COMMUNICATIONS TO THE EDITOR

Reactions of N-Aryliminotriethoxyphosphoranes with Benzaldehydes

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Alkenephosphorane (**1**), iminophosphorane (**2**), and Phosphine oxide (**3**) are among the most important double bonds involving phosphorous atom[1]. The chemistry of the phosphonium yield (**1**) has been extensively studied in regard to its synthetic utility[1,2]. In contrast, relatively little is known about the reactions of the

$R_3P=CR_2'$ $R_3P=NR'$ $R_3P=O$

1 **2** **3**

closely related iminophosphoranes (**2**). The literature results indicate that the imino nitrogen of **2** (R = alkyl or aryl) is a typical nucleophile undergoing reactions such as alkylation, acylation, halogenation, and carbonyl addition[3,4]. The hydrolysis of N-phenyliminotriethoxyphosphorane has also been studied[5].

As part of our ongoing program directed at exploring the chemistry of iminophosphoranes, we have synthesized N-aryliminotriethoxyphosphoranes and investigated their reactions with benzaldehydes. In this communication, we report that **4** reacts readily with benzaldehydes to form the corresponding imines in good yields (Eq.1).

$$XC_6H_4CHO + (EtO)_3P=NC_6H_4Y \rightarrow XC_6H_4CH=NC_6H_4Y + (EtO)_3P=O \quad (1)$$

4

N-Aryliminotriethoxyphosphoranes (**4**) were prepared by reacting triethylphosphite (50 mmol) with appropriate substituted azidobenzenes[6] (50 mmol) in absolute ether for 2 hours at 0-5°C[7]. Evaporation of the ether and vacuum distillation afforded **4** in 80-92% yields. The reactions of **4** with benzaldehydes were conducted by dropwise addition of **4** (50 mmol) in 30 m*l* dry benzene to a 50 m*l* solution of substituted benzaldehyde (50 mmol) in dry benzene followed by 4 hour reflux. Removal of the solvent and recrystallization of the product from ethanol produced the imines in 50-93% yields.

The results are summarized in Table 1. All of the iminophosphoranes (**4**) used in this study reacted with benzaldehydes to form imines in modest to excellent yields. The imine yield increases with electron withdrawing ability of the substituents of benzaldehyde, although no relationship is readily apparent between the N-aryl substituents of **4** and the product yields. It should be noted that even the least reactive iminophosphorane prepared so for [2,4] exhibit remarkable reactivity in these reactions. The results underline the high nucleophilicity of the imino nitrogen of the iminophosphoranes (**2**).

Table 1. Yields of N-Benzylideneanilines ($XC_6H_4CH=NC_6H_4Y$) from Reactions of N-Aryliminotriethoxyphosphoranes with Benzaldehydes

Entry	X	Y	Yield(%)	mp(°C) (lit. mp)
1	H	H	51	51-53 (52)[8]
2		p-CH_3	88	163-164/3[a] (158-159/3)[a,9]
3		p-Cl	50	62-65 (63-63.5)[10]
4		m-NO_2	74	74-75 (73)[10]
5	p-Cl	H	64	65.66 (63.5-64.5)[11]
6		m-NO_2	68	123-125 (125)[10]
7	p-NO_2	H	90	88-90 (92-93)[9]
8		p-CH_3	93	123-125 (120-123)[12]
9		m-CH_3	79	95-96 (94)[12]
10		p-Cl	58	132-133 (134-136)[13]
11		m-NO_2	71	163-165 (164.5-168.5)[13]

[a]Boiling point in °C/mmHg.

Acknowledgement. This investigation was supported by grants from the Basic Research Institute Program, Korea Ministry of Education (1985) and the Korea Science and Engineering Foundation.

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A New Dehydration Procedure by Ultrasonic Reaction in Homogeneous System

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Recent communications describing an improved modification of many reactions indicate considerable potential for ultrasound in synthesis[1-6]. Most of the papers have described rate accelerations by ultrasound in heterogeneous reaction mixtures. However, ultrasonically induced chemical reactions under homogeneous conditions have little been studied before. We report herein the observed sonochemistry under homogeneous conditions, the dehydration of N-nitroso-3-phenylglycine derivatives(1) and N,N'-dinitroso-p-phenylenediglycine(3) in acetic anhydride solution.

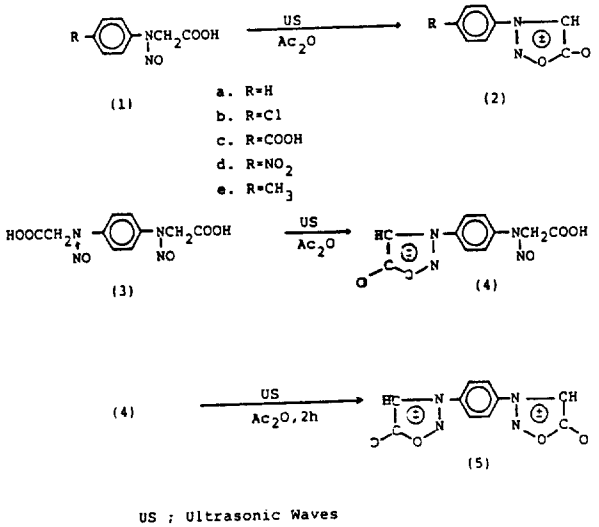
The nitroso compounds (1 and 3) were chosen for our studied because of their well-studied physical and chemical properties[7]. Conventionally, sydnone and disydnone (2 and 5) are normally prepared by refluxing the corresponding nitroso compounds (1 and 3) with excess Ac_2O or standing at room temperature for a few days. The best dehydration method by now was the use of trifluoro acetic anhydride[12], but we were able to obtain better results with acetic anhydride in the water bath of an ultrasonic laboratory cleaner at 25-30°C. These results are listed in Table 1.

All of the examined nitroso compounds gave the corresponding sydnones in fair to excellent yields with no concern for substituent groups. And the reaction times for the dehydration of compounds 1d, 3 and 4 were remarkably decreased.

Table 1. A comparison of Results Between Ultrasonic Wave and Conventional Methods

Reactant	Product	Ultrasonic wave method[a]		Conventional method[8-12]	
		Yield, %	Time, h	Yield, %	Time, h
1a	2a	94	2	87	2[b]
1b	2b	98	2	82	2[b]
1c	2c	92	1	70	1[b]
1d	2d	90	1	low	14 days[c]
1e	2e	94	4.5	35	2[b]
3	4	98	5	low	10 days[c]
3	5	98	7	17	5 days[c]
4	5	90	2	17.7	5 days[c]
				71	2[d]

[a]Reactions were run at 25-30°C in Ac_2O isolated yields with > 95% purity by NMR. [b]Reaction temperature was 80-90°C in Ac_2O. [c]Allowed to stand at room temperature in Ac_2O. [d]Stirring in room temperature with trifluoro acetic anhydride in THF.



But there were no considerable differences in the reaction times between with and without ultrasonic waves for compounds 1a, 1b, 1c, and 1e. Furthermore, when N,N'-dinitroso-p-phenylenediglycine(3) was sonificated for 5 hours, only compound(4) was obtained and detected by TLC; Lieberman test for nitroso group was positive; ν_{max} 1755, 1687, 1445, 1396 cm^{-1}. And when excess acetic anhydride was added to the solution and it was further treated with ultrasonic waves for 2 hours, we obtained compound(5); the test for nitroso group was negative; ν_{max} 1760, 733 cm^{-1}. When we also examined the compound(3) with excess acetic anhydride for 7 hours by ultrasonic waves, only compound(5) was obtained and detected by TLC. Compared with the synthetic methods of sydnones reported hitherto, the present method is more convenient and gives better yields. The reasons why these results are obtained are not clearly known. We are, at present, doing some research in mechanistic studies in order to find out why dehydration is promoted by ultrasonic waves.

A typical reaction procedure is as follows: a mixture of 2.82g (0.01 mol) of compound(1) and 5.1g (0.05 mol) of dry acetic anhydride in round bottomed flask was irradiated in an ultrasoic laboratory cleaner bath, (Bransonic 12,80W, 117V Ac) at 25-30°C for 1-5 hours. The resulting solution was cooled to room temperature and the excess of acetic anhydride was removed in vacuo. The solid was collected, and recrystallized. Each product was characterized by IR, NMR, and elementary analysis. These results matched to authentic