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CHEMICAL REACTIVITY OF PENTALENE DERIVATIVES

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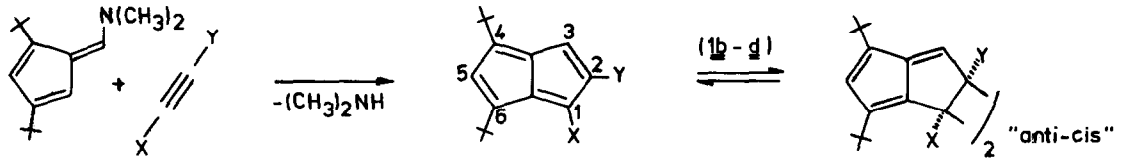
In previous papers[1,2] we described a facile synthesis of the pentalene derivatives 1 from 1,3-di-tert.-butyl-6-dimethylaminofulvene and acetylenes. Although several syntheses of other stable pentalenes have been reported in the literature[3], knowledge of their chemical reactivity is only meager at present. Therefore we have investigated the chemistry of the pentalenes 1. Where-



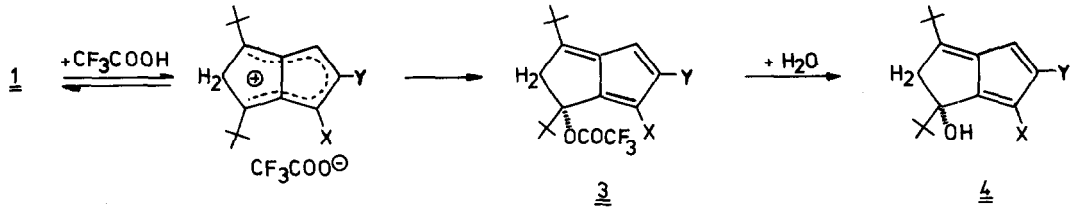
1 2

: $(CH_3)_3C$

	X	Y
a	$COOCH_3$	$COOCH_3$
b	H	$COOCH_3$
c	H	CHO
d	H	CN

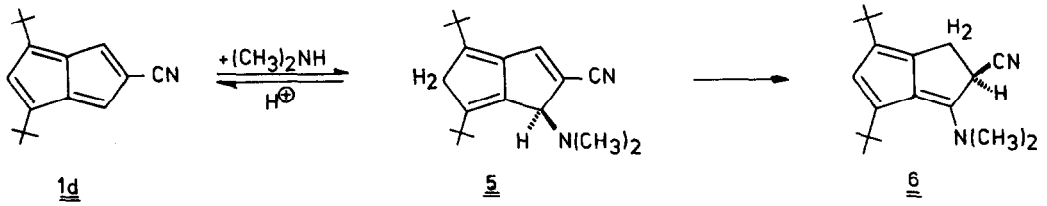
as 1a is stable as such, both in solution and in crystalline state, 1b - 1d are in equilibrium with their dimers 2 in solution[2]. The pentalenes 1 are stable in air but sensitive to both acids and bases. When 1a was treated with trifluoroacetic acid in methylene chloride at 25°C, the alcohol 4a[4] was isolated in 50% yield after chromatography on silica gel[5], indicating a protonation at the 5-position of the pentalene system, followed by the formation of the trifluoroacetate 3a, which was hydrolyzed on silica gel.

Direct evidence for the position of protonation was obtained by monitoring the reaction of 1d with CF_3COOD in $CDCl_3$ by nmr spectroscopy. After a reaction period of about 30 min at ambient temperature, a band at δ 4.90 due to the proton at C-5 of 1d disappeared almost completely,



whereas all other absorptions of 1d were about one-half as strong as the initial intensities. A new set of peaks appeared which were attributable to the corresponding trifluoroacetate 3d [δ 1.o3(9H,s), 1.37(9H,s), 6.24(1H,bs), 7.12(1H,bs)]. This proves that pentalenes 1, when treated with trifluoroacetic acid, are first protonated at the 5-position, followed by the formation of addition products of type 4[6].

Nucleophiles attack the 1-(≡3)position of the pentalenes 1. When dimethylamine was bubbled into a methylene chloride solution of 1d, a quick color change from green to orange was observed. Chromatography of this orange solution on silica gel regenerated 1d partly (70%) and the pale yellow product 6 was isolated (28%). On the other hand, if the above orange solution was kept at 25°C for 2 h before chromatography, only a small amount of 1d was recovered and 6 was obtained in 73% yield. This result suggests the primary formation of an unstable intermediate,



1d 5 6

which can either eliminate dimethylamine on a silica gel column to form 1d, or tautomerize to the stable fulvenoid 1.2-dihydropentalene derivative 6. The strucutre of the intermediate, the 1.5-dihydropentalenederivative 5, was concluded from the nmr spectrum of the crude reaction mixture, which contains 5 (δ 1.22(18H,s), 2.39(6H,s), 3.38(2H,bs), 4.5o(1H,s), 7.23(1H,s)) besides 6.

With dienophiles and dienes the pentalenes 1 form cycloadducts. Although dimethyl acetylenedicarboxylate and tetracyanoethylene were not susceptible, dicyanoacetylene reacted with 1a, 1b and 1c in refluxing benzene under formation of the adducts 7a[7], 7b and 7c in 57, 56 and 25%

7

isolated yields respectively. The attack of the acetylene at the 4,5-position of 1 was supported by the nmr and uv spectra of the adducts.

Accordingly pentalenes 1 react with dienophiles on the electron-rich five-membered ring, even when this portion of the molecule is substituted by bulky groups. Attempts to isomerize 7 like the adducts of 1,3-bis(dimethylamino)pentalenes[8] and 1.3.5-tri-tert.-butyl-pentalene[3] with acetylenes to azulene derivatives have met with no success so far.

In contrast to the above reaction, the pentalenes 1 add dienes at the electron-poor five-membered ring in a Diels-Alder reaction. E.g. 1a and 1d reacted at 140°C with cyclopentadiene, generated in situ from its dimer, to single adducts 8a (58%) and 8d (61%). The endo-structure of 8

8

was deduced from their nmr spectra, which exhibit a doublet (J=5Hz) at δ 3.7, attributable to the methine proton derived from the pentalene part. The regio-selectivity, which is also found in the reaction of 1a with dicyanoacetylene (vide supra), can be explained by the π-bond localization in this non-symmetrical pentalene system. A single crystal x-ray analysis[9] of 1a confirmed this suggestion and revealed that the bonds C(2)-C(3) and C(5)-C(6) are much shorter than the bonds C(1)-C(2) and C(4)-C(5). In accordance with that, [4+2]cycloadditions with dienes take place at the double bond C(2)-C(3), carrying an electron-withdrawing group, while those with dicyanoacetylene occur as [8+2]cycloadditions at C(4)-C(5) of the electron-rich moiety of the bicyclic tetraene system.

In summary, the pentalenes 1 show a marked reactivity towards acids, bases, dienophiles and dienes, with a high regio-selectivity.

Physical Properties of the Compounds 4 - 8

compound mp (C°)	^{1}H-nmr spectra in $CDCl_3$ (60 MHz, TMS-internal standard)	uv-visible spectra (λ_{max}(nm) (log ε)	ir-spectra (cm^{-1})
4a yellow syrup	0.88(9H,s), 1.33(9H,s), 3.17(1H,d,J=19.5Hz), 3.43(1H,d,J=19.5Hz), 3.82(6H,s), 6.81(1H,s).	366(2.81)[a] 298(4.22) 245(4.14)	3460[c] 1725 1690
6 yellow prisms 122-123°	0.97(9H,s), 1.19(9H,s), 3.05(6H,s), 3.13(1H,m), 3.41(2H,m), 6.21(1H,d,J=1.5Hz).	344(3.85)[b] 304(3.81) 265(3.71)	
7a orange needles 147-149°	1.09(9H,s), 1.38(9H,s), 3.83(3H,s), 3.88(3H,s), 4.53(1H,s), 6.58(1H,s).	418(2.97)[a] 310(4.00) 233(4.29)	2220[d] 1710
7b yellow blocks 142-143°	1.08(9H,s),1.42(9H,s), 3.85(3H,s), 4.48(1H,s), 6.66(1H,d,J=1Hz), 7.06(1H,d,J=1Hz).	408(2.74)[a] 307(3.96) 232(4.32)	
7c yellow prisms 208-209°	1.09(9H,s), 1.44(9H,s), 4.50(1H,s), 6.73(1H,bs), 7.05(1H,bs), 9.93(1H,s).	397(2.73)[a] 309(4.02) 244(4.35)	
8a red oil	1.12(9H,s), 1.20(9H,s), 1.82(2H,m), 3.13(1H,m), 3.30(1H,m), 3.66(1H,d,J=5Hz), 3.70(3H,s), 3.80(3H,s), 5.95(2H,m), 6.30(1H,s).	419(2.71)[b] 273(4.07)	
8d yellow plates 90-90.5°	1.15(9H,s), 1.19(9H,s), 1.97(2H,m), 3.22(2H,m), 3.67(1H,d,J=4.5Hz), 5.81(2H,m), 6.08(1H,s), 6.22(1H,s).	397(2.82)[b] 260(4.00)	2220[d]

a): in dioxane b): in hexane c): neat d): KBr

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REFERENCES AND NOTES

[1] K. Hafner and M. Suda, Angew.Chem. 88, 341(1976); Angew.Chem.Int.Ed.Engl. 15, 314(1976).

[2] M. Suda and K. Hafner, Tetrahedron Lett. 1977, preceding paper.

[3] K. Hafner and H.U. Süss, Angew.Chem. 85, 626(1973); Angew.Chem.Int.Ed.Engl. 12, 575 (1973); K. Hafner, H. Diehl and H.U. Süss, Angew.Chem. 88, 121(1976); Angew.Chem.Int.Ed.Engl. 15, 104(1976) and references cited therein.

[4] All new compounds gave correct elementary analyses.

[5] The same alcohol 4 was obtained when 1a was chromatographed on aluminum oxide.

[6] The reaction of 1a with CF_3COOD in $CDCl_3$ was so fast that the H-D exchange could not be observed. The product was the trifluoroacetate 3a as judged from the nmr spectrum ($CDCl_3$): δ 0.95(9H,s), 1.38(9H,s), 3.83(3H,s), 3.87(3H,s), 7.18(1H,s).

[7] By addition of dicyanoacetylene in 5,6-position an isomeric adduct was formed as a minor product (10%) [nmr ($CDCl_3$): δ 1.03(9H,s), 1.43(9H,s), 3.83(3H,s), 3.85(3H,s), 4.49(1H,s), 6.95(1H,s)].

[8] K. Hafner, Pure Appl. Chem. 28, 153 (1971).

[9] H.J. Lindner and B. Kitschke, Tetrahedron Lett. 1977, following paper.