Tetrahedron Letters Vol. 21, pp 611 - 612
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0040-4039/80/0208-0611$02.00/0

PREPARATION AND CHARACTERIZATION OF "FURANORADIALENE" (TETRAMETHYLENE - TETRAHYDROFURAN)

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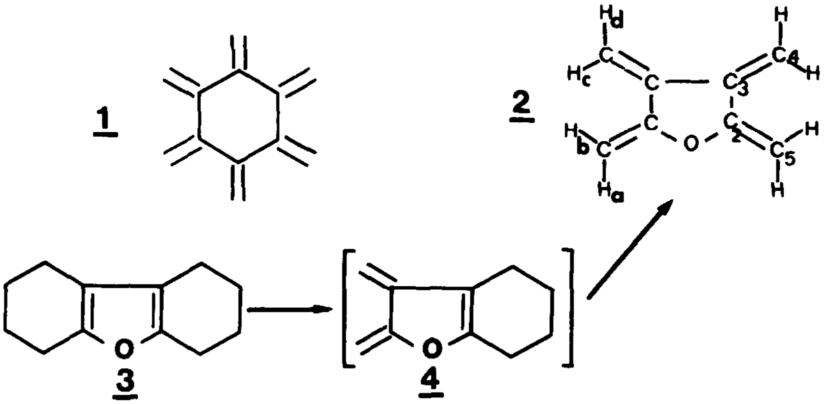
Summary : Tetramethylene-tetrahydrofuran has been prepared by flash vacuum thermolysis. This coumpound is stable in solution below -50° C, and was characterized by NMR and mass spectrometry.

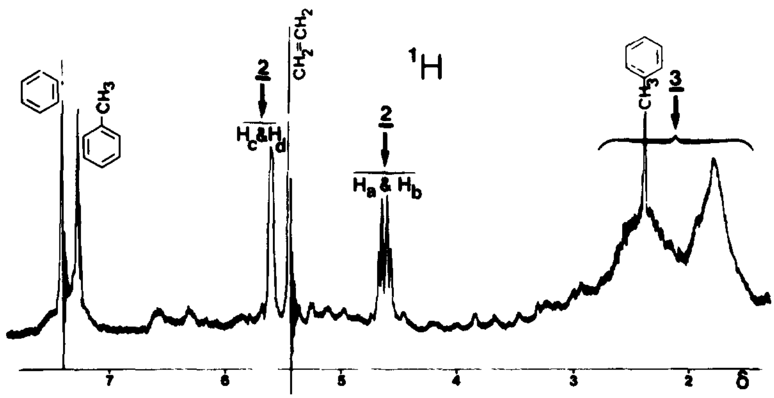
Recently, the reactive and theoretically interesting hexaradialene 1 has been obtained by flash vacuum thermolysis from various precursors[1,2,3]. In the present paper, the first synthesis of the "heteroradialene", 2, is described. Compound 2, the furanic homolog of 1, was obtained by flash vacuum thermolysis[4] from 1,2,3,4,6,7,8,9-octahydrodibenzofuran 3 through a two step retro-Diels-Alder reaction.

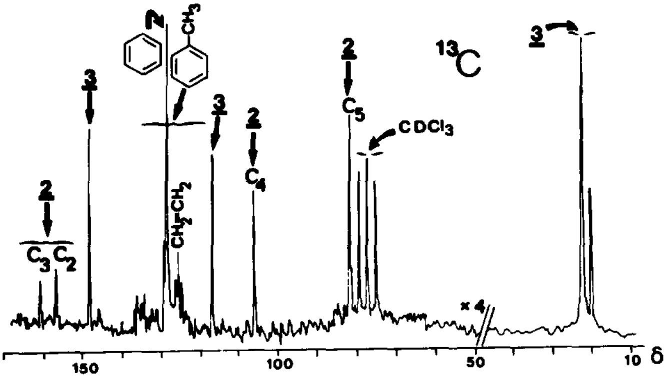


The reaction was carried out at a pressure of about 0.1 Torr, with amounts of starting material 3 ranging from 0.5 to 1 g. In order to determine the temperature at which the yield of 2 would be maximun, the flash thermolyser was coupled to a mass spectrometer so that the mass spectrum of the pyrolysate could be recorded for different reactor temperatures[5]. The optimum temperature appears to be between 920 and 940° C ; at higher temperatures, further degradations become increasingly important :

$$2 \longrightarrow \text{benzene} + CH_2{=}C{=}O \quad \text{and} \quad 2 \longrightarrow \text{toluene} + CO$$

In order to ascertain the structure of compound 2, the pyrolysate was trapped in a $CDCl_3$ matrix on a cold finger, and its low temperature (< -50°), ^{1}H RMN spectrum was recorded. It shows together with characteristic peaks of benzene, toluene, ethylene and starting material 3, two signals which disappear when temperature is raised above -40° with simultaneous formation of a white, unsoluble material. The quartet at δ 4,61 (AB systems,





J = 2.5 Hz, 4H) corresponds to the methylene H_a and H_b : the J and δ values being nearly the same as those reported for 2,5 bis (methylene)-2,5 dihydrofuran [6]. The broad singlet at δ 5.59 (4H) is attributed to the quasiequivalent protons H_c and H_d, the δ being just slightly higher than that of 5.31 reported for hexaradialene 1[2].

Integration of the ^{1}H NMR signals shows that the pyrolyzate contains 15 to 20% of the "furanoradialene" 2, the main component being the starting material 3 ~ 70% together with small amounts of benzene (~ 5%) and toluene (~ 7%).

The ^{13}C RMN spectrum of 2 (CDl_3 at - 60°) presents two methylene carbon signals at δ 81.8 and 106.2 [assigned respectively to C (5) and C (4)] and two ring carbon signals at 156.6 and 160.5 [assigned respectively to C (3) and C (2)].

The intermediate product 4 could not be isolated. Its unstability seems normal, owing to the presence of both diene and dienophile moieties within the molecule[5].

Acknowledgement : We thank Mr. C. ZAUG for technical assistance.

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(Received in France 12 November 1979)