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A NOVEL POLYCYCLIC TRIAMINE DERIVATIVE OF TRIDEHYDRO[12]ANNULENE AND ITS NITROXIDES

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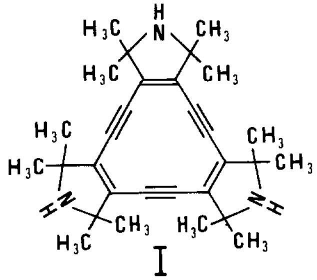
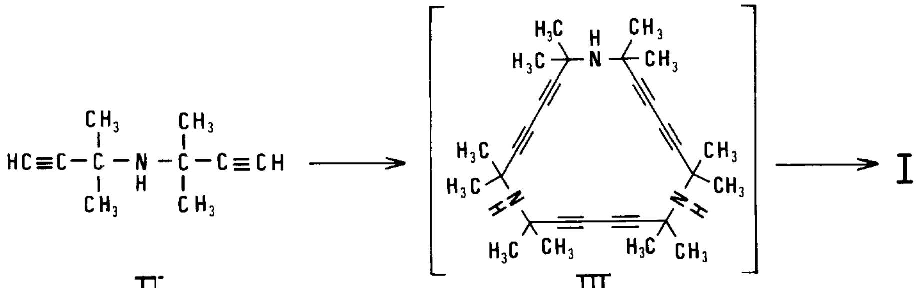
As part of a study on acetylenic amines and their related nitroxides, we wish to report the synthesis of the novel polycyclic compound tri(2,2,5,5-tetramethylpyrrolo)[aei]3,7,11-tridehydro[12]annulene (I), prepared in one step by oxidative coupling of di(1,1-dimethylpropyn-2-yl)amine (II), the latter synthesized by a known literature method[1]. We applied to II the oxidative coupling method of Hay[2]. Using a CuCl/pyridin/O_2 complex reaction proceeded rapidly with an oxygen consumption of 0.75 mole per mole of the monomer (i.e. 150% of theory). After removal of the pyridin and the copper salt, t.l.c. (silicagel, aceton) of the resulting dark brown oil gave two components, the first a brown material (R_f=0) and the second a red solid (R_f=0.3). Recrystallization of the latter from n-heptane gave a 7% yield of a red crystalline solid, stable in air; m.p. 266-267°C (decomp.); elemental analysis C 81.23, H 8.70, N 9.70 %; UV/VIS λ_{max}^{EtOH} in nm (ε): ca. 244 sh. (43,000), 251 (57,600), ca. 299 sh. (3800), ca. 318 sh. (2500), 467 (260), 500 (250), 560 (170); NMR (CCl_4)τ9.05; mass spec. m/e 441 (M^+); IR (KBr) in cm^{-1}: 3360 (w), 2980 (s), 2930 (m), 2870 (m), 2190 (w), 1560 (m), 1440 (m), 1420 (m), 1375 (s), 1360 (s), 1325 (m), 1265 (m), 1210 (m), 1160 (s), 1140 (w), 1070 (w), 1010 (w), 930 (w), 800 (w), 700 (s), 630 (m), 540 (w), 470 (s).

We did not investigate the R_f=0 band further. However, in view of the high oxygen consumption during the coupling reaction we believe that it consists of cross-linked polymeric material. Because there is no strong band in the infrared spectrum at ca. 3300 cm^{-1} and no peak at ca. 8 τ in the NMR spectrum and in addition no precipitate is formed with $AgNO_3$ solution, the red solid is a cyclic compound. This is striking because the oxidative coupling procedure, used in the preparation of this compound, has been claimed previously to give solely linear polymers[3]. The mass spectrum and the elemental analysis give a molecular formula $C_{30}H_{39}N_3$ which is consistent with a cyclic trimer of II. Because the UV/VIS spectrum is almost identical to that of 1,5,9-tridehydro[12]annulene as reported by Untch & Wysocki[4] and by Wolovsky & Sondheimer[5], we assign to the red compound the structure I :



I

We assume that I is formed by valence isomerization from the intermediate cyclic hexaacetylenic triamine III, as follows :



II III

Model studies show that III is a highly crowded molecule and that the α-diacetylene groupings, due to the methyls, can only take positions very close to each other, making valence isomerization to I not surprising. More examples of valence isomerization of polyacetylenic compounds are known in the literature[6,7]. In this context it is very interesting that the cyclic trimer of 1,6-heptadiyne, cycloheneicosa-1,3,8,10,15,17-hexayne, exists[8]. The UV spectrum of this compound reveals no interaction between the α-diacetylene groupings[8] and in a model these groupings can be wide apart.

The stability of I is very striking compared with that of the parent tridehydro [12] annulene[4], the pyrroline rings and the methyl groups obviously giving an effective protection of the unsaturated ring against oxygen. Attempts to fully hydrogenate I were unsuccessful, possibly for the same reason. With Raney nickel in ethanol only 3.5 molar equivalent of H_2 was consumed (1 atm.) giving a colourless solution with an UV spectrum much broader than that of I: 204 nm (ε 19600, calculated upon starting material); 230 sh. (15600); 270 sh. (7100). Evaporating the solvent gave a yellow product, insoluble in ethanol and not further characterized.

The nitroxides of I

Oxidation of I by excess p-nitroperbenzoic acid (PNPBA) in toluene gave an ESR spectrum of seven equally spaced lines, intensity ratio 1:3:6:7:6:3:1, hyperfine splitting constant 4.8 G, g=2.0061. We attribute this spectrum to the trinitroxide of I, having a spin exchange coupling constant J much greater than the hfs constant[9,10]. Partial oxidation of I in the same manner gave two additional ESR spectra with the same g-value 2.0061; the first consisted of three equally spaced lines, hfs constant 14.4 G, the second of five equally spaced lines, intensity ratio 1:2:3:2:1, hfs constant 7.2 G. These two spectra we attribute to the mono- and dinitroxides of I respectively. The ESR spectra of the di- and trinitroxides did not show any linewidth alternation, which is consistent with their rigid structure[10,11]. The hfs constant of the mononitroxide is one Gausz smaller than a_N which we found for the nitroxide of II and, because in general the pyrroline and the pyrrolidine nitroxides have hyperfine splitting constants a_N significantly smaller than the piperidine and the dialkylnitroxides[12], this difference is sufficient to give extra support to structure I.

Further details of I and its nitroxides, including ESR in isotropic and anisotropic media will be published shortly.

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