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Geometrical Isomerism of 2,4-Dinitrophenylhydrazones of Some Pyruvic Esters

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Synopsis. Visible, IR, and PMR spectra of 2,4-dinitrophenylhydrazones (DNPH) of some pyruvic esters were studied. It is suggested that each α-isomer with a higher R_f-value involves an intramolecular hydrogen bond between the imino hydrogen and the ester carbonyl group, to which the *Z*-structure is assigned. The *E*-structure is assigned to each β-isomer with a lower R_f-value.

Formation of various phenylhydrazones is usually utilized for the identification of pyruvic acid and its esters. The problem of geometrical isomerism of the hydrazones has been studied for many years by a number of investigators. However, only a few investigations deal with the geometrical isomerism of DNPH of pyruvic esters, *cf.* H. van Duin,[1] and P. Juvvik and B. Sundby.[2]

Van Duin[1] prepared DNPH of pyruvic esters by the reaction of the corresponding alcohols with DNPH of pyruvoyl chloride and separated two geometrical isomers of DNPH of each ester by partition column chromatography, and assigned *E*(*anti*)-structure to the isomer with the smaller retention volume (α-isomer) and *Z*(*syn*)-structure to the other (β-isomer). His assignment was based on the fact that the wavelength of the absorption maximum in the visible spectra for each α-isomer is very close to that for DNPH of normal ketones. Recently, Juvvik and Sundby[2] assigned, on the basis of the IR spectra (no data given), *E*-structure to DNPH of ethyl pyruvate obtained from the ester and the hydrazine reagent in an aqueous hydrochloric acid solution, no detail being given except for the UV-visible spectral data for the DNPH.

We report the results of the observations on the visible, IR, and PMR spectra for the geometrical isomers of DNPH of pyruvic esters. It is suggested that van Duin's assignment is inconsistent.

Experimental

Methyl and ethyl pyruvates (Sigma Chemical Co.) were distilled before use. Isopropyl and *t*-butyl pyruvates were prepared by esterification of pyruvic acid. DNPH of diethyl mesoxalate was prepared from 2,4-dinitrophenylhydrazine and the ester which was obtained by the oxidation of diethyl bromomalonate with dimethyl sulfoxide.

When DNPH of pyruvic esters were formed in an alcoholic sulfuric acid solution, followed by separation of the resulting mixture of isomers by means of column chromatography on

TABLE 1. MELTING POINTS, ELEMENTARY ANALYSES, CRYSTALLINE FORMS, AND R_f-VALUES OF DNPH OF PYRUVIC ESTERS (**1**) AND OF DIETHYL MESOXALATE (**2**)

Compd		Mp (°C)[a]	Analysis (%) Found (Calcd) C	H	N	Formula	Crystalline form[f]	R_f-Value[g]
	α	184.5—185	42.56	3.34	20.13		Needles	0.38
1, R=Me			(42.56	3.57	19.85)	$C_{10}H_{10}N_4O_6$		
	β	151.5—152	42.77	3.37	20.04		Prisms	0.11
	α	154.5—155	44.41	3.97	19.08		Prisms	0.42
1, R=Et			(44.60	4.08	18.91)	$C_{11}H_{12}N_4O_6$		
	β	126.5—127[b]	44.37	4.03	19.18		Scales	0.12
	α	159.5—160.5	46.22	4.39	17.93		Scales	0.49
1, R=*i*-Pr			(46.45	4.55	18.06)	$C_{12}H_{14}N_4O_6$		
	β	119.5—120[c]	46.65	4.48	18.33		Prisms	0.14
	α	146—147[d]	48.25	4.73	17.33		Scales	0.61
1, R=*t*-Bu			(48.15	4.97	17.28)	$C_{13}H_{16}N_4O_6$		
	β	148.5—149.5[e]	48.11	4.73	17.37		Prisms	0.19
2		118—118.5	43.86	3.85	16.00		Prisms	0.30
			(44.07	3.98	15.82)	$C_{13}H_{14}N_4O_8$		

a) Uncorrected. b) 115—117°C.[1] c) 115.5 °C.[1] d) 151.5 °C.[1] e) 117.5—119.5 °C.[1] f) Recrystallized from ethanol. g) TLC on silica gel utilizing benzene as the developing solvent.

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silica gel with benzene as an eluting solvent, the main product was the α-isomer with a higher R_f-value. On the other hand, the lower R_f-value was found for the main product of the reaction of pyruvic esters with the hydrazine reagent in a dilute aqueous hydrochloric acid solution with subsequent separation.

Results and Discussion

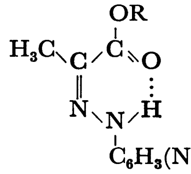
Melting points, elementary analyses, crystalline forms, and R_f-values of DNPH of pyruvic esters (**1**, α and β) together with those for diethyl mesoxalate (**2**) are summarized in Table 1.

The visible, IR, and PMR spectral data for **1** and, for comparison, for **2** and DNPH of acetone (**3**) are given in Table 2. We see that, (a) absorption maxima in the visible spectra for all the α-isomers lie at the longer wavelengths than those for all the corresponding β-isomers, (b) extinction coefficients at the absorption maxima for all the α-isomers are larger than those for all the corresponding β-isomers, (c) both N–H and C=O stretching bands in the IR spectra appear at wave numbers for all the α-isomers smaller than those for all the corresponding β-isomers, (d) all the α-isomers show NH signals in the PMR spectra at lower magnetic fields than all the corresponding β-isomers.

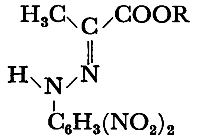
TABLE 2. VISIBLE, IR, AND PMR SPECTRA FOR **1**, **2**, AND **3**

Compd		Visible (in EtOH)[a]		IR (Nujol mull)[b]		PMR (in $CDCl_3$)[c]
		λ_{max} (nm)	ε $\times 10^{-4}$	ν_{N-H} (cm^{-1})	$\nu_{C=O}$ (cm^{-1})	δ_{NH} (ppm)
1, R=Me	α	360	2.67	3148	1695	14.0
	β	348	2.37	3304	1727	11.1
1, R=Et	α	360	2.62	3200	1697	14.1
	β	349	2.37	3320	1723	11.1
1, R=*i*-Pr	α	361	2.64	3173	1685	14.0
	β	350	2.52	3316	1706	11.1
1, R=*t*-Bu	α	362	2.71	3220	1696	14.0
	β	351	2.45	3312	1708	11.1
2		349 373	2.17 2.34	3190	1691 1724	14.1
3		360	2.03	3305	—	10.9

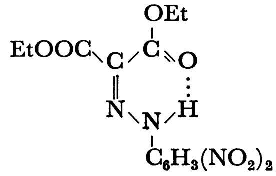
a) Recorded on a Hitachi Recording Spectrophotometer ESP-3. b) Recorded on a Hitachi-Perkin-Elmer IR-Spectrometer 225. c) Recorded at 60 MHz on a Hitachi-Perkin-Elmer High Resolution NMR-Spectrometer R-20B.



1-*Z* (α)



1-*E* (β)



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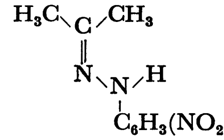

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R=Me, Et, *i*-Pr, *t*-Bu

TABLE 3. IR SPECTRA FOR **1**, **2**, AND **3** IN CCl_4 AT VARIOUS CONCENTRATIONS

Compd		0.01 M (cm^{-1})		0.005 M (cm^{-1})		0.001 M (cm^{-1})	
		ν_{N-H}	$\nu_{C=O}$	ν_{N-H}	$\nu_{C=O}$	ν_{N-H}	$\nu_{C=O}$
1, R=Me	α	3200[a]	1707[a]			3205	1708
	β	3316	1725			3315	1720
1, R=Et	α	3206	1700	3205	1696	3205	1701
	β	3316	1714	3316	1713	3315	1714
1, R=*i*-Pr	α	3202	1694			3205	1695
	β	3318	1713			3315	1708
1, R=*t*-Bu	α	3200	1695			3195	1692
	β	3317	1709			3312	1705
2		3195	1695 1732			3195	1695 1730
3		3320	—			3320	—

a) Saturated solution.

Infrared spectral data for **1**, **2**, and **3** in carbon tetrachloride at various concentrations are given in Table 3. We see that both N–H and C=O stretching bands for all the α-isomers appear at wave numbers smaller than those for all the corresponding β-isomers as in the case with Nujol mull. The observation may suggest that each α-isomer involves an intramolecular hydrogen bond between the imino hydrogen and the ester carbonyl group.

The results suggest that the *Z*-structure (**1**-*Z*) is assigned to the α-isomers and the *E*-structure (**1**-*E*) to the β-isomers. Similar suggestions were reported on the geometrical isomerism of DNPH of α-keto acids,[3,4] and of phenylhydrazones of α-keto acids,[5] pyruvamide,[6] and methyl[6] and ethyl[7] pyruvates. The assignment is just the opposite to that of van Duin. **3** gives an absorption maximum in the visible spectra at the wavelength close to those given by the α-isomers of **1** as was reported by him. However, **2** shows two absorption bands, the stronger band appearing at a longer wavelength than for **3**. Thus, the mere agreement of the wavelength, at which the maximum absorption in the UV-visible spectra occurs, cannot be taken to indicate the coincidence of geometrical structure. The IR and PMR spectral data for **2** and **3** also support our assignment (Tables 2 and 3).

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