Chemistry of Heterocyclic Compounds, Vol. 34, No. 9, 1998

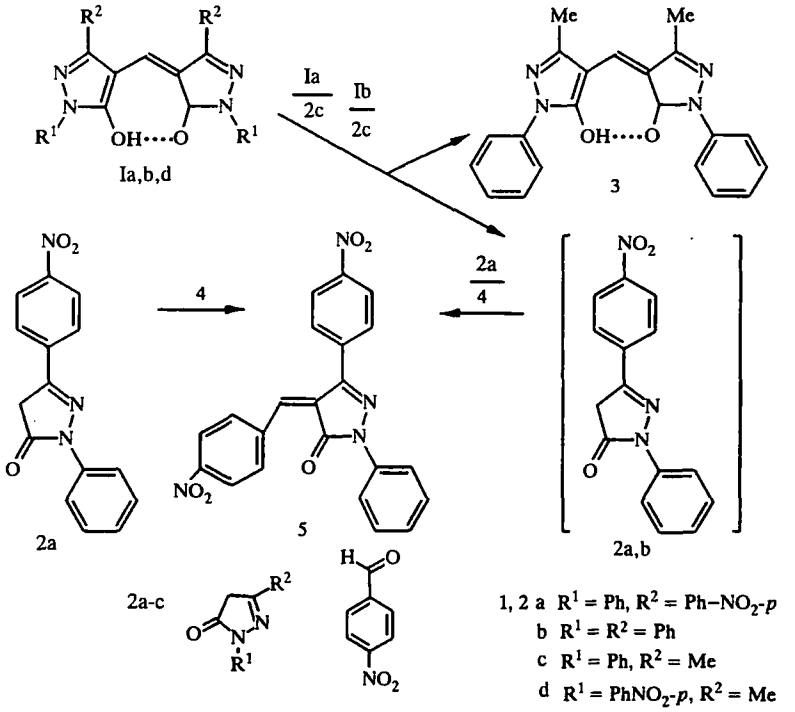
REACTION OF DIPYRAZOLYLMETHANES WITH 1-PHENYL-3-METHYLPYRAZOL-5-ONE

Yu. A. Azev and I. V. Teplyashina

The first derivatives of dipyrazolylmethane (**3**, scheme below) were prepared in low yield by treatment of 5-methyl-6-phenyl-1,2,4-triazine-4-oxide with pyrazolone **2c** in the presence of triethylamine [1]. Formation of this compound was also observed previously when treating 5-azauracil [2], 5-azacytosine [3], and fervenuline-4-oxide [4] with pyrazolone **2c** in the absence of a basic catalyst. A simple method for preparing this compound by the reaction of pyrazolone 2c with orthoformic ester has been reported by us in [3].

The crystalline structure of dipyrazolylmethane **3** was studied using x-ray analysis. In this way it was shown that the molecule of **3** is symmetrical relative to the axis passing through C_1 and the H bonded atoms. The central H bond of the eight-membered ring is characterized by the coplanar distribution of the nonhydrogen atoms. The hydrogen atom is situated halfway in distance between the oxygen atoms of the pyrazole fragments [1].

In our work we have found that dipyrazolylmethanes **Ia, b** react with pyrazolone **2c** by heating in refluxing butanol to form the known derivative **3** in 35-55% yield. Work up of the mother liquors from the reaction mass after removal of compound **3** with p-nitrobenzaldehyde **4** gave the styryl derivative of the pyrazolone **5**.

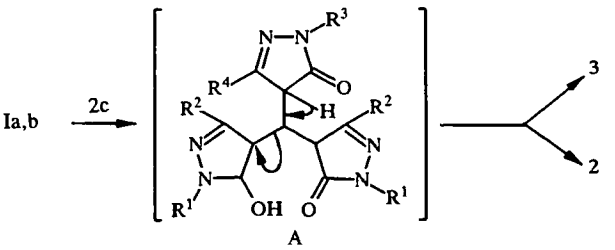


The styryl derivative **5** was also obtained by heating the known pyrazolone **2a** with aldehyde **4**. It was of interest that derivative **Id** did not react with **2c** under the same conditions.

Ural Science Research Institute for the Technology of Medicinal Preparations, Yekaterinburg 620219, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1269-1270, September, 1998. Original article submitted August 9, 1998.

0009-3122/98/3409-1091$20.00

The discovered exchanges of pyrazole residues in the dipyrazolylmethanes **Ia, b** evidently proceed via a stage of formation of the intermediate adducts, which are derivatives of tripyrazolylmethane of type A, and these undergo decomposition to form dipyrazolylmethane **3** and the displaced pyrazolones **2**.



It should be particularly noted that the reported reaction occurs in the absence of base, i.e., does not require activation of the reagent by a charge.

Reaction of Compounds Ia,b with Pyrazolone 2a. Compound Ia (0.12 g, 0.2 mmole) was refluxed with pyrazolone 2a (0.075 g, 0.4 mmole) in butanol (3 ml) for 6 h. The reaction product was cooled and the precipitated **3** was filtered off to give product (0.04 g, 53%). p-Nitrobenzaldehyde (**4**, 0.075 g, 0.5 mmole) was added to the mother liquor and the product refluxed for 5 min. The reaction mixture was cooled to room temperature and the precipitate of **5** filtered off (0.05 g, 28%) with mp 252-253°C. Mass spectrum, m/z 414 (M^+, calculated for $C_{22}H_{14}N_4O_5$ = 414).

The reaction of **Ib** with **2a** occurred similarly. Yield of **3** was 35%.

1-Phenyl-3-(p-nitrophenyl)-4-(p-nitrophenylidene)pyrazol-5-one (5). 1-Phenyl-3-(p-nitrophenyl)pyrazol-5-one (56 mg, 0.2 mmole) and p-nitrobenzaldehyde (32 mg, 0.2 mmole) were refluxed for 15 min. The product was cooled and the precipitate of **5** was filtered to give 20 mg (27%), mp 252-253°C. The product obtained was identical to compound **5** described above.

REFERENCES

1. Yu. A. Azev, H. Neunhoeffer, S. Foro, H. J. Lindner, and S. V. Shorshnev, Mendeleev Commun., No. 6, 229 (1995).
2. Yu. A. Azev, Mendeleev Commun., No. 4, 164 (1997).
3. Yu. A. Azev, I. V. Teplyashina, and B. V. Golomolzin, Khim. Geterotsikl. Soedin., No. 9, 229 (1997).
4. Yu. A. Azev and I. V. Teplyashina, Khim.-Farm. Zh., No. 2, 42 (1998).