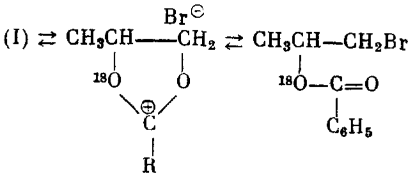

CONCLUSIONS

2-Bromopropyl benzoate has been obtained labeled with the isotope ^{18}O. The isomerization of 1(2)-bromoprop-2(1)-yl benzoates occurs via an acyloxonium mechanism.

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CONDENSATION OF PHTHALONITRILE WITH WEAKLY BASIC DIAMINES

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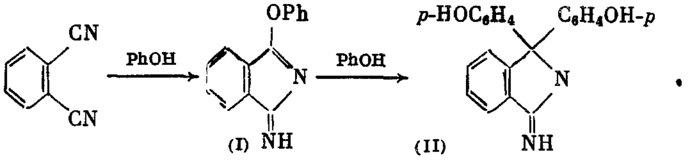
and N. A. Klyuev

UDC 542.953:547.584'052.2:
547.553.1

We have previously studied in detail the kinetics and mechanism of the reaction of phthalonitrile (PN) with aromatic amines in phenol solution [1]. It was shown that the first stage of the reaction involves addition of phenol to the PN:



(1)

A macroheterocycle is then formed by reaction of the phenoxy, then the imino-group in (I) with the diamine [2].

Compound (I) is extremely unstable [3]. In the absence of a diamine it rapidly adds a molecule of phenol, followed by a rearrangement to give 1,1-bis-(4-hydroxyphenyl)-3-imino-isondoline (II).

Hence, two competing reactions of the phenoxy-group (I) are possible in the condensation of PN with diamines in phenol, namely reaction with the amino-group of the diamine, or with phenol to give (II).

It has been shown [4] that condensation of PN with diamines with pK_a values of 6.2-3.3 results in the formation of macroheterocycles. The observation that neither (I) nor (II) could be detected by either TLC or mass spectrometry in the reaction mixture or in the products of this reaction shows that (I) reacts much more readily with the diamine than with phenol.

It may be assumed that as the basicity of the diamine is decreased, the role of side reaction (1) will increase. The object of the present investigation was to examine the reaction of PN with diamines of low basicity, namely 4,4'-diaminodiphenyl sulfone (DPS) (pK_a 2.7) [5] and 3,6-diamino-2,7-dimethylacridine (Acridine Yellow, AY) [6].

Examination of the products of the reaction of PN with DPS in phenol showed that, in contrast to all the previously studied diamines, DPS did not give a macroheterocycle with PN.

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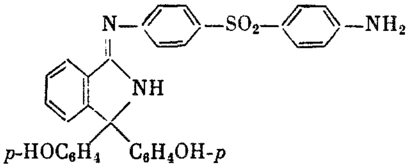
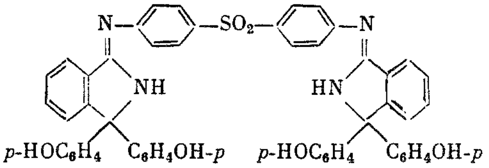
0568-5230/88/3709-1926$12.50

The products of the reaction of PN with DPS were examined by mass spectrometry. On ionization by electron impact, the mass spectrum of the mixture showed $[M]^+$ peaks of m/z 223, 316, and 547. Chromatographic separation on a silica gel column gave two products, which were examined by IR spectroscopy and elemental analysis. The IR spectra of both compounds showed absorption (cm^{-1}) at 1660 (C=N), 3340 (NH), and 3400-3600 (OH). Following acylation with benzoyl chloride, the absorption corresponding to the NH and OH groups disappeared, and absorption at 1650 and 1740 cm^{-1} appeared, corresponding to the CONH and COO groups. These findings give reason to suppose that the reaction of PN with DPS gives (III) and (IV):



(III)



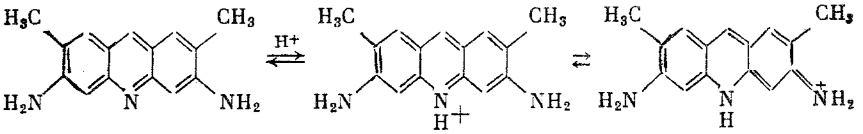
(IV)

It appears that the low basicity of DPS results in the rate of its reaction with (I) being less than the rate of formation of (II), the reaction of which with the diamine gives (III) and (IV).

A more complex situation exists in the condensation of PN with AY. The amino-groups in AY differ considerably in their basicity. The powerful electron-acceptor ability of the acridine ring results in the cyclic nitrogen being highly basic (pK_a 9.8) and the primary amino-groups weakly basic [6]. The pK_a value of the amino-group in 2-aminoacridine is 1.2 [6], and that in 3,6-diaminoacridine 1.5 [7].

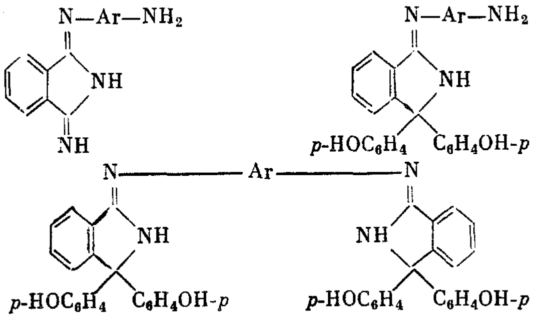
The reaction of PN with AY was carried out under the same conditions as with DPS. It was found that although the condensation of PN with DPS proceeds to 95-98% completion, the extent of reaction of PN with AY was no greater than 60-65%. This leads one to suppose that a considerable proportion of the AY reacts with the PN at one amino-group only.

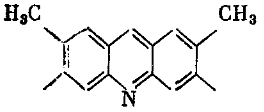
From literature information on the structures of protonated 2-aminoacridine and 3,6-diaminoacridine [7-9], it may be assumed that in a protic solvent (phenol), the AY molecule will be present in the ionized form:



In this case, one of the amino-groups becomes virtually nonreactive. The fact that in a more acidic medium than phenol (m-chlorophenol) the reaction proceeds only to the extent of 35% is in favor of this interpretation.

The products of the reaction of PN with AY were examined by TLC. According to TLC, the mixture contained six products, separation of which by recrystallization or reprecipitation did not appear possible, since they differed little in solubility. Chromatographic separation was prevented by the close similarity of their R_f values in a variety of eluents. We therefore used mass spectrometry to establish the composition of the reaction products. For readily volatile compounds, electron impact ionization was used, the spectrum showing $[M]^+$ peaks with m/z 223 [compound (I)], 316 (II), and 365. For the detection of compounds of high molecular mass, fast atom bombardment (FAB) [10] was employed. Peaks for the protonated molecular ions $[M + H]^+$ were obtained by selective detection of ion currents [11], as a result of which peaks with m/z 537 and 835 were seen. These findings lead to the conclusion that the products of the reaction of PN with AY in phenol are as follows:



where Ar =  .

It is therefore proposed that the mechanism of the condensation of PN with AY in phenol is basically similar to that of the condensation of PN with DPS.

EXPERIMENTAL

Mass spectra were obtained on a Varian 311-A. The following current sources were used: electron impact (recording conditions: ionizing voltage 70 eV, cathode emission current 1 mA, accelerating voltage 3 kV, direct sample introduction) and fast atom bombardment (FAB) [10] (recording conditions: glycerol matrix on a copper surface with a nominal angle of incidence of 65°, neutral Xe atoms, incident particle energy 3-8 kV). Glycerol cluster ions were calculated from the FAB mass spectrum.

Condensation of Phthalonitrile with 4,4'-Diaminodiphenyl Sulfone. In a previously dried flask fitted with a stirrer, reflux condenser, and a capillary for the introduction of argon were placed 0.25 g (0.001 mole) of DPS and 0.128 g (0.001 mole) of PN. Phenol (6 ml) and a solution of 0.0042 g of LiCl in 0.5 ml of dry methanol were added, and condensation carried out at 175-180°C for 40-50 h, until the evolution of ammonia had slowed down to a considerable extent. The mixture was poured into ethanol, and the solid which separated was filtered off, dried at 100°C (0.01 mm), and purified by reprecipitation from DMF with ethanol.

Compounds (III) and (IV) were separated by chromatography on silica gel, eluent DMF. For (III), found: C 70.69; H 4.63; N 7.49; S 5.29%. $C_{32}H_{25}N_3SO_4$. Calculated: C 70.18; H 4.50; N 7.67; S 5.86%. For (IV), found: C 73.27; H 4.50; N 6.39; S 5.85%. $C_{52}H_{38}N_4SO_6$. Calculated: C 73.74; H 4.53; N 6.01; S 3.78%.

The condensation of PN with AY was carried out similarly.

CONCLUSIONS

It has been found that, in contrast to the condensation of phthalonitrile with diamines with $pK_a > 2.7$, the principal products from which are macroheterocycles, reaction of phthalonitrile with diamines with $pK_a \leq 2.7$ gives linear condensation products of the reactants.

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OXIDATION OF UNSATURATED TERTIARY AMINES, AMIDES, AND IMIDES BY MOLECULAR OXYGEN CATALYZED BY PALLADIUM COMPLEXES

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and U. M. Dzhemilev

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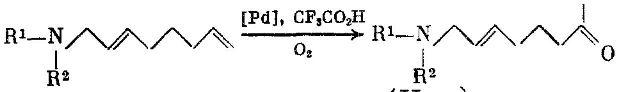
547.333.3

The oxidation of olefins by molecular oxygen in the presence of palladium salts has potential as a route for the synthesis of ketones of various structures [1-5]. On the other hand, there is very little information in the literature on the application of this method to the conversion of unsaturated tertiary amines, amides, and imides into the corresponding carbonyl compounds. This is evidently connected with the fact that amines, added to a $PdCl_2$–CuCl catalyst composition, completely block the oxidation of olefins by molecular O_2 on account of the formation of coordination-saturated complexes of Pd and Cu which are only feebly active in the oxidation of unsaturated compounds.

It might be expected that introduction of protonic acids, capable of bonding with the nitrogen in the initial unsaturated amine, amide, or imide molecule into the palladium catalyst composition would make it possible to oxidize these compounds to the corresponding ketones.

We have established that the presence of a protonic acid in the system, with a ratio amine:acid = 1:3 and amide or imide:acid = 1:1, is a necessary condition for the conversion of the amine, amide, or imide to a ketone. Oxidation by O_2 is carried out in the presence of a $PdCl_2$–CuCl catalyst (Pd:Cu:amine/amide/imide = 1:10:5 to 20) at a temperature of 60-65°C with a reaction time of 6 h in THF as solvent. The highest yields of amino-, amido-, and imidoketones are obtained on oxidation of the unsaturated amine, amide, or imide in the presence of a catalyst and CF_2CO_2H



(Ia-m) (IIa-m)

$R^1 = R^2 = (CH_3)$(a); $R^1 + R^2 = (CH_2)_5$(b); $R^1 + R^2 = (CH_2)_2\text{—}O\text{—}(CH_2)_2$(c); $R^1 = CH_3$, $R^2 = C_6H_5$(d); $R^1 = COC_6H_5$, $R^2 = C_6H_5$(e); $R^1 = COCH_3$, $R^2 = C_6H_5$(f); $R^1 = COCH_3$, $R^2 = CH_3$(g); $R^1 = COCH_3$, $R^2 = o\text{-}C_6H_4CH_3$(h); $R^1 = COCH_3$, $R^2 = m\text{-}C_6H_4F$(i); $R^1 = COCH_3$, $R^2 = p\text{-}C_6H_4O_2$(j), $R^1 = COH$, $R^2 = H$(k); $R^1 = COH$, $R^2 = C.H_{13}$(ℓ); $R^1 + R^2 = (COCH_2)_2$(m).

On oxidation of N-methyl-N-(2E,7-octadienyl)aniline (Id), 1,3E-6E-octatriene and methylaniline were formed in addition to (IId), these being the decomposition products of the original amine (Id).

On oxidation of N,N-bis(2E,7-octadienyl) derivatives of methylamine (IIIa) and benzylamine (IIIb), the corresponding mono- and diketones (IVa-c) and (Va-b) were formed:

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