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9-HYDROXY[7]METACYCLOPHANE

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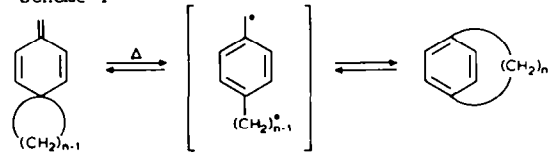
Abstract - A new pyrolytic access to a metacyclophane has been found by the flash vacuum thermolysis of spiro[5,7]trideca-1,4-dien-3-one (4) which gave 9-hydroxy[7]metacyclophane (7), and 4-(6-heptenyl)phenol (8). The mechanism of formation of 7 and 8 from the intermediate diradical 6 is discussed.

INTRODUCTION

We have reported that short-bridged [n]paracyclophanes (1; n=7,8) can be conveniently prepared by flow pyrolysis of the methylenespirocyclohexadienes 2.[1] In this reaction, diradicals 3 were postulated as intermediates (Scheme 1).

Scheme 1



2 3 1

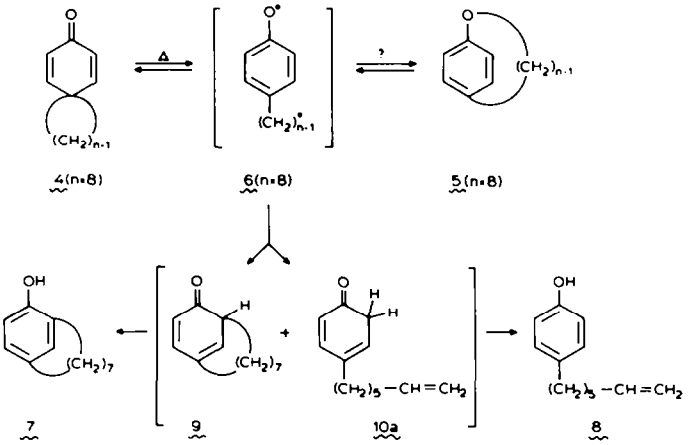
It appeared of interest to investigate the flash vacuum thermolysis (F.V.T.) of the corresponding spirocyclohexadienones 4[2] as a possible route to the unknown oxa[n]paracyclophanes 5 which, by analogy, might be expected to arise by ring closure of the intermediate diradicals 6 (Scheme 2).

We now describe the F.V.T. of 4 (n=8) which, however, did not furnish 5, but instead the novel 9-hydroxy[7]metacyclophane 7, together with 4-(6-heptenyl)phenol (8).

RESULTS AND DISCUSSION

In a recovery of about 90%, F.V.T. of 4 yielded a pyrolysate which contained only 7 and 8 besides starting material; its composition was temperature dependant (Table 1).

Scheme 2



4(n=8) 6(n=8) 5(n=8)

7 9 10a 8

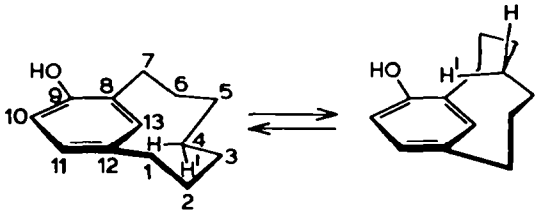
Table 1. Product distribution in the pyrolysis of 4 (%)*

T(°C)	4	7	8
520	38	29	23
560	14	23	53
600	0	15	75
650	0	0	90

* Determined from integral ratios of ^{1}H-NMR spectra of the pyrolysate

The products were isolated by preparative GLC, and their structure was determined from their spectral data (see Experimental). The metacyclophane structure of 7 follows from the great similarity of its ^{1}H-NMR spectrum with that of [7]metacyclophane.[3] Typical are the low field shift of the proton H(13) between the bridge ($\Delta\delta$= +0.53 ppm compared to H(3) in 2,4-dimethylphenol[4]) and the temperature dependence: the high field multiplet at δ= -0.01 ppm (2H, H(4) and H(4')) (Scheme 3))

Scheme 3



7a 7b

coalesces at T_c= -11°C and reappears (in part) at T= -36.5°C at δ= -1.20 ppm (H(4) in 7a), while H(4') at lower field is masked by other methylene protons. Hirano et al. have explained similar dynamic phenomena for [7]metacyclophane by a flipping motion of the heptamethylene bridge from one side of the benzene ring to the other (T_c= -28°C; $\Delta G^{\ddagger}$= 11.5 kcal.mol^{-1})[3]. In our case, $\Delta G^{\ddagger}$ is temperature independant (250 MHz: T_c= -11°C, $\Delta G^{\ddagger}$= 11.6 kcal.mol^{-1}; 90 MHz: T_c= -23°C, $\Delta G^{\ddagger}$= 11.6 kcal.mol^{-1}), suggesting that $\Delta S^{\ddagger} \approx 0$ e.u. and $\Delta H^{\ddagger}$= 11.6 kcal.mol^{-1}. Thus, the hydroxyl group has no marked influence on this conformational motion.

A surprising outcome of this investigation is the dramatic difference in product formation from 2 and from 4. Still, we feel that the first step is the same, i.e. homolytic cleavage of one of the spiro bonds to yield the benzyl radical 3[1,5,6] or the phenoxy radical 6, respectively. The different ring closure from 3 and 6 probably reflects differences in spin distribution, as 3 is expected to have the highest spin density at the benzylic carbon atom,[7] whereas phenoxy radicals are known to have higher spin densities at the ortho and para positions.[8] Ring closure of 6 at the ortho position will yield 9 which, after rearomatization, leads to 7.

The formation of 8 from 6 requires the transfer of a hydrogen atom from the aliphatic side chain to the phenoxy part of the molecule. It is unlikely that this process is intermolecular under the low pressure reaction conditions; furthermore, no dimeric reaction products could be detected in the pyrolysate.[9] By pyrolysing pure 7 at 800°C, it was demonstrated that 7 is not a precursor of 8; 7 was recovered in 90% yield as the only detectable product. It must be concluded that 7 and 8 are formed independently from 6. The formation of 8 requires a higher enthalpy of activation as it is formed at the expense of 7 at higher temperatures. It cannot be decided at the moment, whether the hydrogen is transferred to the ortho-position leading to 10a, or to the para-position (10b, not shown) before rearranging to give 8.

In line with earlier experience on [7]metacyclophane,[3] the properties of 7 indicate that this compound is only slightly strained. The UV-spectrum (0.4% NaOH; λ_{max} in nm (log ε): 241 (4.01) 302 (3.52)) shows a minor bathochromic shift compared to 2,4-dimethylphenol[4] (0.4% NaOH; λ_{max} in nm (log ε): 238 (3.87), 296 (3.48)). As far as investigated, the chemical reactivity of 7 is normal contrary to more strained metacyclophanes;[10] it is, for example, stable at room temperature towards acid[11] (CF_3COOH) and towards dienophiles (tetracyanoethene).

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EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker WH-250 spectrometer at a frequency of 250 MHz). All products were analyzed by GCMS, using a Finnigan-4000 mass spectrometer; exact mass measurements were performed with a Varian CH-5 DF mass spectrometer at an ionization potential of 70 eV. Ultra violet spectra were recorded on a Cary 114 spectrometer.

Spiro[5,7]trideca-1,4-dien-3-one (4).
4 Was prepared according to a reported procedure.[2] 4: ^{1}H-NMR (250 MHz, $CDCl_3$, δ in ppm) 7.02 and 6.22 (AB-system, J_{AB}= 10.2 Hz, 4H), 1.67 (m, 14H). Mass spectrum m/z (%): 190 (63) $4^{+\cdot}$, 107 (100); calc. for $C_{13}H_{18}O$, 190.1358, found 190.1362.

Flash vacuum thermolysis (F.V.T.)
The F.V.T. apparatus was modelled after the design of R.F.C. Brown, Pyrolytic Methods in Organic Chemistry, Academic Press, New York, 1980, p.31, with modifications by Dr. J.M.J. Verlaak, Ph.D. Thesis, Catholic University of Nijmegen, 1983.
We thank Prof. B. Zwanenburg, Dr. A.J.H. Klunder and their coworkers for assistance and advice.
In our experiments, a 28 cm aluminium oxide heating tube was used at a pressure of 0.04 mbar. In a typical run, 4 was vaporized into the hot zone at a rate of 50 mg per hour, using a sublimation furnace (Büchi GKR50) to heat the sample bulb. The pyrolysate was trapped in a cold trap, cooled with dry ice in acetone at -70°C. After pyrolysis of the substrate the pyrolysate was collected from the cold trap by washing with diethyl ether. The solvent was evaporated at reduced pressure; the residue was ~90% by weight. Products were isolated by preparative GLC (15% SE-30 on Chromosorb W, length 1.5 m at 180°C). The products were identified on the basis of their spectral data.

9-Hydroxy[7]metacyclophane (7).
M.P. 76-78°C (uncorrected). ^{1}H-NMR ($CDCl_3$, δ in ppm, room temperature) 7.30 (d, ^4J= 2.0 Hz, 1H, H(13)), 6.83 and 6.71 (AB-system; J_{AB}= 7.9 Hz; on A part ^4J= 2.0 Hz; 2H; A= H(11), B= H(10)), 4.59 (bs, 1H, OH), 2.72 (vbs, 2H, benzylic H), 2.61 (vbs, 2H, benzylic H), 1.45 (vbs, 8H, CH_2), -0.01 (m, 2H, H(4) and H(4')). UV (0.4% NaOH, λ_{max}[nm](log ε)) 241 (4.01), 302 (3.52). Mass spectrum m/z (%): 190 (58.9) $7^{+\cdot}$, 120 (100); calc. for $C_{13}H_{18}O$ 190.1358, found 190.1363.

4-(6-heptenyl)phenol (8).
Colourless liquid: ^{1}H-NMR (250 MHz, $CDCl_3$, δ in ppm; J obtained by computer simulation with PANIC (Bruker)) 7.05 and 6.76 (AB-system, J_{AB}= 8.4 Hz, 4H, aryl-H), 5.82, 5.00 and 4.94 (ABX-system, J_{AB}= 1.5 Hz, J_{AX}= 17 Hz, J_{BX}= 10.2 Hz, 3H, CH_2=CH-), 4.61 (bs, 1H, OH), 2.54 (t, ^3J= 7.9 Hz, 2H, benzylic CH_2), 2.05 (m, ^3J= 6.7 Hz, ^3J= 7.2 Hz, ^4J= 1.0 Hz, 2H, allylic CH_2), 1.59 (m, 1H), 1.39 (m, 5H). Mass spectrum m/z (%): 190 (24.4) $8^{+\cdot}$, 107 (100), calc. for $C_{13}H_{18}O$ 190.1358, found 190.1358.

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