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THE ISOLATION AND INTERCONVERSION OF TAUTOMERS OF 2-ARYLHYDRAZONES OF 1-PHENYLBUTANE-1,2,3-TRIONE

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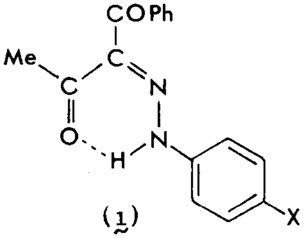
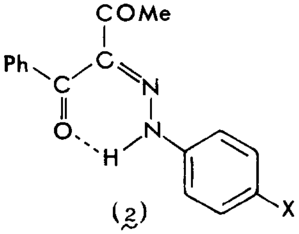
2-Arylhydrazones of 1,2,3-tricarbonyl compounds, prepared by coupling diazonium salts with β-diketones or β-ketoesters, exist exclusively in an intramolecularly hydrogen-bonded keto-amine tautomeric form.[1-3] In the case of compounds derived from unsymmetrical β-diketones such as benzoylacetone (2-arylhydrazones of 1-phenylbutane-1,2,3-trione) there are two possible keto-amine tautomers (**1** and **2**).



(**1**)

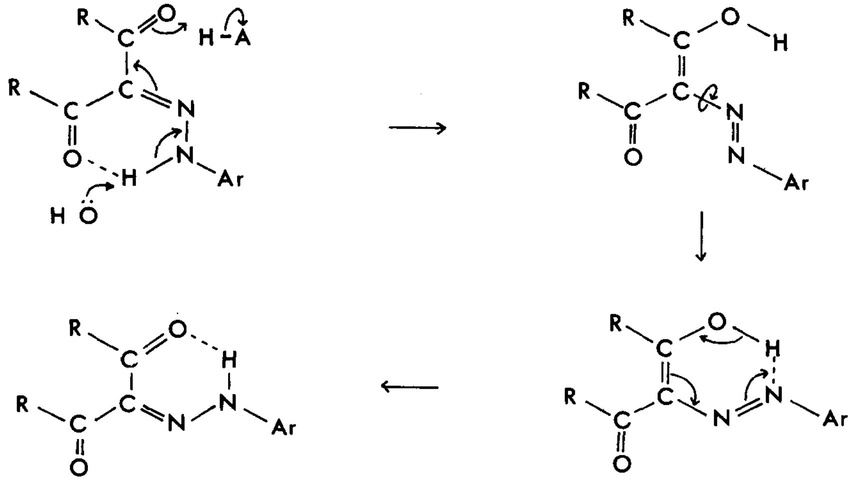


(**2**)

We wish to report that several 2-arylhydrazones of 1-phenylbutane-1,2,3-trione can be isolated in both possible keto-amine tautomeric forms (X=Cl, Br, COOEt). The tautomer (**2**) was obtained by crystallization of the product derived from coupling of the appropriate diazonium salt with benzoylacetone. If this tautomer was sublimed and crystallized from hexane with the rigorous exclusion of traces of acid or base, the tautomer (**1**) could be isolated in a pure condition. These results are in contrast to those reported for the

2-phenylhydrazone which was always isolated as the tautomer (1).[1,2] Subsequently we have shown that irrespective of the nature of the substituent in the arylhydrazone, a solution of either tautomerin chloroform containing a trace of acid or base contains 85-90% of tautomer (1) and 15-10% of tautomer (2). The ability to isolate tautomer (2) of a particular arylhydrazone is dependent on this tautomer having a lower solubility than tautomer (1).

The interconversion of the two tautomers is catalysed either by acid or base. The scheme depicts a possible mechanism for the acid-catalysed process. A similar scheme can be drawn for the base-catalysed interconversion. In the presence of deuterium oxide n.m.r. studies have shown that the rate of exchange of the enolic proton is equal to the rate of isomerization.[4] This is consistent with the proposed mechanism.



The results indicate that (1) is the thermodynamically more stable tautomer presumably because this has the stronger hydrogen-bond. Studies on diacetylbenzoylmethane and acetyldibenzoylmethane indicated that the preferred tautomers in both instances were those in which a benzoyl group rather than an acetyl group was excluded from the enolic system.[5] The more polar tautomer (**2**) is favoured in polar solvents such as DMSO.

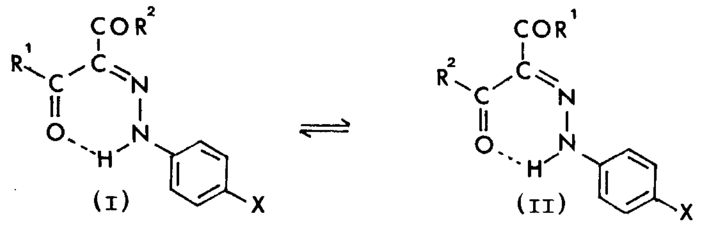
Structures were assigned to the two tautomers on the bases of their i.r. and n.m.r. spectra. The i.r. spectra clearly indicate whether the acetyl or benzoyl group is not involved in the enolic system. Thus the i.r. spectra of the tautomers (**1**) and (**2**) have carbonyl absorptions at ca. 1640 and 1680 cm^{-1} respectively (see Table). The carbonyl absorptions of arylhydrazones derived from dibenzoylmethane and acetylacetone are at ca. 1640 and 1680 cm^{-1} respectively in agreement with these assignments. The intramolecularly hydrogen-bonded protons in the n.m.r. spectra of the tautomers (**1**) and (**2**) appear at ca. δ 14.5 and 12.5 respectively (The precise position depends on the nature of the substituent in the arylhydrazone group.) from which it can be adduced that the signal due to this proton appears at lower field when an acetyl rather than a benzoyl group is involved in the chelate ring. The positions of the methyl signals are also different in the two tautomers being at slightly higher field in tautomer (**1**).

Similar results have been obtained with arylhydrazones of other 1,2,3-tricarbonyl systems and will be reported in detail later.

REFERENCES

1. H. C. Yao, *J. Org. Chem.*, **29**, 2959, (1964).
2. J. Elguero, R. Jacquier and G. Tarrago, *Bull. Soc. Chim. France*, 1966, 2981.
3. A. K. Bose and I. Kugajevsky, *Tetrahedron*, **23**, 1489 (1967).
4. Followed by observing the signals due to the methyl protons in the two tautomers.
5. D. C. Nonhebel, *Tetrahedron*, **26**, 4443 (1970).

TABLE <u>I.R. and N.M.R. Spectra of 2-Arylhydrazones of 1,2,3-Triketones</u>



R'	R^2	X	δ_{NH}(I)	δ_{NH}(II)	δ_{Me}(I)	δ_{Me}(II)	ν_{CO}(I)	ν_{CO}(II)	Equilibrium % I (in $CHCl_3$)	Form(s) isolated
Me	Me	COOEt	14.50		2.58,2.46		1675		–	
Me	Me	Cl	14.60		2.57,2.45		1680		-	
Me	Me	Br	14.65		2.60,2.48		1680		-	
Me	Me	H	14.65		2.58,2.46		1680		-	
Me	Ph	COOEt	14.55	12.25	2.64	2.55	1640	1675	85	I,II
Me	Ph	Cl	14.65	12.62	2.61	2.54	1640	1675	85	I,II
Me	Ph	Br	14.70	12.67	2.61	2.51	1640	1675	85	I,II
Me	Ph	H	14.75	12.80	2.60	2.53		a	90	I
Me	Ph	Me	14.90	13.10	2.60	2.55		a	95	I
Ph	Ph	H	13.45				1640		-	

[a] ν_{CO} not resolved in mixture of tautomers