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# REACTION OF 4-ARYLIDENE-3-METHYL-1-PHENYL-5-PYRAZOLONES WITH AMINES

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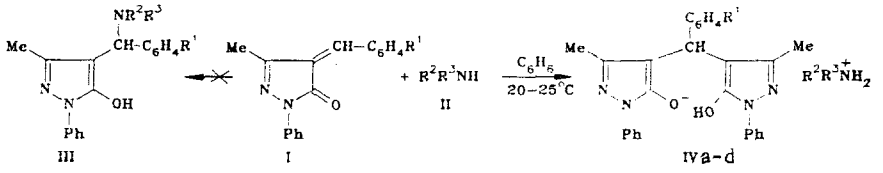
The reaction of primary and secondary amines with 4-arylidenepyrazolones gives the corresponding ammonium salts of 4,4'-benzylidenebis-5-pyrazolone derivatives but not adducts on the exocyclic C=C bond as was previously believed.

The reactions of 4-arylidene-5-pyrazolones with nucleophiles have been the subject of numerous studies [1]. In particular, it has been reported [2] that with secondary amines (piperidine, morpholine) addition products (III) are formed on the exocyclic C=C bond. Compounds of this type are of interest to us as intermediates in the synthesis of dyes, therefore we have studied the reaction of two 4-arylidene-3-methyl-1-phenyl-5-pyrazolones (I) with primary and secondary amines (II).




IV a $R^1=R^2=H$, $R^3=i$-Bu; b $R^1=H$, $R^2=R^3=Et$; c $R^1=H$, $R^2+R^3=(CH_2)_5$; d $R^1=p$-MeO, $R^2=H$, $R^3=i$-Bu

In accordance with the findings of [2], the reaction proceeds readily even at room temperature and in all cases white crystalline addition products IVa-d are obtained (Table 1). However, their composition and PMR spectra do not correspond to the previously proposed structure of III. As can be seen from Table 2, for adducts IVa, b, d the ratio of intensities of the signals from the methyl groups in the pyrazoline ring and in the amine fragment is not 1:2 as in structure III, but 1:1. Moreover, there is a signal from only one arylidene proton in the spectra, while for compound IVd there is a signal from only one methoxyl group, in other words, the addition products have a symmetrical structure that contains two pyrazoline fragments, a CH group with an aryl substituent, and one amine molecule.

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TABLE 1. 4,4'-Arylidenebispyrazolone Salts IV

| Compound | mp, °C | Found, % | | | Empirical formula | Calculated, % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | | C | H | N | |
| IVa | 159...161 | 73,5 | 6,7 | 13,4 | $C_{27}H_{23}N_4O_2 \cdot C_4H_{12}N$ | 73,1 | 6,9 | 13,7 | 95* |
| IVb | 160...162 | 73,3 | 6,7 | 13,6 | $C_{27}H_{23}N_4O_2 \cdot C_4H_{12}N$ | 73,1 | 6,9 | 13,7 | 88 |
| IVc | 187...189† | 73,7 | 6,8 | 13,3 | $C_{27}H_{23}N_4O_2 \cdot C_5H_{12}N$ | 73,7 | 6,8 | 13,4 | 90 |
| IVd | 133...137 | 71,4 | 6,8 | 13,3 | $C_{28}H_{25}N_4O_3 \cdot C_4H_{12}N$ | 71,2 | 6,9 | 13,0 | 92 |

*With half the quantity of amine the yield is 87%.
†The adduct of benzylidenepyrazolone and piperidine (I, $R^1$ = H) as reported in [2] has mp 209°C.

TABLE 2. PMR Spectra of Adducts IV (δ, ppm)

| Compound | $CH_3$, 6H, s | CH, 1H, s | Aromatic protons | $R^2$, $R^3$ |
|---|---|---|---|---|
| IVa | 2.13 | 4.67 | 7.10...7.57 (11H, m), 8.03 (4H, d*) | 0.86 [6H, d†, $(CH_3)_2$], 1.65...1.90 (1H, m, CH), 2.60 (2H, d, $CH_2$) |
| IVb | 2.10 | 4.58 | 6.97...7.40 (11H, m), 7.95 (4H, d*) | 1.00 (6H, t, $CH_3$), 2.73 (4H, q, $CH_2$) |
| IVc | 2.12 | 4.59 | 6.97...7.45 (11H, m), 7.95 (4H, d*) | 1.33...1.64 (6H, m, 3-...5-H)‡ 2.73...2.98 (4H, m, 2- and 6-H)‡ |
| IVd | 2.17 | 4.67 | 6.84 (2H, d**), 7.10...7.63 (8H, m), 8.13 (4H, d*1) | 0.83 [6H, d, $(CH_3)_2$], 1.63...1.97 (1H, m, CH), 2.57 (2H, d, $CH_2$) |

*1 ortho-Protons of $C_6H_5$–N, $^3J$ ~8 Hz.
† In alkyl substituents, $^3J$ 6.5-7.5 Hz.
‡ For piperidine ring.
** meta-Protons of p-$MeOC_6H_4$ group, $^3J$ ~8 Hz. Methoxyl protons give a singlet at 3.70 ppm.

TABLE 3. Intensity of Characteristic Peaks in Mass Spectra of Adducts IV and Bispyrazolone V

| Compound | I (% of max.) for m/z | | |
|---|---|---|---|
| | 262 | 185 | 174 |
| IVa | 35 | 46 | 100 |
| IVb | 46 | 51 | 68 |
| IVc | 27 | 31 | 26 |
| IVd | 2* | 2 | 34 |
| V | 18 | 27 | 19 |

*For ion with m/z 292.

Taking this into consideration, the PMR spectra of the adducts almost unequivocally suggest a structure of IV in which the equivalence of the heterocyclic fragments is achieved by a degenerate migration of the hydroxyl proton that is rapid on the time scale of NMR. Similar salt-like compounds were previously obtained [3] in a number of 3-methylisoxazolone derivatives.

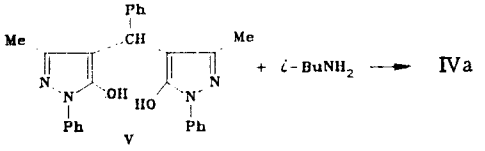
The $^{13}C$ NMR spectrum of compound IVb is also consistent with the structure proposed by us and rules out a structure of type III for it. The criterion here is the chemical shift of the benzyl carbon atom. If, as in the case of III, an amino group is bonded to it together with the pyrazolone ring and phenyl radical, a signal would be expected at ~60 ppm [4]. On the other hand, in structure IV, analogous to bispyrazolone V, the chemical shift value must be ~30 ppm [5]. The experimental value is 31.91 ppm.

The validity of structure IV is supported by the mass spectra of the adducts, in which the heaviest ion has a mass corresponding to 4-arylidene-5-pyrazolone and characteristic ions with m/z 185 and 174 are present (Table 3). This type of fragmentation is typical for 4,4'-arylidenebis(3-methyl-1-phenyl-5-pyrazolones), the formation of which is very likely to occur by separation of an amine molecule from adducts IVa-d. The peaks with m/z 262 (or 292) and

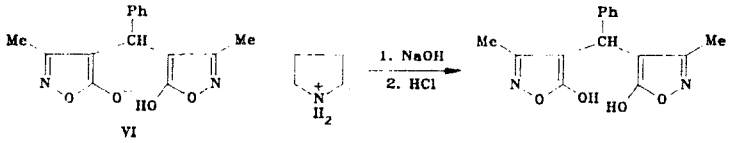
174 occur as a result of a McLafferty rearrangement of the bispyrazolone ion, and the peak with m/z 185 is formed by separation of an aryl residue from the resulting arylidene derivative.

Finally, structure IV can be proved by purely chemical methods. The reaction was carried out with equimolar quantities of compounds I and II. Since one molecule of amine reacts with two molecules of 4-arylidenepyrazolone, half the quantity of amine should also be sufficient. In accordance with this, when the quantity of amine was halved we did not observe any substantial reduction in yield of adduct IVa (Table 1). According to the reaction stoichiometry, when salts IV are formed one of the two arylidene residues must be lost. It transpires that in this reaction it is converted to the corresponding aldehyde, which we determined as its 2,4-dinitrophenylhydrazone.

The reaction of amines II with 4,4'-benzylidenebis(3-methyl-1-phenyl-5-pyrazolones) (V) must lead directly to products IV, and the interaction of isobutylamine with both benzylidenepyrazolone (I, $R^1$ = H) and bispyrazolone V [6] in actual fact gives identical products.




When bisisoxazolone salt VI is dissolved in alkali and subsequently treated with hydrochloric acid, bisisoxazolone itself is obtained [3].




The corresponding bispyrazolones are similarly isolated from our products. Bispyrazolone V was also obtained when the purification of adduct IVa by column chromatography on silica gel was attempted.

Thus, on the basis of the results obtained we can assume that reaction of amines II with 4-arylidene-5-pyrazolones I leads not to addition products on the C=C bond of structure III but to salt-like compounds of type IV. The question naturally arises as to the possible reasons for the discrepancy between our results and the findings of [2]. The following should be noted in this connection. We carried out all experiments repeatedly (several were performed more than 10 times), and in all cases products separated out with identical PMR spectra and having the structure IV. However, the crystals of these salts appeared to capture solvent molecules readily, so in order to obtain reproducible data of elemental analysis the products had to be dried for a considerable time (for at least 12 h) under vacuum in a drying pistol. Since the structure of III in [2] was demonstrated only from elemental analysis data, it cannot be ruled out that in that case these were distorted because of contamination of the products with solvent.

## EXPERIMENTAL

PMR spectra were recorded on an EM-360 spectrometer as solutions in DMSO-$d_6$ with HMDS as internal standard. Mass spectra were recorded on a Varian MAT CH-6 mass spectrometer, and IR spectra were recorded on a UR-20 instrument.

The properties of the synthesized compounds are given in Tables 1-3.

Synthesis of Compounds IVa-d. To a solution of 5 mmole of pyrazolone I in 20 ml of benzene was added 5 mmole of amine II, and the mixture was left for 12 h. The precipitate was filtered off, dried, and recrystallized from ethanol or ethyl acetate. $^{13}C$ NMR spectrum of salt IVb [Bruker MSL-300 spectrometer (75 MHz), DMSO-$d_6$]: 8.02 ($CH_3CH_2$), 10.1 ($CH_3C$), 31.91 (CH), 38.4 ($CH_3CH_2$), 99.0 ($C_{(4)}$), 143.8 ($C_{(3)}$), 154.3 ($C_{(5)}$); N–$C_6H_5$ 116.1 ($C_o$), 124.3 ($C_p$), 125.2 ($C_m$), 137.8 ($C_i$); C–$C_6H_5$ 125.8 ($C_p$), 126.3 ($C_o$), 128.2 ($C_m$), 142.9 ($C_i$) ppm.

Reaction of 4,4'-Benzylidenebispyrazolone V with Isobutylamine. To a suspension of 1.3 g (3 mmole) of bispyrazolone V [6] in 10 ml of benzene was added 0.22 g (3 mmole) of

isobutylamine. After 12 h the precipitate was filtered off, dried, and recrystallized from ethyl acetate. The product obtained was identical in every respect (mp, IR, PMR, and mass spectra) with adduct IVa. Yield 1.4 g (90%).

Hydrolysis of Salt IVa. Adduct IVa (0.5 g, 1 mmole) was dissolved in 10 ml of an aqueous solution of NaOH (2 M), the solution was then neutralized with hydrochloric acid (2 M). The white precipitate formed was filtered off, dried, and recrystallized from ethanol, mp 164-166°C. The product obtained had identical mp, IR, PMR, and mass spectra to those of a known sample of 4,4'-benzylidenebis(3-methyl-1-phenyl-5-pyrazolone) (V).

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# SPIROBUTYROLACTONE DERIVED FROM 1-PHENYL-3-METHYL-2-PYRAZOLIN-5-ONE


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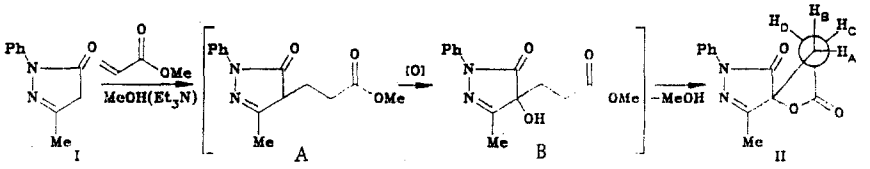
X-ray diffraction and NMR spectral examination have shown that 1-phenyl-3-methyl-2-pyrazolin-5-one reacts with methyl acrylate in methanol to give spiro[(1-phenyl-3-methyl-2-pyrazolin-5-one)-4,5'-butyrolactone]. The conformation has been shown to be the same in the crystal and in solution, the pyrazoline ring has been found to be nonplanar, the reasons for the acoplanarity established, stabilizing and destabilizing interactions studied, and the orientation of the phenyl substituent relative to the pyrazolin-5-one ring determined.


The reaction of 1-phenyl-3-methyl-2-pyrazolin-5-one (I) with methyl acrylate has given the novel spiro[(1-phenyl-3-methyl-2-pyrazolin-5-one)-4,5'-butyrolactone] (II), the formation of which may be rationalized as oxidation of the intermediate monoalkylated compound A by atmospheric oxygen, followed by cyclization of the hydroxyacid ester B:




The signals in the $^1H$ NMR spectrum of the spirolactone (II) were assigned on the basis of descreening of the $CH_2CO$ protons as compared with $CH_2C$, which is in accordance with the high absolute $^2J_{gem}$ value for the $CH_2CO$ protons, and on the descreening of the and $H_D$ protons by the CO group in the pyrazoline ring, as in [1]. The observed values for $^3J$ are in accordance with the dihedral angles found by x-ray diffraction analysis*: $^3J_{BD}$ (162.7°) > $^3J_{AC}$ (42.5°)

*In the x-ray structural examination, atoms $H_A$, $H_B$, $H_C$, and $H_D$ are designated 1-H, 2-H, 3-H, and 4-H (Fig. 1 and Table 1).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