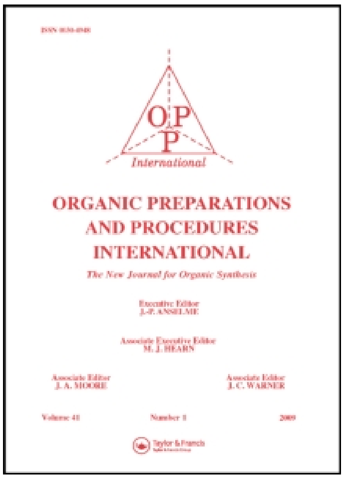

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SYNTHESIS OF ISOXAZOLYL 2-PYRAZOLINES

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OPPI BRIEFS

SYNTHESIS OF ISOXAZOLYL 2-PYRAZOLINES

Submitted by (07/15/87)
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The cycloaddition of diazomethane to 1,2-disubstituted alkenes often requires high pressure and prolonged reaction time.[1] de Suray et al. have found that the presence of a nitro group on stilbene permitted the reaction to occur to a certain degree under less drastic conditions. We now report that the cycloaddition of diazomethane to 3-methyl-4-nitro-5-styrylisoxazoles[2] in dry ether for 2 hrs furnished 4-aryl-3-(3-methyl-4-nitro-5-isoxazolyl)-2-pyrazolines (II) in reasonable yields. The initially formed 1-pyrazolines evidently underwent prototropic rearrangement to give II. The absence of the isomeric 3-aryl-4-(3-methyl-4-nitro-5-isoxazolyl)-2-pyrazoline may be ascribed to the polarisation of the ethylenic double bond in I towards the isoxazole nucleus by the nitro group thus rendering the β-carbon positively charged. The structure of II was established from analytical and spectral data. Mass spectral fragmentation of IIa (styrene at m/e 104) also supports the structure assigned.

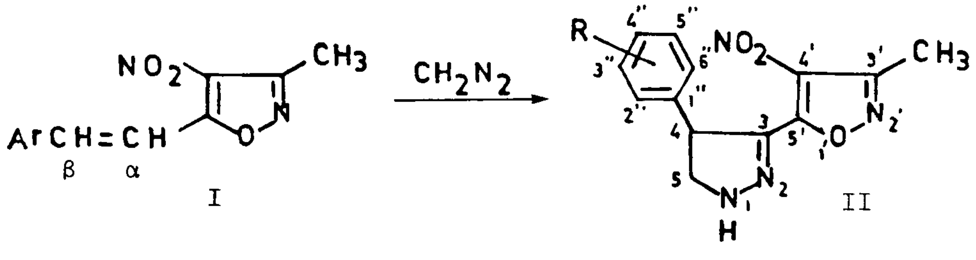

TABLE 1. Yields, mps and Elemental Analyses

Comp.	Ar	Yield (%)	mp. (°C)	Elemental Analyses (Found) C	H	N
IIa	C_6H_5	50	157^a	57.35 (57.37)	4.41 (4.40)	20.58 (20.59)
IIb	p-MeOC$_6$H$_4$	70	140^a	55.62 (55.63)	4.63 (4.62)	18.54 (18.53)
IIc	p-MeC$_6$H$_4$	75	150^b	58.74 (58.72)	4.89 (4.90)	19.58 (19.57)
IId	o-ClC$_6$H$_4$	40	154^a	50.98 (50.97)	3.59 (3.58)	18.30 (18.31)
IIe	p-ClC$_6$H$_4$	50	125^b	50.98 (50.96)	3.59 (3.60)	18.30 (18.29)
IIf	2,4-Cl$_2$C$_6$H$_3$	40	162^a	45.88 (45.89)	2.94 (2.95)	16.47 (16.45)
IIg	3,4-(OCH$_2$O)C$_6$H$_3$	35	178^b	53.16 (53.15)	3.79 (3.78)	17.72 (17.73)
IIh	p-BrC$_6$H$_4$	60	123^a	44.57 (44.58)	3.14 (3.15)	16.0 (16.0)

a) Crystallized from pet. ether and benzene. b) Crystallized from methanol.

TABLE 2. C-13 NMR Spectral Data^a of IIb^b and II^c

Carbon atoms	δ_C ppm IIb	IIc	Carbon atoms	δ_C ppm IIb	IIc
CH$_3$ (q)	11.5	11.5	C-5' (s)	140.1	139.8
C-3 (s)	176.7	176.7	C-1"	162.6	162.5
C-4 (d)	49.3	49.7	C-2" & C-6"^{c}	114.7	127.4
C-5 (t)	58.3	58.4	C-3" & C-5"^{c}	128.6	129.9
C-3'(s)	156.1	156.1	C-4"	159.4	136.8
C-4'(s)	131.8	137.6		55.3 (OCH$_3$-q)	21.0 (CH$_3$-q)

a) These assignments are based on our previous publication.[3] b) ^{13}C NMR spectra were recorded in CDCl$_3$. c) These carbons appeared as a single peak.

TABLE 3. Spectral Data of Compounds II[a]

	^{1}H NMR (ppm)					
Comp.	NH[b]	Ar-H	CH_3	CH_2	CH	Others
IIa[c]	5.5	7.2-7.3	2.4	4.2	4.9	--
				(J_{MX} = 11.9Hz)	(J_{XA} = 6.8Hz)	
				(J_{MA} = 10.4Hz)	(J_{XM} = 11.9Hz)	
				3.7		
				(J_{AX} = 6.8Hz)		
				(J_{AM} = 10.4Hz)		
IIb[d]	9.5	6.7-7.1	2.5	4.2	4.9	3.6
				(J_{MX} = 11.7Hz)	(J_{XA} = 6.8Hz)	(OCH_3)
				(J_{MA} = 10.4Hz)	(J_{XM} = 11.7Hz)	
				3.7		
				(J_{AX} = 6.8Hz)		
				(J_{AM} = 10.4Hz)		
IIc	7.5	7.0-7.3	2.5	4.2	4.9	2.3
				(J_{MX} = 11.9Hz)	(J_{XA} = 6.6Hz)	(CH_3)
				(J_{MA} = 10.5Hz)	(J_{XM} = 11.9Hz)	
				3.8		
				(J_{AX} = 6.6Hz)		
				(J_{AM} = 10.5Hz)		
IId	6.8	7.3-7.6	2.6	4.2	4.9	--
				(J_{MX} = 11.9Hz)	(J_{XA} = 6.8 Hz)	
				(J_{MA} = 10.4Hz)	(J_{XM} = 11.9Hz)	
				3.8		
				(J_{AX} = 6.8Hz)		
				(J_{AM} = 10.4Hz)		

a) NMR spectra of all compounds were recorded in $CDCl_3$. b) These hydrogen peaks disappeared on shaking the sample with D_2O. c) Mass spectrum of compound IIa: m/e 272 (55), 226 (100), 212 (25), 144 (30), 116 (60), 104 (70), 119 (45). d) Mass spectrum of compound IIb: m/e 302 (60), 226 (100), 212 (25), 174 (25), 145 (70), 134 (50), 119 (35), 103 (25).

All compounds showed an NH band at ∿3300 cm^{-1}.

The pyrazolines are stable and have very long shelf life as indicated by the unchanged mps over a long period of time. This is the first report of cycloaddition of diazomethane to isoxazole derivatives.

EXPERIMENTAL SECTION

All mps were determined in open capillary tubes using Toshniwal melting point apparatus and are uncorrected. IR spectra were recorded in Nujol on Perkin-Elmer 282 instrument. The ^{1}H NMR spectra were obtained on Varian 100 MHz spectrum using TMS as internal standard and chemical shifts are expressed in ppm. 20 MHz ^{13}C NMR spectra were run on Varian FT-80A instrument. Mass spectra were determined on a JEOL-JMS-300 spectrometer at 70 eV. Microanalyses were performed at Regional Research Laboratories, Hyderabad, India. The purity of the compounds were monitored by TLC, performed on silica gel plates (Merck) and using benzene-ethyl acetate as the eluent.

4-Aryl-3-(3-methyl-4-nitro-5-isoxazolyl)-2-pyrazolines (II). _General Procedure_.- To a solution of 3-methyl-4-nitro-5-styrylisoxazole (0.01 mol) in dry benzene (25 ml), was added slowly a solution of diazomethane (0.01 mol) in dry ether (25 ml) and the mixture was stirred for 2 hrs. Evaporation of the solvent at ambient temperature, followed by trituration of the gummy product with pet. ether gave the crude product. Recrystallization from suitable solvent gave the pure product (Table 1).

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