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STRUCTURE AND ABSORPTION SPECTRA OF 2-PHENACYLPYRIDINES—II*

C-AROYL DERIVATIVES

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Abstract—Features of the I.R. and U.V. spectra of seven C-aroyl derivatives of 2-phenacylpyridine are reported. Three of these derivatives form two solid isomers, and these are shown to be the *cis* OH/Py and *trans* OH/Py isomers of the enolic form. The remaining four compounds yield only one isomer and this is shown to be the *trans* OH/Py in each case.

INTRODUCTION

IT HAS been shown[1] that aroylation of 2-phenacylpyridine yields C-aroyl derivatives rather than O-aroyl derivatives. This work is now confirmed and extended by synthesis of additional compounds. Furthermore, three out of seven compounds examined form two distinct isomers in the solid state. These isomers are distinguished by different I.R. spectra and melting points, and the particular isomer obtained depends upon the solvent used for recrystallization. That they are indeed isomers is proved by their ultimate analysis, by the fact that they can be interconverted by crystallization from suitable solvents and by the fact that their U.V. spectra are identical in various solvents. The compounds examined are listed in Table 1.

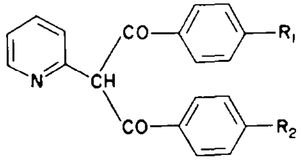

TABLE 1. THE C-AROYL DERIVATIVES OF 2-PHENACYLPYRIDINE

Compound No.	R_1	R_2	Isomers	M.p.s	I.R. spectra in double bond region* (cm^{-1})		
1	H	H	Form A	118°	1636	—	
			Form B	140°	1636	1677	
2	Cl	H	Form A	110°	1636	—	
			Form B	126°	1636	1658	1686
3	Br	H	Form A	119°	1639	—	—
			Form B	148°	1639	1672	1689
4	Cl	Br	One form	150°	1630	—	—
5	CH_3	H	One form	113°	1632	—	—
6	NO_2	H	One form	174°	1634	—	—
7	Cl	Cl	One form	150°	1634	—	—

* Solid state in nujol.

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* Part I. Previous paper.

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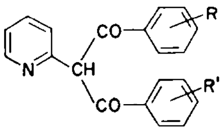
[1] A. H. Beckett and K. A. Kerridge, *J. Chem. Soc.* 2948 (1954).

In general, the isomer of lower melting point (form A) is isolated from hydrocarbon solvents (benzene/petroleum ether), and the isomer of higher melting point (form B) is isolated from ethanol. If the hydrocarbon solution of the lower melting form is evaporated rapidly, instead of allowing slow crystallization, the higher melting form is obtained. Furthermore, when the two isomers are intimately mixed, the melting point of the mixture is identical to that of the higher melting form.

The reason for the failure to isolate isomers in the case of four compounds is not yet understood.

Structures of the isomers

The C-aroyl derivatives of 2-phenacylpyridine can exist with any of the structures shown in I to V. If bond equalization by resonance takes place to a great extent,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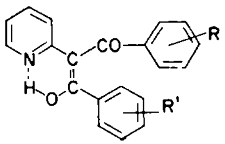
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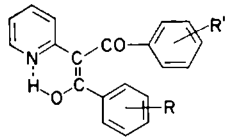
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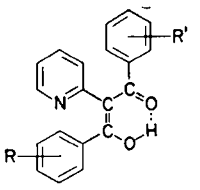
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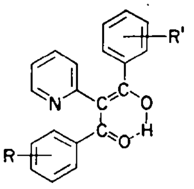
V

then it will be difficult to distinguish between forms IV and V. When R = R′, forms IV and V, and II and III are identical. Forms II and III will be referred to as *cis* OH/Py, and forms IV and V as *trans* OH/Py.

The possibility of geometrical isomerism in these compounds, established by the present work, has been discussed in a preliminary note.[2] It was pointed out that the *cis* OH/Py compounds can form a planar arrangement of the benzene ring, the pyridine ring and the hydrogen bonded chelate ring, with the aroyl group at right angles to this plane. On the other hand, the *trans* OH/Py compounds will contain three aromatic rings which will tend to be non-coplanar due to steric hindrance.

Results and discussion of I.R. spectra

The structure can be decided by the following considerations of the I.R. spectra. Thus, I should show the typical spectrum of a β-diketone in the diketo form, II and III should show a normal, conjugated carbonyl group, and absence of normal OH absorption, and IV and V should show absence of conjugated carbonyl absorption and absence of OH absorption due to conjugate chelation.

Furthermore, in principle it should be possible to decide the direction of enolization, and so decide between forms II and III, by measurement of the C=O frequency. This should vary with the Hammett sigma value of the substituent in the ring attached to the C=O group.[3]

Examination of the spectra of the three compounds which form isomers reveals

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[2] R. F. Branch, *Nature Lond.* **179**, 42 (1957).

[3] Part I, previous paper.

that in each case the lower melting isomer shows no normal C=O absorption, but that the higher melting isomer does show normal C=O absorption. The four compounds which form only one isomer show no normal C=O absorption. These results are recorded in Table 1. None of the solids showed any normal OH absorption.

Two of the three higher melting forms showed two peaks in the C=O region, and this might suggest the diketo form in which it is known that mechanical coupling produces a doublet.[4] However, the presence of a strong band near 1636 cm^{-1}, which corresponds to the 1640 cm^{-1} band due to C=C in simple 2-phenacylpyridine enols,[3] suggests that these isomers are of the form II or III.* This splitting of the C=O absorption does not occur in the unsubstituted benzoyl derivative (compound 1), and it is due to an effect not yet established. This splitting removes the possibility of determining the direction of enolization by measurement of the C=O frequency.

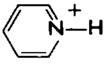
Thus, we conclude that the lower melting forms A, obtained from hydrocarbon solvents, have structures IV or V i.e. *trans* OH/Py, and the forms isolated when only one isomer is obtained are also *trans* OH/Py. The higher melting forms B from ethanol, on the other hand, have structures II or III i.e. *cis* OH/Py.

Results and discussion of U.V. spectra

The U.V. spectra are shown in Table 2, and a typical spectrum is shown in Fig. 1. Both enol forms (*cis* or *trans*) absorb in the conjugated carbonyl region near 250 mμ, as expected, but the position of the band at longer wavelengths due to the enol depends upon the solvent used. Two isomers of the same compound give identical spectra when examined in the same solvent. This confirms the interconvertibility of the isomers, which change can proceed via the diketo form, and that the preferred form in solution depends upon the solvent. In ethanol the enol absorption occurs at 370 mμ, whereas in cyclohexane the enol absorption occurs at 325 mμ. That this is a structural effect, and not merely due to solvent changes, is evident from the spectrum in mixed solvents (90% cyclohexane/10% ethanol) in which both enol bands are present (Fig. 1). Furthermore, the enol band in simple 2-phenacylpyridines remains constant regardless of solvent (Part I). The fact that the U.V. spectra differ according to the solvent used, together with the differences observed between the isomers in the carbonyl region of the I.R. spectrum, shows that the solid isomers are not merely polymorphs. On the basis of the I.R. spectra, the higher-melting isomers, which are isolated from ethanol, exist as the *cis* OH/Py structures, II or III. It is reasonable to suppose that

* The band near 1640 cm^{-1} occurs in both forms as a strong band and is indeed stronger than in the simple phenacyl pyridines and the band in forms IV and V is slightly stronger than that in forms II and III. However, the relative intensities of the bands is a matter of some difficulty because (a) the samples are run in the solid state in nujol, (b) the bands are quite broad and the bands of the aromatic systems are in close proximity (c) the band in the simple 2-phenacyl pyridines is itself quite strong.

† When the ethanolic solutions are acidified the band near 370 mμ in the U.V. spectrum disappears completely into the background and no peak is observed. In the keto region (near 250 mμ) of absorption a very strong band remains with a slight frequency shift. The band here, of course, is a composite band containing aromatic absorptions and also absorption due to



This is the reason why the relative ε values were not quoted. The fact that the 370 mμ band disappears and there is only weak absorption near 324 mμ is sufficient evidence that the diketo form predominates.

[4] R. Mecke and E. Funck, *Z. fur Elecktrochem.* **60**, 1124 (1956).

these structures would be preferred in ethanol solution, and therefore the absorption at 370 mμ can be ascribed to the *cis* OH/Py enol. The lower melting isomers which are isolated from cyclohexane exist as the *trans* OH/Py structures, IV or V. The absorption at 325 mμ is ascribed, therefore, to the *trans* OH/Py enol. The longer wavelength of the absorption due to the *cis* OH/Py structures is to be expected since they contain the longest conjugated system. The failure to isolate isomers from compounds 4–7 is surprising since these compounds show the presence of both *cis* and *trans* enols in the appropriate solvent as evidenced from the U.V. spectra. The only form which is isolated is that which would be expected to be favoured in cyclohexane solution, i.e. the *trans* OH/Py compound. The reason for this failure is not yet understood.

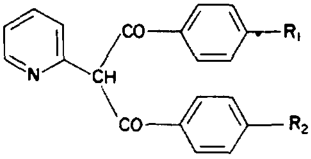


Table 2. The U.V. spectra of C-aroyl derivatives of 2-phenacylpyridine

Compound No.	Compound	Solvent	λ_{max} (mμ)	ϵ_{max}
1	$R_1 = H, R_2 = H$	cyclohexane	249·8	15560
			291	9500
			324·9	11340
		ethanol	250·3	14520
			309·7	8300
			370	9620
5	$R_1 = H, R_2 = CH_3$	cyclohexane	256	17600
			327·5	11500
		ethanol	256·8	16900
			366	8330
2	$R_1 = H, R_2 = Cl$	cyclohexane	256·5	19300
			324	13800
		ethanol	255	17580
			370	11740
		aqueous	247	16720
			365	8455
3	$R_1 = H, R_2 = Br$	cyclohexane	258	18320
			324	13080
		ethanol	251·5	16900
			360	11080
7	$R_1 = Cl, R_2 = Cl$	cyclohexane	260	21780
			326	13150
		ethanol	259	17955
			368	15240
4	$R_1 = Cl, R_2 = Br$	cyclohexane	262·5	22100
			326	13320
6	$R_1 = H, R_2 = NO_2$	cyclohexane	251·5	19440
			317–330	11000
		ethanol	254	—
			370	12660

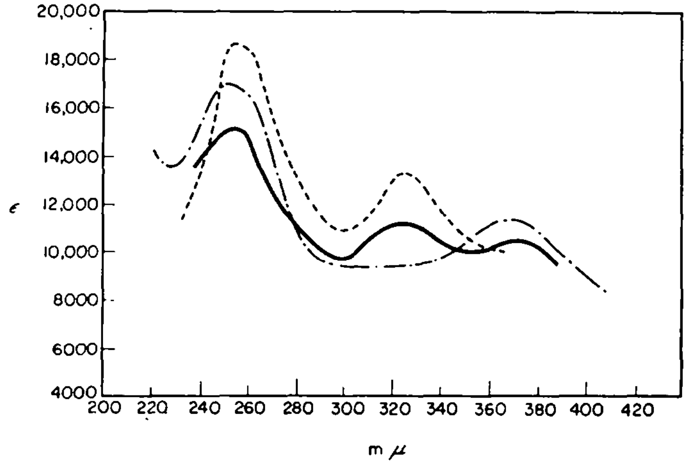


FIG. 1. U.V. Spectra of 1-(4'-bromophenyl)-3-phenyl-2-2'-pyridylpropane-1,3-dione
— — — — — cyclohexane
- - - - - - - - ethanol
———— 90% cyclohexane/10% ethanol.

The effect of addition of acid to the ethanol solutions is to remove the 370 mμ band completely. It appears that in acidic ethanolic solutions the diketo form is the preferred form. (See footnote on p. 415)

EXPERIMENTAL

Spectra. The I.R. Spectra were determined on a Grubb-Parsons G.S.2A spectrophotometer with a 1200 l.p.i. grating. The samples were examined as solids in paraffin. The U.V. Spectra were determined on a Beckman D.K.2. recording spectrophotometer. The compounds were examined in ethanol and cyclohexane or mixtures of these. Concentrations were from 10–20 mg/l. at path length 1 cm. The effect of acid was studied by the addition of 1–2 drops of dil hydrochloric acid to the ethanol solutions.

Preparation of C-aroyl derivatives of 2-phenacylpyridines

General procedure. This was similar to that adopted by Beckett and Kerridge[1] except that sodium hydride instead of sodium amide was used to make the sodium derivatives of the 2-phenacylpyridines. The sodium hydride was in the form of a 50% w/w suspension in mineral oil obtained from Metal Hydrides Ltd. The mineral oil was removed by washing by decantation with dry toluene before use.

2-Phenacylpyridine (or derivative, 1 mole) was stirred in dry toluene with sodium hydride (1 mole) at 80° for at least 6 hr under nitrogen. A yellow suspension of the sodio derivative was formed and hydrogen was evolved. Benzoic anhydride (or derivative) dissolved in dry acetone was added rapidly to the suspension of the sodio derivative with stirring at room temp, and stirring continued for a few min only. When the deep colour of the sodio derivative had faded considerably water was added. The toluene layer was washed with water, dried (Na_2SO_4), filtered and the solvent removed under red. press. To the residual yellow oil an equal volume of ether was added and the product crystallized by cooling.

1,3-*Diphenyl*-2-2'-*pyridylpropane*-1,3-*dione* (compound 1). From 2 g 2-phenacylpyridine and 2·3 g benzoic anhydride, about 1·5 g of crude oil was obtained from which 0·5 g yellow crystals was obtained, m.p. 118°. (Found: C, 79·5; H, 5·07; N, 4·6; Calc. for $C_{20}H_{16}O_2N$; C, 79·9; H, 5·0; N, 4·7%). On recrystallization from ethanol a compound, m.p. 141° identical with that obtained by Beckett and Kerridge[1] was obtained. The isomer m.p. 141° dissolved more slowly in a mixture of equal parts benzene–pet ether (b.p. 60–80°) than the isomer m.p. 118°.

1-(4'-*Chlorophenyl*)-3-*phenyl*-2-2'-*pyridylpropane*-1,3-*dione* (compound 2). From 1 g 2-*p*-chlorophenacylpyridine and 2 g benzoic anhydride, 0·3 g yellow crystals was obtained after crystallization from benzene–pet ether (b.p. 60–80°), m.p. 110–112°. (Found: C, 71·9; H, 4·11; N, 4·22; Cl, 10·5; Calc. for $C_{20}H_{14}O_2NCl$: C, 71·6; H, 4·2; N, 4·2; Cl, 10·55%). On recrystallization from ethanol, a compound m.p. 128°, identical to that obtained by Beckett and Kerridge[1] was obtained. When compound, m.p. 128°, was recrystallized from benzene, it yielded compound, m.p. 110°.

An identical compound, m.p. 110–112° was obtained when the sodio derivative of 2-phenacylpyridine was reacted with *p*-chlorobenzoic anhydride. A colourless by-product m.p. 148–149°, 1,3 *bis*(4′-*chlorophenyl*)-2-2′-*pyridyl*-2-*benzoyl*-*propane*-1,3-*dione* was also obtained. (Found: C, 68·0; H, 3·6; N, 3·0; Cl, 14·8; Equiv. wt. by non-aqueous titration, 470; $C_{27}H_{17}O_3NCl_2$ requires: C, 68·4; H, 3·6; N, 2·95; Cl, 14·97%. Equiv. wt. 474). The yield of the latter was increased when the acylation was carried out an at elevated temp.

1-(4′-*Bromophenyl*)-3-*phenyl*-2-2′-*pyridylpropane*-1,3-*dione* (compound 3). From 0·5 g 2-*p*-bromophenacyl-pyridine and 0·5 g benzoic anhydrate. 0·3 g yellow crystalline product from pet ether (b.p. 60–80°), m.p. 119–121°. (Found: C, 63·4; H, 3·71; N, 3·42; Br, 20·93; $C_{20}H_{14}NO_2Br$ requires: C, 63·2; H, 3·71; N, 3·68; Br, 21·0%).

On recrystallization from ethanol, a compound m.p. 148–150° was obtained. (Found: C, 63·34; H, 3·82; N, 3·84; Br, 21·45; $C_{20}H_{14}NO_2Br$ requires: C, 63·2; H, 3·71; N, 3·68; Br, 21·0%). On recrystallization of compound m.p. 148–150° from benzene–pet ether (60–80°) the compound m.p. 119° was obtained.

An identical compound to that melting at 119° was obtained when 2-phenacylpyridine was acylated with *p*-bromobenzoic anhydride. A by-product, m.p. 155–157°, 1,3-bis(4′-*bromophenyl*)-2-(2′-*pyridyl*)-2-*benzoylpropan*-1,3-*dione* was also obtained. (Found: C, 57·66; H, 3·06; N, 2·7; Br, 28·2. $C_{27}H_{17}NO_3Br_2$ requires: C, 57·55; H, 3·04; N, 2·49; Br, 28·42%).

1-(4′-*Bromophenyl*)-3-(4′-*chlorophenyl*)-2-2′-*pyridylpropan*-1,3-*dione* compound 4). From 1 g 2-*p*-chlorophenacylpyridine and 1 g *p*-bromo-benzoic anhydride, 1·8 g of crude yellow crystals gave from benzene–pet ether a compound m.p. 150°. (Found: C, 58·2; H, 3·32; N, 3·4; $C_{20}H_{13}NO_2BrCl$ requires: C, 57·95; H, 3·2; N, 3·4%). On crystallization from ethanol the m.p. remained constant.

An identical compound to that melting at 150° was obtained when 2-*p*-bromophenacylpyridine was acylated with *p*-chlorobenzoic anhydride.

1,3-*bis*(4′-*chlorophenyl*)-2-2′-*pyridylpropan*-1,3-*dione* (compound 5). From 0·7 g 2-*p*-chlorophenacylpyridine and 0·9 g *p*-chlorobenzoic anhydride, 0·44 g of yellow needles m.p. 150–152° were obtained after recrystallization from benzene–pet ether. (Found: C, 64·98; H, 3·42; N, 3·61; Cl, 19·02; $C_{20}H_{13}NO_2Cl_2$ requires: C, 64·9; H, 3·54; N, 3·78; Cl, 19·16%). On crystallization from ethanol the m.p. remained constant.

1-*Phenyl*-3-(4′-*methylphenyl*)-2-2′-*pyridylpropane*-1,3-*dione* (compound 6). From 1 g 2-*p*-methylphenacylpyridine and 1·2 g benzoic anhydride, 0·3 g yellow crystals m.p. 112° were obtained after recrystallization from benzene–per ether. (Found: C, 80·36; H, 5·39; N, 4·28; $C_{21}H_{17}NO_2$ requires: C 80·0; H, 5·44; N, 4·44%). On crystallization from ethanol the m.p. remained constant.

1-(4′-*Nitrophenyl*)-3-*phenyl*-2-2′-*pyridylpropane*-1,3-*dione* (compound 7). This was prepared according to the method of Beckett and Kerridge.[1] On crystallization from benzene–pet ether no alteration in m.p. was observed. A by-product m.p. 157°, 1,3 *bis*(4′-*nitrophenyl*)-2-2′-*pyridyl*-2-*benzoyl*-*propane*-1,3-*dione* was also obtained. (Found: C, 64·9; H, 3·6; N, 8·6; equiv. wt. 500. $C_{27}H_{17}N_3O_7$ requires: C, 65·5; H, 3·5; N, 8·5%. Equiv. wt. 495).