provided further studies indicate absence of toxicity following local application.

11 November 1988

1. Jag Mohan, *Indian J. Chem.*, 1982, **B21**, 243.
2. Jag Mohan, *Indian J. Chem.*, 1983, **B22**, 270.
3. Jag Mohan and Anjaneyulu, G. S. R., *Polish J. Chem.*, 1987, **61**, 547.
4. Reid, J. R. and Heindel, N. D., *J. Heterocycl. Chem.*, 1976, **13**, 925.
5. Nakahara, H., Ishikawa, T., Sarai, Y., Kondo, T. and Mitsuhashi, S., *Nature (London)*, 1977, **266**, 165.

SYNTHESIS AND CHARACTERIZATION OF SOME NEW 3-ACETYL-4-ARYL-2-PYRAZOLINES

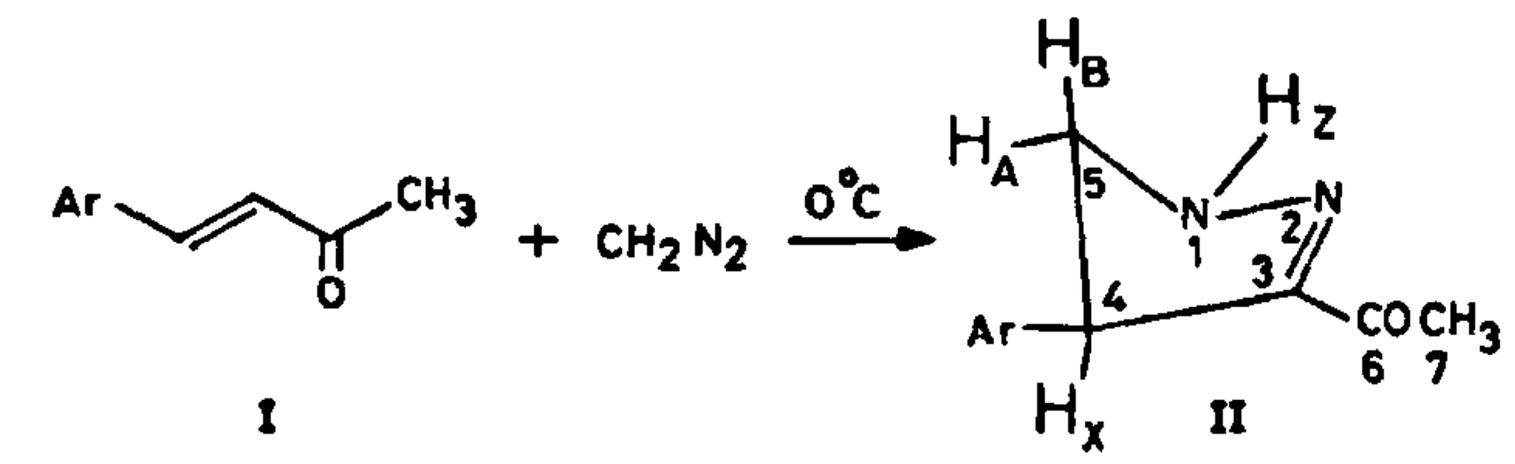
G. V. SUBBA RAJU and KOTHA S. RAO
Department of Chemistry, School of Mathematical and Physical Sciences, Sri Venkateswara University, Tirupati 517 502, India

SYNTHESIS of pyrazolines through cycloaddition of diazomethane to activated olefines has been known for a long time[1]. However, there is no general agreement on the structure of 2-pyrazolines[2–6]. Recently, we have established the structure of 3-aroyl-4-aryl-2-pyrazolines[7]. In continuation of this study, we report in this communication the synthesis and characterization of 3-acetyl-4-aryl-2-pyrazolines (IIa–h).

4-Aryl-3-buten-2-ones (Ia–h) were obtained by crossed aldol condensation of appropriately substituted aldehydes and acetone[8]. The ether solution of diazomethane prepared from nitrosomethylurea[9] was added to butenones (Ia–h) in ether at 0°C to give 3-acetyl-4-aryl-2-pyrazolines (IIa–h). In the case of Ia, the formation of 1-pyrazoline[1] was noticed, but this changed to 2-pyrazoline, IIa.

The IR data (table 1) for the pyrazolines (IIa–h) indicate bands in the regions 3280–3340, 1630–1650 and 1520–1530 cm^{-1} assigned to NH, C=O and C=N stretch vibrations respectively. It is significant to note that $\nu_{C=N}$ shifted to lower frequencies while $\nu_{C=O}$ shifted to higher frequencies compared to those of 3-aroyl-4-aryl-2-pyrazolines[5–7].

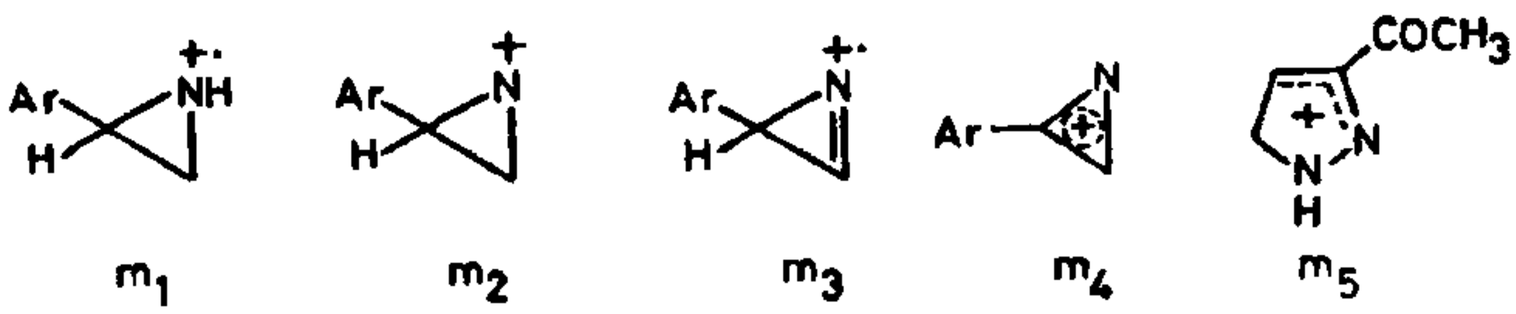
^{1}H NMR spectroscopic data (table 2) contain ABX pattern of signals attributed to 4-methine and 5-methylene protons. It is interesting to note that 200 MHz spectra clearly resolved the NH signal, whereas in 90 MHz spectra the signal could not be traced out. In case of IIb and IIc the coupling with NH proton is also discernible.



I II

Ar

(a) Phenyl
(b) 4-Methylphenyl
(c) 4-N, N-dimethylphenyl
(d) 2-Chlorophenyl
(e) 4-Chlorophenyl
(f) 3,4-Methylenedioxyphenyl
(g) 4-Methoxyphenyl
(h) Furan-2-yl



m_1 m_2 m_3 m_4 m_5

Table 1 *Physical and chemical data for 2-pyrazolines (IIa–h)*

Compound	Reaction time (h)	Yield* (%)	m.p. (°C)	Mol. formula	Found (Calc.) (%) C	H	N	UV (MeOH) (nm)	IR** (cm^{-1}) C=N	C=O	N–H
IIa	60	85	102–103[a]	$C_{11}H_{12}N_2O$	70.58 (70.21)	6.57 (6.30)	14.79 (14.89)	309	1530	1640	3280
IIb	48	92	81–83	$C_{12}H_{14}N_2O$	70.55 (71.29)	7.16 (6.93)	13.05 (13.86)	311	1530	1635	3340
IIc	48	66	124–125	$C_{13}H_{17}N_3O$	66.47 (67.53)	7.62 (7.35)	17.71 (18.18)	308 255	1520	1635	3290
IId	36	83	120–121	$C_{11}H_{11}N_2OCl$	59.62 (59.19)	4.35 (4.93)	12.49 (12.55)	318 304	1530	1630	3280
IIe	24	90	97–99	$C_{11}H_{11}N_2OCl$	59.07 (59.19)	4.64 (4.93)	11.70 (12.55)	308	1520	1630	3310
IIf	24	86	94–95	$C_{12}H_{12}N_2O_3$	62.20 (62.06)	5.75 (5.17)	11.88 (12.07)	307 296	—	1650	3320
IIg	36	62	90–91	$C_{12}H_{12}N_2O_2$	65.84 (66.67)	6.83 (5.56)	12.69 (12.96)	309	1530	1630	3340
IIh	36	75	53–54	$C_9H_{10}N_2O_2$	61.39 (60.67)	5.64 (5.62)	15.43 (15.73)	305	—	1650	3340

*Computed based on isolated compounds. **Samples as KBr pellets (II a, b, c, d, e)/$CHCl_3$ solutions (II f, g, h). [a]Lit.[1] m.p. 100.5–101°C.

Table 2 *^1H NMR spectroscopic data* for pyrazolines (IIa–h)*

Compound	H_A	H_B	H_X	H_Z	J_{AB}	J_{AX}	J_{BX}	J_{BZ}	7-CH_3	Ar-H	Substituents
IIa	3.71	4.03	4.39	6.25	11	5	11	—	2.38	7.19–7.32 (5H, *m*)	—
IIb	3.68	4.03	4.36	6.22	11	5	11	2	2.38	7.05–7.15 (4H, *m*)	2.30 (3H, *s*)
IIc	3.67	3.98	4.31	6.18	11	5	11	2	2.37	6.65 (2H, *d*, *J* = 9Hz) 7.09 (2H, *d*, *J* = 9Hz)	2.90 (6H, *s*)
IId	3.54	4.05	4.81	6.38	11	6	11	—	2.45	6.38–7.39 (4H, *m*)	—
IIe	3.68	4.05	4.38	—	11	5	11	—	2.40	7.10–7.35 (4H, *m*)	—
IIf	3.65	4.01	4.35	—	11	5	11	—	2.42	6.75 (3H, *s*)	5.95 (2H, *s*)
IIg	3.65	4.02	4.35	—	11	5	11	—	2.40	6.82 (2H, *d*, *J* = 9Hz) 7.20 (2H, *d*, *J* = 9Hz)	3.80 (3H, *s*)
IIh	3.88	3.88	4.56	—	—	8	10	—	2.46	6.10 (1H, *m*) 6.30 (1H, *m*) 7.35 (1H, *m*)	—

*Solvent, $CDCl_3$; δ values from TMS; 200 MHz (IIa, b, c, d)/90 MHz (IIe, f, g, h) spectra.

Table 3 *^{13}C NMR spectroscopic data* for pyrazolines (IIa–h)*

Compound	C-3	C-4	C-5	C-6	C-7	Aromatic carbons C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	Substituents
IIa	152.5	47.0	58.1	193.3	25.7	141.0	127.0	128.5	127.0	128.5	127.0	—
IIb	152.9	46.8	58.2	193.3	25.7	136.5	126.9	129.3	138.0	129.3	126.9	20.9
IIc	153.5	46.4	58.1	193.4	25.8	128.8	127.7	112.8	149.6	112.8	127.7	40.5
IId	151.2	44.2	57.3	193.2	25.7	137.9	133.1	129.7	128.3	127.1	127.7	—
IIe	151.9	46.3	57.8	193.2	25.5	139.6	128.4	128.6	132.5	128.6	128.4	—
IIg	152.0	45.8	57.8	193.2	25.3	133.2	127.7	113.6	158.1	113.6	127.7	54.7
IIh	152.4	40.0	55.0	193.1	25.2	—	148.2	105.5	110.1	141.2	—	—

*Solvent; $CDCl_3$; δ values from TMS; 50.16 MHz (IIa,b,c,d)/22.63 MHz (IIe,g,h) spectra; Assignments are supported by SFORD data.

Table 4 *Important mass spectral fragments of IIa–h m/z (%)*

Compound	M^+	M^+–H	M^+–CH_3	M^+–$COCH_3$	m_1	m_2	m_3	m_4	m_5	$ArCHCH_2^+$	$ArCHCH^+$	Other prominent fragments
IIa	188 (100)	187 (15.2)	173 (8.1)	145 (53.5)	119 (14.1)	118 (39.0)	117 (64.6)	116 (42.4)	111 (14.1)	104 (23.2)	103 (10 1)	91(43.4); 90(31.3); 89(42.5); 77(33.3)
IIb	202 (100)	201 (19.2)	187 (5.1)	159 (56.0)	133 (18.2)	132 (53.0)	131 (82.0)	130 (36.4)	111 (12.2)	118 (31.3)	117 (37.4)	105(40.4); 103(29 3); 91(38 4); 77(20.2)
IIc	231 (100)	230 (5.2)	—	188 (1.1)	162 (3.1)	161 (29.4)	160 (33.3)	159 (35.3)	—	147 (5.9)	146 (5.1)	133(7.2); 43(3.1)
IId	222 (5.5)	221 (3.4)	207 (3.4)	179 (12.8)	153 (9.6)	152 (7.8)	151 (13.1)	150 (11.2)	111 (4.1)	138 (5.1)	—	187(100); 125(8 1); 43(97.0)
	224 (5.1)	223 (5.8)	209 (3.1)	181 (4.1)								
IIe	222 (100)	221 (29.3)	207 (8.0)	179 (70.7)	153 (50.0)	152 (50.5)	151 (57.4)	150 (51.5)	111 (14.2)	138 (8.1)	137 (33.3)	116(26.3); 115(30 3); 114(41.4); 110(28.3); 89(69.7)
	224 (33.4)	223 (21.2)	—	181 (31.3)	155 (7.0)	154 (10.1)	153 (50.0)	152 (50.5)		140 (10.1)		
IIf	232 (68.9)	231 (7.2)	—	189 (9.3)	163 (9.8)	162 (33.4)	161 (46.5)	160 (20.2)	111 (3.1)	148 (19.2)	147 (17.2)	135(22.2); 43(100)
IIg	218 (93.9)	217 (11.2)	203 (1.1)	175 (21.4)	149 (12.3)	148 (65.7)	147 (53.1)	146 (28.6)	111 (4.6)	134 (25.0)	133 (10.1)	132(26.9); 121(32.7); 91(17.9), 43(100)
IIh	178 (36.6)	177 (4.2)	163 (5.9)	135 (9.7)	109 (6.2)	108 (32.7)	107 (64.3)	106 (19.4)	—	94 (27.6)	93 (3.1)	43(100)

^{13}C NMR data (table 3) show signals in the regions 40–47 ppm (doublets in SFORD) and 55–58 ppm (triplets) which are interpreted[7] as due to C-4 and C-5 respectively. The chemical shifts of the aromatic carbons show the substituent shifts as expected[10].

The mass spectral fragments (table 4) agree well with the structures assigned. Some of the fragmentation pathways are similar to those for 3-aroyl-4-aryl-2-pyrazolines[5].

From the above it is clear that 3-acetyl-4-aryl-2-pyrazolines have the structure **II**. Such a structure assignment has also been favoured by Smith *et al.*[1], but without any spectroscopic evidence.

3-Acetyl-4-aryl-2-pyrazolines: General procedure

To a solution of Ia (1.46 g, 10 mmol) in ether or chloroform at 0°C was added excess of diazomethane (from 4 g of nitrosomethylurea) and the mixture kept at 0°C for 60 h. The progress of the reaction was monitored over silica gel layers. After completion of the reaction, the solvent was removed under vacuum. The product IIa, 1.6 g, formed was recrystallized from pet. ether–ether; m.p. 102–103°C.

Financial assistance from UGC, New Delhi, is gratefully acknowledged. We thank Prof. G. S. R. Subba Rao, Indian Institute of Science, Bangalore; Dr K. Suseela, USA, and Regional Sophisticated Instrumentation Centre, Lucknow, for spectroscopic data; and Prof. C. B. S. Rao, Andhra University, Visakhapatnam, for encouragement.

15 December 1988

1. Smith, L. I. and Pings, W. B., *J. Org. Chem.*, 1937, **2,** 23; Smith, L. I. and Howard, K. L., *J. Am. Chem. Soc.*, 1943, **65,** 159, 165.
2. Ghate, S. G., Kaushal, R. and Deshapande, S. S., *J. Indian Chem. Soc.*, 1950, **27,** 633.
3. Mustafa, A. and Fleifel, A. M., *J. Org. Chem.*, 1950, **24,** 1740; Mustafa, A., Asker, W., Harhash, A. H. and Fleifel, A. M., *Tetrahedron*, 1965, **21,** 2215.
4. Parham, W. E., Blake, F. D. and Theissen, D. R., *J. Org. Chem.*, 1962, **27,** 2415.
5. Sayed, G. H. and Kjosen, H., *Indian J. Chem.*, 1980, **B19,** 980.
6. Bhaskar Reddy, D., Bhaskara Reddy, D., Subba Reddy, N. and Balaji, T., *Indian J. Chem.*, 1984, **B23,** 983; Bhaskar Reddy, D., Seshamma, T. and Ramana Reddy, B. V., *Acta. Chim. Hung.*, 1986, **122,** 19.
7. Bheemasankara Rao, Ch., Subba Raju, G. V. and Narasimha Raju, P. V., *Indian J. Chem.*, 1986, **B25,** 400.
8. Drake, N. L. and Allen, P. Jr., *Org. Syntheses*, Coll. Vol. 1, (ed.) A. H. Blatt, John Wiley, 2nd edn, 1941, p. 77; Robert, E. L. *et al.*, *J. Org. Chem.*, 1949, **14,** 982; Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G. and Tatchell, A. R., *Vogel's Textbook of Practical Organic Chemistry*, 4th edn, ELBS, London, 1978, p. 147.
9. Vogel, A. I., *Practical Organic Chemistry*, 3rd edn, ELBS, London, 1968, p. 969.
10. Levy, G. C., Lichter, R. L. and Nelson, G. L., *Carbon-13 NMR Spectroscopy*, 1980, 2nd edn, pp. 111, 112.

TWO NANNANDROUS SPECIES OF *OEDOGONIUM* LINK, NEW TO INDIAN ALGAL FLORA

H. M. SHUKLA, IQBAL HABIB, U. C. PANDEY† and G. L. TIWARI*
Mitra Phycology Lab, P.G. Department of Botany, Bareilly College, Bareilly 243 005, India
**Department of Botany, University of Allahabad, Allahabad 211 002, India*

THE genus *Oedogonium* Link, is world-wide in distribution and most of the species are found epiphytic on *Cladophora, Pithophora, Chara* and *Nitella*, and also on larger species of *Oedogonium* and *Bulbochaete*[1]. At present the genus includes more than 531 species[1,2] excluding its varieties and forma. Of these, 171 nannandrous species, completely described, and 10 species, incompletely described, are included in a monograph by Gonzalves[1]. Among them 58 nannandrous species with their 73 taxa are so far reported from India.

During fortnightly collections of epiphytic algae of Mauri Lake, Pratapgarh, UP, from August 1984 to July 1986, 65 taxa of the genus *Oedogonium* were encountered. Among them 18 taxa are nannandrous, of which only two taxa, viz. *Oedogonium sinuatum* (Trans.) Tiffany f. *seriatum* Prescott and *O. westii* (Tiffany *et* Braun) Tiffany, are described here. Both species are new additions to the Indian algal flora.

†For correspondence