equalizing dropping funnel was placed 0.25 g (0.0066 mol) of lithium aluminum hydride stirred in anhydrous ether. A solution of 0.8 g (0.0043 mol) of **5** in 50 mL of anhydrous ether was added dropwise. The reaction was stirred at room temperature for 4 h, at which time 50 mL of wet ether followed by 25 mL of 10% HCl were added. The ether layer was separated and the aqueous layer was extracted with 50 mL of ether. The combined ether layers were dried over anhydrous magnesium sulfate and solvent was removed under reduced pressure. The resulting oily residue was recrystallized five times from hexane to give alcohol **6**: mp 39–40 °C; IR (neat) 3604 (s, free OH), 3505 (s, H-bonded OH), 830 (s), 815 (s), 810 (s) cm^{-1}.

(3S*,5R*)-5-Phenylnortricycl-3-yl Tosylate (4a) and (3S*,5R*)-5-(p-Nitrophenyl)nortricycl-3-yl Tosylate (4b). To a solution of 0.0085 mol of bromides **2a** and **2b** in 30 mL of acetonitrile held at reflux was added 0.0090 mol of silver *p*-toluenesulfonate dissolved in 50 mL of acetonitrile. An immediate turbidity and white flocculent precipitate was observed. Heating was continued for 30 min after which the mixture was cooled and filtered. Removal of solvent left a greenish oil which was crystallized from either methanol, **4a**, or carbon tetrachloride, **4b**. Tosylate **4a** had mp 108–109 °C and was obtained in 22% yield. IR (KBr) 1360 (s, asym S–O str), 1180 (s, sym S–O str), 820 (s), 814 (s), 805 (s) cm^{-1}.

Tosylate **4b** was isolated in 38% yield. The product melted over the range 138–145 °C, the melting point varying with the rate of heating. IR (KBr) 1510 (s, asym N–O str), 1330 (s, sym N–O str), 1355 (s, asym S–O str), 1160 (s, sym S–O str), 820 (s), 810 (s), 800 (s) cm^{-1}.

Treatment of active (−)-**2a** with silver tosylate gave **4a** of unspecified rotation. Hydrolysis of this tosylate in 70% aqueous dioxane at 100 °C for 3 h gave active (+)-**3a**.

(3S*,5R*)-3-Bromo-5-(p-aminophenyl)nortricyclane (2c). A solution of 11.2 g (0.038 mol) of nitrobromide **3b** in 300 mL of methanol was placed in a Parr hydrogenation bottle. A few milligrams of platinum dioxide was added and **3b** was reduced at an average pressure of 36 psi. After the theoretical amount of hydrogen was absorbed, the solution was treated with charcoal and the mixture was filtered. Solvent was removed under reduced pressure leaving a residue that was crystallized from ligroin giving 7.5 g (75%) of slightly off-white crystals, mp 86–87.5 °C. IR (KBr) 3400 (m, N–H str), 820 (s), 810 (s) cm^{-1}.

Amine **2c** was further purified by conversion to the hydrochloride salt and reconversion to the amine.

(3S*,5R*)-3-Bromo-5-(p-aminophenyl)nortricyclane Hydrochloride. Through a solution of 2.35 g (0.088 mol) of amine **2c** in 30 mL of anhydrous ether was passed hydrogen chloride formed by dropping concentrated H_2SO_4 onto ammonium chloride. Shortly after the addition of HCl began, a turbidity and white crystal formation was observed. HCl addition was continued for 15 min. A yield of 2.54 g (96%) of white crystals, mp 175–177 °C, was recovered.

3-Nortricyclyl Tosylate (10). The method of Hanack and Kaiser (*3*) was used to prepare 3-nortricyclyl tosylate, **8**, from 3-hydroxynortricyclane. A colorless oil was obtained which could be crystallized from hexane to give a 28% yield of product, mp 34–37 °C. These crystals slowly sublimed at 60 °C (2 Torr) to give white crystals, mp 42.5–43 °C (lit. (*3*) 41–43 °C). Tosylate **8** was also prepared by stirring 4.28 g (0.025 mol) of 3-bromonortricyclane in 10 mL of acetonitrile with 7.0 g (0.025 mol) of silver *p*-toluenesulfonate in 25 mL of acetonitrile. The mixture was stirred for 2 h, the precipitate of silver bromide was removed by filtration, and solvent was removed under reduced pressure. The residual oil was recrystallized from pentane to give 2.1 g (32%) of tosylate **10**.

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Synthesis and Spectral Properties of ω-Aroylacetophenone, Benzaldehyde, and Acetophenone Hydrazone Derivatives

Yousuf A. Al-Farkh, Farouk H. Al-Hajjar,* and Hayat S. Hamoud
Petroleum and Petrochemicals Division, Kuwait Institute for Scientific Research, Kuwait

The structures of ω-aroylacetophenone, benzaldehyde, and acetophenone *N*-(acyl- or benzoyl)hydrazones (IIIa–o, Va–i, and Vj–r, respectively) are supported by their NMR spectra, and the AB system, which appeared in the spectra of the former compounds, is discussed. The electronic spectra of ω-aroylacetophenone *N*-(acyl- or benzoyl)hydrazones (IIIa–o) are discussed in relation to those of the corresponding benzaldehyde *N*-(acyl- or benzoyl)hydrazones (Va–i).

In a previous publication (*1*), it was reported that the reaction of aroylphenylacetylenes (Ia–c) with the hydrazide derivatives (IIa–c) gave ω-aroylacetophenone *N*-(acyl- or benzoyl)hydrazones (IIIa–i).

In order to study the spectral properties of these compounds, six more derivatives, in which the phenyl group is substituted by a chlorine atom (IIIj–l) and a methoxy group (IIIm–o), were prepared (cf. Figure 1) as described previously (*1*).

The structure of the reaction products (IIIa–o) was identified on the basis of spectroscopic evidence based on IR, NMR, and UV spectra (Tables I and II). The IR spectra show a sharp band in the region 3460–3300 cm^{-1} (ν(NH)) and a strong band in the region 1640–1620 cm^{-1} (ν(C=O)). The NMR spectra, however, support structure III, since they show a broad signal in the region δ 5.47–5.00 (NH) and a quartet (2 H) representing an AB system (J = 18 Hz) (*2*). The fact that these methylene groups behave as an AB system can be interpreted as being due to either the large anisotropic effect of the C=N– and the nitrogen lone pair or the restriction of the rotation by the weak

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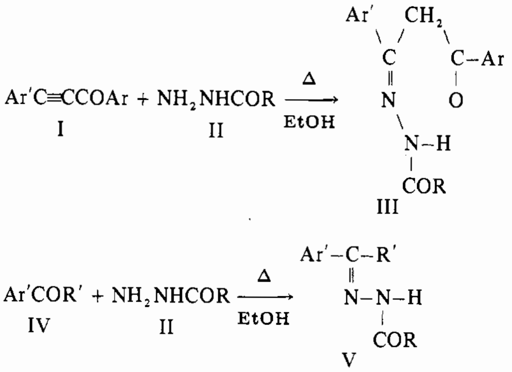


$$\underset{\text{I}}{Ar'C{\equiv}CCOAr} + \underset{\text{II}}{NH_2NHCOR} \xrightarrow[\text{EtOH}]{\Delta} \underset{\text{III}}{Ar'C(=N{-}NH{-}COR)CH_2{-}C({=}O){-}Ar}$$

$$\underset{\text{IV}}{Ar'COR'} + \underset{\text{II}}{NH_2NHCOR} \xrightarrow[\text{EtOH}]{\Delta} \underset{\text{V}}{Ar'{-}C(R'){=}N{-}N(H){-}COR}$$

I a, Ar = Ar′ = C_6H_5-
 b, Ar = p-ClC_6H_4, Ar′ = C_6H_5-
 c, Ar = p-$CH_3OC_6H_4$, Ar′ = C_6H_5-
 d, Ar = C_6H_5, Ar′ = p-ClC_6H_4-
 e, Ar = C_6H_5, Ar′ = p-$CH_3OC_6H_4$-
II a, R = C_6H_5-
 b, R = $C_6H_5CH_2$-
 c, R = α-$C_{10}H_7CH_2$-
III a, Ar = Ar′ = R = C_6H_5-
 b, Ar = Ar′ = C_6H_5-, R = $C_6H_5CH_2$-
 c, Ar = Ar′ = C_6H_5-, R = α-$C_{10}H_7CH_2$-
 d, Ar = p-ClC_6H_4, R = C_6H_5-, Ar′ = C_6H_5-
 e, Ar = p-ClC_6H_4, R = $C_6H_5CH_2$-, Ar′ = C_6H_5-
 f, Ar = p-ClC_6H_4-, R = α-$C_{10}H_7CH_2$-, Ar′ = C_6H_5-
 g, Ar = p-$CH_3OC_6H_4$-, R = C_6H_5-, Ar′ = C_6H_5-
 h, Ar = p-$CH_3OC_6H_4$-, R = $C_6H_5CH_2$-, Ar′ = C_6H_5-
 i, Ar = p-$CH_3OC_6H_4$-, R = α-$C_{10}H_7CH_2$-, Ar′ = C_6H_5-
 j, Ar′ = p-ClC_6H_4-, R = C_6H_5-, Ar = C_6H_5-
 k, Ar′ = p-ClC_6H_4-, R = $C_6H_5CH_2$-, Ar = C_6H_5-
 l, Ar′ = p-ClC_6H_4-, R = α-$C_{10}H_7CH_2$-, Ar = C_6H_5-
 m, Ar′ = p-$CH_3OC_6H_4$-, R = C_6H_5-, Ar = C_6H_5-
 n, Ar′ = p-$CH_3OC_6H_4$-, R = $C_6H_5CH_2$-, Ar = C_6H_5-
 o, Ar′ = p-$CH_3OC_6H_4$-, R = α-$C_{10}H_7CH_2$-, Ar = C_6H_5-
IV a, Ar′ = C_6H_5-, R′ = H-
 b, Ar′ = p-ClC_6H_4-, R′ = H-
 c, Ar′ = p-$CH_3OC_6H_4$-, R′ = H-
 d, Ar′ = C_6H_5-, R′ = CH_3-
 e, Ar′ = p-ClC_6H_4-, R′ = CH_3-
 f, Ar′ = p-$CH_3OC_6H_4$-, R′ = CH_3-
V a, Ar′ = R = C_6H_5-, R′ = H-
 b, Ar′ = C_6H_5-, R = $C_6H_5CH_2$-, R′ = H-
 c, Ar′ = C_6H_5-, R = α-$C_{10}H_7CH_2$-, R′ = H-
 d, Ar′ = p-ClC_6H_4-, R = C_6H_5-, R′ = H-
 e, Ar′ = p-ClC_6H_4-, R = $C_6H_5CH_2$-, R′ = H-
 f, Ar′ = p-ClC_6H_4-, R = α-$C_{10}H_7CH_2$-, R′ = H-
 g, Ar′ = p-$CH_3OC_6H_4$-, R = C_6H_5-, R′ = H-
 h, Ar′ = p-$CH_3OC_6H_4$-, R = $C_6H_5CH_2$-, R′ = H-
 i, Ar′ = p-$CH_3OC_6H_4$-, R = α-$C_{10}H_7CH_2$-, R′ = H-
 j, Ar′ = R = C_6H_5-, R′ = CH_3-
 k, Ar′ = C_6H_5-, R = $C_6H_5CH_2$-, R′ = CH_3-
 l, Ar′ = C_6H_5-, R = α-$C_{10}H_7CH_2$-, R′ = CH_3-
 m, Ar′ = p-ClC_6H_4-, R = C_6H_5-, R′ = CH_3-
 n, Ar′ = p-ClC_6H_4-, R = $C_6H_5CH_2$-, R′ = CH_3-
 o, Ar′ = p-ClC_6H_4-, R = α-$C_{10}H_7CH_2$-, R′ = CH_3-
 p, Ar′ = p-$CH_3OC_6H_4$-, R = C_6H_5-, R′ = CH_3-
 q, Ar′ = p-$CH_3OC_6H_4$-, R = $C_6H_5CH_2$-, R′ = CH_3-
 r, Ar′ = p-$CH_3OC_6H_4$-, R = α-$C_{10}H_7CH_2$-, R′ = CH_3-

Figure 1. Reactions of acetylenic ketones, aldehydes, and acetophenone derivatives with different hydrazides.

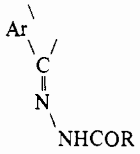
hydrogen bonding between the NH and the carbonyl of the aroyl group. The latter interpretation appears to be more plausible. This is because when the spectra of hydrazones IIIa–o were run in $(CD_3)_2SO$ instead of in $CDCl_3$ the quartet coalesced to a singlet in the region δ 3.57–3.38. It indicates that the appearance of the AB system should be attributed to the weak hydrogen bonding between the NH and CO group, which cleaved in highly polar solvents. The IR spectra of Va–s show a broad band at 3320–3180 cm^{-1} (ν(NH)) and a strong band in the region 1670–1630 cm^{-1} (ν(C=O)) (*3*). The NMR spectra of these compounds are reported in Tables III and IV.

Table I. UV and NMR Spectral Data of the ω-Aroylacetophenone *N*-(Acyl- or benzoyl)hydrazone Derivatives IIIa–i[a]

compd	UV bands (EtOH) λ_{max}, nm	log ϵ_{max}	NMR values, δ	assign
			in $CDCl_3$	
IIIa	287	4.39	7.83 m	ArH
			5.27 br	NH
			3.78 d 3.47 d	CH_2CO
IIIb	295–290 sh	4.35	7.63 m	ArH
	283	4.39	5.12 br	NH
			4.18 s	$NCOCH_2$
			3.73 d, 3.37 d	CH_2CO
IIIc	295–290 sh	4.46	7.88 m	ArH
	283	4.49	5.15 br	NH
			4.67 s	$NCOCH_2$
			3.77 d, 3.40 d	CH_2CO
IIId	292	4.36	7.78 m	ArH
			5.73 br	NH
			3.83 d, 3.47 d	CH_2CO
IIIe	295–290 sh	4.44	7.57 m	ArH
	283	4.45	5.07 br	NH
			4.28 d, 4.15 d (J = 14 Hz)	$NCOCH_2$
			3.70 d, 3.30 d	CH_2CO
			in Me_2SO	
			7.55 m	ArH
			4.03 s	$NCOCH_2$
			3.53 s	CH_2CO
IIIf	295–290 sh	4.45	7.78 m	ArH
	283	4.47	5.13 br	NH
			4.63 s	$NCOCH_3$
			3.74 d, 3.32 d	CH_2CO
IIIg	292	4.41	7.50 m	ArH
			5.40 br	NH
			3.37 s	$ArOCH_3$
			3.69 d, 3.38 d	CH_2CO
IIIh	294–289 sh	4.41	7.26 m	ArH
	283	4.43	4.98 br	NH
			4.08 s	$NCOCH_2$
			3.70 s	$ArOCH_3$
			3.63 d, 3.27 d	CH_2CO
IIIi	295–290 sh	4.41	7.27 m	ArH
	284	4.43	4.98 br	NH
			4.57 s	$NCOCH_2$
			3.70 s	$ArOCH_3$
			3.66 d, 3.31 d	CH_2CO

[a] Abbreviations: s = singlet; m = multiplet; br = broad; d = doublet; sh = shoulder.

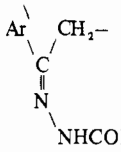
The electronic spectra of the hydrazones IIIa–o are identical (cf. Tables I and II) and are practically not affected by the type of substituent in the aroyl group. However, the expected red shift is caused by auxochromic substituents in the phenyl group. This shows that their absorption should be attributed to perturbation in chromophore A or C and not in chromophore B or D. It follows that the absorption characteristics of these compounds are attributed to chromophore A rather than C.



A

$-CH_2COAr$

B



C

$-COAr$

D

Also, this conclusion was inferred from the following evidence.

Table II. IR, UV, and NMR Spectral Data of the ω-Benzoylacetophenone *N*-(Acyl- or benzovl)hydrazone Derivatives IIIk-p

compd	IR bands in KBr, cm^{-1}	assign	UV bands (EtOH) λ_{max}, nm	UV bands (EtOH) log ϵ_{max}	NMR values, δ CDCl$_3$	NMR values, δ Me$_2$SO	NMR values, δ assign
IIIk	3460	NH	300	4.36	7.69 m	7.54 m	ArH
	1620	C=O			5.43 br		NH
					3.67 d, 3.36 d	3.57 s	CH$_2$CO
IIIl	3380	NH	302-294 sh	4.38	7.57 m	7.45 m	ArH
	1640	C=O	290	4.39	5.00 br		NH
					4.12 s	4.05 s	NCOCH$_2$
					3.67 d, 3.30 d	5.52 s	CH$_2$CO
IIIm	3400	NH	293	4.42	7.65 m	7.53 m	ArH
	1640	NH	290-282 sh	4.41	5.00 br		NH
					4.55 s	4.50 s	NCOCH$_2$
					3.65 d, 3.28 d	3.53 s	CH$_2$CO
IIIn	3460	NH	303	4.42	7.54 m	7.49 m	ArH
	1625	C=O			5.47 br		NH
					3.82 s	3.78 s	ArOCH$_3$
					3.69 d, 3.38 d	3.38 s	CH$_2$CO
IIIo	3320	NH	307-300 sh	4.38	7.24 m	7.17 m	ArH
	1640	C=O	294	4.41	5.13 br		NH
					4.10 s	4.02 s	NCOCH$_2$
					3.83 s	3.80 s	ArOCH$_3$
					3.62 d, 3.31 d	3.50 s	CH$_2$CO
IIIp	3300	NH	307-300 sh	4.36	7.60 m	7.32 m	ArH
	1640	C=O	294	4.44	5.33 br		NH
			288-281 sh	4.39	4.67 s	4.07 s	NCOCH$_2$
					3.93 s	3.93 s	ArOCH$_3$
					3.74 d, 3.43 d	3.57 s	CH$_2$CO

Table III. IR, UV, and NMR Spectral Data of Benzaldehyde *N*-(Acyl- or Benzoyl)hydrazone Derivatives Va-i

compd	IR bands in KBr, cm^{-1}	assign	UV bands (EtOH) λ_{max}, nm	UV bands (EtOH) log ϵ_{max}	NMR values (δ) in CDCl$_3$	assign
Va	3200	NH	330-397 sh	4.31	8.43 br	NH
	1640	C=O	294	4.31	7.65 m	ArH + =CH
Vb	3300, 3180	NH	309-302 sh	4.05	10.50 br	NH
	1660	C=O	296-289 sh	4.25	7.50 m	ArH + =CH
			284	4.29	4.08 s	CH$_2$CO
Vc	3180	NH	305-299 sh	4.10	9.40 br	NH
	1660	C=O	296-289 sh	4.31	7.62 m	ArH + =CH
			284	4.32	4.57 s	CH$_2$CO
Vd	3280, 3150	NH	305	4.36	8.37 s	NH
	1630	C=O	301-297 sh	4.35	7.60 m	ArH + =CH
Ve	3180	NH	310-305 sh	4.11	10.35 br	NH
	1660	C=O	298-293 sh	4.28	7.55 m	ArH + =CH
			288	4.32	4.12 s	CH$_2$CO
Vf	3180	NH	311-305 sh	4.16	9.61 br	NH
	1660	C=O	294	4.38	7.51 m	ArH + =CH
			289-282 sh	4.39	4.50 s	CH$_2$CO
Vg	3200	NH	304	4.39	8.50 br	NH
	1630	C=O	292-288 sh	4.32	7.34 m	ArH + =CH
					3.73 s	ArOCH$_3$
Vh	3220	NH	307-300 sh	4.34	10.75 br	NH
	1660	C=O	291	4.40	7.50 m	ArH + =CH
					4.03 s	CH$_3$CO
					3.83 s	ArOCH$_3$
Vi	3200	NH	308-302 sh	4.34	9.83 br	NH
	1660	C=O	294	4.39	7.30 m	ArH + =CH
			287-284 sh	4.33	4.53 s	CH$_2$CO
					3.85 s	ArOCH$_3$

(i) The electronic spectra of ω-aroylacetophenone *N*-(acyl- or benzoyl)hydrazones IIIa-i are similar to those of the corresponding benzaldehyde *N*-(acyl- or benzoyl)hydrazones Va-c but different from those of acetophenone *N*-(acyl- or benzoyl)hydrazones Vj-l. (ii) The electronic spectra of ω-benzoylacetophenone *N*-(acyl- or benzoyl)hydrazones IIIj-o are similar to those of the corresponding benzaldehyde hydrazone derivatives Vd-i but different from those of the corresponding acetophenone hydrazones Vm-r. Benzaldehyde hydrazones are shown to absorb at a longer wavelength than the corresponding acetophenone hydrazones (*4*). (iii) Experimentally, the difference between the spectrum of ω-benzoylacetophenone *N*-phenylacetylhydrazone (IIIb) and benzaldehyde *N*-phenylacetylhydrazone (Vb) shows bands at about 309 nm (ε 1000) and 270

Table IV. IR, UV, and NMR Spectral Data of Acetophenone *N*-(Acyl- or benzoyl)hydrazone Derivatives Vk-s

compd	IR bands in KBr, cm^{-1}	assign	UV bands (EtOH)		NMR values, δ in CDCl$_3$	assign
			$\lambda_{\max}$, nm	log $\epsilon_{\max}$		
Vk	3180	NH	287	4.23	9.17 br	NH
	1630	C=O			7.75 m	ArH
					2.33 s	=CCH$_3$
Vl	3210, 3180	NH	276	4.28	9.40 br	NH
	1670	C=O			7.37 m	ArH
					4.13 s	CH$_2$CO
					2.20 s	=CCH$_3$
Vm	3180	NH	294-290 sh	4.18	9.20 br	NH
	1660	C=O	281	4.27	7.69 s	ArH
			275-270 sh	4.27	4.53 s	CH$_2$CO
					2.08 s	=CCH$_3$
Vn	3270	NH	295	4.32	10.13 br	NH
	1640	C=O			7.52 m	ArH
					2.3 s	=CCH$_3$
Vo	3320, 3180	NH	281	4.36	9.52 br	NH
	1670	C=O			7.55 m	ArH
					4.12 s	CH$_2$CO
					2.18 s	=CCH$_3$
Vp	3200, 3170	NH	294-288 sh	4.25	9.37 br	NH
	1660	C=O	282	4.32	7.67 m	ArH
					4.55 s	CH$_2$CO
					2.03 s	=CCH$_3$
Vq	3200	NH	298	4.31	10.15 br	NH
	1640	C=O			7.43 m	ArH
					3.82 s	ArOCH$_3$
					2.35 s	=CCH$_3$
Vr	3220, 3180	NH	286	4.37	8.98 br	NH
	1670	C=O			7.44 m	ArH
					4.12 m	CH$_2$CO
					3.85 s	ArOCH$_3$
					2.17 s	=CCH$_3$
Vs	3210	NH	297-292 sh	4.43	9.43 br	NH
	1660	C=O	284	4.32	7.30 m	ArH
					4.53	CH$_2$CO
					3.78	ArOCH$_3$
					2.00	=CCH$_3$

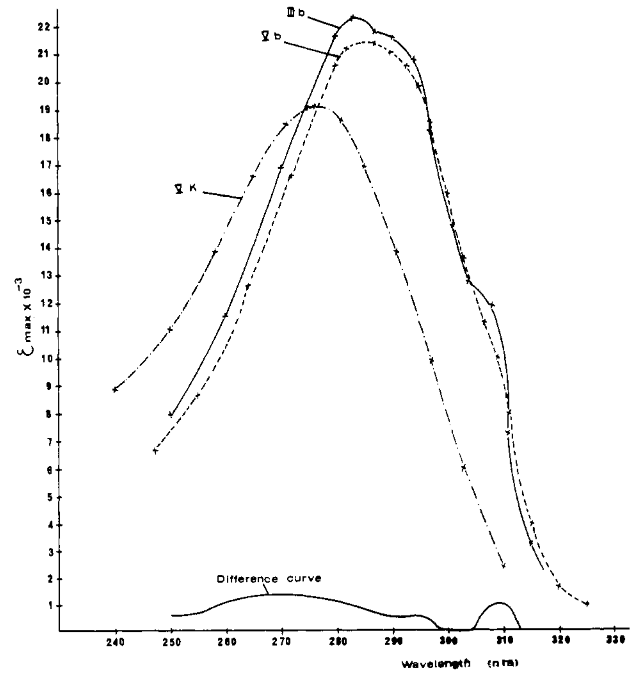


Figure 2.

Table V. Results for ω-Benzoylacetophenone Hydrazone Derivatives[a] IIIa-o

compd	mp, °C	yield, %	formula[b]
IIIa	105-106	87	$C_{22}H_{18}N_2O_2$
IIIb	135-136	85	$C_{23}H_{20}N_2O_2$
IIIc	165-166	78	$C_{27}H_{22}N_2O_2$
IIId	173-174	78	$C_{22}H_{17}ClN_2O_2$
IIIe	153-154	81	$C_{23}H_{19}ClN_2O_2$
IIIf	160-161	75	$C_{27}H_{21}ClN_2O_2$
IIIg	137-138	72	$C_{23}H_{20}N_2O_3$
IIIh	129-130	80	$C_{24}H_{22}N_2O_3$
IIIi	133-134	81	$C_{28}H_{24}N_2O_3$
IIIj	157-158	79	$C_{22}H_{17}ClN_2O_2$
IIIk	94-95	87	$C_{23}H_{19}ClN_2O_2$
IIIl	155-156	82	$C_{27}H_{21}ClN_2O_2$
IIIm	190-192	71	$C_{23}H_{20}N_2O_3$
IIIn	130-131	68	$C_{24}H_{22}N_2O_3$
IIIo	155-156	78	$C_{23}H_{24}N_2O_3$

[a] Elemental analyses (C, H, N, Cl) in agreement with theoretical values were obtained and submitted for review. [b] Compounds IIIa, f, g were crystallized from benzene--cyclohexane and IIIb-e, h-o from cyclohexane.

nm (ε 14 000) (Figure 2). This is attributed to the absorption of the acetophenone chromophore. Furthermore, the same conclusion was substantiated by the fact that the same difference in spectrum was obtained when the spectrum of an alcoholic solution of a known molar concentration of IIIb was determined using as reference an alcoholic solution of the same molar concentration of benzaldehyde Vb.

Experimental Section

General Information. Melting points are uncorrected. IR spectra were recorded using a Perkin-Elmer 577 grating infrared spectrophotometer (KBr). NMR spectra were measured on a Jeol JNM-PM spectrometer using Me_4Si as internal standard. UV

Table VI. Results for Acetophenone and Benzaldehyde Hydrazones[a] Va-r

compd	mp, °C	yield, %	formula[b]
Va	208-209	98	$C_{14}H_{12}N_2O$
Vb	135-136	91	$C_{15}H_{14}N_2O$
Vc	210-211	87	$C_{19}H_{16}N_2O$
Vd	176-177	88	$C_{14}H_{11}ClN_2O$
Ve	175-176	92	$C_{15}H_{13}ClN_2O$
Vf	228-229	95	$C_{19}H_{15}ClN_2O$
Vg	159-160	92	$C_{15}H_{14}N_2O_2$
Vh	170-171	85	$C_{16}H_{16}N_2O_2$
Vi	185-186	88	$C_{20}H_{18}N_2O_2$
Vj	155-156	89	$C_{15}H_{14}N_2O$
Vk	157-158	96	$C_{16}H_{16}N_2O$
Vl	172-173	95	$C_{20}H_{18}N_2O$
Vm	204-205	93	$C_{15}H_{11}ClN_2O$
Vn	164-165	89	$C_{16}H_{13}ClN_2O$
Vo	184-185	92	$C_{20}H_{17}ClN_2O$
Vp	167-168	89	$C_{16}H_{16}N_2O_2$
Vq	167-168	88	$C_{17}H_{18}N_2O_2$
Vr	170-171	97	$C_{21}H_{20}N_2O_3$

[a] Elemental analysis (C, H, N, Cl) in agreement with theoretical values were obtained and submitted for review. [b] Compounds Va-d, k, l were crystallized from benzene-cyclohexane and Ve-j from benzene.

spectra were measured on a Beckman spectrophotometer ACTA MVI using a scan speed of 0.25 nm/s and chart rate of 10 nm/in. (ethanol). The purity of the analytical samples was checked by TLC (silica gel). Microanalyses were determined by Alfred Bernhardt, West Germany.

Reaction of Hydrazide Derivatives IIa-c with Acetylenic Ketones Ia-c, Benzaldehydes IVa-c, and Acetophenones IVd-f. General Procedure. The reported procedure (*5*) for the reaction of acetylenic ketones with hydrazide was used in this work. The compounds ω-aroylacetophenone, benzaldehyde, and acetophenone *N*-(acyl- or benzoyl)hydrazones (IIIa-p, Va-i, and Vk-s, respectively) were obtained by refluxing the hydrazide II (1 mol equiv) with the acetylenic ketones I (1 mol equiv), benzaldehydes IVa-c (1 mol equiv), and acetophenones IVd-f in ethanol for 5 h. The precipitated solid left after evaporation of the solvent was crystallized from a suitable solvent to give the corresponding hydrazone (Tables V and VI).

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Synthesis of Novel Bis(amides) by Means of Triphenyl Phosphite Intermediates

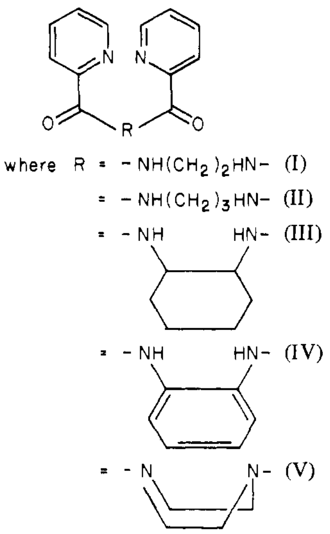
D. J. Barnes, R. L. Chapman, R. S. Vagg,* and E. C. Watton

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

The synthesis, via a triphenyl phosphite intermediate, of a series of bis(amides) of pyridine-2-carboxylic acid and various diamines is reported. Products isolated are of the form $(C_5H_5NCO)_2R$ where R = (I) $-NH(CH_2)_2NH-$, (II) $-NH(CH_2)_3NH-$, (III) $-NH\overline{CH(CH_2)_4CH}NH-$, (IV) $-NH(o\text{-}C_6H_4)NH-$, and (V) $\underline{H_2CN(CH_2)_2NCH_2}$. The compounds were characterized by microanalysis, melting point, and NMR, IR, and mass spectral data.

This paper reports the synthesis of some new bis(amides) by means of a triphenyl phosphite intermediate. The following compounds have been prepared: *N*,*N'*-bis(2-pyridinecarboxamide)-1,2-ethane (I); *N*,*N'*-bis(2-pyridinecarboxamide)-1,3-propane (II); *N*,*N'*-bis(2-pyridinecarboxamide)-1,2-cyclohexane (III); *N*,*N'*-bis(2-pyridinecarboxamide)-1,2-benzene (IV); *N*,*N'*-bis(2-pyridylcarboxamide)piperazine (V).

Gardiner et al. (*1*) synthesized the 4-pyridyl analogue of I for possible chemotherapeutic use in the treatment of tuberculosis. Castle (*2*) reported the same compound as a reaction product from the attempted synthesis of 2-(4'-pyridyl)imidazoline. Ojima (*3*) condensed methyl picolinate with the corresponding diamines to produce both I and II. Compounds III-V have not appeared in the literature. The synthetic method used here was first reported by Mitin and Glinskaya (*4*) and has been discussed in detail by Yamazaki and Higashi (5, 6). Several other methods, including the use of acid chloride intermediates and dicyclohexylcarbodiimide or ethyl chloroformate as dehydrating agents, were attempted initially. In all cases yields were found to be considerably lower than for that reported here. Physical and spectroscopic data for the compounds are given in Table I.



Experimental Section

General Methods. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected.

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