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FRONTIER ORBITAL CONTROL IN HYDRAZINO BRIDGED [14]ANNULENES[1)]

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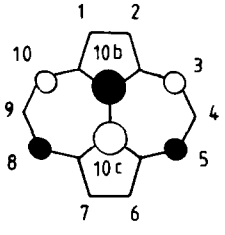
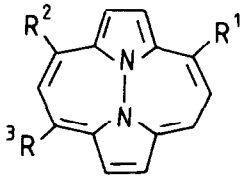
SUMMARY: [10b,10c]Diazapyraceheptylenes **1b** and **1c** were obtained from olefinic precursors **6**. Treatment of **7** under the same conditions does not allow a synthesis of the parent compound **1a** which may be explained by frontier orbital considerations.

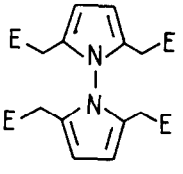
Previous investigations led us to assume, that the properties of [10b,10c]diazapyraceheptylenes **1** might be deduced from the eigenvector **A** of the highest occupied molecular orbital (HOMO) of the isoconjugate dianion of pyraceheptylene[2)]. We synthesized the ester derivatives **1b** and **1c** to corroborate this assumption and present a preliminary report of the results of our investigations.



A

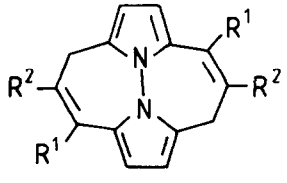


1a $R^1 - R^3 = H$
1b $R^1 = R^3 = E$, $R^2 = H$
1c $R^1 = R^2 = E$, $R^3 = H$

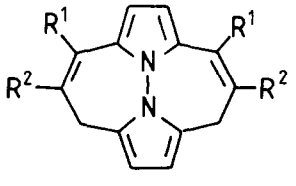


2

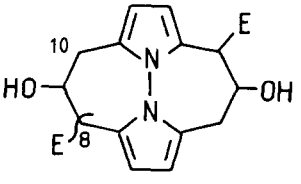
$E = CO_2C_2H_5$



3a $R^1 = E$, $R^2 = OH$
4a $R^1 = E$, $R^2 = Cl$
6a $R^1 = E$, $R^2 = H$
7a $R^1 = R^2 = H$



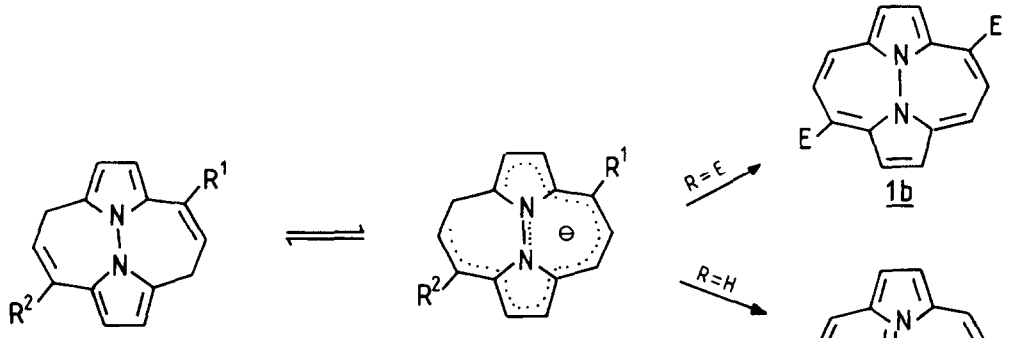
3b
4b
6b
7b



5a 8-E
5b 10-E

Dieckmann condensation of the tetraester 2[2a,3] resulted in 60-70% of a crystalline mixture of the β-ketoesters **3a** and **3b**[2b,4] which, following ^{1}H NMR spectroscopy, are completely enolized[5]. From a reaction of the mixture **3a/b** with triphenylphosphane and carbon tetrachloride in 1,2-dichlorethane 74% of the chloro derivatives **4a/b** were obtained which could be separated by chromatography yielding mainly **4a**[4]. Attempts of a reductive elimination of the chlorine atoms failed.

A reduction of **3a/b** with sodium borohydride in the presence of $(PPh_3)_2PdCl_2$[6] led to diastereomeric mixtures of the hydroxy esters **5a/b** (64%)[4]. This reaction was also effected with the pure isomers, and proved to be difficult in the absence of the transition metal catalyst: at -9°C in ethanol a 22-43% yield of **5a/b** was obtained together with 29-38% of an isomeric mixture of hydroxy ketones[1]. Dehydration of **5a** and **5b** with sodium carbonate in boiling ethanol gave the olefins **6a** and **6b** in 58% yield[4].



6a $R^1=R^2=E$
7a $R^1=R^2=H$
8 $R^1=E, R^2=H$

1b

9

In the course of early attempts to dehydrogenate **7a/b** with potassium tert.-butoxide in DMSO we obtained, instead of **1a**, the bridged bisimino-[14]annulene **9**[2b]. The rearrangement was rationalized using the eigenvector **A**[7] of the HOMO of the isoconjugate pyraceheptylene dianion the eigenvalue of which should be lowered by splitting of the antibonding (10b-10c)-relation.

A prediction was made simultaneously proposing that in the presence of additional structural features stabilizing the HOMO **A** the rearrangement should fail in favour of a dehydrogenation. A suitable candidate should contain one or two electron attracting substituents in positions 3,5,8 and/or 10[2]. This assumption is in complete agreement with our experiments: Treatment of **6a/b** under the conditions used for the rearrangement of **7** gave the [10b,10c]diazapyraceheptylene derivatives **1b/c**[4,5].

Apart from a product control of the reactions of **6** and **7** with potassium tert.-butoxide in DMSO mechanistic arguments are conceivable which allow to explain differences of product formation depending on the substitution pattern of the precursors. We now try to synthesize the monoester **8** the reaction of which should furnish information concerning these alternatives.

ACKNOWLEDGEMENT

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4) Experimental conditions: **3a/3b**: From **2** using reaction conditions previously described but extending the reaction time from 3 h to 16 h. Pure **3a** (m.p. 128°C, 200 mg) and **3b** (m.p. 174°C, 60 mg) were obtained by fractional crystallization of the mixture **3a/b** (1g) from ethanol.
4a/4b: A solution of **3a/3b**, PPh_3 and CCl_4 (1:4:4) in $C_2H_4Cl_2$ is refluxed for 3 h. Chromatography (silica gel, CH_2Cl_2) and recrystallization from ethanol/n-heptane gave 60% **4a** (m.p. 212°C) and 15% **4b** (m.p. 248°C).

5a/b: A solution of **3a/b**, $(PPh_3)_2 \cdot PdCl_2$ and $NaBH_4$ in methanol is stirred for 10 min., acidified to pH = 5-6 using 2N HCl and evaporated. Water is added and extracted with chloroform. Evaporation and chromatography (silica gel, petrol ether/ethyl acetate = 2:1) gave 64% **5a/b**.
6a/b: **5a/b** was dissolved in ethanol. An excess of Na_2CO_3 was added and the mixture refluxed for 2 h. Chromatography (silica gel, petrol ether/ethyl acetate = 2:1) gave 58% of **6a/b**.

1b/c: A solution of **6a/b**, potassium tert.-butoxide and a trace of dibenzo-18-crown-6 is refluxed in toluene for 5 min. and stirred subsequently for 30 min. at r.t. Chromatography (silica gel, toluene/ethyl acetate = 30:1) gave 38% **1b/c**. The same yield was obtained from **5a/b** by heating to 80°C for 10 min. and stirring at r.t. subsequently.

5) All compounds were characterized by elemental analyses as well as by their spectra. Selected data: **3a**: ^{1}H NMR ($CDCl_3$): δ = 13.24 (s; 2H, OH) 6.20, (d; 2H, J = 4.0 Hz; H-2, H-7), 6.02 (d; 2H, J = 4.0 Hz; H-1, H-6), 4.37, 4.16 (q; 4H, J = 7.1 Hz O-CH_2), 3.64 (d; 2H, J = 14.5 Hz), 3.43 (d; 2H, J = 14.5 Hz), 1.33 (t; 6H, J = 7.1 Hz CH_3); **3b**: ^{1}H NMR ($CDCl_3$): δ = 13.30 (s; 2H, OH), 6.28 (s; 2H, H-1, H-2), 5.93 (s; 2H, H-6, H-7), 4.37, 4.20 (q, 4H, J = 7.1 Hz O-CH_2), 3.68 (d; 2H, J = 14.4 Hz), 3.37 (d; 2H, J = 14.4 Hz), 1.33 (t; 6H, J = 7.1 Hz; CH_3).**6a**: ^{1}H NMR (Acetone-d_6): δ = 7.06 (dd, 2H, J = 5.6 Hz, J = 8.6 Hz; H-4, H-9), 6.42 (d; 2H, J = 4.2 Hz; H-2,7), 5.93 (d; 2H, J = 4.2 Hz; H-1, H-6), 4.16 (2q; 4H, J = 7.1 Hz O-CH_2), 3.64 (dd; 2H, J = 8.6 Hz, J = 14.7 Hz), 3.53 (dd; 2H, J = 5.6 Hz, J = 14.7 Hz), 1.26 (t; 6H, J = 7.1 Hz, CH_3); **6b**: ^{1}H NMR (Acetone-d_6): δ = 7.22 (dd; 2H, J = 5.6 Hz, J = 8.6 Hz; H-4, H-9), 6.52 (s; 2H H-1, H-2), 5.78 (s, 2H, H-6, H-7) 4.20 (2q; 4H, J = 7.2 Hz; OCH_2), 3.52 (dd; 2H, J = 8.6 Hz, J = 15.0 Hz), 3.34 (dd; 2H, J = 5.6 Hz, J = 15.0 Hz), 1.29 (t; 6H, J = 7.2 Hz; CH_3). **1b**: ^{1}H NMR (Acetone-d_6)): δ = 9.18 (d; 2H, J = 5.4 Hz; H-2, H-7), 8.70 (d; 2H, J = 10.5 Hz; H-4, H-9), 8.56 (d; 2H, J = 5.4 Hz; H-1, H-6), 8.23 (d; 2H, J = 10.5 Hz; H-5, H-10), 4.58 (q, 4H, J = 7.0 Hz; OCH_2), 1.52 (t; 6H, J = 7.0 Hz; CH_3); **1c**: ^{1}H NMR (Acetone-d_6): δ = 9.16 (s; 2H, H-1, H-2), 8.68 (d; 2H, J = 10.5 Hz; H-4, H-9), 8.60 (s; 2H, H-6, H-7), 8.32 (d; 2H, J = 10.5 Hz; H-5, H-10), 4.60 (q; 4H, J = 7.0 Hz; OCH_2), 1.53 (t; 6H, J = 7.0 Hz; CH_3).

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7) HMO calculation: $C_{3,5,8,10} = \pm 0.368$; $C_{10b,10c} = \pm 0.0476$. SCF-calculation: A. DasGupta and N. DasGupta, Cand. J. Chem. 52, 155 (1974).

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