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Reactions of Nitrosobenzene, *o*-Nitrosotoluene, and Pyridine *N*-Oxide with Phosphorus Pentachloride

ROBERT C. DUTY* AND GARY LYONS

Illinois State University, Normal, Illinois 61761

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The products of the reaction of phosphrous pentachloride with nitrosobenzene (**1**), *o*-nitrosotoluene (**2**), and pyridine *N*-oxide (**3**) were identified by vpc with known samples. In all three compounds, phosphorus pentachloride deoxygenated the nitrogen and formed chlorinated aniline, toluidine, and pyridine products, respectively, in the anhydrous solvent methylene chloride.

This study investigated the products of the reaction of phosphorus pentachloride with nitrosobenzene (**1**), *o*-nitrosotoluene (**2**), and pyridine *N*-oxide (**3**) in the solvent methylene chloride. The purpose of the investigation was to ascertain whether the tetrachlorophosphonium cation (PCl_4^+) would deoxygenate the nitrogen and chlorinate the ring. As expected, the oxygen from the nitroso group was removed to form phosphoryl chloride along with the hydrochloride salts of the chlorinated aromatic amines. Nitrosobenzene has been deoxygenated previously with triethyl phosphite. Bunyan and Cadogan[1] converted nitrosobenzene into azoxybenzene which subsequently can be converted into azobenzene with excess reagent.[2]

In the reaction with pyridine *N*-oxide, the phosphorus pentachloride would not react at the refluxing temperature of methylene chloride. Previously, Murakami and Matsumura[3] had treated pyridine *N*-oxide with solid phosphorus pentachloride at 140° to form 4-chloropyridine. Consequently, the reactants were placed in a sealed Pyrex tube and heated to 130° for 90 min. The solution turned a light brownish black, but no black-tarry residue remained as was the case with the nitroso compounds.

When phosphorus pentachloride dissolves in methylene chloride, the molecular ions, $(PCl_4^+)(PCl_6^-)$, are formed in equilibrium with molecular phosphorus pentachloride. This is substantiated from our experiments with 9-xanthone and 9-thioxanthone which immediately formed brilliant yellow and red complex ions, respectively, with the $(PCl_4^+)(PCl_6^-)$ molecular ions from phosphorus pentachloride.[4] Therefore, when nitroso compounds are added to a methylene chloride solution of phosphorus pentachloride, the initial reaction is undoubtedly the electrophilic attack of the tetrachlorophosphonium cation, (PCl_4^+), onto the negative end of the oxygen–nitrogen dipole of the nitroso group with the subsequent loss of a chloride ion.

The chlorination of the aromatic ring, as revealed from Table I, is probably an intermolecular chlorination. If intramolecular chlorination were occurring, one would expect the ratio of ortho/para isomers to be greater than 1; however, for both compounds **1** and **2** the ortho/para ratios were much less than 1 with values of 0.65 and 0.024, respectively.

TABLE I

REACTIONS OF PHOSPHORUS PENTACHLORIDE WITH NITROSOBENZENE, *o*-NITROSOTOLUENE, AND PYRIDINE *N*-OXIDE

Product	Yield, %
Nitrosobenzene: $POCl_3$, 61.2%	
Aniline	3.5
4-Chloroaniline	20.0
2,4-Dichloroaniline	18.5
2-Chloroaniline	13.0
2,4,6-Trichloroaniline	2.2
Total	57.2
o-Nitrosotoluene: $POCl_3$, 68.1%	
o-Toluidine	0.8
4-Chloro-*o*-toluidine	20.8
2,4-Dichloro-*o*-toluidine	18.7
2-Chloro-*o*-toluidine	0.5
Total	40.8
Pyridine *N*-Oxide: $POCl_3$, 55.0%	
Pyridine	65.4
2-Chloropyridine	10.2
3-Chloropyridine	10.2
4-Chloropyridine	1.9
Total	87.7

The actual species responsible for chlorination was not definitely established in this study. However, the additional experiments performed with chlorine, phosphorus trichloride, and phosphoryl chloride eliminated some of the possible precursors to chlorination. Phosphorus trichloride and phosphoryl chloride have previously been reported to chlorinate aromatic rings simultaneously with their ability to deoxygenate such compounds as pyridine *N*-oxide,[5] substituted pyridine *N*-oxides,[5,6] quinoline *N*-oxides,[5] lutidine *N*-oxides,[7] picoline *N*-oxides,[7] and pyrazine *N*-oxides.[8] Consequently, we treated compound **2** with excess quantities

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of both phosphorus trichloride and phosphoryl chloride, and the results are shown in Table II. Yields were considerably lower than with phosphorus pentachloride, but both compounds deoxygenated and chlorinated compound **2** with no trace of starting material remaining. However, considerable quantities of a black-intractable residue resulted. These data, in conjunction with data from Table I, suggest that phosphorus pentachloride is responsible for the major portion of the deoxygenation and chlorination reactions.

TABLE II

REACTION OF *o*-NITROSOTOLUENE WITH PHOSPHORYL CHLORIDE AND PHOSPHORUS TRICHLORIDE

Product	Yield, %	
	$POCl_3$	PCl_3
o-Toluidine	0.2	5.9
2-Chloro-*o*-toluidine	0.3	1.0
4-Chloro-*o*-toluidine	4.1	3.2
2,4-Dichloro-*o*-toluidine	4.2	1.1
Total	8.8	11.2

An Orton rearrangement[9,10] also could explain the isomer distribution, especially so, if an *N*-chloro intermediate existed in the medium. The *N*-chloroacetanilide rearrangement was proved to be an intermolecular chlorination with molecular chlorine as the chlorinating agent. To rule out the molecular chlorine possibility, we treated *o*-nitrosotoluene with phosphorus pentachloride in the presence of equal molar quantities of acetanilide. Acetanilide was recovered unchanged with no trace of 4-chloroacetanilide present.

Since deoxygenation of nitroso compounds generates nitrenes,[1,11] the gas chromatograms from the nitrosobenzene reaction products were examined for the presence of azobenzene. No trace was found, but this was not expected since the nitroso solutions were highly acidic from the excess hydrogen chloride generated in the reactions. In the case of pyridine *N*-oxide, the reaction temperature was 130°. Since phosphorus pentachloride can dissociate into phosphorus trichloride and chlorine at 130°,[12] it was necessary to investigate the reaction of molecular chlorine with pyridine in the presence of phosphoryl chloride. Since the formation of pyridine from pyridine *N*-oxide with either phosphorus trichloride or phosphoryl chloride had been reported previously,[5,6,13] it was possible for both products, pyridine and the chloropyridines, to be produced from the reaction and decomposition products of phosphorus pentachloride. To prove that the chloropyridines did not result from either the molecular chlorine or the phosphoryl chloride reacting with pyridine, a sealed tube reaction was run at 130° with pyridine, phosphoryl chloride, and excess chlorine in methylene chloride. Under these conditions, no chloropyridines were formed.

If one examines Table I, a striking difference exists between the products for pyridine *N*-oxide and the nitroso compounds. The phosphoryl chloride yield is 28% less than the total yield of pyridine products. In addition the chlorinated pyridines are 66% less than the yield of pyridine, and the ortho/para ratio is 5.4. Undoubtedly, phosphoryl chloride and phosphorus trichloride play a significant role in the deoxygenation and chlorination since these compounds have already been shown to deoxygenate and chlorinate pyridine *N*-oxide.[5,6]

Experimental Section

Nitrosobenzene–PCl_5.—A 25-ml solution of methylene chloride containing 0.990 g (0.00935 mol) of nitrosobenzene (Aldrich Chemical Co.) was added dropwise to a 25-ml solution of methylene chloride containing 1.90 g (0.00913 mol) of sublimed reagent grade phosphorus pentachloride (Allied Chemical Co). The reaction was exothermic (+11°), and the solution turned a brownish black. After all the nitrosobenzene was added, the solution was cooled in an ice bath and rotary evaporated under vacuum (0.5 Torr). The last traces of distillate were removed from a steam bath. The distillate was collected in a Dry Ice trap for immediate vpc analysis. The residue was made basic with 5% sodium hydroxide and steam-distilled which left a black tarry residue in the steam distillation flask. The distillate was extracted with ether and dried over anhydrous magnesium sulfate prior to vpc analysis. If the reaction mixture was allowed to reflux before rotary evaporation, the yields would be reduced approximately 50%. This was also noted for *o*-nitrosotoluene.

***o*-Nitrosotoluene–PCl_5**—A 20-ml solution of methylene chloride containing 1.00 g (0.00827 mol) of *o*-nitrosotoluene (Aldrich Chemical Co.) was added dropwise to an ice-cooled solution of 20 ml of methylene chloride containing 1.94 g (0.00932 mol) of reagent grade (Allied Chemical Co.) phosphorus pentachloride. The separation of products was performed in the exact manner as given above for nitrosobenzene.

Pyridine *N*-Oxide–PCl_5.—A 20-ml solution of methylene chloride containing 0.880 g (0.00925 mol) of pyridine *N*-oxide (Aldrich Chemical Co.) and 1.93 g (0.00925 mol) of reagent grade phosphorus pentachloride (Allied Chemical Co.) reacted in a sealed Pyrex tube at 130° for 90 min. The products were separated and analyzed exactly as for the nitroso compounds.

Pyridine–Chlorine–Phosphoryl Chloride.—A 20-ml solution of methylene chloride containing 2.3 g (0.029 mol) of chlorine (Matheson Coleman and Bell), 0.48 g (0.0059 mol) of pyridine (Baker Reagent Grade), and 0.92 g (0.0060 mol) of reagent grade phosphoryl chloride (Matheson Coleman and Bell) reacted in a sealed Pyrex tube at 130° for 90 min. Products were separated and analyzed in the identical manner as for pyridine *N*-oxide.

***o*-Nitrosotoluene–Acetanilide–PCl_5.**—A 20-ml solution of methylene chloride containing 1.00 g (0.00827 mol) of *o*-nitrosotoluene (Aldrich Chemical Co.) and 1.13 g (0.00832 mol) of acetanilide (Eastman White Label) was added to a 20-ml solution of methylene chloride containing 1.71 g (0.00823 mol) of reagent grade phosphorus pentachloride (Allied Chemical Co.). The reaction temperature and color were similar to the *o*-nitrosotoluene-PCl_5 reaction. After the addition, the reaction mixture was added to approximately 30 ml of water, and the aqueous layer was separated and extracted with two 30-ml ether fractions. The combined organic fractions were dried over anhydrous potassium carbonate and concentrated to 3 ml for vpc analysis.

***o*-Nitrosotoluene–$POCl_3$.**—A 20-ml solution of methylene chloride containing 1.00 g (0.00827 mol) of *o*-nitrosotoluene (Aldrich Chemical Co.) was added dropwise at room temperature to a 20-ml solution of methylene chloride containing 1.89 g (0.0346 mol) of phosphoryl chloride (Matheson Coleman and Bell reagent grade). After stirring for 30 min, the solvent was removed by rotary evaporation, and 100 ml of water was added to the residue. The water layer was extracted with three 25-ml portions of ether which was dried over anhydrous potassium carbonate prior to vpc analysis.

***o*-Nitrosotoluene–PCl_3.**—This reaction was run and analyzed in same manner as the above reaction with phosphoryl chloride.

Solvent.—Reagent grade methylene chloride (Mallinckrodt Chemical Co.) was dried over phosphorus pentoxide and distilled prior to use.

Vpc Analysis.—Phosphoryl chloride was analyzed on a 6 ft × $^1/_4$ in. column containing 10% OV-17 (50% phenyl silicone) substrate at 100°. Benzene was used as the internal standard for the quantitative determinations. The nitrosobenzene

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products were analyzed on an 8 ft × $^1/_4$ in. 3% SE-30 column at 120°. Calibration curves with areas of known chlorinated anilines were used to determine per cent yield. The chloropyridines were analyzed on an 8 ft × $^1/_4$ in. column containing 3% Carbowax 20M and 5% KOH at 100°. Morpholine was used as the internal standard for quantitative measurements. For the chloro-*o*-toluidines a 6 ft × $^1/_8$ in. column containing 10% Carbowax 1540 (polyethylene glycol) and 5% KOH at 200° was used. Quantitative measurements were made with aniline as the internal standard. Acetanilide and 4-chloroacetanilide were analyzed on a 6-ft 3% SE-30 column at 170°.

Only two compounds were not commercially available for vpc identification: 2,4-dichloro-6-methylaniline (mp 183–185° of acetanilide derivative, lit.[14] 186°) and 4-chloroacetanilide (mp 177–179°, lit.[15] 179°). The 2,4-dichloro-6-methylaniline was prepared from 4-chloro-2-methylaniline (Aldrich Chemical Co.) by chlorinating the acetanilide derivative.[16]

Registry No.—**1**, 586-96-9; **2**, 611-23-4; **3**, 694-59-7; phosphorus pentachloride, 10026-13-8; phosphoryl chloride, 10025-87-3; phosphorus trichloride, 7719-12-2.

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A Nuclear Magnetic Resonance Study of Some Nitrogen-15 Substituted Azo Heterocycles

C. H. YODER,* R. C. BARTH, W. M. RICHTER, AND F. A. SNAVELY

Department of Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania 17604

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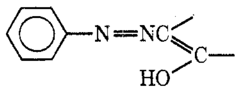
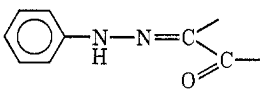
Six ^{15}N-substituted azo heterocycles have been prepared and their tautomeric structures studied by means of nmr spectroscopy. A phenylazo-3-pyrazolone and a phenylazo-4-pyrazolone exist in the azo form in $CDCl_3$, DMSO, and C_5H_5N. Phenylazothioindoxyl and the phenylazo derivative of diphenylbarbituric acid exist predominantly in the phenylhydrazone form in DMSO at room temperature. The phenylazo derivatives of coumaran-2-one and 4-hydroxycoumarin exhibit phenylhydrazone geometric isomerism in DMSO and $CHCl_3$, respectively.

The determination of the structure of azo heterocycles by the usual spectroscopic techniques is often plagued by the ambiguities inherent in peak assignment. In an attempt to eliminate these ambiguities in our own investigations, we have prepared and studied the ^{15}N isotopomers of six heterocycles containing the structural feature A or B.



A

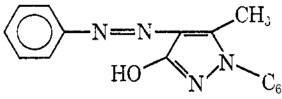


B

Each of the compounds can exist in at least two different tautomeric forms; all but the above two forms can be eliminated by conventional techniques.

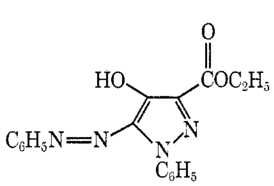
The ^{15}N isotopomers were prepared by diazotization of ^{15}*N*-aniline and coupling to the appropriate heterocycle. The probability of isotopic scrambling under the conditions used (*vide infra*) has been shown to be very low and the heterocycles can therefore be safely assumed to carry the ^{15}N attached to the benzene ring.[1] Since the ^{15}N isotope has a spin quantum number of $^1/_2$, the NH proton resonance of form B would be a low-field doublet with coupling constant of 90–100 Hz. The OH proton resonance of A will be, of course, a low-field singlet. If the compound exists as a mixture of A and B and if the proton exchanges intermolecularly between the ^{15}N of B and the oxygen of A or between two molecules of B, the shape of the peak(s) will depend upon the rate of exchange. If the exchange is fast and intramolecular, the shape depends upon the coupling constant in pure B and the composition of the mixture.[2]

The nmr spectrum of 5-methyl-4-phenylazo-1-phenyl-3-pyrazolone (**1**), whose structure has previously been determined to be the azo form shown (and for which no simple hydrazone tautomeric structure can be written),[3] showed the expected singlet for the acidic proton in both the ^{14}N and ^{15}N derivatives in $CDCl_3$ from 38 to −51°, in DMSO at 38°, and in pyridine at 38 to −23°. The chemical shifts of all compounds are listed in Table I.



1

The acidic proton resonance for 3-carboethoxy-1-phenyl-5-phenylazo-4-pyrazolone (**2**) in all three solvents was a singlet, an observation which could be interpreted as indicative of only the azo form or of rapid intermolecular exchange. The similarity of chemical shifts and peak shapes to those of **1** favors the



2

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