Phenylpropiolic Acids. Part IX.[1] Reaction of Arylpropiolic Acids with Hydrazine and Phenylhydrazine

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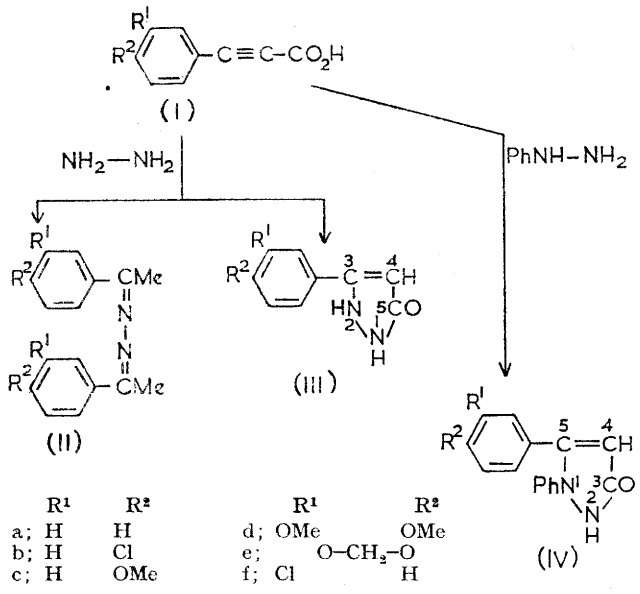
Phenyl-, *p*-chlorophenyl-, and 3,4-methylenedioxyphenyl-propiolic acids react with hydrazine to give, in each case, a mixture of the corresponding pyrazol-5-one and azine. *p*-Methoxyphenyl-, and 3,4-dimethoxyphenyl-propiolic acids give azines only. Phenyl-, *p*-chlorophenyl-, and *m*-chlorophenyl-propiolic acids react with phenylhydrazine to give the corresponding 5-aryl-1-phenylpyrazol-3-ones.

THE reaction of phenyl- (Ia), *p*-chlorophenyl- (Ib), and 3,4-methylenedioxyphenyl-propiolic acid (Ie), with excess of 99% hydrazine hydrate gave the corresponding 3-arylpyrazol-5-ones (IIIa), (IIIb), and, (IIIe), respectively, together with the respective aryl methyl azines (IIa), (IIb), and (IIe). In the first two cases, the pyrazolone constituted the main reaction product. With *p*-methoxyphenyl- (Ic), and 3,4-dimethoxyphenyl-



SCHEME

(Id) propiolic acid only the aryl methyl azines (IIc) and (IId), respectively could be isolated in fairly good yield. The reaction of phenylhydrazine with phenyl- (Ia), *p*-chlorophenyl- (Ib), and *m*-chlorophenyl- (If) propiolic acids gave, in each case, the corresponding 5-aryl-1-phenylpyrazol-3-one (IVa), (IVb), and (IVf).

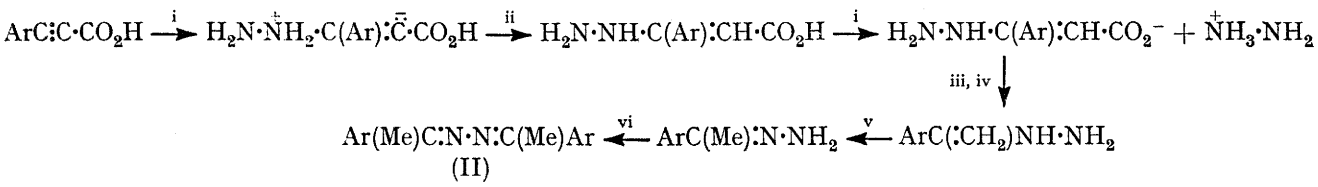
Structure of the Azines.—The two products (IIa) and (IIc) are known compounds, and were characterised both by analysis and by their identity with authentic specimens.[2] The structure assigned to the azines (IIb), (IId), and (IIe), is justified both by their analytical data, and the similarity of their spectroscopic behaviour to that of (IIa), and (IIc). The i.r. spectra of the azines show bands at 1592—1582 cm.$^{-1}$; values for particular compounds are (IIa) 1592, (IIb) 1587, (IIc) 1587, (IId) 1592, and (IIe) 1582 cm.$^{-1}$. These values are close to the absorption at 1635 cm.$^{-1}$ reported for α-furylazine,[3] which has been correlated with the C=N stretching frequency. The regularity observed in the u.v. absorption of compounds (IIa)—(IIe) (*cf.* Table 1) affords further support for the similarity of the structures. The bathochromic shift and hyperchromic effect in (IIb)—(IIe) can be attributed to the auxochromic character of the substituent groups. The two peaks at 271 and 296 mμ observed with (IIa) are probably due to vibrational fine-structure.

TABLE 1

U.v. absorption of the azines in cyclohexane

Compound (II)	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
a	271	26,214	238	7754
	296	25,414	290	25,414
b	274	30,324	237	9530
c	315	34,273	242	8828
d	275—285infl	18,541	249·5	13,597
	322	32,138		
e	270—280infl	16,200	254	14,850
	325	37,800		

The formation of the azines is undoubtedly initiated by nucleophilic attack by hydrazine at the β-acetylenic carbon of the arylpropiolic acid, and probably involves the following reaction sequence.



Reagents: i, hydrazine; ii, $-H^+$, $+H^+$; iii, $-CO_2$; iv, $+H^+$; v, αγ-proton shift; vi, ArC:C·CO$_2$H.

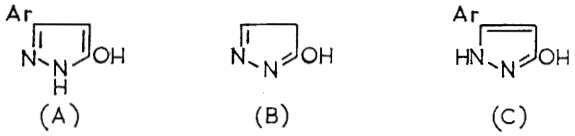
Structure of the Pyrazolones.—The characterisation of the reaction product (IIIa) as the known 3-phenylpyrazol-5-one followed from its identity with an authentic

[1] Part VIII, F. G. Baddar, G. E. M. Moussa, and M. T. Omar, *J. Chem. Soc.* (*C*), 1968, 110.
[2] T. Curtius, *J. prakt. Chem.*, 1890, [2] **44**, 167.
[3] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1960, p. 270.

specimen.[4,5] The latter procedure [5] was used to prepare an authentic specimen of 3-*p*-chlorophenylpyrazol-5-one which proved to be identical with the reaction product (IIIb). The similarity of the i.r. and u.v. spectra of (IIIa) and (IIIb) with that of (IIIe), justifies the pyrazolone structure assigned to the last named product (*cf.* following discussion of spectra).

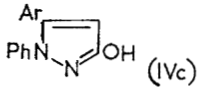
The structure of (IVa) was established by its identity with an authentic specimen [6] and that assigned to the substituted analogues (IVb) and (IVf) was based on spectroscopic evidence.

The 3-arylpyrazol-5-ones (IIIa), (IIIb), and (IIIe) as well as (IVa), (IVb), and (IVf) exhibited similar i.r. absorption in the functional-group region. Absorption at 1710—1705 cm.$^{-1}$, reported by Gagnon *et al.*[7] for the carbonyl stretching frequency in a series of 4-alkyl-1,3-diphenylpyrazol-5-ones was absent in the pyrazolones under discussion. On the other hand, these compounds exhibited rather strong absorption at 1620—1580 cm.$^{-1}$ which can be correlated with the stretching frequency of the cyclic C=N group.[7,8] The absence of carbonyl absorption suggests the existence of the pyrazol-5-ones (IIIa), (IIIb), and (IIIe) in the following tautomeric forms.



(A) (B) (C)

Tautomeric structures for (III)

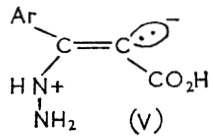


(IVc)

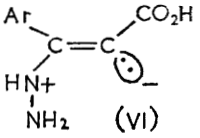
For the pyrazol-3-ones (IVa), (IVb), and (IVf) the only possible non-ketonic structure is the lactim form (IVc). The presence of the hydroxy-group in the pyrazolones under discussion is further substantiated by the appearance of strong broad bands in the 3μ region.

The u.v. absorption data of (IIIa), (IIIb), and (IIIe), and (IVa), (IVb), and (IVf) (Table 2) indicate a similarity of their chromophoric systems and suggest the lactim form (C) as the more probable structure for the first three compounds. Variations in the values of $\lambda_{max.}$ and $\varepsilon_{max.}$ can be interpreted in terms of conjugative or steric effects of substituents. Thus, the pronounced bathochromic shift and intensification of absorption in (IIIe) compared with (IIIa), and (IIIb), is expected from the extended conjugation brought by the *para*-substituent auxochrome. The hypsochromic shifts observed in the last three compounds (IVa), (IVb), and (IVf) can be attributed to a steric inhibition of conjugation.

The failure to obtain pyrazolones for the methoxy-substituted acids (Ic) and (Id), as well as the relatively poor yield obtained for (Ie), can be reasonably explained with the assumption that the reaction initially involves nucleophilic attack at the β-acetylenic carbon. Out of the two possible configurations for the intermediate carbanion, configuration (V) is the one that can eventually lead to cyclo-dehydration. In the above mentioned



(V)



(VI)

acids, repulsive forces involving the electron-rich aromatic ring (+*M* effect of the substituents) may retard the formation of configuration (V). The alternative mechanistic route involving initial hydrazide formation

TABLE 2

U.v. absorption data of pyrazolones in ethanol

Compound	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
(IIIa)	252	14,725	224	5778
(IIIb)	254	16,306	226	6819
(IIIe)	266	20,400	341	11,730
	300	13,260	290	12,240
(IVa)	238	17,228	222	13,688
(IVb)	244	18,315	225	12,679
(IVf)	240	18,935	230	16,771

followed by nucleophilic attack at the β-acetylenic carbon, cannot satisfactorily explain the above mentioned observation, since the argument that such nucleophilic attack may be retarded by the +*M* of the *para*-oxygens is readily rejected in view of the fact that particularly in the case of (Ic) and (Id), a fairly good yield of the ketazines (IIc) and (IId) was obtained.

The formation of (IVa), (IVb), and (IVf), from the corresponding arylpropiolic acids, is in contrast to the known behaviour of arylpropiolic esters which normally yield 3-aryl-1-phenylpyrazol-5-ones with phenylhydrazine.[5] It is believed that in the case of acids, protonation of the more basic β-nitrogen converts phenylhydrazine into its conjugate acid with the α-nitrogen available for nucleophilic attack at the β-acetylenic carbon.

EXPERIMENTAL

I.r. and u.v. spectra were measured with Perkin-Elmer Infracord Model 137 and Spectracord Model 4000A, Spectrophotometers, respectively. All i.r. measurements were carried out with KBr discs.

General Procedure for the Reaction of Arylpropiolic Acids with Hydrazine.—A mixture of the arylpropiolic acid and excess of 99% hydrazine hydrate (1 ml./1 g. acid) in n-butanol (5 ml./g. acid) was heated under reflux for 5 hr. and then set aside overnight at room temperature. For (Ia), (Ic), and (Id), the solvent was removed under reduced pressure and the yellow azines (IIa), (IIc), and (IId) were extracted from the oily residue by being repeatedly heated under reflux with light petroleum (b.p. 100—120°); with phenylpropiolic acid (Ia) this procedure left the pyrazolone

[4] A. Michaelis and W. Rassmann, *Annalen*, 1907, **352**, 158.
[5] V. Rothenburg, *Ber.*, 1894, **27**, 783.
[6] A. Michaelis and W. Willert, *Annalen*, 1907, **358**, 159.
[7] P. E. Gagnon, J. L. Boivin, and R. J. Paquin, *Canad. J. Chem.*, 1953, **31**, 1025.
[8] J. R. Randal, 'Infrared Determination of Organic Structures,' van Nostrand, New York, 1949, p. 222.

TABLE 3

Reactant acid	Product	Yield (%)	Solvent	M.p.	Found (%) C	H	N	Formula	Required (%) C	H	N
(Ia)	(IIa) *	20	P ‡	121—122°	81·6	6·8	12·0	$C_{16}H_{16}N_2$	81·3	6·8	11·9
	(IIIa) *	56	Dil. AcOH	238—239	67·2	5·1	17·3	$C_9H_8N_2O$	67·5	5·0	17·5
(Ib)	(IIb)	38	P §	152—153	62·8	4·6	9·5	$C_{16}H_{14}Cl_2N_2$ ¶	62·9	4·6	9·2
	(IIIb) †	50	Bu^nOH	242	55·5	3·9	14·1	$C_9H_7ClN_2O$ ‖	55·5	3·6	14·4
(Ic)	(IIc) *	60	P §	197—198	72·1	6·7	10·15	$C_{18}H_{20}N_2O_2$	72·9	6·7	9·45
(Id)	(IId)	60	P §	195—196	66·8	6·7	7·5	$C_{20}H_{24}N_2O_4$	67·4	6·8	7·9
(Ie)	(IIe)	30	P §	183—184	66·6	5·2	8·7	$C_{18}H_{16}N_2O_4$	66·7	5·0	8·6
	(IIIe)	20	EtOH	239	58·8	4·0	13·6	$C_{10}H_8N_2O_3$	58·8	3·95	13·7

* Already known compounds. † This compound was also prepared by the reaction of hydrazine with ethyl *p*-chlorophenylpropiolate according to a procedure described by Rothenburg.[5] ‡ Light petroleum (b.p. 60—80°). § Light petroleum (b.p. 100—120°). ¶ Analysis (%) for Cl: Found 24·25 (Calc. 23·7). ‖ Analysis (%) for Cl: Found 18·3 (calc. 18·25).

TABLE 4

Reactant acid	Product	Yield (%)	Solvent	M.p.	Found (%) C	H	Cl	N	Formula	Required (%) C	H	Cl	N
(Ia)	(IVa) *	75	B–P †	256°	75·5	4·95		12·5	$C_{15}H_{12}N_2O$	76·25	5·1		11·9
(Ib)	(IVb)	50	Dioxan	284—285	66·2	4·3	12·5	10·0	$C_{15}H_{11}ClN_2O$	66·5	4·0	12·8	10·7
(If)	(IVf)	40	B–P ‡	222—223	66·5	4·0	12·55	10·0	$C_{15}H_{11}ClN_2O$	66·5	4·0	12·8	10·7

* Already known compound. † Benzene–light petroleum (b.p. 40—60°). ‡ Benzene–light petroleum (b.p. 60—80°).

(IIIa). For (Ib) the reaction mixture was diluted with ether and left for few days in an ice-box during which time the pyrazolone (IIIb) was precipitated. The mother liquor was concentrated and cooled for a few days to give the yellow azine (IIb). With (Ie) treatment similar to that described for (Ib) gave the yellow azine (IIe) and then the pyrazolone (IIIe); results are given in Table 3.

General Procedure for Reaction of Arylpropiolic Acids with Phenylhydrazine.—A solution of the arylpropiolic acid [(Ia), (Ib), and (If)] and phenylhydrazine (1 ml./g. acid) in benzene (25 ml./g. acid) was heated under reflux for 20 hr., and then set aside overnight at room temperature. Concentration and dilution with light petroleum (b.p. 40—60°) precipitated a solid which was treated with 10% sodium carbonate solution. The insoluble material was then crystallised from a suitable solvent. Results are recorded in Table 4.

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