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$\mathbf{4}$,7-BISDIALKYLAMINOTRICYCLO[5.2.1.$0^{4,10}$]DECA-1^{10},2,5,8-TETRAENES AS POTENTIAL PRECURSORS TO ACEPENTALENEDIIDE[1]

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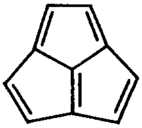
Abstract: Trihalotriquinacenes **3** react with secondary amines to yield 4,7-bis(dialkylamino)dihydroacepentalenes **4**. Upon reduction with sodium the tetraenes **4** apparently form radical anion intermediates **5** which disproportionate to tris(dialkylamino)trienyl anions **6** and possibly acepentalenediide **2**.

As simple MO calculations reveal, acepentalene (**1**) with its cross-conjugated 10π electron system has two singly occupied degenerate HOMO's[2] and should accordingly be highly reactive. The mere fact that **1** has not yet been generated although numerous attempts have undoubtedly been made[3], may be taken to indicate its high degree of instability. Even the closed-shell 12π acepentalendiide (**2**) which should be sufficiently stable, has so far escaped experimental detection. We here report a convenient synthesis of bifunctional dihydroacepentalenes which should be suitable precursors to **2** under appropriate conditions.



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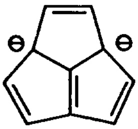
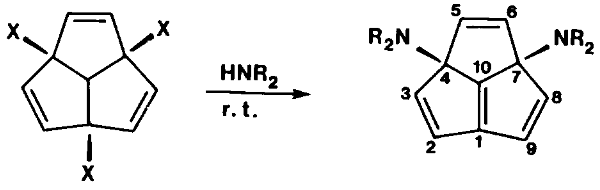


2

Secondary amines react with 1-halo- and 1,4-dihalotriquinacenes with complete allylic rearrangement, thus following a S_N2' mechanistic scheme[4] and thereby differing markedly from the methoxide nucleophile[5]. On the contrary, dimethylamine ($HNMe_2$) was found to cause a threefold elimination-addition sequence just like methoxide[5] when acting upon 1,4,7-trichlorotriquinacene, as proven by a deuterium labelling experiment with $DNMe_2$[6]. Surprisingly, secondary amines with alkyl groups larger than methyl are hindered to add in the final step and therefore leave the bis(dialkylamino)-tetraenes **4** untouched. The interesting new dihydroacepentalene derivatives

4a - **4d** with a variety of substituents are thus obtained in fair to very good yields. The oxygen sensitive oils were purified by low temperature (-30°C) column chromatography on silica gel or, in the case of the bis(diethylamino) derivative **4a**, by "Kugelrohr" distillation, and unequivocally characterized by their ^{1}H- and ^{13}C-nmr spectra (see table 1). In the UV spectrum **4a** shows its longest wavelength absorption at 285 nm, probably corresponding to the π-π^* transition of its cross conjugated triene unit.



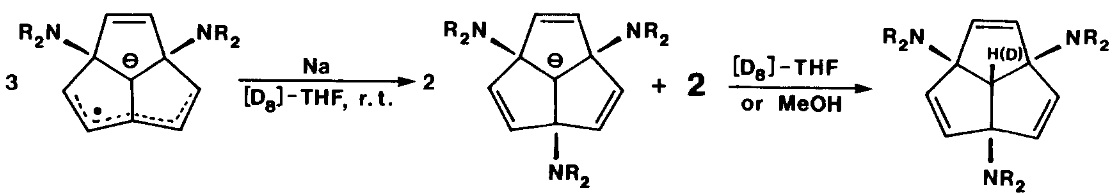
3 X = Cl, Br

4

a) NR_2 = diethylamino (77%)
b) NR_2 = piperidinyl (86%)
c) NR_2 = morpholinyl (86%)
d) NR_2 = 3,5-dimethyl-piperidinyl (36%)
e) NR_2 = dimethylamino (47%)

When the reaction of tribromide **3** (X = Br) with dimethylamine was monitored, a substantial amount of bis(dimethylamino)tetraene **4e** (47%) was found in the mixture after 14 d, identified by its typical ^{1}H-nmr spectrum (see table 1).

With the perspective of generating the acepentalenediide **2**, tetraenes **4a**, **4b** and **4c** in [D_8]-tetrahydrofuran were treated with sodium in nmr tubes sealed under vacuum[7]. Within 6-8 h the originally yellow solutions had turned deep redbrown, the ^{1}H-nmr signals of the educts disappeared, while a single new singlet showed up in the olefinic region at 5.55, 5.31 and 5.45 ppm respectively. These and the ^{13}C-nmr data (doublets around 133 ppm with $^1J_{C,H}$ = 162 Hz, triplets around 88 ppm with $^2J_{C,H}$ = 8 Hz) would have been consistent with the formation of a C_3-symmetric species like **2** in all three cases. However, the species thus generated from **4a**, upon quenching with methanol gave a 53% isolated yield of 1,4,7-tris(diethylamino)triqui-



5

6

7

Table 1. Characteristic data (chemical shifts δ_{TMS} in ppm, coupling constants in Hz) of the new compounds **4** and **7**.

Compounds (NR_2), characteristic data

4a (diethylamino), ^{1}H-nmr (270 MHz, C_6D_6): δ = 1.09(t, 12H, 2'-H, $\underline{J}_{2',1'}$ = 7.2), 2.66 - 2.93(m, 8H, 1'-H), 5.47(s, 5(6)-H), 6.14(d, 3(8)-H, $\underline{J}_{2,3}$ = 5.0), 6.61(d, 2(9)-H). - ^{13}C-nmr (67.91 MHz, C_6D_6): δ = 15.9(C-2'), 45.6 (C-1'), 82.1 (C-4), 128.8(C-5), 135.2(C-3), 148.5(C-2), 162.2(C-1 or C-10), 165.3(C-10 or C-1). - UV (n-Hexane, c = 3.7 10^{-5}M): λ_{max} (log ε_{max}) = 285 (3.584), 235 (3.644), 215(s) nm(4.012).

4b (piperidinyl), ^{1}H-nmr (270 MHz, C_6D_6): δ = 1.25-1.70(m, 12H, 2'-H, 3'-H), 2.70 - 2.95(m, 8H, 1'-H), 5.50(s, 5(6)-H), 6.20(d, 3(8)-H, $\underline{J}_{2,3}$ = 5.0), 6.69(d, 2(9)-H). - ^{13}C-nmr (67.91 MHz, C_6D_6): δ = 25.5(t, C-3', $\underline{J}_{^{13}C,^1H}$ = 128.0), 27.1 (t, C-2', $\underline{J}_{^{13}C,^1H}$ = 128.0), 50.6(t, C-1', $\underline{J}_{^{13}C,^1H}$ = 131.9), 82.1(s, C-4), 129.6(d, C-5, $\underline{J}_{^{13}C,^1H}$ = 165.4), 135.9(d, C-3, $\underline{J}_{^{13}C,^1H}$ = 165.4), 147.8(d, C-2, $\underline{J}_{^{13}C,^1H}$ = 165.4), 163.2(s, C-1 or C-10), 163.4(s, C-10 or C-1).

4c (morpholinyl), ^{1}H-nmr (270 MHz, C_6D_6): δ = 2.57 - 2.79 (m, 8H, 1'-H), 3.67(t, 8H, 2'-H, $\underline{J}_{2',3'}$ = 4.7), 5.41(s, 5(6)-H), 6.27(d, 3(8)-H, $\underline{J}_{2,3}$ = 5.0), 6.56(d, 2(9)-H). - ^{13}C-nmr (67.91 MHz, C_6D_6): δ = 50.6(C-1'), 67.6 (C-2'), 81.6 (C-4), 130.8(C-5), 135.6(C-3), 147.3 (C-2), 161.5(C-1 or C-10), 164.9(C-10 or C-1).

4d (3,5-dimethylpiperidinyl, mixture of <u>cis</u>-<u>trans</u> isomers), ^{1}H-nmr (270 MHz, C_6D_6): δ = 0.80 - 0.87(2d, 12H, 4'-H), 1.50 - 2.14(m, 8H, 2'-H, 3'-H), 3.04 - 3.45(dm, 8H, 1'-H), 5.60 (s, 5(6)-H), 6.21(d, 3(8)-H, $\underline{J}_{2,3}$ = 5.0), 6.72(d, 2(9)-H).

4e (dimethylamino), mixture containing 31% **7e**, ^{1}H-nmr (270 MHz, $CDCl_3$): δ = 2.34(s, 6H, 1'-H), 2.41(s, 6H, 1'-H), 5.68(s, 5(6)-H), 6.21(d, 3(8)-H, $\underline{J}_{2,3}$ = 5.0), 6.75(d, 2(9)-H).

7a (diethylamino), ^{1}H-nmr (270 MHz, $CDCl_3$): δ= 1.01(t, 18H, 2'-H, $^3\underline{J}_{1',2'}$ = 7.2), 2.65(quint, 12H, 1'-H), 2.77(s, 1H, 10-H?), 5.55(s, 6H, 2(3,5,6,8,9) -H). - ^{13}C-nmr (20.17 MHz, $CDCl_3$): δ = 15.8(q, C-2'), 43.8(t, C-1'), 87.3(s, C-1(4,7)), 132.8(d, C-2(3,5,6,8,9)).

7e (dimethylamino), ^{1}H-nmr (270 MHz, $CDCl_3$): δ= 2.45(s, 18H, 1'-H), 3.31 (s, 1H, 10-H), 5.57(s, 6H, 2(3,5,6,8,9)-H).

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nacene **7a** (fully characterized by its ^{1}H-nmr, see table 1, and (high resolution) mass spectrum). Since the only source of the third diethylamino group in **7a** under these conditions could have been the educt **4a** and in addition it was proven that **4a** would not add excess diethylamide if it had been present, it must be assumed that **4a** was initially reduced to a radical anion **5a** which disproportionated to give a 2:1 ratio of 1,4,7-tris(diethylamino)triquinacenyl-10-anion (**6a**) and **2**. Protonation (deuteration) of **6a** to yield **7a** either occurred under the reaction conditions with THF ([D_8]-THF) acting as the proton (deuteron) donor or upon quenching. The acepentalenediide **2** so far could not be unequivocally detected. Although both the ^{1}H- and ^{13}C-nmr spectra show additional signals less intense than those of **6** or **7** with reasonable chemical shifts for **2**[8], all attempts to quench **2** with chlorotrimethylsilane were unsuccessful. The fraction of **5** which eventually loses its NR_2 groups may simply have polymerized under the conditions employed.

References and footnotes

[1] This work was supported by the Stiftung Volkswagenwerk, the Fonds der Chemischen Industrie, the Hoechst AG and the Studienstiftung des Deutschen Volkes (Holger Butenschön).

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