Reference Data

¹H NMR Spectroscopy of Cycloadducts of 1,5- and 1,6-Diazaphenanthrene Phenacylides

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The ¹H NMR spectra of cycloadducts of 1,5- and 1,6-diazaphenanthrene phenacylides with acrylonitrile, ethyl acrylate, dimethyl acetylenedicarboxylate (DMAD), maleic anhydride and ethyl maleate, and those of cycloadducts of 1,5- and 1,6-diazaphenanthrenes with DMAD, are presented.

KEY words Cycloadducts Diazaphenanthrenes Phenacylides ¹H NMR

INTRODUCTION

The ¹H NMR of cycloadducts obtained from 1,6-diazaphenanthrene (dap) 1.5- and phenacylides^{1,2} and from parent daps³ have been investigated. The work was carried out in view of the biological activities of 1,5- and 1,6-daps and their derivatives.4-6

EXPERIMENTAL

The ¹H NMR spectra were recorded on a 100-MHz Tesla BS 497 spectrometer (cw) at DMSO temperature ambient in (concentration $5 \times 10^{-4} \text{ mgl}^{-1}$; 0.5-ml tube) using TMS as internal standard. The values of the chemical shifts and coupling constants were measured directly from the ¹H NMR spectra, based on literature data.7 The computer analysis of the ¹H NMR spectrum of 1,6-dap, recorded on a Jeol FX 90 spectrometer, using the LA0CN3 program,⁸ has shown the identical nature of the δ and J values obtained in this manner with those found directly from the ¹H NMR spectrum.

Compounds 1-10 are products of the 1,3dipolar cycloaddition reaction of the corresponding 1,5- and 1,6-dap phenacylides with acrylonitrile, ethyl acrylate, dimethyl acetylenedicarboxylate (DMAD), maleic anhydride and ethyl maleate;^{1,2} 11 and 12 are cycloadducts of 13 and 14 with DMAD.³ Compounds 1-10 were obtained by treatment of 1,5- and 1,6-dap phenacylides, formed in situ from the corresponding quaternary bromides in the presence of triethylamine, with dipolarophiles in benzene at room temperature;^{1,2,9,10} 11 and 12 were synthesized by the reaction of 1,5- and 1,6-daps with DMAD in benzene at room temperature.³

General procedure for 9

5-Phenacyl-l,5-dap bromide (1 mmol) suspended in benzene (15 ml) was treated with diethyl maleate (1.5 mmol) and triethylamine (1.4 mmol). The mixture was stirred at room temperature for 2 h and allowed to stand for 24 h; the triethylammonium bromide was filtered off.

An excess of *n*-hexane precipitated the crude product, which was purified by preparative chromatography and recrystallization (benzene-n-hexane); orange prisms, m.p. 63-64 °C; yield 31%.

Nomenclature of cycloadducts 2, 9 and 10

The compounds have the following systematic names: 2 = 7-benzoyl-5-cyanopyrido[3', 2':3,4] pyrrolidine [1,2-a]quinoline; 9 = 5benzoyl - 6,7 - diethoxycarbonylpyrido[3',2': 3,4] pyrrolidine [2,1-a] isoquinoline; and 10 = 7-benzoyl-5,6-diethoxycarbonylpyrido [3',2':3,4] pyrrolidine[1,2-a]quinoline.

RESULTS AND DISCUSSION

The ¹H NMR chemical shifts of 1-12 are shown in Table 1; the parent 1,5- and 1,6daps 13 and 14 are included for comparative purposes.

The chemical shifts of the cycloadducts derived from 1,5-dap were compared with those of the parent 1,5-dap (13), and the cycloadducts derived from 1,6-dap were compared with 14.

The presence and the length of the conjugation strongly influence the electron density in these molecules. In all cycloadducts an upfield shift of the H-2 signals is observed in compounds where there is no conjugation between the dap moiety and the fivemembered ring, e.g. 11.

The above results are compatible with those obtained for the series of 1,3-dipolar cycloadducts of 1,5- and 1,6-dap ethoxycarbonylmethylides with the same dipolarophiles.11,12

13





11

Reference Data

								Proton										
Series	Compound	2	3	4	4b	5	6A	6B	7	7a	8	9	10	11	2 × H <i>-o</i>	2 × H-m, H-p	CHz	CH_3
ι	1	8.43	7.43	8.65	—	6.67	4.12– 3.60	3.30- 2.78		-	7.22	8.10	7.63	8.87	8.25	8.10- 7.63		
	3	8.42	7.42	8.90		6.55	4.10– <i>ca</i> 3.50	3.22- ca2.70	_	_	7.20	8.15	7.62	9.78	8.28	8.15 7.62	4.20	1.32
	5	8.72- 8.30	7.70– 7.41	9.00	_	6.95	4	.13	-		7.70 7.41	8.20	7.72	10.00	8.72 8.30	8.20- 7.72	_	3.92 and 3.70
	7	8.85	8.03- 7.57	8.57– 8.27	-	_	7	.45	7.30	—	8.57- 8.27	8.03-	7.57	8.97	8.27- 8.03	8.03- 7.57		
	9	8.70	7.55– 7.38	8.88	_	6.00 5.62 5A 5B		4.22-3.5	0	6.00 5.62	7.55 7.38	6.65	7.00	9.74	8.45– 8.20	8.10 7.60	4.42- 3.50	1.08 and 0.68 2 × CH ₃
	11	8.42- 8.20	8.00	-7.22		6.05 6.90		—		6.30	8.00-7.22		8.42 8.20	_			3.65	
	13	9.23- 8.98	7.81	8.49	-	_			—	9.41	8.28	8.14-	-7.78	9.23- 8.98	~	—	-	
Π	2	8.75	7.52	8.00- 7.60	5.55	4.52- 4.20	3.32 3.02	2.50- 2.20	6.10- 5.82		6.25	7.25	6.87	8.5	0-8.22	8.00– 7.60		_
	4	9.05	8.00- 7.42	8.72		-	4.00- 	3.20- <u>2.72</u>	6.60	-	6.82	8.00- <u>7.42</u>	7.25	10.25	8.30	8.00– 7.42	4.22	1.30
	6	9.12	8.00- 7.40	8.80	_		4	.05	7.22- 6.90	-	7.22– 6.90	8.00	7.40	10.30	8.43	8.00- 7.40	_	3.90 and 3.68
	8	9.21– 9.05	8.05– 7.55	8.84	-	7.29	7	.50	-		8.05– 7.55	8.05-	-7.55	9.21- 9.05	8.27– 8.05	8.05– 7.55	_	
	10	9.05	8.12- 7.47	8.72	5.92	4	.47-3.64		6.26 7A 7B		8.12– 7.47	7.00	7.33	10.26	8.47 8.24	8.12 7.47	4.47- 3.64	1.32 and 1.13
	12	8.62	7.50– 7.15	7.78	6.22	_			6.10 6.90		7.00	7.50-	-7.15	8.20	—	_	-	2 × CH ₃ 3.62
	14	9.16	7.77	8.63	9.40	—	_	_			8.16	8.08-	-7.66	9.01		_		-



Table 1. ¹H NMR chemical shifts (ppm) (DMSO, TMS) of compounds 1-14.



COOEt н COOMe COOMe

4

6



PhCD

8



14

Series II. Compounds derived from 14

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Received 14 February 1991; accepted (revised) 28 May 1991