

Reaction of Aroylphenylacetylenes with Hydrazine Derivatives

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The reaction of aroylphenylacetylenes (I) with acyl- or aroylhydrazines (II) gave ω -aroylacetophenone-*N*-acyl or *N*-aroylhydrazones (IV). The latter gave upon treatment with methanolic potassium hydroxide and with acetic anhydride in the presence of sodium acetate, the corresponding pyrazoles (V) and the *N*-acetylpyrazoles (VII and VIII), respectively. The acetylenic ketones (I) also reacted with methylhydrazine and 1,1-dimethylhydrazine to give 5-aryl-1-methyl-3-phenylpyrazoles (XII), and 1,1-dimethylhydrazine derivatives (XIII), respectively. When the latter compounds were heated with acetic anhydride, they gave the *N*-methylpyrazoles (XII).

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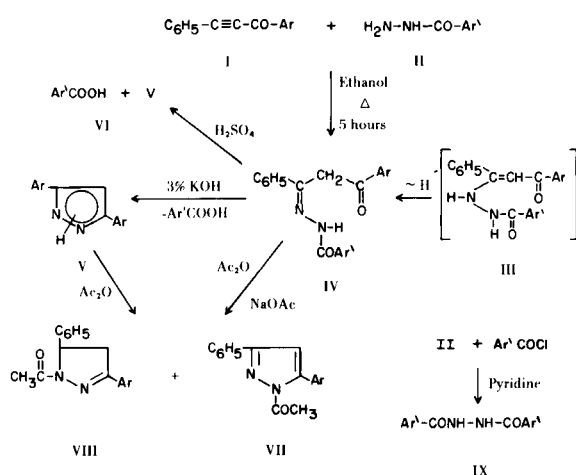
In the present investigation, aroylphenylacetylenes (Ia-e) were allowed to react with acyl- or aroylhydrazines (IIa-d), methylhydrazine, and 1,1-dimethylhydrazine, to study the mechanisms of the reactions and to prepare new substituted pyrazoles.

(A) Reaction with Acyl- and Aroylhydrazines (II).

When the pure and freshly prepared aroylphenylacetylenes (Ia-e) were refluxed with an alcoholic solution of benzoyl- (IIa), phenylacetyl- (IIb), α -naphthoyl- (IIc) and α -naphthylacetyl- (IId) hydrazines, they gave ω -aroylacetophenone-*N*-benzoyl- (IVa,e,i,o), *N*-phenylacetyl (IVb, f,j,m,p), *N*- α -naphthoyl (IVc,g,k) and *N*- α -naphthylacetyl (IVd,h,l,n,q) hydrazones, respectively, (cf. Scheme 1).

The structure of the above products was established spectroscopically and chemically. Thus, their ir spectra reveal the absence of $\nu \text{C}\equiv\text{C}$ and the presence of a band in the region $3540\text{--}3300 \text{ cm}^{-1}$ (νNH) (2a). They also show a strong band in the region $1667\text{--}1630 \text{ cm}^{-1}$ ($\nu \text{C}=\text{O}$) (2b)

Scheme 1



Compounds	Ar	Compounds	Ar'
I, V, VII, VIIIa	C_6H_5	II, VI, IXa	C_6H_5
b	<i>p</i> - $\text{CH}_3\text{-C}_6\text{H}_4$	b	$\text{CH}_2\text{C}_6\text{H}_5$
c	<i>p</i> - $\text{Cl-C}_6\text{H}_4$	c	$\alpha\text{-C}_{10}\text{H}_7$
d	3,4- $\text{OCH}_2\text{OC}_6\text{H}_3$	d	$\alpha\text{-CH}_2\text{C}_{10}\text{H}_7$
e	<i>p</i> - $\text{CH}_3\text{-C}_6\text{H}_4$		

Compounds III and IV

No.	Ar	Ar'	No.	Ar	Ar'
a	C_6H_5	C_6H_5	i	<i>p</i> - $\text{Cl-C}_6\text{H}_4$	C_6H_5
b	C_6H_5	$\text{CH}_2\text{C}_6\text{H}_5$	j	<i>p</i> - $\text{Cl-C}_6\text{H}_4$	$\text{CH}_2\text{C}_6\text{H}_5$
c	C_6H_5	$\alpha\text{-C}_{10}\text{H}_7$	k	<i>p</i> - $\text{Cl-C}_6\text{H}_4$	$\alpha\text{-C}_{10}\text{H}_7$
d	C_6H_5	$\alpha\text{-CH}_2\text{C}_{10}\text{H}_7$	l	<i>p</i> - $\text{Cl-C}_6\text{H}_4$	$\alpha\text{-CH}_2\text{C}_{10}\text{H}_7$
e	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	C_6H_5	m	3,4- $\text{OCH}_2\text{OC}_6\text{H}_3$	$\text{CH}_2\text{C}_6\text{H}_5$
f	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	$\text{CH}_2\text{C}_6\text{H}_5$	n	3,4- $\text{OCH}_2\text{OC}_6\text{H}_3$	$\alpha\text{-CH}_2\text{C}_{10}\text{H}_7$
g	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	$\alpha\text{-C}_{10}\text{H}_7$	o	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	C_6H_5
h	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	$\alpha\text{-CH}_2\text{C}_{10}\text{H}_7$	p	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	$\text{CH}_2\text{C}_6\text{H}_5$
			q	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	$\alpha\text{-CH}_2\text{C}_{10}\text{H}_7$

(cf. Table I). This indicates that they have either structure III or IV. Their nmr spectra (cf. Table II), however, show a quartet (2H) representing an AB system ($J_{AB} = 18\text{--}19 \text{ Hz}$; $\Delta \nu/J = 1.00\text{--}1.40$) due to the CH_2CO protons (3), indicating that they have structure IV and not III. The fact that these methylene groups behave as an AB system can be attributed either to the large anisotropic effect of the $\text{C}=\text{N}$ group and the nitrogen lone pair or to the restriction of rotation at the COAr group by the weak hydrogen bonding between the NH and the carbonyl group of the aroyl group. The fact, however, that the quartets coalesced to singlets when the nmr spectra of IV_j and IV_n were measured in DMSO(*d*₆) indicates that the latter interpretation is more probable. The highly polar solvent cleaves the weak hydrogen bonding between the NH and CO group. Compound IV_j, however, shows in addition, a second quartet, representing another AB system ($J_{AB} = 14.0 \text{ Hz}$; $\Delta \nu/J = 0.55$) attributable to NCOCH_2 group (cf. Table II). The nmr spectra of these compounds also show a broad signal in the region $\delta 5.03\text{--}5.98$ which exchanges with deuterium oxide (NH) (3).

The electronic spectra of these compounds (cf. Table I) reveal their identity and show absorption maxima in the range 281-292 nm attributable to $\pi\text{-}\pi^*$ transition bands (3,4).

The following chemical reactions of compounds IVa-q give further evidence for the assigned structures.

(i) They are converted to a mixture of the corresponding 3(5)-aryl-5(3)-phenylpyrazoles (V) and acids (VI) when heated with 3% methanolic potassium hydroxide.

(ii) When refluxed with acetic anhydride in the presence of anhydrous sodium acetate, they gave an inseparable

Table I

The Electronic and Infrared Spectral Data of ω -Aroylaceto-phenone-*N*-aroyl and *N*-acylhydrazones (IVa-q)

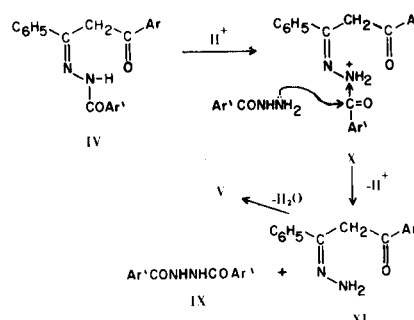
Compound No.	Electronic Spectra (Ethanol)		Infrared Spectra (Potassium bromide)	
	λ max	ϵ	cm^{-1}	ν
IVa	287	24,620	3390 (br.) 1634 (s) 1605 (m)	NH C=O C=N
IVb	283 290-295 (sh)	24,340 22,540	3510 (m) 1667 (s) 1605 (m)	NH C=O C=N
IVc	283 290-295 (sh)	26,860 25,700	3400 (br.) 1633 (s) 1593 (m)	NH C=O C=N
IVd	283 290-295 (sh)	30,720 28,950	3410 (br.) 1652 (s) 1592 (m)	NH C=O C=N
IVe	219 292	31,740 26,170	3515 (m) 1630 (s) 1600 (m)	NH C=O C=N
IVf	215-220 (sh) 284 287-294 (sh)	28,080 25,120 24,630	3350 (br.) 1658 (s) 1590 (m)	NH C=O C=N
IVg	281 290-295 (sh)	26,935 25,350	3460 (br.) 1637 (s) 1618 (m)	NH C=O C=N
IVh	283 290-295 (sh)	26,300 24,200	3410 (br.) 1655 (s) 1600 (m)	NH C=O C=N
IVi	220 292	28,970 23,060	3360 (br.) 1634 (s) 1600 (m)	NH C=O C=N
IVj	220 283 290-295 (sh)	33,220 28,100 27,360	3350 (br.) 1665 (s) 1605 (m)	NH C=O C=N
IVk	220 282 290-295 (sh)	28,100 26,500 25,025	3460 (br.) 1642 (s) 1625 (m)	NH C=O C=N
IVl	220 283 290-295 (sh)	32,220 29,630 28,100	3500 (m) 1660 (s) 1605 (m)	NH C=O C=N
IVm	282 287-292 (sh) 305-312 (sh)	23,650 22,210 15,100	3320 (br.) 1650 (s) 1590 (s)	NH C=O C=N
IVn	282 290-295 (sh) 315	22,600 19,430 11,100	3400 (br.) 1663 (s) 1605 (m)	NH C=O C=N
IVo	292	25,600	3540 (m) 1640 (s) 1615 (s)	NH C=O C=N
IVp	283 289-294 (sh)	26,870 25,440	3310 (br.) 1654 (s) 1597 (m)	NH C=O C=N
IVq	284 290-295 (sh)	26,860 24,980	3490 (m) 1645 (s) 1615 (m)	NH C=O C=N

mixture of the acetyl pyrazoles (VII and VIIIb-e, respectively) [detected by tlc and nmr spectra] (cf. Scheme 1). The identity of the tlc and nmr spectra of these products with those obtained by the direct acetylation of the pyrazoles (Vb-e) with acetic anhydride (3), indicated that the reaction proceeds through the intermediate formation of pyrazole followed by acetylation. (iii) When IVi was treated with concentrated sulfuric acid at room temperature, it gave a mixture of 3(5)-*p*-chlorophenyl-5(3)-phenylpyrazole (Vc) and benzoic acid (cf. Scheme 1).

When the reaction of *p*-toluylphenylacetylene (Ib) or *p*-chlorobenzoylphenylacetylene (Ic) with aroyl- (IIa,c) and acyl- (IIb,d) hydrazines was repeated in the presence of 2 drops of concentrated sulfuric acid, it gave in addition to the corresponding hydrazones (IVe-h and IVi-l), the pyrazoles (Vb,c), 1,2-diaroyl- (IXa,c) and 1,2-diacyl- (IXb,d) hydrazines, respectively. The structure of IXa-d was established by their identity with authentic samples prepared by heating aroyl- (IIa,c) and acyl- (IIb,d) hydrazines with the corresponding aroyl and acyl chlorides in pyridine. The spectral data of these compounds are reported in Table IV.

The electronic spectra of IXa and IXc are similar to the spectra of the corresponding amides (Ar'-CONH₂) (5,6) with double the molecular extinction coefficient, whereas those of IXb and IXd are identical with the spectra of benzene and naphthalene, respectively (7). The formation of the 1,2-diacyl- (IXb,d) and 1,2-diaroyl- (IXa,c) hydrazines appears to proceed according to Scheme 2.

Scheme 2



The acyl- or aroylhydrazone attacks the carbonyl group of the protonated hydrazone (X) by an S_N2 mechanism to give the diacyl- or diaroylhydrazines (IX) and the hydrazone (XI) which readily cyclizes to the pyrazole (V). The formation of an intermediate cation (Ar'CO⁺), which then attacks the acyl- or aroylhydrazone (II) to give the diacyl- or diaroylhydrazone (IX), was excluded, since an attempt to trap this cation by carrying out the reaction in a reactive solvent such as anisole or *N,N*-dimethylaniline rather than in ethanol was not successful.

Conversion of IV to the corresponding acetylpyrazole (VII and/or VIII) by the action of sodium acetate in

Table II

The Nuclear Magnetic Resonance Spectral Data of ω -Aroylaceto-phenone-*N*-aroyl and *N*-acylhydrazone Derivatives (IVa-q) in Deuteriochloroform

Compound No.	δ	No. of protons	Assignment J (Hz) (b)	$\Delta \nu/J$ (b)
IVa	7.33-8.33 (m)	15	ArH	1.00
	5.27 (br)	1	NH	
	3.78 (d) } (a)	1	H	
	3.47 (d) }	1	-C-CO (AB System) 19 H	
IVb	7.33-7.93 (m)	15	ArH	1.19
	5.12 (br)	1	NH	
	4.18 (s)	2	NCOCH ₂	
	3.73 (d) } (a)	1	H	
3.37 (d) }	1	-C-CO (AB System) 18 H		
IVc	7.33-8.33 (m)	17	ArH	1.15
	5.67 (br)	1	NH	
	3.87 (d) } (a)	1	H	
	3.50 (d) }	1	-C-CO (AB System) 19 H	
IVd	7.33-8.43 (m)	17	ArH	1.15
	5.15 (s)	1	NH	
	4.67 (s)	2	NCOCH ₂	
	3.77 (d) } (a)	1	H	
3.40 (d) }	1	-C-CO (AB System) 19 H		
IVe	7.1-8.2 (m)	14	ArH	1.12
	5.43 (br)	1	NH	
	3.73 (d) } (a)	1	H	
	3.39 (d) }	1	-C-CO (AB System) 18 H	
2.32 (s)	3	ArCH ₃		
IVf	7.1-7.93 (m)	14	ArH	1.19
	5.03 (br)	1	NH	
	4.13 (s)	2	NCOCH ₂	
	3.70 (d) } (a)	1	H	
3.34 (d) }	1	-C-CO (AB System) 18 H		
2.30 (s)	3	Ar-CH ₃		
IVg	7.1-8.13 (m)	16	ArH	1.12
	5.43 (br)	1	NH	
	3.73 (d) } (a)	1	H	
	3.39 (d) }	1	-C-CO (AB System) 18 H	
2.31 (s)	3	ArCH ₃		
IVh	7.13-8.47 (m)	16	ArH	1.12
	5.13 (br)	1	NH	
	4.67 (s)	2	NCOCH ₂	
	3.76 (d) } (a)	1	H	
3.41 (d) }	1	-C-CO (AB System) 18 H		
2.32 (s)	3	Ar-CH ₃		
IVi	7.23-8.33 (m)	14	ArH	1.19
	5.73 (br)	1	NH	
	3.83 (d) } (a)	1	H	
	3.47 (d) }	1	-C-CO (AB System) 18 H	

Table II (Continued)

Compound No.	δ	No. of protons	Assignment J (Hz) (b)	$\Delta \nu/J$ (b)		
IVj	7.27-7.87 (m)	14	ArH	0.55		
	5.07 (br)	1	NH			
	4.28 (d)	1	NCOCH ₂ (AB System) 14			
	4.15 (d)	1				
	3.70 (d)	1				
	3.30 (d)	1				
					- $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ -CO (AB System) 18	1.33
	7.87-7.23 (m)	14	ArH			
	4.03 (s)	2	NCOCH ₂			
	3.53 (s)	2	-CH ₂ CO-Ar			
IVk	7.33-8.33 (m)	16	ArH	1.21		
	5.72 (s)	1	NH			
	3.86 (d)	1	- $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ -CO (AB System) 19			
	3.48 (d)	1				
IVl	7.23-8.33 (m)	16	ArH	1.40		
	5.13 (br)	1	-NH			
	4.63 (s)	2	-NCOCH ₂ -			
	3.74 (d)	1	- $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ -CO (AB System) 18			
	3.32 (d)	1				
IVm	6.83-7.93 (m)	13	ArH	1.01		
	5.83 (s)	2	OCH ₂ O			
	4.87 (br)	1	NH			
	4.13 (s)	2	NCOCH ₂			
	3.69 (d)	1	- $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ -CO (AB System) 19			
	3.37 (d)	1				
IVn	7.50-8.27 (m)	15	ArH	1.19		
	5.82 (s)	2	OCH ₂ O			
	5.57 (br)	1	NH			
	4.57 (s)	2	NCOCH ₂ -			
	3.70 (d)	1	- $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ -CO (AB System) 18			
	3.34 (d)	1				
	7.5-8.17 (m)	15	ArH			
	6.18 (s)	2	OCH ₂ O			
	4.53 (s)	2	NCOCH ₂			
	3.67	2	-CH ₂ COAr			
IVo	6.8-8.2 (m)	14	ArH	1.04		
	5.4 (br)	1	NH			
	3.73 (s)	3	ArOCH ₃			
	3.69 (d)	1	- $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ -CO (AB System) 18			
	3.38 (d)	1				
IVp	6.68-7.83 (m)	14	ArH	1.19		
	4.98 (br)	1	NH			
	4.08 (s)	2	-NCOCH ₂ -			
	3.70 (s)	3	ArOCH ₃			
	3.63 (d)	1	- $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$ -CO (AB System) 18			
	3.27 (d)	1				

IVq	6.67-7.87 (m)	16	ArH	
	4.98 (br)	1	NH	
	4.57 (s)	2	-NCOCH ₂ -	
	3.70 (s)	3	ArOCH ₃	
	3.66 (d)	1	H	
	3.31 (d) } (a)	1	-C-CO (AB System) 18	1.19
			H	

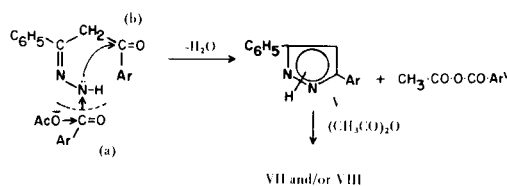
(a) These were calculated from the relation $\nu_A = \nu_0 + \frac{1}{2} \sqrt{mn}$ Hz and $\nu_B = \nu_0 - \frac{1}{2} \sqrt{mn}$ Hz, where ν_0 is the mid-point of the quartet of lines (11). However, the values for this system reported in reference (3) were determined by inspection. (b) All J-values reported in reference (3) should be multiplied by 2, and $\Delta\nu$ and $\Delta\nu/J$ in the same reference are erroneous. (c) In deuteriodimethyl sulfoxide.

Table III

The Nuclear Magnetic Resonance Spectral Data of Acetylpyrazole Derivatives (VII and/or VIII) in Deuteriochloroform

Compound	δ	Assignments (No. of Protons)
VIIa	7.33 (s)	(10) ArH
	6.73 (s)	(1) =CH-
	2.77 (s)	(3) NCOCH ₃
VIIIb or VIIIb	7.13-7.83 (m)	(9) ArH
	6.63 (s)	(1) =CH-
	2.77 (s)	(3) NCOCH ₃
VIIc and VIIIc	2.40 (s)	(3) ArCH ₃
	7.33-8.07 (m)	(9) ArH
	6.73 (s)	(1) =CH-
VIIc and VIIIc	6.7 (s)	(1) =CH-
	2.77 (s)	(3) NCOCH ₃
	2.73 (s)	(3) NCOCH ₃
VIId and VIIId	6.77-8.0 (m)	(8) ArH
	6.67 (s)	(1) =CH-
	6.60 (s)	(1) =CH-
VIIe and VIIIe	6.0 (s)	(2) OCH ₂ O
	2.73 (s)	(3) NCOCH ₃
	2.75 (s)	(3) NCOCH ₃
VIIe and VIIIe	6.83-7.97 (m)	(9) ArH
	6.67 (s)	(1) =CH-
	6.63 (s)	(1) =CH-
VIIe and VIIIe	3.83 (s)	(3) ArOCH ₃
	2.71 (s)	(3) NCOCH ₃

acetic anhydride appears to proceed by a similar mechanism. The acetate ion, which is a strong nucleophile, attacks the carbonyl group (a) simultaneously with the attack of the nitrogen on the carbonyl group (b) with loss of water to give the mixed anhydride (CH₃-CO-O-COAr') and pyrazole (V). The latter compound is then acetylated to give a mixture of the two acetyl derivatives (VII and VIII).



(B) Reaction with Methylhydrazine and 1,1-Dimethylhydrazine.

When the acetylenic ketones (Ia-e) were treated with methylhydrazine, they gave the corresponding 5-aryl-1-methyl-3-phenylpyrazoles (XIIa-e) (*cf.* Scheme 3). The reaction seems to proceed by Michael addition of methylhydrazine to the triple bond of the acetylenic ketone (3), followed by cyclization to give the final products (XIIa-e). The structure of these pyrazoles was inferred from the identity of 5-*p*-chlorophenyl-1-methyl-3-phenylpyrazole with an authentic specimen prepared by reacting the dibromide of *p*-chlorobenzalacetophenone with methylhydrazine in methanolic potassium hydroxide (8). Further evidence concerning the structure of compounds XIIa-e is forthcoming from their spectral data (*cf.* Table V). Thus,

Scheme 3

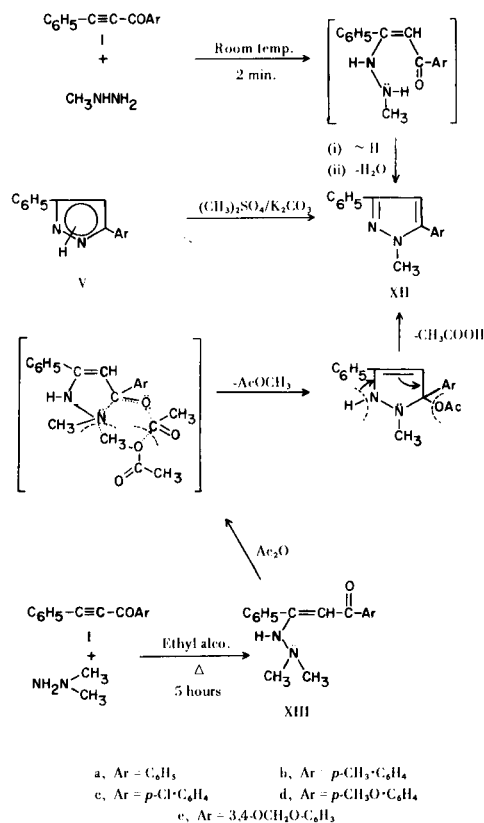


Table IV

The Electronic, Infrared and Nuclear Magnetic Resonance Spectral Data of Diacyl- (IXb,d) and Diaroyl- (IXa,c) hydrazines

Compound No.	Electronic Spectra (Ethanol)		Infrared Spectra (Potassium bromide)		Nmr (Deuteriochloroform)	
	λ max (nm)	ϵ	cm^{-1}	ν	δ	Assignments (No. of Protons)
IXa	229	24,220	3200 (br.)	NH	10.6 (s)	(2) NH (a)
	265-278 (sh)	5,810	1628 (s)	C=O	8.33-7.37 (m)	(10) ArH
IXb	255	273	3200 (br.)	NH	10.22 (s)	(2) NH (a)
			1590 (s)	C=O	7.4 (s)	(10) ArH
					3.53 (s)	(4) ArCH ₂
IXc	222	100,900	3190 (br.)	NH	10.7 (s)	(2) NH (a)
	282	14,700	1605 (s)	C=O	8.93-7.53 (m)	(14) ArH
	287-290 (sh)	14,000				
IXd	224	117,760	3210 (br.)	NH	10.37 (s)	(2) NH (a)
	276	10,730	1610 (s)	C=O	8.47-7.33 (m)	(14) ArH
	282	12,920			3.95 (s)	(4) ArCH ₂
	287-293 (sh)	8,820				
	312	732				

(a) Exchanged with deuterium oxide.

Table V

The Electronic, Infrared and Nuclear Magnetic Resonance Spectral Data of 5-Aryl-1-methyl-3-phenylpyrazoles (XII) and 1,1-Dimethyl-2-[β -(α (3,4-methylenedioxybenzoyl)styryl)]hydrazine (XIIIe)

Compound No.	Electronic Spectra (Ethanol)		Infrared Spectra (Potassium bromide)		Nmr (Deuteriochloroform)				
	λ max (nm)	ϵ	cm^{-1}	ν	δ	Assignments (No. of Protons)			
XIIa	251	31,090	1605 (m)	C=N	8.27-7.2 (m)	(10) ArH			
					6.57 (s)	(1) =CH-			
					3.53 (s)	(3) NCH ₃			
XIIb	252	34,460	1600 (m)	C=N	7.83-7.17 (m)	(9) ArH			
					6.57 (s)	(1) =CH-			
					3.87 (s)	(3) NCH ₃			
					2.33 (s)	(3) ArCH ₃			
XIIc	256	36,790	1515 (w)	C=C	7.87-7.23 (m)	(9) ArH			
					6.6 (s)	(1) =CH-			
					3.87 (s)	(3) NCH ₃			
XIIId	257	37,170	1610 (s)	C=N	7.9-6.87 (m)	(9) ArH			
					6.52 (s)	(1) =CH-			
					3.93 (s)	(3) ArOCH ₃			
					3.78 (s)	(3) NCH ₃			
XIIe	259	38,330	1605 (m)	C=N	7.5-6.77 (m)	(8) ArH			
					6.50 (s)	(1) =CH-			
					5.93 (s)	(2) OCH ₂ O			
					3.83 (s)	(3) NCH ₃			
XIIIe	(a) {	21,300	1590 (s)	C=O	11.60 (br.)	(1) NH (b)			
					30,430	1570 (s)	C=C	7.67-6.73 (m)	(8) ArH
								6.0 (s)	(2) OCH ₂ O
								5.67 (s)	(1) =CH-
								2.47 (s)	(6) -N(CH ₃) ₂

(a) Dimethyl-formamide-water (60:40 w/w). (b) Exchanged with deuterium oxide.

Table VI
 ω -Aroylaceto-phenone-*N*-acyl and *N*-aroylhydrazones (IVa-q)

Compound No.	Yield (%)	M.p., °C	Formula	C	H	Calcd. %	N	Cl	OCH ₃	C	H	Found %	N	Cl	OCH ₃
IVa	87	105-106 (a)	C ₂₂ H ₁₈ N ₂ O ₂	77.17	5.30	8.18		--	--	76.99	5.40	8.32		--	--
IVb	85	135-136 (b)	C ₂₃ H ₂₀ N ₂ O ₂	77.51	5.66	7.86		--	--	77.36	5.79	8.02		--	--
IVc	85	123-124 (c)	C ₂₆ H ₂₀ N ₂ O ₂	79.57	5.14	7.14		--	--	79.32	5.26	7.23		--	--
IVd	78	165-166 (b)	C ₂₇ H ₂₂ N ₂ O ₂	79.78	5.46	6.89		--	--	79.63	5.51	6.77		--	--
IVe	90	160-161 (a)	C ₂₃ H ₂₀ N ₂ O ₂	77.51	5.66	7.86		--	--	77.61	5.72	8.01		--	--
IVf	91	166-167 (a)	C ₂₄ H ₂₂ N ₂ O ₂	77.81	5.99	7.56		--	--	77.89	6.02	7.81		--	--
IVg	88	140-141 (a)	C ₂₇ H ₂₂ N ₂ O ₂	79.78	5.46	6.89		--	--	79.67	5.39	7.11		--	--
IVh	80	113-114 (a)	C ₁₈ H ₂₄ N ₂ O ₂	79.98	5.75	6.66		--	--	80.13	5.90	6.51		--	--
IVi	78	173-174 (c)	C ₂₂ H ₁₇ ClN ₂ O ₂	70.12	4.55	7.43	9.41		--	70.44	4.87	7.65	9.68		--
IVj	81	153-154 (c)	C ₂₃ H ₁₉ ClN ₂ O ₂	70.68	4.90	7.17	9.07		--	70.62	5.02	7.30	8.95		--
IVk	79	197-198 (b)	C ₂₆ H ₁₉ ClN ₂ O ₂	73.15	4.49	6.56	8.30		--	72.97	4.60	6.46	8.44		--
IVl	75	160-161 (a)	C ₂₇ H ₂₁ ClN ₂ O ₂	73.54	4.80	6.35	8.04		--	73.55	4.90	6.37	8.49		--
IVm	65	142-143 (a)	C ₂₄ H ₂₀ N ₂ O ₄	71.99	5.04	7.00		--	--	71.87	5.11	6.99		--	--
IVn	68	248-249 (a)	C ₂₈ H ₂₂ N ₂ O ₄	74.65	4.92	6.22		--	--	74.61	5.13	6.46		--	--
IVo	72	137-138 (a)	C ₂₃ H ₂₀ N ₂ O ₃	74.18	5.41	7.52		--	8.33	74.30	5.45	7.58		--	8.14
IVp	80	129-130 (c)	C ₂₄ H ₂₂ N ₂ O ₃	74.59	5.74	7.25		--	8.03	74.72	5.94	7.68		--	8.21
IVq	81	133-134 (c)	C ₂₈ H ₂₄ N ₂ O ₃	77.08	5.54	6.42		--	7.11	76.80	5.32	6.51		--	7.29

(a) Crystallized from benzene-cyclohexane. (b) Crystallized from benzene. (c) Crystallized from cyclohexane.

their nmr spectra show signals in the ranges δ 6.60-6.50 (s, 1, -NH=) and δ 3.87-3.53 (s, 3, NCH₃). The identity of their electronic spectra reflects their structural analogy, and show good resemblance to the spectra of substituted pyrazoles (9).

The reaction of the above acetylenic ketones (Ia-e) with 1,1-dimethylhydrazine in boiling ethanol was reported to produce the corresponding 1,1-dimethyl-2- β -(α -aroyl-styryl) hydrazines (XIIa-e) (cf. Scheme 3) (10). However, when the latter compounds were heated with acetic anhydride, they gave the corresponding 5-aryl-1-methyl-3-phenylpyrazoles (XIIa-e) (4); i.e., a methyl group was eliminated. The reaction appears to proceed by the intermediate formation of a six-membered cyclic transition state with the elimination of methyl acetate (cf. Scheme 3). The presence of the latter compound in the reaction mixture was established by El-Rayyes and Al-Hajjar (4). It is noteworthy to mention that the methylation of the pyrazole derivatives (Va-e) with dimethyl sulfate and anhydrous potassium carbonate in acetone afforded 5-aryl-1-methyl-3-phenylpyrazoles (XIIa-e) and not 3-aryl-1-methyl-5-phenylpyrazole (cf. Scheme 3) as in the case of 3(5)-*p*-nitrophenyl-5(3)phenylpyrazole (V; Ar = *p*-NO₂·C₆H₄) (4). The abnormal behaviour of the latter compound may be attributed to the strong electron-attracting effect of the *p*-nitrophenyl group, which decreases the nucleophilicity of the neighbouring nitrogen atom.

EXPERIMENTAL

Melting points are uncorrected. Electronic and infrared spectra were measured on Pye-Unicam SP 8000 and SP 700, and SP 1000 and Beckman IR 12 spectrophotometers, respectively. Nmr spectra were run on Varian T 60 A, using TMS as the internal standard. The purity of the analytical samples was checked by tlc (silica gel). Microanalyses were determined by Alfred Bernhardt, West Germany.

1,2-Diacyl- and diaroylhydrazines (IX).

The acyl or aroyl chloride (0.01 mole) was added dropwise to a stirred solution of acyl- or aroylhydrazine (II) (0.01 mole) (prepared by stirring the corresponding ester with hydrazine hydrate on a boiling water bath for one hour) in pyridine (50 ml.) at room temperature, and kept for one hour. The reaction mixture was diluted with water and filtered off. The colorless solids were crystallized from pyridine-water to give the corresponding 1,2-diacyl- or diaroylhydrazines (IX) as colorless leaflets.

1,2-Dibenzoylhydrazine (IXa).

This compound had m.p. 234-235° (12), yield = 98%.

Anal. Calcd. for C₁₄H₁₂N₂O₂: C, 69.99; H, 5.04; N, 11.66. Found: C, 69.90; H, 5.15; N, 11.59.

1,2-Di(phenylacetyl)hydrazine (IXb).

This compound had m.p. 243-244° (13), yield = 92%.

Anal. Calcd. for C₁₆H₁₆N₂O₂: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.65; H, 6.10; N, 10.41.

1,2-Di(α -naphthoyl)hydrazine (IXc).

This compound had m.p. 265-266° (14), yield = 88%.

Anal. Calcd. for C₂₂H₁₆N₂O₂: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.33; H, 4.75; N, 7.90.

1,2-Di(α -naphthylacetyl)hydrazine (IXd).

This compound had m.p. 292-293°, yield = 72%.

Anal. Calcd. for C₂₄H₂₀N₂O₂: C, 78.24; H, 5.47; N, 7.60. Found: C, 77.97; H, 5.53; N, 7.47.

Reaction of Aroylphenylacetylenes (I) with Acyl- or aroylhydrazines (II).

A mixture of the pure and freshly prepared aroylphenylacetylene (Ia-e) (0.01 mole) (3) and acyl- or aroylhydrazine (IIa-d) (0.01 mole) was refluxed in ethanol (50 ml.) for 5 hours. The reaction mixture was concentrated, and the product precipitated on cooling was crystallized from a suitable solvent to give the corresponding *w*-aroylaceto-phenone-*N*-acyl- or *N*-aroylhydrazones (IV). The results are reported in Table VI.

When the reaction of acyl- or aroylhydrazines (IIa-d) with the acetylenic ketones (Ib or Id) was repeated under the above mentioned conditions in ethanol containing 2 drops of concentrated sulfuric acid, it gave a mixture of the corresponding hydrazone (IV) (yield = 70-75%), 1,2-diacyl- or diaroylhydrazines (IX) (yield = 10-15%) and the corresponding pyrazole (V) (yield = 5-8%). The components of the mixture were separated from the mixture by heating with benzene and filtering off the insoluble hydrazine derivative (IX). The compounds remaining in the mother liquor were isolated by tlc plates using benzene-cyclohexane (1:2) as eluent. The same products were also obtained when the reaction medium was either a mixture of ethanol-anisole (50% v/v) or ethanol-*N,N*-dimethylaniline (50% v/v).

Action of Acetic Anhydride and Sodium Acetate on ω -Aroylaceto-phenone-*N*-acyl- and *N*-aroylhydrazones (IVa-q).

A mixture of the hydrazone derivative (IV) (1.0 g.), anhydrous sodium acetate (0.2 g.) and acetic anhydride (5 ml.) was heated in an oil-bath at 125-130° for one hour. The cold reaction mixture was worked up as previously mentioned (4) to give the corresponding *N*-acetylpyrazole derivative (VII and/or VIII) (cf. Table VII). IVa-d and IVe-h gave a single acetyl derivative (VII or VIII) (a and b, respectively), whereas the remaining hydrazone derivatives (IVi-g) gave a mixture of the corresponding *N*-acetyl derivatives (VII and VIII) (tlc). Similar results were obtained by acetylating 3(5)-aryl-5(3)-phenylpyrazoles (V) (3) with acetic anhydride.

Action of Alcoholic Potassium Hydroxide on ω -Aroylaceto-phenone-*N*-acyl or *N*-aroylhydrazones (IVa-q).

The hydrazone derivatives (IVa-q) (0.01 mole) were refluxed on a boiling water-bath with 3% methanolic potassium hydroxide (20 ml.) for 30 minutes. The reaction mixture was worked up as previously reported (3) to give 3(5)-aryl-5(3)-phenylpyrazoles (Va-e) in 90-95% yield, identified by m.p. and mixed m.p. (3). The mother liquor obtained from the alkaline solution of V was acidified with dilute sulfuric acid to give the corresponding acid (VI), identified by m.p. and mixed m.p.

The reaction of concentrated sulfuric acid on IVi at room temperature, however, gave a mixture of benzoic acid (20% yield) and 3(5)-*p*-chlorophenyl-5(3)-phenylpyrazole (Vc) (yield = 80%), separated by sodium hydrogen carbonate solution.

5-Aryl-1-methyl-3-phenylpyrazoles (XIIa-e).

These were prepared by the following two methods.

(i) A mixture of the acetylenic ketone (I) (1.0 g.) and methylhydrazine (3 ml.) was left for 5 minutes at room temperature. The reaction mixture was diluted with water and filtered off. The colorless solid was crystallized from *n*-hexane to give the corre-

Table VII

Acetylpyrazole Derivatives VII and/or VIII

Compound No.	Yield (%)	M.p., °C	Formula	Calcd. %				Found % (b)			
				C	H	N	COCH ₃	C	H	N	COCH ₃
VIIa	83	87-88	C ₁₇ H ₁₄ N ₂ O	77.84	5.39	10.69	16.41	77.76	5.42	10.82	16.05
VIIb or VIIIb	85	90-91	C ₁₈ H ₁₆ N ₂ O	78.24	5.84	10.14	15.58	77.92	5.87	10.24	15.16
VIIc and VIIIc	82	81-82	C ₁₇ H ₁₃ ClN ₂ O	68.81	4.42	9.44	14.51	68.91	4.27	9.11	14.01
VIIId and VIIIId	77	111-112	C ₁₈ H ₁₄ N ₂ O ₃	70.58	4.61	9.15	14.05	70.31	4.71	9.25	14.46
VIIe and VIIIE	88	99-100	C ₁₈ H ₁₆ N ₂ O ₂	73.92	5.51	9.58	14.72	73.83	5.35	9.70	15.01

(a) Crystallized from light petroleum (60-80°). (b) These were analyzed as the purified mixture of the two acetyl pyrazole derivatives.

Table VIII

5-Aryl-1-methyl-3-phenylpyrazoles (XIIa-e)

Compound No.	Yield (%)	M.p., °C(a)	Formula	Calcd. %			Found %		
				C	H	N	C	H	N
XIIa	97	60-61 (15)	C ₁₆ H ₁₄ N ₂	82.02	6.02	11.96	82.03	6.00	12.04
XIIb	96	139-140	C ₁₇ H ₁₆ N ₂	82.22	6.50	11.28	82.14	6.52	11.33
XIIc	96	129-130	C ₁₆ H ₁₃ ClN ₂	71.51	4.88	10.42	71.61	4.92	10.51
XIIId	98	94-95	C ₁₇ H ₁₆ N ₂ O	77.25	6.10	10.66	77.34	6.18	10.73
XIIe	95	112-113	C ₁₇ H ₁₄ N ₂ O ₂	73.37	5.07	10.07	73.32	5.02	10.17

sponding 5-aryl-1-methyl-3-phenylpyrazole (XIIa-e) as colorless crystals.

(ii) A mixture of dimethyl sulfate (8.0 ml.), anhydrous potassium carbonate (16.0 g.) and 3(5)-aryl-5(3)-phenylpyrazole (Va-e) (1.0 g.) in dry acetone (60 ml.) was refluxed on a boiling water-bath for 12 hours, cooled and filtered. The solids separated after evaporation of the acetone were crystallized from *n*-hexane to give the corresponding 5-aryl-1-methyl-3-phenylpyrazoles (XIIa-e), identical with those prepared by the first method. The results are reported in Table VIII.

An authentic sample of XIIc was prepared by the reaction of the dibromide of *p*-chlorobenzalacetophenone with methylhydrazine (8). 1,1-Dimethyl-2-β-[α-3,4-methylenedioxybenzoyl]hydrazine (XIIIe).

This compound was prepared as reported in reference (10), crystallized from cyclohexane and had m.p. 117-118°, yield = 77%.

Anal. Calcd. for C₁₈H₁₈N₂O₃: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.89; H, 5.80; N, 9.14.

Action of Acetic Anhydride on the Hydrazine Derivatives (XIIIa-e).

General Procedure.

The mixture of the hydrazine derivative (XIIIa-e) (10) (1.0 g.) and acetic anhydride (3 ml.) was heated in an oil-bath at 130-135° for 2 hours. The cold reaction mixture was worked up as previously reported (10) to give the corresponding 5-aryl-1-methyl-3-phenylpyrazole (XII) in 87-92% yield, identified by m.p. and mixed m.p.

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