

A Study of the Pyrazoles formed by Reaction between *p*-Carboxyphenylhydrazine and some β -Diketones

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It has been stated previously that pyrazole derivatives, crystallising with 1 mole of water, and not *p*-carboxyphenylhydrazones, are formed when reacting β -diketones with *p*-carboxyphenylhydrazine. This statement has been corroborated by investigating the UV- and the IR-absorption of the derivatives as well as their titration curves when titrated as acids and as bases.

Some 10 years ago it was proposed to use *p*-carboxyphenylhydrazine as a reagent for the identification of carbonyl compounds, the *p*-carboxyphenylhydrazones formed by the condensation reaction being titratable as acids and thus of value in determining the equivalent weight of the carbonyl compound investigated¹.

It is well known that β -diketones, when reacting with hydrazine derivatives, do not form mono- or bis-hydrazones but, by ring closure of the initial monohydrazones, pyrazole derivatives. This means that when calculating the molecular weight of the carbonyl compound from that of the *p*-carboxyphenylhydrazine-derivative one has to use the formula $E = E_{p\text{-Carb.}} - 116.1$ instead of the formula $E = E_{p\text{-Carb.}} - 134.1$ ordinarily used, as two molecules of water have been eliminated during the condensation reaction.

If was found, on the other hand, that when isolated and purified as usually (recrystallised from ethanol or aqueous ethanol) acetylacetone, benzoylacetone and dibenzoylmethane gave derivatives which titrated as the ordinary *p*-carboxyphenylhydrazones, not as the corresponding pyrazoles. When, however, these derivatives were dried *in vacuo* over phosphorus pentoxide at 56° or at atmospheric pressure at 130°, they titrated as pyrazoles. Recrystallised from ethanol they once more titrated as *p*-carboxyphenylhydrazones. It was, without further proof, stated that the pyrazoles crystallise with 1 mole of water of crystallisation which is removed by drying and taken up again by recrystallisation¹, thus ignoring the possibility that ring closure might take place when drying the substances, ring opening during their recrystallisation.

In order to settle this question finally we decided to compare the UV- and the IR-absorption of the dried and the recrystallised preparations with the UV- and the IR-absorption of a genuine *p*-carboxyphenylhydrazone of a monoketone with a CH_2 -group instead of one of the carbonyl groups in the β -diketones.

Besides, we determined the titration curves of these substances when titrated as acids with sodium hydroxide and as bases with perchloric acid in glacial acetic acid, this last mentioned method making an estimation of the $\text{p}K_{\text{B}}$ -values possible ².

The result of this investigation is a corroboration of the previous statement. The absorption curves of the dried and of the dried and recrystallised preparations are within the limit of the experiment identical and different from the absorption curves of *p*-carboxyphenylhydrazones. The titration curves, too, indicate the identity of the dried and the dried and recrystallised preparations and their difference from a *p*-carboxyphenylhydrazone structure.

EXPERIMENTAL PART

All substances were prepared as described ¹ and showed the m.p.'s indicated above.

Drying of the derivatives of acetylacetone (I), benzoylacetone (II) and dibenzoylmethane (III). Samples were dried at 56° *in vacuo* over phosphorus pentoxide. Loss of weight was: I, 8.37 %, II, 6.56 %, III, 6.54 %, calculated for 1 mole of water, I, 7.69 %, II, 6.08 %, III, 5.03 %.

Titration of the derivatives as acids. 1 mmole of the substances, once before drying, then after drying and finally after recrystallisation of the dried sample, was dissolved in 50 ml of ethanol and titrated with 0.1 N sodium hydroxide. At the same time the *p*-carboxyphenylhydrazones of methyl propyl ketone (IV) and of propiophenone (V) were titrated. Table 1 gives the equivalent weights found.

Table 1. Titration of the derivatives with NaOH.

	I			II		
	Undried	Dried	Recryst.	Undried	Dried	Recryst.
E found	235.9	214.7	234.3	295.6	278.6	297.4
E calc.	234.3	216.3	234.3	296.3	278.3	296.3
	III			IV	V	
E found	362.6	342.9	362.4			218.1
E calc.	358.4	340.4	358.4	220.3	268.3	

Ultraviolet absorption of I–V. Fig. 1 shows that the absorption curves of I, II and III are of the same type, especially in the region 2 700 Å–3 000 Å, and in this region quite different from the absorption of IV and V. No significant difference between the dried and the recrystallised preparations can be observed.

Infrared absorption of I–V. The absorption in the region from 3 700 cm^{-1} to 670 cm^{-1} was determined, using a Beckman IR 2 spectrophotometer and applying the potassium bromide disk technique.

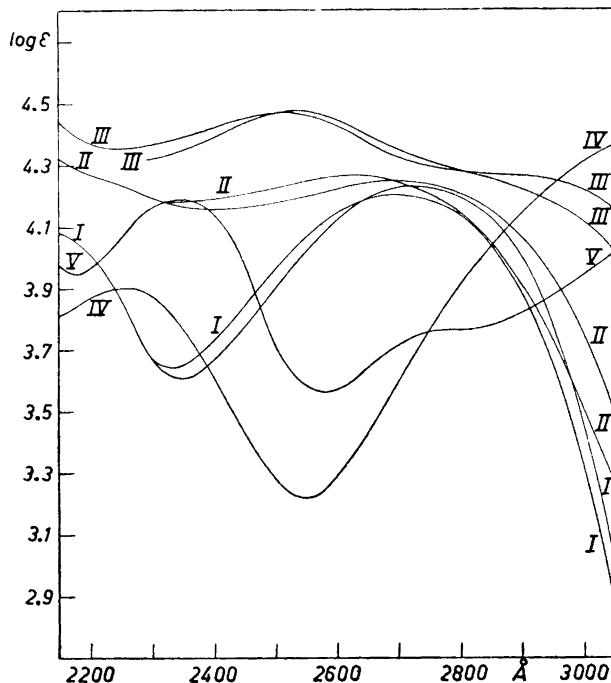


Fig. 1. UV-absorption curves of the substances investigated. I. Acetylacetone-derivative. II. Benzoylacetone-derivative. III. Dibenzoylmethane-derivative. IV. Methyl propyl ketone-*p*-carboxyphenylhydrazone. V. Propiophenone-*p*-carboxyphenylhydrazone.

Neither the genuine *p*-carboxyphenylhydrazones (IV–V) nor the genuine pyrazoles (I–III dried *in vacuo*) possess absorption bands sufficiently characteristic to decide from such bands alone whether or not ring closure has taken place.

The spectra of the undried and of the dried and recrystallised specimens are identical for each of the substances I, II and III respectively. Of the dried specimens, II shows a spectrum identical with that of the other specimens of II, whereas in I insignificant changes in the relative intensities of adjacent bands at 870 cm^{-1} , 1 130 cm^{-1} and 1 260 cm^{-1} , and in III similar insignificant changes at 765 cm^{-1} , 810 cm^{-1} and 1 430 cm^{-1} could be observed.

The spectra of the 3 specimens of I, II and III were, however, for each substance so closely identical that the identity of structure of the 3 specimens is unambiguous, the slight differences observed being possibly caused by the presence of water of crystallisation in the two specimens, whereas the third is anhydrous.

Titration of the derivatives as bases. 1 mmole of I, II, IV and V was dissolved in 50 ml of glacial acetic acid and titrated with 0.0985 N perchloric acid in glacial acetic acid, using a glass electrode and a calomel electrode as reference electrode. III is so sparingly soluble in glacial acetic acid that its titration under comparable conditions could not be carried through.

Table 2 shows that here, too, the dried and the recrystallised preparations are identical, the jump of potential being somewhat greater for the anhydrous preparations than for those with water of crystallisation, in accordance with the fact that water always will decrease the jump of potential in these titrations.

Table 2. Titration of *p*-carboxyphenylhydrazine-derivatives with perchloric acid.

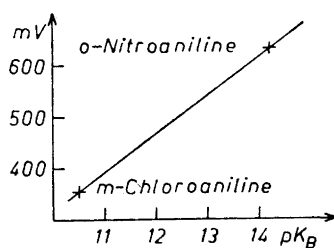
ml HClO ₄	MV					
	I		II		IV *	V
	Dried	Recryst.	Dried	Recryst.		
0	385	370	360	343	355	365
1	454	450	502	485	424	543
2	468	465	520	514	446	565
3	477	474	530	527	458	582
4	485	481	539	536	468	591
5	492	490	545	545	479	600
6	500	497	554	554	490	609
7	508	506	562	562	505	619
8	519	517	574	574	530	627
9	531	535	590	584	628	640
10	559	580	620	601	663	655
11	673	652	658	640	675	667
12	687	668	675	660	680	678

* Only 0.85 millimole

Table 3 gives the half-neutralisation potentials and the pK_B -values (taken from fig. 2, giving the slope of the line indicating the dependency between half-neutralisation potentials and pK_B for the particular glass electrode and potentiometer used ²). It is seen

 Table 3. Half-neutralisation potentials and pK_B -values.

	II		I		IV	V
	Dried	Recryst.	Dried	Recryst.		
Half-neutralisation potential	493	491	546	546	470	601
$pK_{B(H_2O)}$	12.4	12.3	13.1	13.1	12.1	13.7


 Fig. 2. Dependency of half-neutralisation potentials and $pK_{B(H_2O)}$.

that there is no great difference in basic properties of the pyrazoles and the *p*-carboxy-phenylhydrazones, the influence of the substituents being, however, somewhat greater in the latter than in the former group of derivatives.

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