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INDOLE DERIVATIVES. 120.* SYNTHESIS OF HIGHER ω-(3-INDOLYL)ALKANOIC ACIDS BY ALKYLATION OF INDOLE LACTONES

B. Ya. Eryshev and N. N. Suvorov

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The alkylation of indole with the tridecanolide, pentadecanolide, and oxo lactones of ω-hydroxyethoxyundecanoic and ω-hydroxybutoxyundecanoic acids was investigated. Higher indolylalkanoic acids, viz., ω-(3-indolyl)undecanoic, ω-(3-indolyl)tridecanoic, and ω-(3-indolyl)pentadecanoic acids, were obtained. The scheme of the alkylation of indole with oxo lactones, and the difference in the rates of the reactions of the ester and lactone bonds, were established from the reaction products.

Methods for the preparation of γ-(3-indolyl)butyric acid by the reaction of indole with γ-butyrolactone in the presence of alkali in an autoclave at 250°C and in a solvent at normal pressure are known [2].

It seemed of interest to ascertain the possibility of the preparation of higher 3-indolylalkanoic acids by this method, and the use of other less aggressive catalysts. For this, we used lactones, such as the tridecanolide, pentadecanolide, and oxo lactones of ω-hydroxyethoxyundecanoic acid and ω-hydroxybutoxyundecanoic acid, and various weak bases as the catalysts.

The studies showed that the tridecanolide and pentadecanolide react with indole to give the corresponding acids in 62-95% yields. Under the given conditions, oxo lactones IIa and IIb form ω-(3-indolyl)undecanoic acid in 10-15% yield. In addition to the acid, a substance that, according to the results of elementary analysis and IR spectroscopy, has the 3-indolylethyl decyl ether structure, was isolated from the neutral reaction products by thin-layer chromatography (TLC). On the basis of the results, it may be stated that both the lactone and ether bond participate in the alkylation of indole with oxo lactones under the conditions presented above via the scheme:

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*See [1] for communication 119.

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TABLE 1. Characteristics of the Compounds Obtained

Structural formula	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %	Note
		C	H	N		C	H	N		
γ-(3-Indolyl)butyric acid*	124–125				$C_{12}H_{13}O_2N$				82	
ω-(3-Indoyl)undecanoic acid†	89–89,5				$C_{19}H_{27}O_2N$				10–15	
ω-(3-Indolyl)tridecanoic acid	96,5–97,5	76,4	9,7	4,0	$C_{21}H_{31}O_2N$	76,6	9,5	4,2	62	pyrrole ring ν_{NH} 3420–3340 cm⁻¹ ν_C carboxyl 1715–1695 cm⁻¹ $\nu_{-CH_2-O-CH_2-}$ 1140–1090 cm⁻¹
ω-(3-Indolyl)pentadecanoic acid	98,5	77,7	9,6	4,1	$C_{23}H_{35}O_2N$	77,3	9,9	3,9	95	
Ethyl 3-Indolyldecylate	30,5–32,0	81,4	9,2	4,9	$C_{20}H_{31}ON$	81,0	9,5	4,3	2–3	

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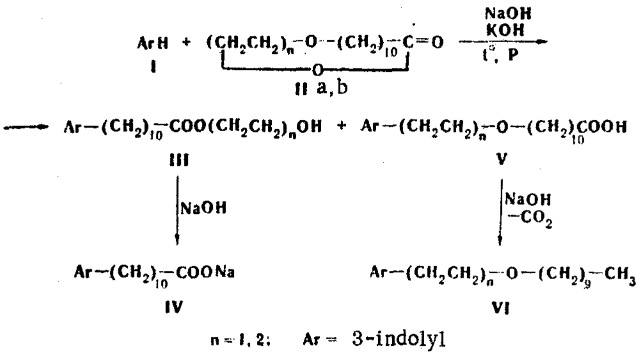
*According to the data in [3], this compound has mp 124°C.

†According to the data in [4], this compound has mp 89-90°C.



Judging from the yields of the reaction products, the lactone bond undergoes alkylation at a higher rate than the ether bond, since the yield of the product of decarboxylation of the indolyloxy acid is 2-3%. A study of the structures of IV and VI by mass spectrometry and PMR spectroscopy showed that the side chains have the normal structure [5].

In a search for milder catalysts we investigated a number of bases such as $Ba(OH)_2$, BaO, CH_3COONa, and a mixture of CH_3COONa with KOH in equal molar ratios with the lactones presented above and γ-butyrolactone at 200-350°C. It was established that they all display very weak activity and that the yields of the acid do not exceed 5-10%. Primary hydrolysis of the lactones to give ω-hydroxy acids occurs at 200-250°C, while pronounced resinification of the starting compounds and the reaction products is observed at 300-350°C.

EXPERIMENTAL

A steel assay autoclave was charged while heating with 0.06 mole of indole, 0.05 mole of lactone, and 0.09 mole of KOH or NaOH, after which the autoclave was sealed hermetically, placed in a heater, and heated with stirring to 250°C. Heating was continued for 18 h, after which the autoclave was cooled, and the reaction products were removed and subjected to steam distillation to isolate the unchanged indole. The residue was separated from the resinous residues by filtration, and the acid was isolated from the filtrate by neutralization with acetic or formic acid with respect to Congo. The acid was purified by recrystallization from alcohol or benzene. The indole that was isolated from the cooled distillate was dried and used in the next experiment. Data on the synthesized compounds are given in Table 1.

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POLAROGRAPHIC REDUCTION OF NONQUATERNIZED AND QUATERNIZED PYROPHTHALONES IN PROTOGENIC MEDIA

Ya. P. Stradyn', Yu. A. Benders,
V. P. Kadysh, É. S. Lavrinovich,
and Yu. É. Fridmanis

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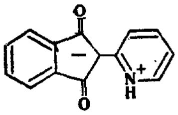
The polarographic reduction potentials were determined by classical polarography, millicoulometry, preparative electrolysis, and cyclical voltammetry, and the course of the electrochemical process for nonquaternized and quaternized pyrophthalones in 20% buffer solutions in aqueous dimethylformamide was studied. In the case of α and γ isomers of pyrophthalones, two-electron irreversible electrical reduction leads to the formation of an indan-1-on-3-yl-1,4-dihydropyridine, which exists in two protolytic forms. The compound was isolated and its structure was proved by means of mass spectrometry. The polarographic reduction of β-pyrophthalones is similar to the electrical reduction of 2-phenylindane-1,3-dione. The tautomeric-protolytic equilibria of quaternized and nonquaternized α-, β-, and γ-pyrophthalones were studied, and it was ascertained that individual tautomeric-protolytic forms participate in the electrochemical process at various pH values.

Various products are formed in the reduction of 2-pyridylindane-1,3-diones (all of the isomers, which we have designated by the general term "pyrophthalones" [1]); depending on the reduction conditions, either the indanedionyl or pyridinium fragment of the molecule, or both, are involved [2].

To characterize the individual possible steps in the reduction, and to determine the corresponding electrode potentials, we chose a polarographic method and undertook a systematic polarographic study of diverse pyrophthalones.

Rather stable anion radicals, the unpaired electron in which is localized primarily in the 5 and 6 positions of the indanedionyl fragment of the molecule, are formed in the polarographic reduction of quaternary isomeric 2-pyridylidane-1,3-diones in aprotic dimethylformamide (DMF) media as a result of transfer of the first electron [3]. The next step in the electrical reduction involves the indanedionyl fragment of the molecule and only at extremely negative potentials, and the pyridinium fragment of the molecule evidently also undergoes reduction.

As a rule, the transition from aprotic to protogenic media gives rise to more profound destruction of the starting molecules during the electrical reduction of organic compounds.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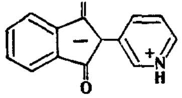
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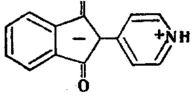
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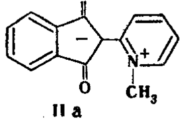
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