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The reaction between hydrazonoyl halides and *N*-arylbenzamidines leads to the simultaneous formation of products derived from a substitution and a cycloaddition reaction *via* two independent paths.

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Fusco and co-workers (1,2) have investigated the behaviour of hydrazonoyl halides towards reaction with benzamidine. They reported the formation of 1,2,4-triazole or imidazolin-2-one derivatives, depending on the nature of the hydrazonoyl halide employed.

In connection with our research concerning the use of 1,3-dipoles (3) in heterocyclic synthesis we studied the reaction between methyl α -chloroglyoxylate phenylhydrazone (1) and some *N*-arylbenzamidines (2). In all cases which were investigated, the reaction gave a mixture of products which, separated by fractional crystallization associated with column chromatography, proved to be 1-aryl-2-phenyl-4-phenylhydrazonoimidazolin-5-ones (3), 1,5-diphenyl-3-methoxycarbonyl-1,2,4-triazole (4), arylamines originally bonded to amidine (5), methyl α -aminoglyoxylate phenylhydrazone (6), and 1,5-diphenyl-3-methoxycarbonyl-4-aryl-1,2,4-triazolium salt (7) isolated as the perchlorate.

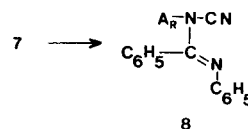
The main characteristics of products 3 and 7 are summarized in Table 1.

The characteristics of 1,5-diphenyl-3-methoxycarbonyl-1,2,4-triazole (4) and of arylamines (5) agree with those reported in the literature (4), whereas the identity of 6 was established by comparison with an authentic sample prepared from methyl α -chloroglyoxylate phenylhydrazone and ammonia. Analytical and spectroscopic data (ir and nmr) of compounds 3 and 7 are consistent

with their structural assignments.

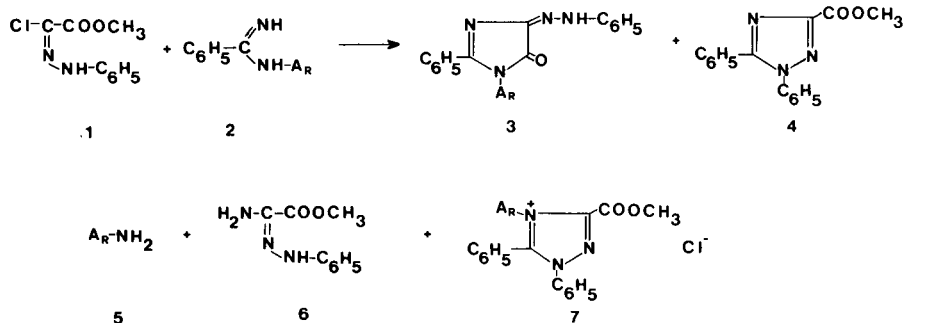
In the case of 7, its chemical behaviour also supports the structural assignment. Treatment with aqueous potassium carbonate prompts the detachment of the methoxycarbonyl group followed by cleavage of the heterocyclic ring with the formation of *N'*-aryl-*N'*-cyano-*N*-phenylbenzamidine (8). This is in accordance with the known behaviour of 3-acetyl or 3-methoxycarbonyl substituted 1,2,4-triazolium salts (5).

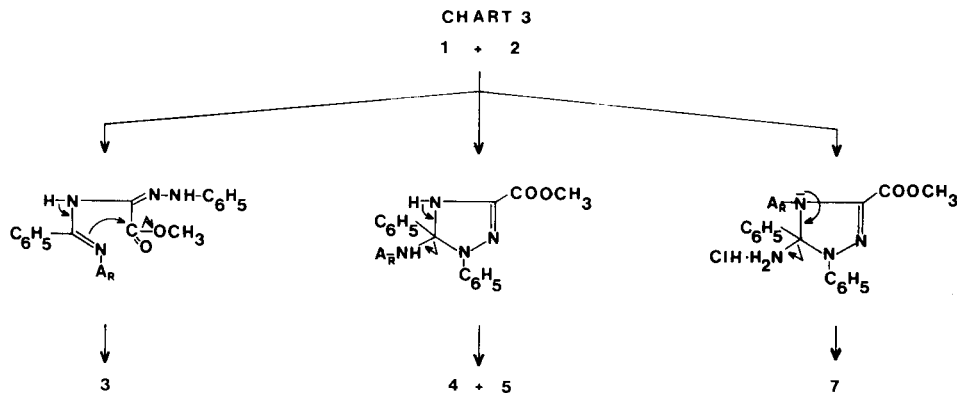
CHART 2



The simultaneous formation of all the products of the reaction can be explained by the fact that amidines combine the properties of the azomethine-like C=N double bond with an amide-like C-N single bond. Thus, the reaction with hydrazonoyl halides can follow two independent paths. The first involves the nucleophilic attack of the more basic amidinic nitrogen atom on the electrophilic center of the 1,3-dipole giving a ring closure to the imidazolin-5-one system *via* a prototropic hydrogen shift. In the second path, the cycloaddition of the 1,3-dipole to both tautomeric forms of the amidines affords two cyclo-

CHART 1





Compound No	Ar	M.p. (°C)	Relative Yield %	Molecular Formula	Analysis						Ir (Chloroform) Cm^{-1}	
					Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	ν NH	ν CO
3a	C_6H_5	212-214	25	$\text{C}_{21}\text{H}_{16}\text{N}_4\text{O}$	74.10	4.74	16.46	74.25	4.70	16.18	3365	1725
3b	$\text{C}_6\text{H}_4\text{-CH}_3$ (<i>p</i>)	184-186	28	$\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}$	74.75	5.12	15.81	74.75	5.31	16.00	3350	1720
3c	$\text{C}_6\text{H}_4\text{-NO}_2$ (<i>p</i>)	190-192	30	$\text{C}_{21}\text{H}_{15}\text{N}_4\text{O}_3$	65.45	3.92	18.17	65.15	3.86	18.03	3360	1720
3d	$\text{C}_6\text{H}_4\text{-OCH}_3$ (<i>p</i>)	196-198	22	$\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2$	71.33	4.90	15.13	71.54	4.76	15.26	3365	1725
3e	$\text{C}_6\text{H}_4\text{-F}$ (<i>p</i>)	218-220	24	$\text{C}_{21}\text{H}_{15}\text{FN}_4\text{O}$	70.30	4.22	15.72	70.36	4.30	15.85	3360	1720
7a	C_6H_5	265-270	42	$\text{C}_{22}\text{H}_{18}\text{ClN}_3\text{O}_6$	58.04	3.96	9.24	57.94	4.01	9.30		
7b	$\text{C}_6\text{H}_4\text{-CH}_3$ (<i>p</i>)	253-255	42	$\text{C}_{23}\text{H}_{20}\text{ClN}_3\text{O}_6$	58.84	4.26	9.95	58.62	4.31	9.78		
7c	$\text{C}_6\text{H}_4\text{-NO}_2$ (<i>p</i>)	298-300	48	$\text{C}_{22}\text{H}_{17}\text{ClN}_3\text{O}_6$	52.80	3.40	11.20	52.62	3.63	11.34		
7d	$\text{C}_6\text{H}_4\text{-OCH}_3$ (<i>p</i>)	257-259	40	$\text{C}_{23}\text{H}_{20}\text{ClN}_3\text{O}_7$	56.90	4.12	8.65	57.03	4.02	8.78		

adducts, which by elimination of a molecule of ammonia and arylamine, respectively, gain aromaticity.

The main difference between the previously reported (2) reactivity of benzamidine and that of the *N*-aryl-substituted derivatives is that the latter can give both a substitution and a cycloaddition reaction. A similar dual reaction may be expected for all cases but the different behaviour may merely reflect the basicity of the two series of benzamidines. The unsubstituted benzamidine, which is more basic, gives preferentially the substitution reaction whereas the less basic *N*-aryl substituted derivatives give cycloaddition products as the major course of the reaction.

EXPERIMENTAL

Melting points are uncorrected. Nmr spectra were recorded with a Varian A-60 spectrometer (TMS as internal standard). Ir spectra were recorded on a Perkin-Elmer 377 spectrophotometer in ca. 2% chloroform solution.

N-Arylbzamidines.

These are known compounds and were prepared following the standard method (6) described for *N*-phenylbenzamidine.

Reaction Between Methyl α -Chloroglyoxylate Phenylhydrazone (1) and *N*-Arylbzamidine (2). General Procedure.

Triethylamine (0.01 mole) was added dropwise to a solution of methyl α -chloroglyoxylate phenylhydrazone (1) (7) (0.01 mole) and *N*-arylbzamidine (2) (0.01 mole) in chloroform (50 ml.). The mixture was stirred for 4 hours and the solvent evaporated. The residue was taken up

with benzene and the precipitate filtered off.

The benzene solution containing four components (tlc) was fractionated by column chromatography on silica gel. Elution with benzene-ethyl acetate (90:10) gave 1-aryl-2-phenyl-4-phenylhydrazonoimidazolin-5-ones (3) with arylamines (5). The mixture was separated by treatment with 10% aqueous hydrochloric acid, which dissolved the amine and left the unaffected imidazolin-5-one derivatives. These were finally crystallized from benzene (Table 1). Further elution with benzene-ethyl acetate (75:25) gave 1,5-diphenyl-3-methoxycarbonyl-1,2,4-triazole (4) together with methyl α -aminoglyoxylate phenylhydrazone (6). The solution was extracted with 10% aqueous hydrochloric acid. Evaporation of the organic layer gave 4 as white needles, m.p. 158-160° [benzene-isopropyl ether (90:10)], yield 20%.

Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$: C, 68.80; H, 4.69; N, 15.05. Found: C, 68.65; H, 4.65; N, 15.24.

Treatment of the acid solution with 10% aqueous sodium carbonate precipitated 6. The product was purified from benzene-isopropyl ether (80:20), m.p. 130-132°, yield 35%; ir: ν NH 3350, CO 1710 cm^{-1} .

Anal. Calcd. for $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2$: C, 55.95; H, 5.74; N, 21.75. Found: C, 56.06; H, 5.46; N, 21.80.

The first precipitate obtained from benzene was dissolved in water. The solution was decolorized with charcoal and treated with 60% aqueous perchloric acid to give triazolium derivatives (7) (Table 1), purified from acetic acid.

Preparation of an Authentic Sample of 6.

A solution of methyl α -chloroglyoxylate phenylhydrazone (1) (0.01 mole) in dioxane (25 ml.) was saturated with ammonia and allowed to stand overnight. The solvent was evaporated and the residue chromatographed [silica gel; benzene-ethyl acetate (75:25)] to give methyl α -aminoglyoxylate phenylhydrazone (6) m.p. 130-132°.

Reaction of 7b with Potassium Carbonate.

Potassium carbonate (0.5 g.) was added portionwise to a well stirred solution of triazolium perchlorate (7b) (1 g.) in water (25 ml.). The mixture was stirred 15 minutes. The precipitate was collected by filtration and washed with water. The *N'*-cyano-*N'*-tolyl-*N*-phenylbenzamidine (8) was purified from benzene, m.p. 129-132°, yield 78%; ir: ν C=N 2220 cm^{-1} .

Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{N}_3$: C, 81.00; H, 5.50; N, 13.50. Found: C, 81.03; H, 5.47; N, 13.50.

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