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CONVERSION OF 2-ACYL-1-ARYLHYDRAZIDES OF DIARYLGLYCOLIC ACIDS TO 1-ACYLAMINO-3,3-DIARYLOXINDOLES*

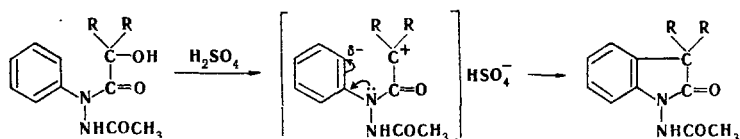
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UDC 547.298'75

2-Acyl-1-arylhydrazides of diarylglycolic acids are cyclized in the presence of concentrated sulfuric acid to 1-acylamino-3,3-diaryloxindoles through the intermediate formation of a halochromic salt.

1,2-Diacylhydrazines are readily converted to 2,5-disubstituted 1,3,4-oxadiazoles by the action of zinc chloride, phosphorus oxychloride, thionyl chloride, and other condensing agents [2]. Diacylhydrazines are cyclized to 1,3,4-oxadiazole or 1,2,4-triazole derivatives by the action of concentrated sulfuric or polyphosphoric acids [3].

We have established that 2-acetyl- or formyl-1-arylhydrazides of diarylglycolic acids [4] in the presence of concentrated sulfuric acids give a halochromic coloration that vanishes as the mixtures stand; this is associated with the conversion of the initially formed halochromic salt to 1-acylamino-3,3-diaryloxindoles (Table 1).



Compounds I and XVI were reduced with Raney nickel, during which the N-N bond was cleaved in both cases to give 3,3-diphenyloxindole [5]; this proves the structures of the synthesized compounds.

As compared with the IR spectrum of the starting hydrazide, the ν_{OH} and ν_{C-OH} bands vanished in the IR spectrum of III, and this proves splitting out of the OH group during the reaction. The spectrum of III above 3000 cm^{-1} contains one band at 3245 cm^{-1} (at 3400 cm^{-1} in the spectrum of a solution); there are two bands at 1736 and 1680 cm^{-1} (as compared with 1690 and 1680 cm^{-1} in the spectrum of the starting compound) corresponding to two amide carbonyl groups in the region of carbonyl group vibration. The band at 1736 cm^{-1} corresponds to the $\nu_{C=O}$ band from the carbonyl group in the oxindole ring [6], and a band with the same frequency is also observed in the spectrum of 3,3-diphenyloxindole.

As compared with the UV spectra of the starting hydrazides, absorption at $250\text{--}260\text{ nm}$, which, according to the data in [7], can be linked with the indole ring, appeared in the UV spectra of I and VI (Fig. 1).

*Communication CI from the series "Substituted Hydrazides of Hydroxy Carboxylic Acids." See [1] for communication C.

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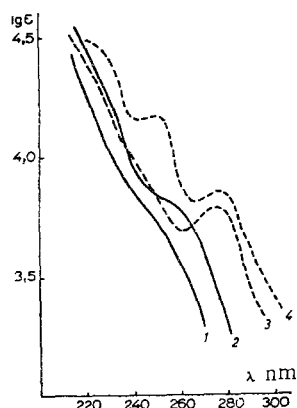


Fig. 1. UV spectra: 1) benzilic acid 2-acetyl-1-phenylhydrazide; 2) I; 3) di(p-anisyl)glycolic acid 2-acetyl-1-phenylhydrazide; 4) VI.

TABLE 1. 1-Acetamido and 1-Formamido-3,3-diaryloxindoles

Compound	X	R	R'	mp, °C *	Empirical formula	N, %		Yield, %
						found	calc.	
I		C ₆ H ₅		231—235	C ₂₂ H ₁₈ N ₂ O ₂	7.9	8.2	94
II		<i>o</i> -CH ₃ C ₆ H ₄		157—159	C ₂₄ H ₂₂ N ₂ O ₂	7.4	7.6	95
III		<i>m</i> -CH ₃ C ₆ H ₄		212.5—213.5	C ₂₄ H ₂₂ N ₂ O ₂	7.5	7.6	96
IV	H	<i>p</i> -CH ₃ C ₆ H ₄		222.5—223.5	C ₂₄ H ₂₂ N ₂ O ₂	7.5	7.6	98
V		<i>o</i> -CH ₃ OC ₆ H ₄		214—215	C ₂₄ H ₂₂ N ₂ O ₄	6.8	6.0	94
VI		<i>p</i> -CH ₃ OC ₆ H ₄		213—214	C ₂₄ H ₂₂ N ₂ O ₄	7.1	7.0	96
VII		<i>p</i> -ClC ₆ H ₄	CH ₃	123—124	C ₂₂ H ₁₆ Cl ₂ N ₂ O ₂	6.7	6.8	96
VIII		C ₆ H ₅		209—210	C ₂₃ H ₂₀ N ₂ O ₂	7.7	7.9	97
IX		<i>o</i> -CH ₃ C ₆ H ₄		127—128	C ₂₅ H ₂₄ N ₂ O ₂	7.0	7.3	94
X	5-CH ₃	<i>m</i> -CH ₃ C ₆ H ₄		194—195	C ₂₅ H ₂₄ N ₂ O ₂	7.0	7.3	92
XI		<i>p</i> -CH ₃ C ₆ H ₄		197—198	C ₂₅ H ₂₄ N ₂ O ₂	7.0	7.3	95
XII		C ₆ H ₅		240—241	C ₂₃ H ₂₀ N ₂ O ₂	7.8	7.9	94
XIII	7-CH ₃	<i>o</i> -CH ₃ C ₆ H ₄		156—158	C ₂₅ H ₂₄ N ₂ O ₂	7.0	7.3	98
XIV		<i>m</i> -CH ₃ C ₆ H ₄		218—219	C ₂₅ H ₂₄ N ₂ O ₂	7.1	7.3	96
XV		<i>p</i> -CH ₃ OC ₆ H ₄		206—207	C ₂₅ H ₂₄ N ₂ O ₄	6.9	6.7	91
XVI		C ₆ H ₅		178—180	C ₂₁ H ₁₆ N ₂ O ₂ †	8.4	8.5	95
XVII		<i>p</i> -CH ₃ C ₆ H ₄		204—205	C ₂₃ H ₂₀ N ₂ O ₂	7.8	7.9	96
XVIII	H	<i>p</i> -CH ₃ OC ₆ H ₄	H	208—209	C ₂₃ H ₂₀ N ₂ O ₄	7.3	7.3	98
XIX		<i>p</i> -ClC ₆ H ₄		103—105	C ₂₁ H ₁₄ Cl ₂ N ₂ O ₂	7.1	7.0	98

*Compounds IV and XIV were recrystallized from benzene-petroleum ether, V and XVIII were recrystallized from glacial acetic acid, and the remaining compounds were recrystallized from alcohol.

†Found: C 76.8; H 5.0%. Calculated: C 76.6; H 4.9%.

EXPERIMENTAL

The IR spectra of mineral oil suspension and CCl₄ solutions of the compounds were measured with a UR-20 spectrometer. The UV spectra of alcohol solutions of the compounds were obtained with an SF-16 spectrophotometer.

1-Acetamido-3,3-diphenyloxindole (I). A concentrated sulfuric acid solution was added in small portions to a solution of 7.2 g (0.02 mole) of benzilic acid β-acetyl-α-phenylhydrazide in 20 ml of glacial acetic acid until the formation of a vanishing green coloration ceased. The mixture was then poured into water, and the resulting precipitate was removed

by filtration to give 6.5 g (94%) of a substance that was insoluble in water and petroleum ether, only slightly soluble in benzene and toluene, and more readily soluble in alcohol and glacial acetic acids. Recrystallization from alcohol gave prisms with mp 234-235°. Found: C 77.2; H 5.4%. $C_{22}H_{18}N_2O_2$. Calculated: C 77.2; H 5.3%.

Compounds II-XIX were similarly obtained.

Reduction of I. A solution of 1 g of I in 60 ml of alcohol was gently refluxed with 25 g of freshly prepared Raney nickel for 3 h, after which the mixture was filtered, and the filtrate was evaporated. The residue was crystallized from benzene to give prisms with mp 225-226° (in agreement with the melting point reported for 3,3-diphenyloxindole [5]). No melting-point depression was observed for a mixture of this product with a genuine sample. The IR spectra of the two substances were also identical.

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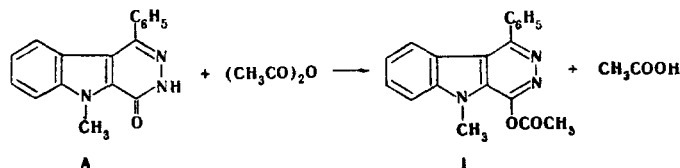
ACETYLATION OF PYRIDAZINO[4,5-b]INDOLES AND THEIR DIHYDRO AND TETRAHYDRO DERIVATIVES. III*

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Acetylation of pyridazino[4,5-b]indol-4-ones with acetic anhydride gives the O-acetyl derivatives, and acetylation of 1,2-dihydropyridazino[4,5-b]indol-4-ones leads to the 2-acetyl and 2,4-diacetyl derivatives. Tetrahydropyridazino[4,5-b]indoles, obtained by reduction of the dihydro derivatives, undergo substitution by an acetyl group at the 2 position.

Pyridazino[4,5-b]indoles [1, 2] are capable, as we have observed, of readily undergoing acetylation. It has been reported [3] that the acylation of pyridazino[4,5-b]indol-4-ones with benzoyl chloride leads to 3,5-dibenzoyl derivatives. In the case of 5-methylpyridazino[4,5-b]indole (A) we have observed that the introduction of an acetyl group is accompanied by the appearance of a single absorption band at 1770 cm^{-1} , which is characteristic for the ester group.



*See [1] for communication II.

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