SOME PYRAZOLID-3-ONE DERIVATIVES

IV. Bromination of 1-Phenylpyrazolid-3-ones*

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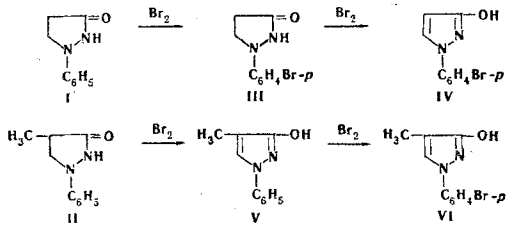
The bromination of 1-phenylpyrazolid-3-one (phenidone) and of 4-methyl-1-phenylpyrazolid-3-one (methylphenidone) with bromine in acetic acid has been studied. Phenidone is brominated by an equimolar amount of bromine with the formation of 1-(p-bromophenyl)pyrazolid-3-one, while methylphenidone is oxidized to 3-hydroxy-4-methyl-1-phenylpyrazole. On bromination with a twofold excess of bromine, phenidone gives 1-(p-bromophenyl)-3-hydroxypyrazole, and methylphenidone is converted into 1-(p-bromophenyl)-3-hydroxy-4-methylpyrazole.

1-Phenylpyrazolid-3-one and some of its derivatives are widely used as development activators in the processing of black-and-white light-sensitive materials [1, 2]. Of the chemical properties of compounds of this series, only hydroxylation [3], aminomethylation with ketene [5] have been described.

For a study of the bromination reaction, we selected 1-phenylpyrazolid-3-one (I) and 4-methyl-1-phenylpyrazolid-3-one (II), which are similar in structure and photographic properties [6]. It appeared likely that the behavior on bromination would also be similar.

The results of the experiments showed that compound (I) first brominates in position 4 of the phenyl nucleus with the formation of 1-(p-bromophenyl)pyrazolid-3-one (III) which, under the action of a second mole of bromine, is oxidized to 1-(p-bromophenyl)-3-hydroxypyrazole (IV). (On the structure of the products of the oxidation of pyrazolidone see, for example, [7]). However, in the case of compound II the opposite pattern was observed: first oxidation to 3-hydroxy-4-methyl-1-phenylpyrazole (V) took place and then bromination with the formation of 1-(p-bromophenyl)-3-hydroxy-4-methylpyrazole (VI).



Thus, a CH_3 group in position 4 of the pyrazolidone ring increases the capacity of the latter for oxidation.

It is known that compound I is less stable in an alkaline medium than compound II [8]. According to our observations, on being boiled with hydrochloric acid, compound I undergoes an opening of the pyrazolidone ring with the formation of N_1-(β-ethoxycarbonyl)-phenylhydrazine, while compound II is unaffected under these conditions. Consequently, in this case, also, the introduction of a CH_3 group into the pyrazolidone ring sharply changes its reactivity.

The structure of the pyrazolidone III was confirmed by independent synthesis from p-bromophenylhydrazine and methyl acrylate in the presence of sodium butoxide [9]. The bromination of substance I with a twofold excess of bromine and the bromination of compound III with an equimolecular amount of bromine led to one and the same substance IV. The structure of compound V was shown by its formation on when II was oxidized with ferric chloride [10].

The compound obtained by the bromination of II with a twofold excess of bromine proved to be identical with compound VI obtained by the bromination of V with an equimolecular amount of bromine by a known method [11].

EXPERIMENTAL

1-(p-Bromophenyl)pyrazolid-3-one (III). A) A solution of 8 g of bromine in 10 ml of glacial acetic acid was added dropwise to a solution of 8.1 g of I in 20 ml of glacial acetic acid in such a way that the temperature of the reaction mixture did not exceed 50° C, and then the hot mass was poured into water, and the precipitate was filtered off, washed with water, dried, and crystallized from benzene. Yield, 1.8 g (15%). Colorless needles becoming pink in the light, with mp 133–133.5° C. λ_{max} 225 nm, log ε 4.13 (ethanol). Found, %: C 44.93; H 3.58; Br 33.07; N 11.49. Calculated for $C_9H_9BrN_2O$, %: C 44.83 H 3.76; Br 33.14; N 11.62.

B) At 25–30° C, 14.5 g of p-bromophenylhydrazine hydrochloride [12] was added to a solution of sodium butoxide obtained from 6.9 g of Na and 110 ml of butanol, and the mixture was stirred at 80° C for 30 min and cooled to 25° C after which 13 g of methyl acrylate and 100 ml of butanol were slowly added. The reaction mixture was then heated to 110–115° C, and kept at this temperature for 1 hr, cooled to 30° C, treated with 100 ml of water, stirred until the solid matter had dissolved, poured into a beaker, and neutralized with 50% acetic acid. The ethanolic layer was separated off and the bulk of the butanol was distilled off in the vacuum of a water pump, after which the hot residue was transferred to a beaker and cooled with stirring. The precipitate that deposited was filtered off, washed with petroleum ether, and crystallized from benzene. Mp 133.5–134° C. A mixture with the substance obtained by method (A) gave no depression of the melting point.

1-(p-Bromophenyl)-3-hydroxypyrazole (IV). A) This was obtained in the same way as **III** from 8.1 g of I and 16 g of bromine (temperature about 80° C). Yield 3.8 g (31%). Colorless prisms with mp 215–216° C (from toluene). λ_{max} 281 nm, log ε 4.32 (ethanol). Found, %: C 45.17; H 2.90; N 11.73. Calculated for $C_9H_7BrN_2O$, %: C 45.21; H 2.95; N 11.71.

B) From 0.6 g of **III** and 0.4 g of bromine, by the method described above for **III**, a substance with mp 214–215° C (from toluene) was obtained. A mixture with the substance obtained by method (A) gave no depression of the melting point.

3-Hydroxy-4-methyl-1-phenylpyrazole (V). This was obtained in the same way as **III** from 8.8 g of II and 8 g of bromine (temperature about 60° C). Yield 3.2 g (37%). Colorless plates with mp 205–206° C

*For part III, see [13].

(from ethanol). λ_{max} 279 nm, log ε 4.25 (ethanol). A mixture with the substance obtained by the oxidation of **II** with ferric chloride gave no depression of the melting point.

1-(p-Bromophenyl)-3-hydroxy-4-methylpyrazole (VI). This was obtained in the same way as **III** from 8.8 g of **II** and 16 g of bromine (temperature about 70° C). Yield 4.5 g (36%). Colorless prisms with mp 239-240° C (from ethanol). λ_{max} 287 nm log ε 4.40 (ethanol). A mixture with the substance obtained by the bromination of **V** with an equimolecular amount of bromine gave no depression of the melting point.

N_1-(β-Ethoxycarbonyl)phenylhydrazine. A mixture of 10 g of **I** and 70 ml of conc HCl was heated at 100° C for 5 hr and was cooled, and, after evaporation, the hydrochloride of the desired substance was obtained. Yield 7.7 g (58%). Colorless prisms with decomp. p. 228° C (from ethanol). Found, %: C 49.88; H 5.83; Cl 16.00; N 12.87. Calculated for $C_9H_{12}N_2O_2 \cdot HCl$, %: C 49.89; H 6.04; Cl 16.36; N 12.93.

The treatment of the hydrochloride with a saturated aqueous solution of sodium acetate yielded the substance in the form of colorless plates with mp 96-97° C (from benzene). Found, %: C 60.02; H 6.70; N15.64. Calculated form $C_9H_{12}N_2O_2$, %: C 59.98; H 6.71; N 15.55.

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