DIPYRAZOLODIAZOCINES

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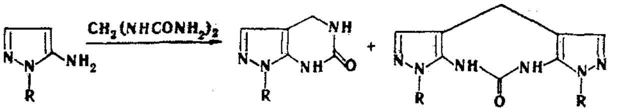
Substituted dipyrazolo[3,4-d:4',3'-g][1,3]diazocines – representatives of a new heterocyclic system – were obtained by reaction of methylenebisurea and benzalbisurea with 1-R-aminopyrazoles.

We have previously [1] shown that pyrazolo[3,4-d]pyrimidines (I) are formed in the reaction of 1-substituted 5-aminopyrazoles with methylenebisurea in acetic acid when the reagent ratio is 1 : 2.



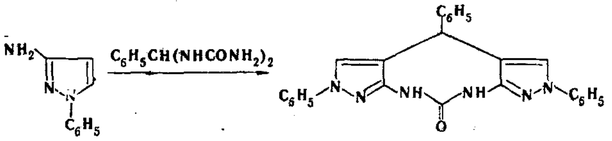
I II

I, II a $R = C_6H_5$; b $R = CH_2C_6H_5$

A compound that differed from I was isolated when this condensation was carried out with an equimolecular ratio of the reagents. Absorption bands at 1665 and 3260 cm^{-1} (NH) were present in the IR spectrum of this compound; moreover, judging from the negative qualitative reaction, the compound did not contain an NH_2 group. The UV spectrum of the compound was similar to the UV spectrum of the starting pyrazole. Signals of methylene protons at 3.53 (s),* of pyrazole ring protons at 7.74 (s), and of aromatic protons at 7.43 ppm (m) with an intensity ratio of 1 : 1 : 5 were present in the PMR spectrum. On the basis of the data presented above, the determination of the molecular weight, and the results of elementary analysis, the 1,7-diphenyl-9-oxodipyrazolo[3,4-d:4',3'-g][1,3]diazocine structure (IIa) was assigned to the compound obtained.

Condensation of equimolecular amounts of 1-benzyl-5-aminopyrazole with methylenebisurea proceeds similarly to give dipyrazolodiazocine IIb, the structure of which was also proved by analytical and spectral data and determination of the molecular weight.

It has been reported [2] that 1-phenyl-3-aminopyrazole reacts with benzalbisurea to give a complex mixture, one of the components of which is 1-phenyl-3-ureidopyrazole, which is readily formed from 1-phenyl-3-aminopyrazole and the urea present in the reaction medium. In a further investigation of this reaction, we isolated yet another compound, which, judging from the qualitative reaction, does not have an NH_2 group but contains NH (3420 cm^{-1}) and CO (1700 cm^{-1}) groups. On the basis of these data and the empirical formula, as well as in analogy with the preceding case, we assigned the 2,4,6-triphenyl-9-oxodipyrazolo[3,4-d:4',3'-g][1,3]diazocine structure (III) to this compound.



III

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* The following abbreviations are used here and elsewhere: s is singlet and m is multiplet.

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Of the condensed derivatives of diazocines that have been described, most of the compounds are dibenzo[1,5]- and dibenzo[1,3]diazocines [3,4]; dipyrido[3,2-b:3',2'-f][1,5]diazocine [5] was synthesized from heterocyclic compounds including a diazocine ring. Pyrazolodiazocines have not been described, and II and III consequently are members of a new heterocyclic system – dipyrazolo[1,3]diazocine.

EXPERIMENTAL

The IR spectra of KBr pellets (c 0.25%) were recorded with a UR-20 spectrometer. The PMR spectra of d_6-dimethyl sulfoxide solutions were recorded with a Varian A56/60A spectrometer with hexamethyldisiloxane (HMDS) as the internal standard. The molecular weights were determined with an MS-902 mass spectrometer.

1,7-Diphenyl-9-oxodipyrazolo[3,4-d:4',3'-g][1,3]diazocine (IIa). A 1.0 g (6.3 mmole) sample of 1-phenyl-5-aminopyrazole was refluxed for 2 h with 0.83 g (6.3 mmole) of methylenebisurea [6] in 10 ml of glacial CH_3COOH. The mixture was cooled, and the precipitate was removed by filtration, washed with acetic acid, and dried over NaOH to give 0.13 g of IIa with mp 358-362°. Found, %: C 67.2; H 4.5; N 23.3. Mol. wt. 356. $C_{20}H_{16}N_6O$. Calculated, %: C 67.4; H 4.5; N 23.6. Mol. wt. 356.

The filtrate was poured into water, and the aqueous mixture was neutralized with $NaHCO_3$ and extracted with $CHCl_3$. The chloroform extracts were dried with $MgSO_4$, and the chloroform was removed by distillation to give 0.1 g of Ia [1].

1,7-Dibenzyl-9-oxodipyrazolo[3,4-d:4',3'-g][1,3]diazocine (IIb). This compound was obtained in 10% yield by the method used to prepare IIa by reaction of 1-benzyl-5-aminopyrazole and methylenebisurea. The product had mp 359-359°. Found, %: N 21.6. Mol. wt. 384. $C_{22}H_{20}N_6O$. Calculated, %: N 21.8. Mol. wt. 384. IR spectrum: 1650 cm^{-1} (CO). PMR spectrum, δ, ppm: 3.44 (4-CH_2, s), 5.84 (1,7-di-CH_2, s), 7.40 (3-H, s), 7.20 (1,7-di-C_6H_5, m) with an intensity ratio of 1 : 2 : 1 : 5.

2,4,6-Triphenyl-9-oxodipyrazolo[3,4-d:4',3'-g][1,3]diazocine (III). A 1.59 g (0.01 mole) sample of 1-phenyl-3-aminopyrazole and 2.08 g (0.01 mole) of benzalbisurea were refluxed for 2 h with 20 ml of glacial CH_3COOH. The yellowish solution was poured into 300 ml of water, and the precipitate was removed by filtration, dried, and washed thoroughly with ether to give 1.6 g of a substance with mp 160-170°. Four recrystallizations from 50% alcohol gave III with mp 223-225°. Found, %: C 67.8; H 4.9; N 19.7. Mol. wt. 432. $C_{26}H_{20}N_6O$. Calculated, %: C 67.6; H 4.5; N 19.4. Mol. wt. 432.

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