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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 synthesis¹⁻⁶. 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.

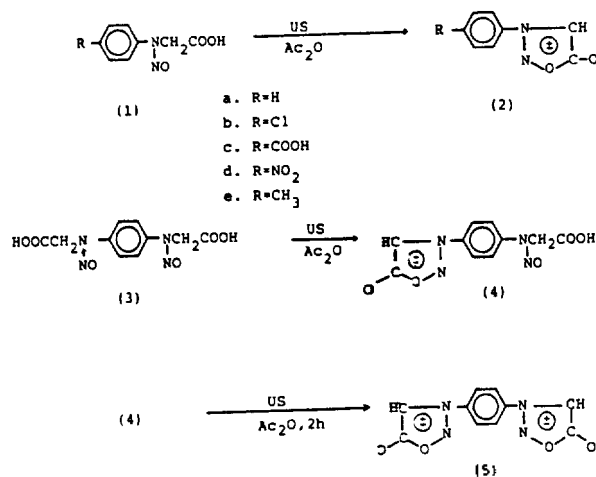
The nitroso compounds (1 and 3) were chosen for our studied because of their well-studied physical and chemical properties⁷. Conventionally, sydnone and disydnone (2 and 5) are normally prepared by refluxing the corresponding nitroso compounds (1 and 3) with excess Ac₂O or standing at room temperature for a few days. The best dehydration method by now was the use of trifluoro acetic anhydride¹², 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 ^{b, 12}	
		Yield, %	Time, h	Yield, %	Time, h
1a	2a	94	2	87	2 ^a
1b	2b	98	2	82	2 ^a
1c	2c	92	1	70	1 ^a
1d	2d	90	1	low	14 days ^c
1e	2e	94	4.5	35	2 ^a
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 ^a

^aReactions were run at 25-30°C in Ac₂O isolated yields with > 95% purity by NMR. ^bReaction temperature was 80-90°C in Ac₂O. ^cAllowed to stand at room temperature in Ac₂O. ^dStirring in room temperature with trifluoro acetic anhydride in THF.



US ; Ultrasonic Waves

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 sonicated 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 ultrasonic 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

samples.

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New Methods for the Preparation of Nitriles and Isothiocyanates Using Di-2-pyridyl Carbonate

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In connection with our ongoing research program on the synthetic utility of 2-pyridyl related active esters and carbonates, we have reported that di-2-pyridyl carbonate (2-DPC) is an efficient coupling reagent for the direct esterification of carboxylic acids^{1,2} and a carbonyl transfer reagent for the formation of cyclic carbonates from 1,2- and 1,3-diols³. We now wish to report that nitriles can be prepared from aldoximes in high yields under mild conditions (eq. 1) and triethylammonium dithiocarbamates, easily prepared from amines, carbon disulfide, and triethylamine, are cleanly converted into the corresponding isothiocyanates (eq. 2) by the use of 2-DPC, respectively.

Conversion of aldoximes into nitriles using 2-DPC was carried out in the presence of bases such as triethylamine, 4-dimethylaminopyridine (DMAP), and 1,8-diazabicyclo-

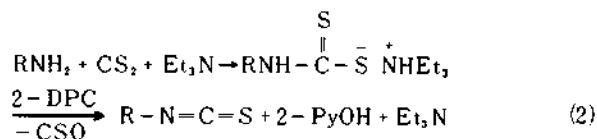
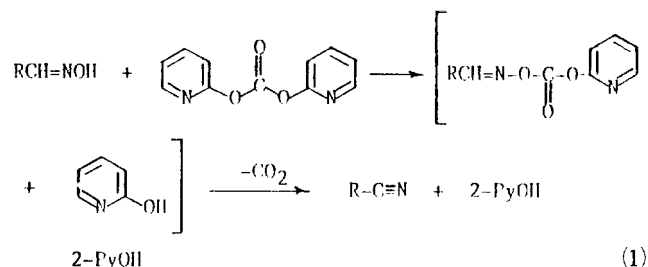


Table 1. Preparation of Nitriles from Aldoximes

Aldoxime	Method ^a	Time, h	Yield, %	b.p./torr or m.p.	
				found ^a	reported
C ₆ H ₅ CH=NOH	A	3	83	68-69/9	190/760 ¹⁰
p-CH ₃ C ₆ H ₄ CH=NOH	A	2	95	62-64/1.5	91/11 ¹⁰
p-CH ₃ O-C ₆ H ₄ CH=NOH	A	5	82	60	60 ⁶
	B	0.5	94		
p-Cl-C ₆ H ₄ CH=NOH	A	0.5	91	92-93	91-92 ⁶
	B	0.7	90		
p-NO ₂ -C ₆ H ₄ CH=NOH	A	0.1	93	145-146	146-147 ⁶
	B	0.5	90		
c-C ₆ H ₁₁ CH=NOH	A	12	87	65-67/9	66/9 ⁶
	B	2	88		
CH ₃ (CH ₂) ₇ CH=NOH	A	12	84	60-62/1	224/760 ¹⁵
	B	2	84		
C ₆ H ₅ CH=CH-CH=NOH	A	12	85	90-91/1.1	136-138/19 ⁷
	B	1.5	89		

^aMethod A: with 0.1 equiv of DBU in CH₂Cl₂ at room temperature. Method B: in refluxing toluene. ^bAll nitriles obtained here are known compounds identified by physical and spectral data (m.p., b.p., IR, and ¹H-NMR).