[CONTRIBUTION FROM THE CHEMICAL LABORATORY, COTTON COLLEGE OF GAUHATI.]

CONDENSATION OF 1-PHENYL-3-METHYL-5-PYRAZOLONE WITH ANHYDRIDES.

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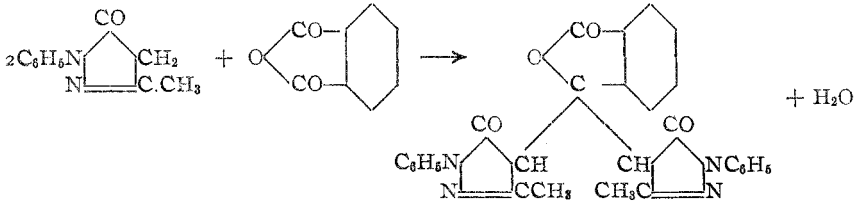
It is well known that the hydrogen atoms of the $>CH_2$ group in 1-phenyl-3-methyl-5-pyrazolone are highly reactive and it is by virtue of this reactivity that the substance so readily undergoes condensation with aldehydes and ketones forming a series of highly colored compounds[1] containing the chromophore —CO—C=C—. It appeared to be of interest to study the reactivity of pyrazolone towards anhydrides and to compare the colors of the products thus obtained with those of the aldehydic compounds prepared by Knorr and Tambor. The anhydrides chosen for the purpose were phthalic, benzoic and succinic—these being typical representatives of the class of closed-chain aromatic, open-chain aromatic and closed-chain aliphatic anhydrides, respectively.

The condensation took place readily in all these cases, yielding deep red compounds.

At first we attempted to bring about the reactions with acetic anhydride as the condensing agent in the manner adopted by Marchese[2] for the condensation of phthalic anhydride with diketohydrindine. But excepting in the case of phthalic anhydride this did not yield satisfactory results. It was subsequently found, however, that the condensation could be effected most readily by simply heating an intimate mixture of the two reacting substances up to a definite temperature.

We commenced by using equi-molecular proportions of the anhydrides and the pyrazolone and expected that this would lead to the condensation with the elimination of a molecule of water, by the union of the hydrogen atoms of the methylene group with an oxygen atom of either one of the CO groups or with the anhydric oxygen.



Formula I.

Subsequently the proportions were adjusted accordingly.

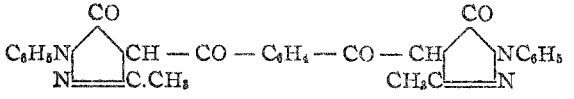
During the heating however it was observed that a part of the phthalic anhydride sublimed in the upper parts of the tube, and analysis of the

[1] Knorr, *Ann.*, 238, 139–219; Tambor, *Ber.*, 33, 864–871 (1900).

[2] *Gazz. chim. ital.*, [2] 37, 303–309 (1907).

purified product indicated that the reaction had taken place between two molecules of the pyrazolone and one of the anhydride, with the elimination of a molecule of water.

The above equation is based on the assumption that it is the oxygen atom of one of the CO-groups, which is removed as water. Of course, as is the case with the condensation of phthalic anhydrides with phenols, which under different experimental conditions leads to the formations of derivatives of either anthraquinone or of phthalo-phenone, there is also the possibility here of the hydrogen atoms uniting with the anhydric oxygen, in which case the following constitution would have to be attributed to the substance:



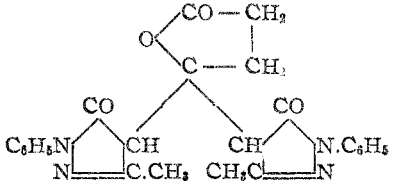
Formula II.

This, however, would lead to the complete opening up of the side-ring, which does not appear very probable. Besides it may be pointed out that in the condensation of phenols which take the place of the pyrazolone in the present case it is only where the reaction takes place in molecular proportions that the anhydric oxygen is attacked, as in the preparation of oxyanthraquinone from ordinary phenol, or of quinizarine from hydroquinone, or of anthragallol from pyrogallol.

But when the condensation occurs between two molecules of the phenol with one of the anhydride, as in the preparations of phenolphthalein, fluorescein, gallin and the rhodamines etc., it is one of the carbonyl oxygen atoms which is removed as water.

In the present instance, therefore, where the reaction has taken place between two molecules of the pyrazolone and one of the anhydride, we may, by analogy, assign Formula I to our condensation product.

Succinic anhydride reacts in a manner precisely similar to phthalic anhydride and the compound obtained in this case, has probably the following constitutions:



Like the other two anhydrides, benzoic anhydride appears to condense readily with the pyrazolone. But in this case the substance could not be obtained in a pure condition. Incidentally we also attempted to condense camphoric anhydride, first by sample heating, and also by using

zinc chloride and acetic anhydride as condensing agents. But in no case was any satisfactory results obtained.

Experimental.

Phthalic Anhydride and 1-Phenyl-3-methyl-5-pyrazolone.—An intimate mixture of the pyrazolone (6.96 g.) and phthalic anhydride (2.96 g.) was introduced into a boiling tube and heated in an oil-bath up to 180° for half an hour. At a temperature of about 15° above the melting point of the mixture, a lively reaction was noticed. On cooling, the product was dissolved out with absolute alcohol, filtered and precipitated by the addition of water. The precipitate was at first slightly gummy but on repeated crystallization from methyl alcohol it was obtained in the form of bright red and fairly large needles, melting at 212°.

Subs., 0.122: CO_2, 0.3138; H_2O, 0.0533.
Subs., 0.1205: N_2, 13 cc. at 28° C. and 748 mm.
Calc. for $C_{28}H_{22}N_4O_4$: C, 70.29; H, 4.6; N, 11.7. Found: C, 70.1; H, 4.8; N, 11.6.

It is fairly soluble in ether, chloroform, toluene and acetic acid. It is also somewhat soluble in hot but is altogether insoluble in cold water. With conc. sulfuric acid, it produce a bright yellow color. It dissolves in dilute solutions of caustic alkalies forming a bright red solution.

Succinic Anhydride and 1-Phenyl-3-methyl-5-pyrazolone.—This was prepared in almost the same way as was the previous product, by heating two molecular proportions of the pyrazolone with one of the anhydride. The temperature of the oil-bath was, however, not allowed to rise in this case above 165° and the crystallization was effected from about 60% ethyl alcohol. The presence of a drop or two of dil. sulfuric acid appears to facilitate the crystallization greatly. It forms bright red needles which melt at 184°.

Subs., 0.1827: CO_2, 0.4493; H_2O, 0.0886.
Subs., 0.1934: N_2, 21.6 cc. at 19° and 762 mm.
Calc. for $C_{24}H_{22}N_4O_4$: C, 66.9; H, 5.1; N, 13. Found: C, 67; H, 5.3; N, 12.8.

Like the previous compound it is fairly soluble in all ordinary solvents with the exception of cold water. Conc. sulfuric acid changes its color to straw-yellow.

Benzoic Anhydride and 1-Phenyl-3-methyl-5-pyrazolone.—A mixture of one molecular proportion of the anhydride with two of the pyrazolone was heated to 145° as before. On dissolving the crude reaction product in absolute alcohol and subsequently treating it with water, a deep red viscous liquid separated out and settled at the bottom. Notwithstanding repeated attempts this could not be obtained in the crystalline condition and therefore nothing further was done with it.

We take this opportunity of expressing our best thanks to Principal F. W. Südmersen for his kind encouragement.

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