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Transformations of *N*-Hydroxyimides.[1] Mechanistic Aspects of the Reaction between *N*-Hydroxyimides, Phenols, Diethyl Azodicarboxylate, and Triphenylphosphine

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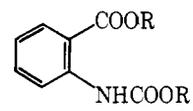
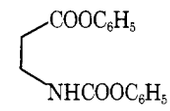
Recently it has been shown that the reaction of alcohols with *N*-hydroxyphthalimide in the presence of equimolar amounts of diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) leads to *N*-alkoxyphthalimides.[1a] Under the same conditions alcohols react with phenols to give alkyl aryl ethers.[2] These observations suggested the possibility of a direct route to *N*-aryloxyphthalimides through arylation of *N*-hydroxyphthalimide with phenols. In this paper we present our studies on the reactions of *N*-hydroxyphthalimide and *N*-hydroxysuccinimide with phenols in the presence of DEAD and TPP.

As a result of the reaction of equimolar amounts of *N*-hydroxyphthalimide, phenol, DEAD, and TPP in tetrahydrofuran as solvent, instead of the expected *N*-phenoxyphthalimide, we obtained phenyl *N*-phenoxycarbonylanthranilate **1**, whose properties (cf. Table I and Experimental Section) were identical with those of a substance obtained earlier in the reaction of *N*-hydroxyphthalimide-*O*-triflate with sodium phenoxide.[3] Likewise, phenyl *N*-phenoxycarbonyl-β-alanate **5** obtained in this laboratory displayed identical properties with those of the compound described by Chapman.[3] Compounds **2**, **3**, and **4** were also obtained by the above procedure.

Under conditions of equimolar amounts of substrates the reaction yield did not exceed 30%; this became understandable after the structure of products had been established. When the proportion of substrates was changed so that per 1 mol of *N*-hydroxyimide, 1 mol of DEAD, 1 mol of TPP, and 2 mol of phenol were used, the reaction yields increased about twofold (Table I). We suggest the reaction mechanism in Scheme I.

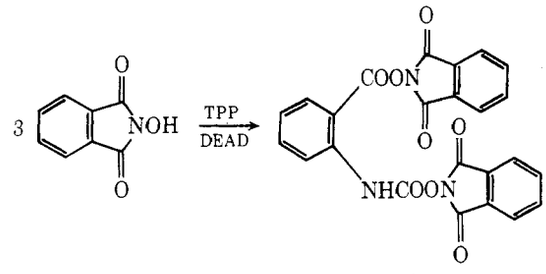


1, R = C_6H_5
2, R = p-$C_6H_4CH_3$
3, R = p-$C_6H_4OCH_3$
4, R = p-C_6H_4Br



5

At the first stage betaine I, postulated by Morrison,[4] is formed and gives with *N*-hydroxyphthalimide present in the reaction mixture ion pair II. We postulate an equilibrium between ion pairs II and III;[5] this postulate is based on our earlier observations of the properties of *N*-hydroxyphthalimide which in the presence of other reagents in the discussed type of reaction plays the part of a nucleophilic agent (e.g., in the reaction with alcohols[1a]) or of a electrophilic agent (e.g., in the reaction with carboxylic acids[1c]). Such a nature of *N*-hydroxyphthalimide was confirmed experimentally; namely, the reaction of *N*-hydroxyphthalimide (3 mol) with DEAD (1 mol) and TPP (1 mol) afforded **6** in high yield.



6

At the next stage of the suggested mechanism, as a result of reaction with a phenol molecule, ion pair III is transformed into a new ion pair IV accompanied by formation of a molecule of diethyl hydrazodicarboxylate. Subsequently the phenolate anion attacks the carbonyl group, thus causing the opening of the imide ring, Lossen rearrangement to isocyanate, and reaction with the second molecule of phenol. The results of the reaction confirm that $OPPh_3$ is a very good leaving group (cf. structure V), being transformed into the neutral molecule of phosphine oxide. All our observations supporting the proposed reaction mechanism are in agreement[7] with the results of Chapman obtained for the nucleophilic reactions of *N*-hydroxyimide-*O*-triflates[3] and with the results of Bittner concerning the Lossen rearrangement of hydroxamic acids in the presence of betaine I.[6] In addition, it has to be stressed that the occurrence of steric hindrance in phenols either greatly

Table I. Products of the Title Reactions

Compd	Registry no.	Yield, %	Mp, °C	Anal., % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
1	33067-24-2	69	95–96	72.1	4.5	4.2	72.2	4.6	4.4
2	65956-55-0	75	147–148	73.1	5.3	3.9	73.1	5.3	3.9
3	65956-56-1	72	123–124	67.1	4.9	3.6	66.7	4.9	3.6
4	65956-57-2	68	155–156	48.9	2.7	2.9	48.8	2.8	3.0
5	41580-56-7	75	82–83	67.4	5.3	4.9	67.5	5.4	4.8
6	65956-58-3	61	192–193	61.2	2.8	8.9	61.2	2.7	8.9

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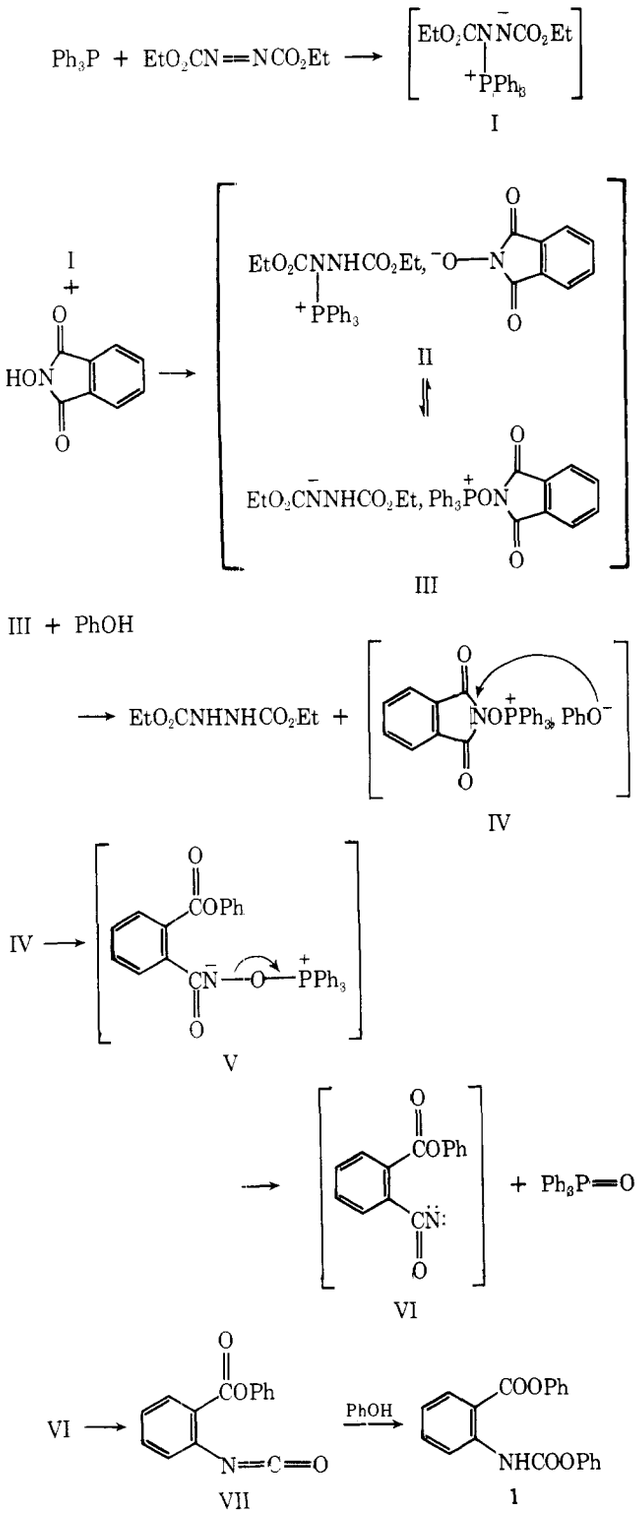
Scheme I



limits their reactivity (in case of 2,4-xylenol the reaction yield is much decreased) or it renders them completely unreactive (e.g., 2,6-di-*tert*-butyl-4-methylphenol); this behavior is quite clear in the light of the proposed mechanism.

Experimental Section

General. Melting points are uncorrected. Infrared spectra were obtained as KBr disks with a Unicam SP-200 spectrophotometer. ^{1}H-NMR spectra were recorded with a Jeol JNM-4H-100 spectrometer for $CDCl_3$ solutions (δ scale, Me_4Si = 0 ppm), silica gel G Merck was used for TLC, and silica gel 100–200 mesh Macherey-Nagel was used for column chromatography.

Phenyl *N*-Phenoxycarbonylanthranilate (1). A solution of *N*-hydroxyphthalimide (326 mg, 2 mmol), phenol (376 mg, 4 mmol), and TPP (524 mg, 2 mmol) in 10 mL of THF was treated with 380 mg (2.2 mmol) of DEAD and left overnight at room temperature. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel column with a mixture of benzene and ether (9:1 v/v) as eluent affording 460 mg (69%) of **1**: IR 3300, 3050, 1740, 1700, 1250–1130 cm^{-1}; ^{1}H NMR (δ 7.05–7.75 (complex, 12 H, aromatic), 8.25 (dd, 1 H, J_1 = 1.5 Hz, J_2 = 8.0 Hz, aromatic), 8.6 (d, 1 H, J_3 = 7.5 Hz, aromatic), 10.8 (s, 1 H, NH).

The compounds **2, 3, 4, 5,** and **6** were obtained in the same manner.

***p*-Methylphenyl *N*-*p*-Methylphenoxycarbonylanthranilate (2):** IR 3300, 3050, 1745, 1700, 1260–1130 cm^{-1}; ^{1}H NMR δ 2.35, 2.4 (2s, 6 H, $2CH_3$), 6.95–7.35 (complex, 9 H, aromatic), 7.6 (t, 1 H, J_1 = 7.5 Hz, aromatic), 8.3 (dd, 1 H, J_2 = 1.5 Hz, J_3 = 8.0 Hz, aromatic), 8.55 (d, 1 H, J_4 = 7.5 Hz, aromatic), 10.6 (s, 1 H, NH).

***p*-Methoxyphenyl *N*-*p*-Methoxyphenoxycarbonylanthranilate (3):** IR 3350, 3020, 1760, 1695, 1260–1140 cm^{-1}; ^{1}H NMR δ 3.8, 3.85 (2s, 6 H, $2OCH_3$), 6.85–7.4 (complex, 9 H, aromatic), 7.6 (t, 1 H, J_1 = 7.5 Hz, aromatic), 8.3 (dd, 1 H, J_2 = 1.5 Hz, J_3 = 8.0 Hz, aromatic), 10.7 (s, 1 H, NH).

***p*-Bromophenyl *N*-*p*-Bromophenoxycarbonylanthranilate (4):** IR 3350, 3100, 1755, 1700, 1255–1130 cm^{-1}; ^{1}H NMR δ 7.0–7.8 (complex, 10 H, aromatic), 8.3 (dd, 1 H, $J_1 \sim 1.0$ Hz, J_2 = 8.0 Hz, aromatic), 8.55 (d, 1 H, J_3 = 7.5 Hz, aromatic), 10.5 (s, 1 H, NH).

Phenyl *N*-Phenoxycarbonyl-β-alaninate (5): IR 3300, 3050, 1745, 1720, 1695, 1280–1150 cm^{-1}; ^{1}H NMR δ 2.8 (t, 2 H, $J_1 = J_2$ = 7.5 Hz, CCH_2O), 3.6 (q, 2 H, J_3 = 7.5 Hz, CCH_2N), 5.7 (broad t, 1 H, NH), 6.9–7.55 (complex, 10 H, aromatic).

Phthalimidyl *N*-Phthalimidoxycarbonylanthranilate (6): IR 3300, 3050, 1810, 1795, 1745, 1250–1130 cm^{-1}; ^{1}H NMR δ 7.5–8.1 (complex, 10 H, aromatic), 8.33 (dd, 1 H, $J_1 \sim 1.0$ Hz, J_2 = 8.0 Hz, aromatic), 8.4 (d, 1 H, J_3 = 7.5 Hz, aromatic), 10.3 (s, 1 H, NH).

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Registry No.—DEAD, 1972-28-7; TPP, 603-35-0; *N*-hydroxyphthalimide, 524-38-9; *N*-hydroxysuccinimide, 6066-82-6; phenol, 108-95-2; *p*-methoxyphenol, 150-76-5; *p*-methylphenol, 106-44-5; *p*-bromophenol, 106-41-2.

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Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Furazans and Related Systems[1]

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Introduction

In the past few years, nitrogen-15 nuclear magnetic resonance spectroscopy, ^{15}N NMR, has shown considerable utility in solving organic structural problems.[2-4] A particular advantage of ^{15}N NMR is the large range of chemical shifts and

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