

## Pyrazole Studies

## XII.\* The Hydrazobenzene-catalysed Oxidation of 1:2-Diphenyl-4-butylpyrazolidine-3:5-dione (Butazolidine)

STIG VEIBEL, S. LINHOLTER and P. SØRENSEN

*Department of Organic Chemistry, University of Technology, Copenhagen, Denmark*

The oxidation by air of alkaline-ethanolic solutions containing 1:2-diphenyl-4-butylpyrazolidine-3:5-dione and hydrazobenzene has been studied. The oxidation products were found to be butyltartronic acid mono-(N:N'-diphenyl)hydrazide and azobenzene. No 4-hydroxybutazolidine could be isolated.

It was found that the oxidation of butazolidine and of hydrazobenzene proceed simultaneously.

In previous papers the oxidation by air of 4-substituted pyrazol-5-ones<sup>1,2</sup> and 1:4-disubstituted pyrazolidine-3:5-diones<sup>3</sup> was studied. We found that triethylamine or sodium ethylate are catalysts for the oxidation, the result of which is the formation of 4-hydroxysubstituted pyrazolones or pyrazolidinediones.

Recently Sokolova and Magidson<sup>4</sup> announced that during the preparation of butazolidine from hydrazobenzene and ethyl butylmalonate a by-product was formed which they identified as 1:2-diphenyl-4-butyl-4-hydroxypyrazolidine-3:5-dione. This substance, they state, can be prepared, in a rather poor yield though, by dissolving butazolidine and hydrazobenzene (equimolar quantities) in ethanol, adding 1 equiv. of sodium ethylate and slowly distilling off the ethanol, passing a stream of air through the solution during the distillation. From the residue 60 % of butazolidine were recovered and the 4-hydroxy compound was isolated in a 9 % yield.

The hydroxy compound is very easily hydrolysed by aqueous bases to butyltartronic acid mono-(N:N'-diphenyl)hydrazide.

We tried to reproduce this result, following as exactly as possible the directions given by Sokolova and Magidson. We did not succeed, however, unchanged butazolidine, hydrazobenzene and azobenzene being the only crystalline products obtained by us.

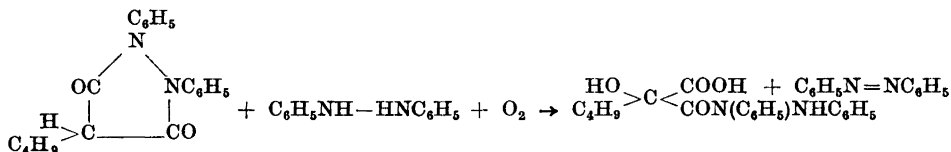
Using the oxidation-technique described previously<sup>1</sup> we were, on the other hand, able to establish the absorption of one molecule of oxygen per

\* Part XI: Preceding paper.

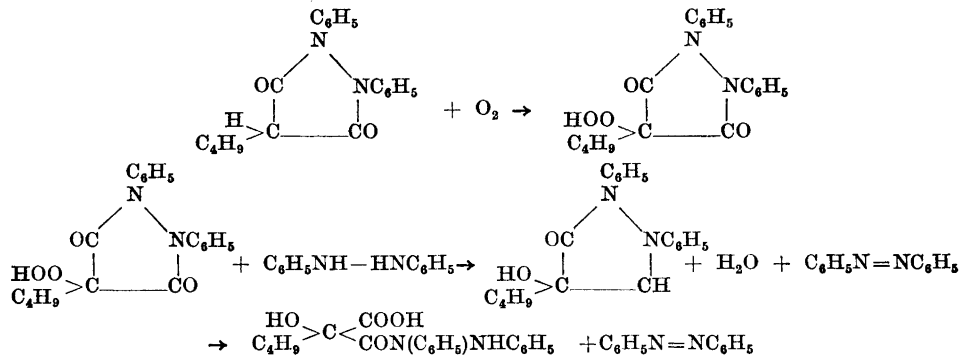
molecule of butazolidine when a solution of this substance and hydrazobenzene in absolute ethanol containing sodium ethylate is agitated in an oxygen atmosphere. The oxidation proceeds extremely slowly at room temperature, 6 days and nights being necessary for the absorption of the calculated volume of oxygen. This means that both the butazolidine and the hydrazobenzene must be oxidised during the absorption of oxygen, and we were able to establish that the two oxidations proceed simultaneously, as we in an experiment discontinued the oxidation after the absorption of 70 % of the volume calculated and isolated from the reaction mixture 30 % unchanged butazolidine and 70 % azobenzene.

Even with the technique employed here we were not able to isolate the hydroxybutazolidine, but only the hydrolysed substance, butyltartronic acid mono-(N:N'-diphenyl)hydrazide which was identified by its m.p. and by electro-metric titration with sodium hydroxide.

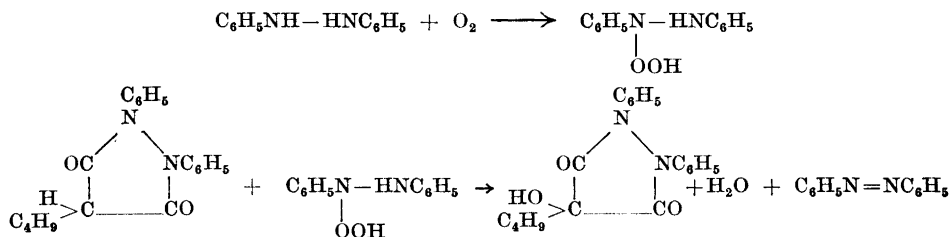
The overall reaction thus is represented by the equation:



Realising that the amine-catalysed oxidation proceeds through the formation of peroxides a possible sequence might be:



As, however, no oxidation takes place in the absence of hydrazobenzene, not even when azobenzene is added, the oxidation possibly starts with the formation of a hydroperoxide of hydrazobenzene so that the sequence might be:



It is seen that during the reaction sufficient water is formed to permit the hydrolysis of the hydroxybutazolidine. Sokolova and Magidson do not state how they have been able to suppress the hydrolysis but they mention that the hydroxy compound is extremely readily hydrolysed in alkaline solution.

#### EXPERIMENTAL PART

A solution of sodium ethylate was prepared from 0.75 g of sodium and 100 ml of absolute ethanol. In this solution 10 g of butazolidine (0.033 mole) and 6 g of hydrazobenzene (0.033 mole) were dissolved and the solvent slowly removed by distillation (5 h), a stream of air passing through the solution. From the residue 8.5 g of butazolidine, 1 g of azobenzene and 4.5 g of hydrazobenzene were recovered. If any, only an insignificant oxidation of butazolidine has thus taken place.

A similar solution was placed in a flask connected to an oxygen-reservoir, enabling the reading of the volume of oxygen absorbed. After 6 days and nights no more oxygen was absorbed, the total volume absorbed being 800 ml (at 20°) or 0.032 mole. The solution was diluted with 500 ml of water, precipitating azobenzene and hydrazobenzene if this substance remains unoxidised. The filtrate was acidified and the substance precipitated filtered off and dried.

The substance precipitated by water was dissolved in light petroleum and recrystallised by slowly evaporating the solvent. Different crops of crystals (*in toto* 5.1 g) were collected. They had the colour of azobenzene and m. p. 65° (azobenzene 68°). In this case practically quantitative oxidation of hydrazobenzene to azobenzene had taken place.

The substance precipitated by acid (9 g) had m. p. 128–132° (uncorr.). Sokolova and Magidson indicate for 4-hydroxybutazolidine m. p. 132–133°. Recrystallised from 50 % methanol, however, the m. p. of our substance was raised to 143–144° (corr.), whereas Sokolova and Magidson indicate the m. p. 145° for butyltartronic acid mono-(N:N'-diphenyl)hydrazide. 0.8600 g consumed (electrometric titration) 24.96 ml of 0.1029 N NaOH. Equiv. wt. found 335, calc. for the hydrazide 342.

In another experiment the reaction was interrupted when 70 % of the calculated volume of oxygen had been consumed. From the solution was recovered 3 g = 30 % of butazolidine, and a mixture of azo- and hydrazobenzene containing 4 g = 70 % of azobenzene was isolated. Besides, butyltartronic acid mono-(N:N'-diphenyl) hydrazide was isolated in a yield of 40 %. It is thus seen that the oxidation of butazolidine is coupled to the oxidation of hydrazobenzene.

Finally we tried to oxidise butazolidine with *tert*-butylhydroperoxide. 0.05 mole of butazolidine, 30 ml of 2 N sodium ethylate solution (0.06 mole) and 7.5 ml of *tert*-butylhydroperoxide (0.08 mole) were dissolved in 75 ml of *tert*-butylalcohol. After 20 min the experiment was discontinued. From the solution a solid was isolated, m. p. 145–46°, equiv. wt 330, titrated with sodium hydroxide (phenolphthalein). Here, again, the only oxidation product isolated was the butyltartronic acid mono-(N:N'-diphenyl)hydrazide.

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