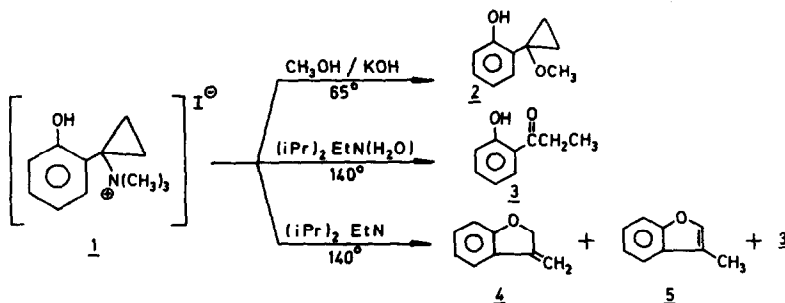
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As part of our interest in cyclopropyl compounds with an exocyclic double bond, we have investigated the quaternary ammonium salt 1, 1-(o-hydroxyphenyl)cyclopropyltrimethylammoniumiodide<sup>2</sup> under alkaline conditions, normally favouring Hofmann elimination.



Heating of 1 with 3.5 eq. of KOH for 36 hrs in refluxing methanol led to substitution of the trimethylamino group by a methoxy group, and isolation of 1-(o-hydroxyphenyl)-1-methoxycyclopropane 2 in 73% yield. The IR spectrum of 2 shows bands at  $3400\text{ cm}^{-1}$  (OH),  $2940$ ,  $2900$  and  $2820\text{ cm}^{-1}$  ( $\text{OCH}_3$ ),  $1025\text{ cm}^{-1}$  (cyclopropyl). The NMR spectrum displays a multiplet with an AA'BB' pattern at

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$\delta = 0.95$  (4H, cyclopropyl), a singlet at  $\delta = 3.07$  (3H, methoxy) and a multiplet at  $\delta = 6.5-7.3$  (4H, phenyl). The mass spectrum gives the parent peak at  $m/e$  164.

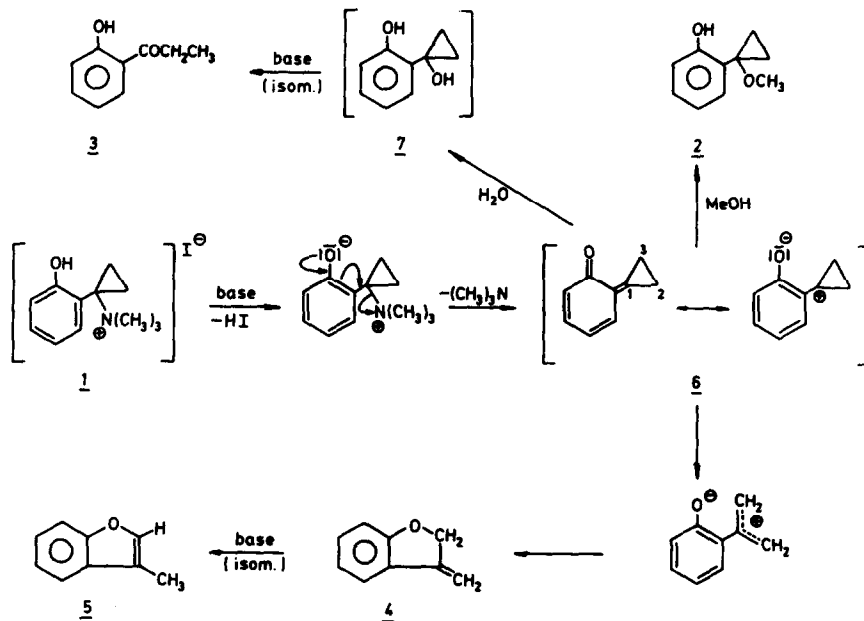
By heating of 1 for 1 hr at  $140^\circ$  with 1.5 eq. of the sterically hindered *N,N*-diisopropylethylamine (not water-free) the only product that could be isolated in 38% yield (VPC) was *o*-hydroxypropiophenone 3. The IR spectrum of 3 shows bands at  $1640\text{ cm}^{-1}$  (C=O conj.),  $1605$ ,  $1490\text{ cm}^{-1}$  (phenyl),  $750\text{ cm}^{-1}$  (4 adj. H-atoms). The NMR spectrum ( $\text{CDCl}_3$ ) shows a triplet at  $\delta = 1.26$  and a quartet at  $\delta = 3.04$  (resp. 3H and 2H,  $\text{CH}_3\text{CH}_2\text{C=O}$ ), a multiplet at  $\delta = 6.7-7.9$  (4H, phenyl) and a broadened singlet at  $\delta = 12.3$  (1H, OH). The molecular weight, determined by mass spectrometry, amounts to 150.06855. Calc. for  $\text{C}_9\text{H}_{10}\text{O}_2$ : 150.06801.

Under similar conditions, the same amine (dried over molecular sieves), reacts with the iodide 1 (dried over  $\text{P}_2\text{O}_5$ ) to give besides 3 (from residual  $\text{H}_2\text{O}$ ) the new products 3-methylene-2,3-dihydrobenzo(b)furan 4 and 3-methylbenzo(b)furan 5 in a total yield of at least 12%. The IR spectrum ( $\text{CHCl}_3$ ) of 4 shows a band at  $1640\text{ cm}^{-1}$  (C=C). The mass spectrum has a parent peak at  $m/e$  132. The 100 MHz NMR spectrum shows three distorted triplets at  $\delta = 4.95$  (1H),  $\delta = 5.07$  (2H) and  $\delta = 5.38$  (1H), and a multiplet at  $\delta = 6.7-7.5$  (4H, phenyl). The simulated spectrum of the  $\text{ABC}_2$  part ( $\delta_A = 5.397$ ;  $\delta_B = 4.974$ ;  $\delta_C = 5.088$ ;  $J_{AB} = 0.50$ ;  $J_{AC} = 3.20$ ;  $J_{BC} = 2.85$ ) is identical with the observed pattern.

The IR spectrum of 5 is identical with that of an authentic sample<sup>3</sup>. The UV spectrum of 5 is almost identical with that of benzo(b)furan<sup>4</sup>.

Compound 4 can readily be converted into its more stable isomer 5 with trifluoroacetic acid in chloroform at room temperature. This reaction is, however, very slow in refluxing *N,N*-diisopropylethylamine.

The experimental results can be explained by postulating 2-cyclopropylidenecyclohexadienone 6 as a key intermediate in all reactions. It is formed in analogy with 2-methylenecyclohexadienone from 2-hydroxybenzyltrimethylammonium iodide<sup>5</sup>.



The substitution products **2** and **7** originate presumably from **6** by nucleophilic addition of methanol and water respectively. Under the alkaline conditions the cyclopropanol **7** isomerizes rapidly to the ring-opened ketone **3** by  $\text{C}_1\text{-C}_2$  bond fission. The isomers **4** and **5** are supposed to be formed by a Woodward-Hoffmann-DePuy ring cleavage of **6** with  $\text{C}_2\text{-C}_3$  bond rupture. This leaves a kind of zwitterion (with the features of a phenolate anion and an allyl cation), which collapses to compound **4**. Its exocyclic double bond migrates slowly into the ring under the influence of base.

#### Acknowledgement

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References

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