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SYNTHESIS OF "DIBENZO-$(CH)_{10}$"-HYDROCARBONS

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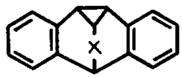

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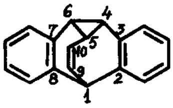
In the course of our previous studies on double bond participation in the solvolysis of dibenzocycloheptatriene systems 1a) and in the decomposition of diazoketones 1b) we obtained the hydrocarbon 1a (X = CH_2), "dibenzobarbaralane" and the ketone 1b (X = CO), "dibenzobarbaralone". As a continuation of these investigations we report here the synthesis of "dibenzobullvalene" (2) and of other two isomeric hydrocarbons 3 and 4.



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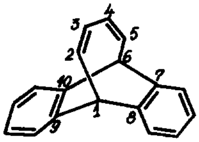

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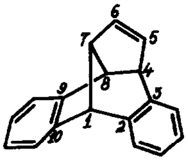

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In view of the great interest in the $(CH)_{10}$-hydrocarbons chemistry 2), recently extended in the area of the "benzo-$(CH)_{10}$"-hydrocarbons 3), the investigation of "dibenzo-$(CH)_{10}$"-hydrocarbons seemed appropriate.

It appeared desirable to study the behaviour of these systems, considering the multiple and facile thermal and photochemical isomerizations which the parent $(CH)_{10}$-hydrocarbons may undergo.

The dibenzobullvalene was prepared through a six-step synthesis starting with 1:2,5:6-dibenzocyclohepta-1,3,5-trienyl-7-acetic acid 4).

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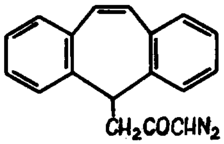
x) Deceased July 28. 1970

The diazoketone 5 x) (m.p. 107-110° ; yellow needles) obtained in 98% yield from the acid chloride of the above mentioned acid with ethereal CH_2N_2, gives rise, by intramolecular ring closure, to the dibenzotricyclic ketone 6 (m.p. 227-228.5° ; 15% yield) ; NMR spectrum ($CDCl_3$, δppm) 7.0-7.4 (m, 8H, H_{arom}) ; 3.88 (t, J = 4.5 ; 1H ; H_1) ; 2.95 (apparently s, 3H, $H_{4,5,6}$) ; 2.82 (d, J = 4.5 ; 2H ; H_9) xx).



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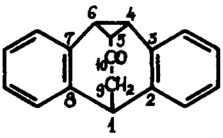

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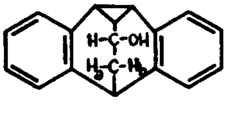

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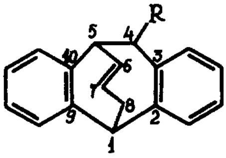

8 a) R = Br b) R = OBu(t)

Reduction of the ketone 6 with $LiAlH_4$ afforded the alcohol 7 (m.p. 120-121° ; 91% yield) ; NMR spectrum ($CDCl_3$, δppm) 7.0-7.4 (m, 8H, H_{arom}) ; 4.35 (sextet, J = 7 ; 7 ; 3.5 ; 1H, H_{10}) ; 3.70 (q, J = 3.5 ; 5.5 ; 1H, H_1) ; 1.8-2.8 (m, 6H, $H_{4,5,6,9a,9b}$, OH) ; this multiplet was resolved with reagent shift $Eu(DPM)_3$ 5), using a complex/alcohol molar ratio of 0.307 (δppm) : 6.92 (H_{9b}) ; 6.30 (H_5) ; 5.58 (H_{9a}) ; 4.18 (H_4) and 3.67 (H_6).

Our attempts to obtain 2 by pyrolysis of 7-OAc, following the procedure used by Doering et al. 2a) for bullvalene itself, failed.

The treatment of the alcohol 7 with PBr_3 gave rise to the dibenzobicyclic bromo-derivative 8a (m.p. 120°, 45% yield) ; NMR spectrum ($CDCl_3$, δppm) 6.9-7.6 (m, 8H, H_{arom}) ; 5.3-6.1 (m, 3H, $H_{6,7}$ and H_4, d, J = 4.5 Hz at 5.79) ; 4.08 (t, J = 4 ; 4 ; 1H, H_1) ; 3.87 (q, J = 4.5 ; 8 ; 1H, H_5) and 2.0-3.0 (m, 2H, H_8). The NMR spectrum of the latter compound compares favourably with that of the ether 8b (m.p. 154-156°) formed on treatment of 8a with t-BuOK in t-BuOH. NMR spectrum ($CDCl_3$, δppm) 7.0-7.5 (m, 8H, H_{arom}) ; 5.3-6.1 (m, 2H, $H_{6,7}$) ; 4.88 (d, J = 5 ; 1H, H_4) ; 4.01 (t, J = 4 ; 4 ; 1H ; H_1) ; 3.72 (q, J = 5 ; 8 ; 1H, H_5) ; 2.0-3.0 (m, 2H, H_8) and 1.23 (s, 9H, t-Bu).

Dehydrobromination of the compound 8a in pyridine (45 min. reflux), afforded the dibenzobullvalene (2) (m.p. 108° ; 15% yield). The NMR spectrum,

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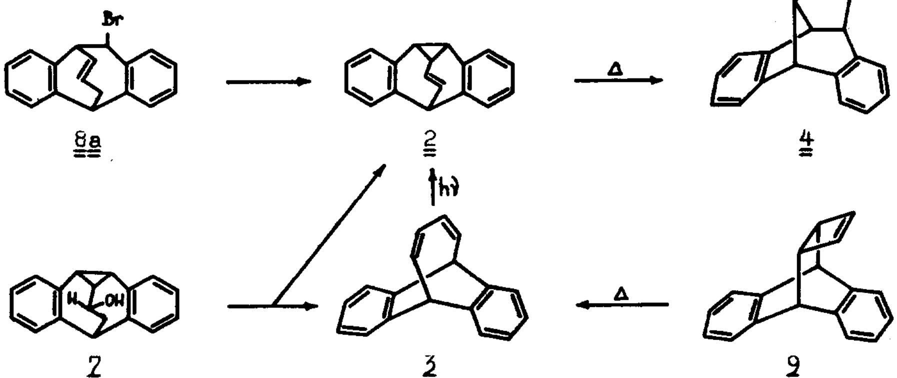
x) All the new compounds gave satisfactory elemental analysis.

xx) NMR spectra were recorded using a 60 MHz, Varian A 60A spectrometer using TMS internal standard.

unchanged until 200°, indicates the return to the dibenzotricyclic structure: ($CDCl_3$, δ ppm) 6.9-7.2 (m, 8H, H_{arom}) ; 5.5-6.1 (m, 2H, $H_{9,10}$) ; 3.68 (q, 1H, H_1) ; 2.20-2.85 ($A_2B(X)$-type spectrum, 3H, $H_{4,5,6}$).

The dehydration of the alcohol 7 with $B(OH)_3$ (at temperatures ranging between 165-200° (0.8 mm Hg) gave rise (60% yield) to a mixture of 2 (65%) and another hydrocarbon m.p. 180-182° (35%), which were separated by recrystallization from methanol. The structure of 9,10-butadieno-9,10-dihydroanthracene (7:8,9:10-dibenzobicyclo [4.2.2]deca-2,4,7,9-tetraene) (3) was assigned to the latter hydrocarbon, from inspection of its NMR spectrum ($CDCl_3$, δ ppm) 7.0-7.3 (m, 8H, H_{arom}) ; 6.0-6.8 (m, 2H, $H_{2,5}$) ; 5.3-5.7 (m, 2H, $H_{3,4}$) and 4.47 (d, J = 9.5 ; 2H, $H_{1,6}$).

Hydrocarbon 3 remained unchanged when heated to 400°. The same hydrocarbon 3 was obtained by pyrolysis at 350-400°, in flow-system, of 7:8,9:10-dibenzotricyclo$[4.2.2.0^{2,5}]$deca-3,7,9-triene (9) - another dibenzo-analogue of a $(CH)_{10}$-hydrocarbon, synthesized in this laboratory [6] (in practically quantitative yield ; 55-85% conversions).



Irradiation of 3 with a Hg-medium pressure UV lamp (130 W, 0.3% acetone solution, Pyrex, 3-6 hrs) afforded dibenzobullvalene (2) in 70% yield.

Another "dibenzo-$(CH)_{10}$" isomer, with m.p. 142-144°, was obtained in nearly 25% yield, by pyrolyzing dibenzobullvalene (2) at 400° in a flow system. The analysis of the NMR spectrum ($CDCl_3$, δ ppm) : 6.8-7.3 (m, 8H, H_{arom}) ; 6.44 (q, 1H, H_6) ; 5.62 (q, 1H, H_5) ; 3.6-4.0 (m, 3H, $H_{1,4,8}$) and 3.35 (q, 1H, H_7), pointed to the structure of 2:3,9:10-dibenzotricyclo $[5.3.0.0^{4,8}]$deca-2,5,9-triene (4).

The thermal conversion of dibenzobullvalene to **4** can be represented by analogy with the rearrangement of vinyl-cyclopropane to cyclopentene 7).

≡ **4**

2

The isomerization probably takes place by a radical mechanism since a concerted process would be forbidden by the Woodward-Hoffmann rules 8). To a certain extent, the thermal and photochemical processes in the "dibenzo-$(CH)_{10}$" series are similar to those encountered in the parent-hydrocarbons series 2). Unlike the latter case, where thermal rearrangements of all hydrocarbons lead to 9,10-dihydronaphthalene, in the present case such processes are made impossible by the two benzene rings.

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