***3-Bromo-4,4-dimethoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8,11-diyl Bismesylate* (14).** To a solution of diol **11** (1.0 g, 3.1 mmol) in dry methylene chloride (100 mL) containing 1.27 g (12.6 mmol) of triethylamine at 0 to −10 °C was added to 1.5 g (7.9 mmol) of methanesulfonyl chloride over a period of 10 min. The solution was stirred for 2 h. The mixture was first extracted with ice water, followed by cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. The methylene chloride solution was dried (Na_2SO_4) and the solvent removed in vacuo to give the crude product as a yellowish oil which crystallized from ethyl ether to give colorless needles of the dimesylate **14** (1.1 g, 70%): mp 131–132 °C; NMR ($CDCl_3$) δ 5.20 (m, 1 H), 4.80 (m, 1 H), 3.57 (s, 3 H, OCH_3), 3.45 (s, 3 H, OH), 3.0–3.3 (m, 6 H, overlaps with the singlet at 3.10), 3.10 (s, 6 H, SO_2CH_3), 2.40 (m, 1 H); mass spectrum, *m/e* (relative intensity) 472 (4.1), 474 (4.5) (molecular ion), 393 (3), 377 (2), 201 (27), 115 (11), 85 (33), 83 (38), 57 (29), 45 (100).

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Supplementary Material Available: Elemental analyses (C, H, N) for the compounds **3–11**, **13**, and **14** (1 page). Ordering information is given on any current masthead page.

Acetylenic Ketones. 8. Synthesis and Spectroscopic Studies of Some Hydrazones

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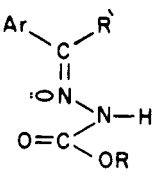
Aroylphenylacetylenes, benzaldehydes, and acetophenones reacted with ethyl and phenyl hydrazinecarboxylates to give the corresponding hydrazone *N*-carboxylic esters of ω-aroylacetophenone (IIIa–f), benzaldehyde (IXa–f), and acetophenone (IXg–l). UV, IR, and NMR spectra of these compounds are presented.

The reaction of some aroylphenylacetylenes with ethyl and phenyl hydrazinecarboxylates has been reported (*1*, *2*). The present work was intended to study the spectral and chemical properties of compounds III and IX in order to establish their structure and configuration. Thus, when phenyl- (Ia), *p*-(chlorophenyl)- (Ib), and *p*-(methoxyphenyl)benzoylacetylenes (Ic) were refluxed with an alcoholic solution of ethyl and phenyl hydrazinecarboxylates, they gave ω-benzoylacetophenone *N*-(ethoxycarbonyl)- (IIIa–c) and *N*-(phenoxycarbonyl)-hydrazone derivatives (IIId–f), respectively (cf. Figure 1). The structures of the products were established chemically and spectroscopically.

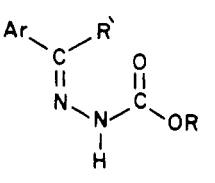
***Chemical Evidence*.** Compounds IIIa–f were easily cyclized by refluxing with acetic anhydride to the corresponding 5-phenyl-1-(ethoxycarbonyl)- (Va–c) and -1-(phenoxycarbonyl)pyrazoles (Vd–f). The structures of the latter compounds were rigidly established by the fact that, when refluxed with 3% methanolic potassium hydroxide, they gave the corresponding 5(3)-aryl-3(5)-phenylpyrazoles (VI), identical with authentic samples prepared by reacting the acetylenic ketones I with hydrazine hydrate. Pyrazoles VI were also directly obtained from hydrazones III by refluxing with 3% methanolic potassium hydroxide. The IR spectra of pyrazoles V show a strong absorption band in the region 1780–1716 cm^{-1} ($\nu_{C=O}$) (*1*, *2*), and their NMR spectra gave a sharp signal in the range δ 6.80–6.69 (cf. Table I) attributable to the olefinic proton. Acetylation of pyrazoles VI by heating with acetic anhydride gave an inseparable mixture (A and B) of acetylpyrazoles VII (cf. Figure 1) (detected by TLC and NMR spectra) (*1*).

***Spectroscopic Evidence*.** The IR and NMR spectra of IIIb,c,e,f are identical with those reported previously (*1*, *2*). Thus, their IR spectra (cf. Table II) show a sharp band in the region 3400–3380 cm^{-1} (ν_{NH}) and a strong band in the region 1722–1690 cm^{-1} with a shoulder at 1715–1680 cm^{-1}. This indicates that these compounds contain two different carbonyl groups and have either structure III, IVA, or IVB (cf. Figure 1). However, the fact that the mass spectrum of IIIa showed a base peak at *m/e* 105, $[C_6H_5CO]^+$, and that the electronic spectra of IIIa–f were similar to those of IX support structure III rather than IVA or IVB. Their NMR spectra (cf. Table II) (*3*) show a broad signal in the region δ 4.57–4.53 (NH) and a quartet (2 H), representing an AB system. The fact that these methylene protons behave as an AB system can be tentatively interpreted by assuming that III exists in solution as the ring tautomer IVB which possesses a chiral carbon atom.

The condensation of benzaldehydes VIIIa,b and acetophenones VIIIc,d with ethyl and phenyl hydrazinecarboxylates II led to the formation of benzaldehyde and acetophenone (*N*-phenoxycarbonyl)hydrazones IXa–h (cf. Figure 2). Their structures were established from their spectral data. The IR spectra (KBr) of compounds IXa–h (cf. Table III) show a broad band at 3300–3195 cm^{-1} (ν_{NH}) and two strong bands in the regions 1748–1710 and 1720–1690 cm^{-1} ($\nu_{C=O}$). Their NMR spectra and TLC, however, indicated that these compounds are pure and are not mixtures of two geometrical isomers. Accordingly, the two bands in the carbonyl region may be attributed to the presence of these compounds as a mixture of the two conformers IX, A and B. The higher stretching frequency



(IXA)



(IXB)

0021-9568/82/1727-0213$01.25/0

Table I. UV, IR, and NMR Spectral Data of 1-(Ethoxycarbonyl)-5-phenyl-3-arylpyrazoles Vb,c and 5-Phenyl-1-(phenoxycarbonyl)-3-arylpyrazoles Ve,f

	electronic spectra (ethanol)		infrared spectra (KBr)		NMR ($CDCl_3$)	
compd	λ_{max}, nm	ϵ	cm^{-1}	υ	δ	assignment (no. of protons)
Vb	265	29 200	1780	C=O	7.25–8.10 (m)	ArH (9)
	~242–237[a]	24 105			6.72 (s)	=CH– (1)
					4.38 (q)	OCH_2CH_3 (2)
					1.28 (t)	OCH_2CH_3 (3)
Vc	269	32 210	1775	C=O	7.10–8.20 (m)	ArH (9)
					6.69 (s)	=CH– (1)
					4.45 (q)	OCH_2CH_3 (2)
					3.91 (s)	OCH_3 (3)
					1.30 (t)	OCH_2CH_3 (3)
Ve	269	26 630	1761	C=O	6.81–8.31 (m)	ArH (14)
	~250–235[a]	21 700			6.80 (s)	=CH– (1)
Vf	272	34 200	1765	C=O	7.11–8.13 (m)	ArH (14)
	~240–235[a]	28 700			6.78 (s)	=CH– (1)
					3.87 (s)	OCH_3 (3)

[a] Shoulder.

Table II. NMR ($CDCl_3$) and IR (KBr) Spectral Data of ω-Aroylacetophenone *N*-(Ethoxycarbonyl)- and *N*-(Phenoxycarbonyl)hydrazones

				υ_A (calcd),	υ_B (calcd),	$\Delta\upsilon$ (calcd),	rel line intensities				IR spectra	
compd	δ	assignments (no. of protons)	J, Hz	Hz	Hz	Hz	calcd	found	$\Delta\upsilon$, J	compd	cm^{-1}	υ
IIIb	7.83–7.27 (m)	ArH (9)								IIIa	3380 (br)	NH
	4.57 (br)	–NH (1)									1696 (s)	C=O
	4.30 (q)	$-CH_2-CH_3$ (2)	7.0								1680 (sh)	
	3.9 (s)	H									1600 (m)	C=N
	3.59 (s)	–C– (3.53 s)[a] (2)	18.0	221.6	201.6	19.90	0.182	0.182	1.11	IIIb	3380 (br)	NH
	3.45 (s)										1690 (s)	C=O
	3.15 (s)	H									1680 (sh)	
	1.27 (t)	$-C_2-CH_3$ (3)	7.0								1610 (s)	C=N
IIIc	7.73–6.80 (m)	ArH (9)								IIIc	3400 (br)	NH
	4.57 (br)	–NH (1)									1718 (s)	C=O
	4.23 (q)	$-CH_2-CH_3$ (2)									1695 (sh)	
	3.80 (s)	$Ar-OCH_3$ (3)									1600 (s)	C=N
	3.87 (s)	H								IIId	3380 (br)	NH
	3.57 (s)	–C– (3.47 s)[a] (2)	18.0	219.6	200.6	19.0	0.182	0.20	1.06		1722 (s)	C=O
	3.43 (s)										1715 (sh)	
	3.13 (s)	H									1610 (m)	C=N
	1.23 (t)	$-CH_2-CH_3$ (3)										
IIIe	7.87–6.96 (m)	ArH (9)										
	4.53 (br)	–NH (1)										
	3.97 (s)	H										
	3.65 (s)	–C– (3.675)[a] (2)	19.0	224	205.5	18.5	0.177	0.20	0.97			
	3.52 (s)											
	3.2 (s)	H										
IIIf	7.8–6.83 (m)	ArH (9)										
	4.53 (br)	NH (1)										
	3.83 (s)	$ArOCH_3$ (3)										
	3.95 (s)	H										
	3.67 (s)	–C– (3.57 s)[a] (2)	18.0	223.99	205.01	18.98	0.177	0.20	1.08			
	3.53 (s)											
	3.20 (s)	H										

[a] In deuteriodimethyl sulfoxide.

stands for conformer IXA and the lower one for the conformer IXB. The higher $\nu_{C=O}$ of conformer IXA is attributed to the electrostatic repulsion between the p orbital of the n electrons of nitrogen and the readily polarizable, negatively charged oxygen of the carbonyl group. This will result in a mutual induction of opposite charge and a decrease in the negative character of the oxygen atom; i.e., the >C=O becomes less polar and accordingly its vibrational frequency will rise (*4*).

The NMR spectra of these compounds (IXa–h) (cf. Table III) show a broad signal (1 H) in the region δ 8.80–7.77, which is attributed to the NH group (exchanged with D_2O). The spectra of the benzaldehyde derivatives (IXa–d) also show a sharp signal at δ 8.07–7.77 (—N=CH proton), whereas those of the acetophenone derivatives (IXe–h) show a sharp signal at δ 2.33–2.17 (—N=C—CH_3 protons).

The UV spectra of benzaldehyde hydrazone carboxylic esters IXa–d show maxima at 287–278 nm; however, the corresponding acetophenone hydrazones IXe–h gave absorption bands at 279–269 nm (cf. Table IV). This band is due to the $\pi-\pi^*$ transition band (*5*). These results indicated that the benzaldehyde hydrazone absorbed at higher wavelength than the corresponding acetophenone hydrazone, which is attributed to steric interaction between the methyl and the hydrazine moiety.

It is noteworthy to mention that the reaction of acetophenone derivatives VIII with phenyl hydrazinecarboxylate gives, in addition to IXg,h, the hydrazine derivatives Xg,h. The structures of the latter compounds were established chemically and spectroscopically. Thus, compound Xg was found to be identical with an authentic sample prepared by heating aceto-

Table III. NMR and IR Spectral Data of Hydrazone *N*-Carboxylic Esters IXb,c,e,f,h,i,k,l and the Hydrazine Derivatives Xk,l

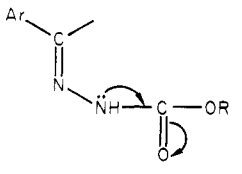
	NMR ($CDCl_3$)		IR spectra (KBr)	
compd	δ	assignments (no. of protons)	cm^{-1}	υ
IXb	8.80 (s)	–NH (1)	3210 (br)	NH
	7.80 (s)	–CH=N– (1)	1733 (m)	C=O
	7.63–7.17 (m)	ArH (4)	1710 (s)	
	4.20 (q)	$-CH_2-CH_3$ (J = 7Hz) (2)		
	1.26 (t)	$-CH_2-CH_3$ (J = 7Hz) (3)		
IXc	8.57 (s)	–NH (1)	3278 (s)	NH
	7.77 (s)	–CH=N– (1)	1710 (s)	C=O
	7.60 (s)		1690 (sh)	
	7.40 (s)	ArH (1)	1610 (s)	C=N
	6.83 (s)			
	6.70 (s)			
	4.20 (q)	$-CH_2-CH_3$ (J = 7Hz) (2)		
	3.67 (s)	$ArOCH_3$		
	1.27 (s)	$-CH_2-CH_3$ (J = 7Hz) (3)		
IXe	10.77 (br)	–NH (1)	3195 (br)	NH
	8.07 (s)	–CH=N– (1)	1737 (s)	C=O
	7.80–7.0 (m)	ArH (9)	1712 (s)	
			1593 (m)	C=N
IXf	8.56 (s)	–NH (1)	3300 (br)	NH
	7.83 (s)	–CH=N– (1)	1725 (s)	C=O
	7.63 (s)	ortho hydrogen (1)	1710 (sh)	
	7.52 (s)		1605 (s)	C=N
	7.50 (s)	C_6H_5 (5)		
	6.92 (s)	meta hydrogen (1)		
	6.78 (s)			
	3.73 (s)	$-OCH_3$ (3)		
IXh	8.03 (br)	–NH (1)	3240 (br)	NH
	7.9–7.6 (m)	ArH (4)	1738 (s)	C=O
	4.37 (q)	$-CH_2CH_3$ (J = 7Hz) (2)	1702 (s)	
	2.18 (s)	$-N=C-CH_3$ (3)	1610 (m)	C=N
	1.35 (t)	$-CH_2CH_3$ (J = 7Hz) (3)		
IXi	7.77 (br)	NH (1)	3218 (br)	NH
	7.80–6.8 (m)	ArH (4)	1736 (s)	C=O
	4.30 (q)	$-CH_2CH_3$ (J = 7Hz) (2)	1708 (s)	
	3.80 (s)	$-OCH_3$ (3)	1615 (s)	C=N
	2.17 (s)	$-N=C-CH_3$ (3)		
	1.35 (t)	$-CH_2-CH_3$ (J = 7Hz) (3)		
IXk	7.90 (br)	–NH (1)	3200 (br)	NH
	7.67–6.93	ArH (9)	1745 (s)	C=O
	2.17 (s)	$-N=C-CH_3$ (3)	1720 (s)	
IXl	7.87 (br)	–NH (1)	3200 (br)	NH
	7.73–6.67 (m)	ArH (9)	1748 (s)	C=O
	3.67 (s)	$-OCH_3$ (3)	1720 (s)	
	2.13 (s)	$-N=C-CH_3$ (3)		
Xk	8.60 (br)	–NH (1)	3318 (s)	NH
	8.07–7.47 (m)	ArH (9)	3255 (br)	
			1747 (s)	C=O
	2.28 (s)	$-N=C-CH_3$ (3)	1675 (s)	
Xl	8.50 (br)	–NH (1)	3315 (s)	NH
	7.92–6.95 (m)	ArH (9)	3250 (br)	
	3.87 (s)	$ArOCH_3$ (3)	1743 (s)	C=O
	2.22 (s)	$-N=C-CH_3$ (3)	1680 (s)	

Table IV. UV Spectral Data of Benzaldehyde (IXb,c,e,f) and Acetophenone (IXh,i,k,l) Hydrazone Carboxylic Esters and the Hydrazine Derivatives (Xk,l)

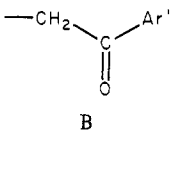
compd	λ_{max}, nm	ϵ	compd	λ_{max}, nm	ϵ
IXb	304–302 (sh)	12 570	IXf	287	25 410
	284	25 570		225	11 190
	226	5 550	IXh	275	24 480
IXc	310–305 (sh)	13 030		~227–222 (sh)	13 090
	286	25 770	IXi	278	22 940
	221	27 360	IXk	275	19 460
IXe	304–301 (sh)	11 330	IXl	274	24 310
	283	22 670	Xk	278	27 665
	226	5 470	Xl	279	28 430

phenone (*N*-phenoxycarbonyl)hydrazone (IXg) with phenyl hydrazinecarboxylate. The spectral data of hydrazine derivatives Xg,h are reported in Table III.

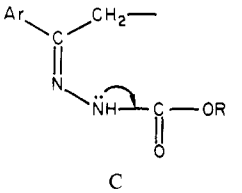
The UV spectra of the hydrazone derivatives IIIa–f are identical (cf. Table V) and are practically not affected by the type of substituent in the aroyl group, and the observed red shift is caused by the auxochromic substituents in the phenyl group. This indicated that their absorption is attributed to perturbation in the chromophore A or C and not in the chromophore B or



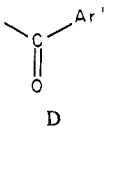
A



B



C



D

Table V. UV Spectral Data of the Hydrazone Carboxylic Esters of ω-Aroylacetophenones IIIa–f, Benzaldehydes IXa–f, and Acetophenones IXg–l in Ethanol

compd	λ_{max}, nm	ε	compd	λ_{max}, nm	ε	compd	λ_{max}, nm	ε
IIIa	279	23 300	IXb	~304–302 (sh)	12 570	IXf	287	25 410
	~226–223 (sh)[a]	12 760		284	25 570		225	11 190
IIIb	285	28 370		226	5 550	IXg	269	16 590
	228	11 640	IXc	~310–305 (sh)	13 030		217	14 910
	225	11 640		286	25 770	IXh	275	24 480
IIIc	287	27 150		221	27 360		~227–222 (sh)	13 090
	227.5	5 380	IXd	~299–297 (sh)	10 680	IXi	278	22 940
IIId	279	23 110		279	21 600	IXj	269	22 340
	~227–223 (sh)	14 300		218	18 200	IXk	275	19 460
IIIe	283	24 150	IXe	~304–301 (sh)	11 330	IXl	274	24 310
IIIf	288	26 880		283	22 670			
IXa	~299–296 (sh)	10 420		226	5 470			
	279	21 250						
	~225–221 (sh)	11 390						

[a] sh = shoulder.

Table VI. Results for the Compounds IIIb,c,e,f, Vb,c,e,f, IXb,c,e,f,h,i,k,l, and Xk,l[a]

compd	mp, °C	yield, %	formula[b]	compd	mp, °C	yield, %	formula[b]
IIIb	174–175	92	$C_{18}H_{17}ClN_2O_3$	IXc	110–111	97	$C_{11}H_{14}N_2O_3$
IIIc	160–161	87	$C_{19}H_{20}N_2O_4$	IXe	211–212	83	$C_{14}H_{11}ClN_2O_2$
IIIe	163–164	87	$C_{22}H_{17}ClN_2O_3$	IXf	180–181	87	$C_{15}H_{14}N_2O_3$
IIIf	131–132	82	$C_{23}H_{20}N_2O_4$	IXh	143–144	94	$C_{11}H_{13}ClN_2O_2$
Vb	128–129	78	$C_{18}H_{15}ClN_2O_2$	IXi	132–133	93	$C_{12}H_{16}N_2O_3$
Vc	136–137	79	$C_{19}H_{18}N_2O_3$	IXk	160–161	62	$C_{15}H_{13}ClN_2O_3$
Ve	158–159	82	$C_{22}H_{15}ClN_2O_2$	IXl	152–153	52	$C_{16}H_{16}N_2O_3$
Vf	165–166	72	$C_{23}H_{18}N_2O_3$	Xk	220–221	88	$C_{16}H_{15}ClN_4O_3$
IXb	150–151	95	$C_{10}H_{11}ClN_2O_2$	Xl	214–215	90	$C_{17}H_{18}N_4O_4$

[a] Elemental analyses (C, H, N, Cl) agree well with theoretical values. [b] Compounds IIIb,e and Vb,c,e,f were crystallized from cyclohexane, IIIc,f and IXb,c,e,i,k from benzene–cyclohexane, and IXf–i from ethanol.

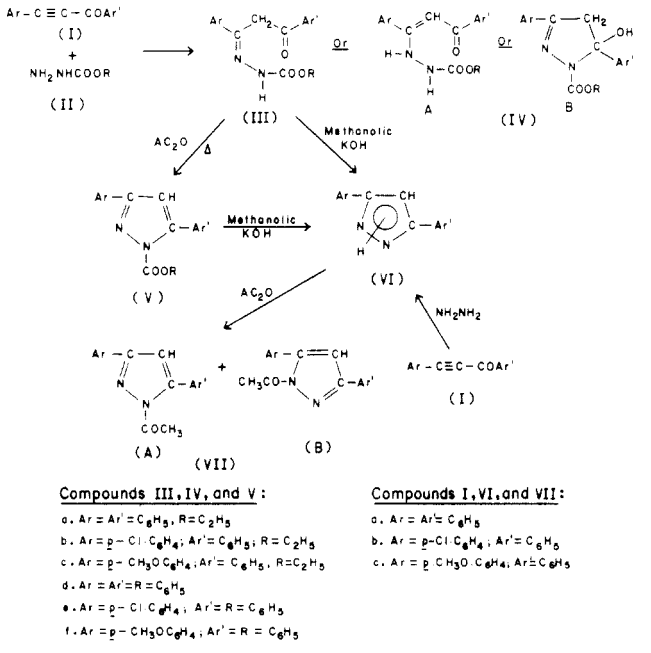


Figure 1. Reaction of aroylphenylacetylenes with hydrazine derivatives.

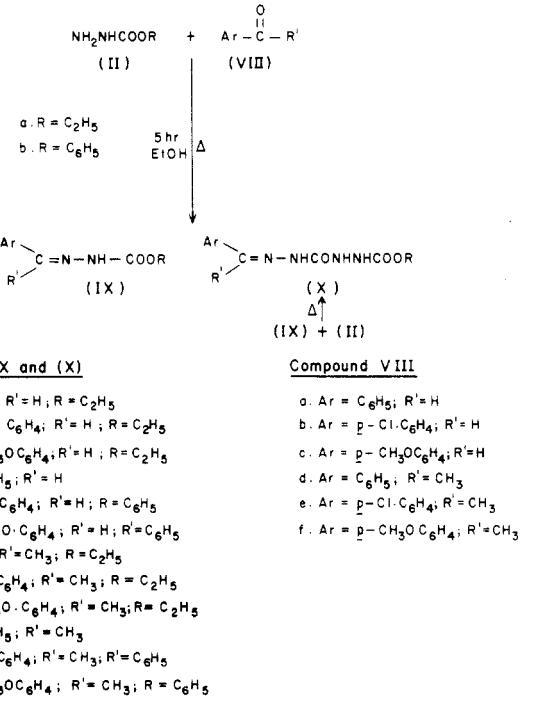


Figure 2. Reaction of benzaldehyde and acetophenone derivatives with hydrazinecarboxylates.

D. However, it appears that the absorption characteristics of these compounds are attributed to the chromophore A rather than C. This conclusion was inferred from the fact that the UV spectra of the ω-benzoylacetophenone hydrazone carboxylic esters IIIa–f are very similar to those of the corresponding benzaldehyde hydrazone derivatives IXa–f but different from those of the corresponding acetophenone hydrazone derivatives IXg–l (cf. Table V).

Experimental Section

General Information. UV and IR spectra were measured on Pye-Unicam SP 8000, SP 700, and Cary 17 and on SP 1000

and Beckman IR 12 spectrophotometers, respectively. NMR spectra were run on Varian T 60 A using Me_4Si as internal standard (sweep width, 100 and 500 Hz). Microanalyses were determined by Alfred Bernhardt, West Germany.

Reaction of Acetylenic Ketones Ia,b, Benzaldehydes VIIIa,b, and Acetophenones VIIIc,d with Hydrazine Carboxylic Esters II. ω-Aroylacetophenone (IIIb,c), benzaldehyde (IXa-c), and acetophenone *N*-(ethoxycarbonyl)hydrazones (IXg-i) were obtained by refluxing ethyl hydrazinecarboxylate IIa (1 mol) with acetylenic ketones Ib,c (1 mol), benzaldehydes VIIIa-c (1 mol), and acetophenones VIIId-f in ethanol for 5 h. The reaction product was worked as previously reported (*1*, *2*). ω-Aroylacetophenone (IIIe,f) and benzaldehyde *N*-(phenoxycarbonyl)hydrazones (IXd-f) were similarly prepared by using the phenyl ester IIb instead of the ethyl ester of hydrazinecarboxylic acid. Under similar conditions, the acetophenones VIIIe,f reacted with phenyl hydrazinecarboxylate IIb to give the corresponding hydrazine derivatives Xk,l in 88-92% yield, and the results are reported in Table VI. However, when phenyl hydrazinecarboxylate IIb (1 mol) was refluxed with excess of the acetophenones VIIIe,f (5 mol) in ethanol for 5 h, the product was a mixture of the acetophenone *N*-(phenoxycarbonyl)hydrazones IXk,l and the hydrazine derivatives Xk,l in which the former were predominant. Compounds IX were separated from X by extraction with cyclohexane and recrystallization from the same solvent as colorless needles (cf. Table VI), whereas compounds X, which were insoluble in cyclohexane, were crystallized from methanol-chloroform as colorless needles. The purity of all compounds was established by TLC. Compound XI was found to be identical with an authentic sample prepared by heating a mixture of acetophenone *N*-(phenoxycarbonyl)hydrazone IXl (0.01 mol) and phenyl hydrazinecarboxylate (0.01 mol) in an oil bath at 150-160 °C for 90 min.

Heating of the hydrazone derivatives IIIb,c,e,f with acetic anhydride at 120-125 °C for 3 h afforded the corresponding pyrazole derivatives Va,b,c,e,f as colorless crystals (Table VI). When the hydrazone derivatives III or the pyrazoles V were refluxed with 3% methanolic potassium hydroxide for 30 min, they gave the corresponding 5(3)-aryl-3(5)-phenylpyrazole VI identified by melting point and mixed melting point with authentic samples prepared by allowing arylbenzoylacetylene to react with hydrazine hydrate at room temperature for 2-3 min. 3-(5)-*p*-(Chlorophenyl)-5(3)-phenylpyrazole VIa had mp 214-215 °C (*2*). 3(5)-*p*-(Methoxyphenyl)-5(3)-phenylpyrazole VIb had mp 168-169 °C (*2*). Acetylation of these pyrazoles with acetic anhydride gave a product which was proved by TLC to be a mixture of VIIA and VIIB.

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Reactions of Substituted Hydrazines with Glyoxal

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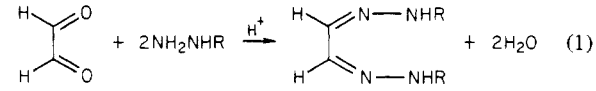
Substituted hydrazines have been reacted with glyoxal to yield bis(hydrazone) derivatives. Cyclized products were not observed. Thermal decomposition of the glyoxal adducts was investigated.

The reactions of amides and urethanes with glyoxal have been shown to yield interesting and unusual products (*1-4*). However, the reactions of glyoxal with hydrazine derivatives have received less attention. This reaction has now been studied with a variety of substituted hydrazines and found to give bis(hydrazones) as the major products.

Glyoxal derivatives, **1-14** (Table I), were generally prepared by reaction of an aqueous solution of glyoxal with 2 equiv of an alcoholic solution of a hydrazine derivative, in the presence of a trace of acid. The products precipitate from solution within hours as microcrystalline solids. With few exceptions (**11** and **12**), these compounds were very insoluble. The limited solubility made isolation of these compounds easy, but purification and further reactions were hindered by the difficulty in finding suitable solvents. Fortunately, as shown by elemental analyses, the compounds were usually of reasonable purity as isolated from the reaction mixtures. In order to maintain this purity, no attempts were made to maximize yield.

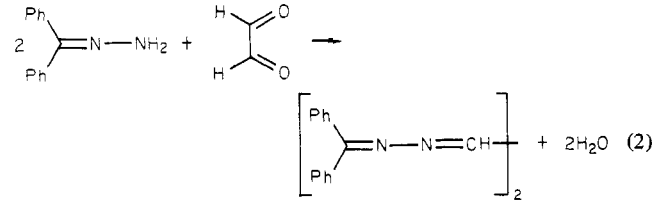
Many reaction pathways are available for the addition of hydrazine derivatives to glyoxal, and we were especially concerned about the formation of cyclic products or further reaction of the initially formed hydrazones with starting material. Proton NMR spectra of saturated solutions of the glyoxal adducts in Me_2SO-d_6 were very useful in determining structure. NMR spectra, along with IR spectra and elemental analyses, showed the compounds to be of structure I. Unusual addition products similar to those seen in the reaction of glyoxal with alcohols, amides, and urethanes were not formed. The glyoxal derivatives are simple 2:1 adducts formed by nucleophilic attack on the aldehyde followed by elimination of water (eq 1).



(1)

I

Compound **13** was prepared by the reaction of 2 equiv of benzophenone hydrazone with glyoxal (eq 2).



(2)

13

In addition to information obtained from spectra, the structural assignments of the bis(hydrazones) are supported by the synthesis of some of these adducts by alternative routes.

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