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Nitrous Acid Deamination of 1,1-Disubstituted Aromatic Hydrazines

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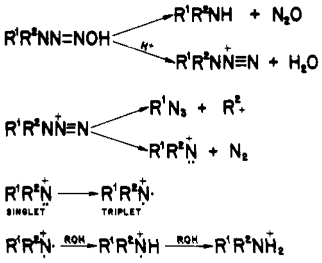
The nitrous acid deamination of *N*-methyl-*N*-phenylhydrazine, 1,1-diphenylhydrazine, and 9-aminocarbazole gave as products *N*-methylaniline, diphenylamine, and carbazole, respectively. *N*-*tert*-Butyl-*N*-phenylhydrazine gave *N*-*tert*-butylaniline and phenyl azide as products. These reactions were carried out in methanol, *n*-butanol, and benzene with isoamyl nitrite–HBF_4 and isoamyl nitrite–acetic acid as the deamination reagents. Nitrous oxide was produced in all reactions. The yield of nitrous oxide is always less than that of the secondary amine formed in each reaction. This demonstrates that secondary amines are formed in two processes. It is proposed that the initially formed *N*-nitrosohydrazines can also give an *N*-diazonium ion. This species can decompose to give a nitrenium ion and nitrogen or phenyl azide and a carbonium ion. When the deamination of *N*-*tert*-butyl-*N*-phenylhydrazine was carried out in methanol, the carbonium ion fragment was trapped as the methyl ether. The formation of phenyl azide and methyl *tert*-butyl ether is evidence for the existence of an *N*-diazonium ion. The products expected from a singlet nitrenium ion derived from *N*-*tert*-butyl-*N*-phenylhydrazine were prepared. No evidence was found for their formation. Evidence is presented that nitrogen-centered radicals are not formed. The results indicate that the nitrenium ions generated by deamination are different from similar species produced from *N*-chloroanilines. This difference appears to be related to the manner in which the positive charge develops. It is proposed that the decomposition of the *N*-diazonium ion generates a nitrenium ion in which the positive charge is localized on nitrogen and that this leads to an enhanced rate of spin inversion. The secondary amines observed are formed by hydrogen atom abstraction by a triplet nitrenium ion and, as previously observed, with the formation of nitrous oxide.

Scheme I



Nitrenium ions[2,3] have been proposed as intermediates in the reactions of *N*-chloroamines,[2,3a,4-9] *N*-bromo amines,[10] *N*-chloro amides,[11] *N*-chloro sulfinates,[12] organic azides,[13] hydroxylamines,[2,3a,c,14] and hydroxylamine derivatives.[14,15] They have also been prepared electrochemically.[16-19] A potential route to nitrenium ions is the nitrous acid deamination of 1,1-disubstituted hydrazines. This is analogous to the formation of carbonium ions during the nitrous acid deamination of certain primary amines.[20] Early studies by Fisher and Thiele on the deamination of 1,1-disubstituted hydrazines such as *N*-methyl-*N*-phenylhydrazine showed that a secondary amine and nitrous oxide are produced.[21] Recently benzimidazole was obtained from the deamination of 1-aminobenzimidazole.[22] The putative mechanism for the deamination process is[23,24] given in eq 1. Several groups have investigated the possibility of forming nitrenium ions by this path.[25,26] The nitrous acid deamination of 2-amino-3,3,4-trimethyl-2-azabicyclo[2.2.1]heptane has been reported to give a product derived from the rearrangement of a nitrenium ion intermediate and the corresponding secondary amine.[25]

$$R^1R^2NNH_2 + HONO \rightarrow R^1R^2NNHNO \rightarrow R^1R^2NN{=}NOH \rightarrow R^1R^2NH + N_2O \quad (1)$$

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[12] T. Sheradsky and S. Avramovici-Grisaru, *Tetrahedron Lett.*, 2325 (1978).

[13] For a discussion on this see R. A. Abramovitch and E. P. Kyba in "The Chemistry of the Azido Group", S. Patai, Ed., Wiley-Interscience, New York, 1971, pp 223–42.

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Table I. Nitrous Acid Deamination of 1,1-Disubstituted Aromatic Hydrazines

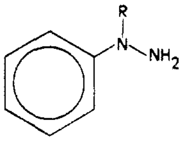
hydrazine	reaction conditions[a,b]				product yields,[c] %		
	solvent	acid[d]	amt LiOAc, g	time, h	PhN_3	PhNHR	N_2O
1[g]	MeOH	HBF_4		20	trace	58	10
1	MeOH	AcOH	12.0	20		61	16
1	*n*-BuOH	AcOH	1.0	20		68	22
1	C_6H_6	AcOH	0.20	20		90	15
2	MeOH	HBF_4		20	8	78	20
2	MeOH	AcOH	6.0	20[e]	12	45	21
2	*n*-BuOH	AcOH	0.50	20	16	63	21
2	C_6H_6	AcOH	0.20	20	16	57	14
3	MeOH	HBF_4		0.5		80	20
3	MeOH	AcOH	12.0	4		62	13
3	*n*-BuOH	AcOH	1.0	4		71	21
3	C_6H_6	AcOH	0.20	4		87	31
4	MeOH	HBF_4		20		65[f]	14
4	MeOH	AcOH	6.0	20		52[f]	15
4	*n*-BuOH	AcOH	0.50	20		75[f]	28
4	C_6H_6	AcOH	0.20	20		72[f]	44

[a] All reactions run at 50 ± 2 °C. [b] Reactions of 1 and 3 run on 1.80 mmol of hydrazine in 50.0 mL of solvent. Reactions involving 2 and 4 where run on 0.90 mmol of hydrazine in 25.0 mL of solvent. [c] Based on recovered starting material. [d] 12.0 or 6.0 mmol or acid used. [e] Methyl *tert*-butyl ether was also formed. [f] Carbazole. [g] PhNRNO was obtained as a product (5% yield) only for this set of conditions.

An attempt to cyclize *N*-aminoazacyclonane to indolizidine has been reported.[26] Nitrous oxide was detected in both studies. In this study we report on the nature of the nitrenium ions generated by the nitrous acid deamination of aromatic 1,1-disubstituted hydrazines.

Results and Discussion

The nitrous acid deamination of the 1,1-disubstituted hydrazines 1–4 was studied in methanol, *n*-butyl alcohol, and benzene. Deamination reactions were run with isoamyl nitrite–HBF_4 or isoamyl nitrite–acetic acid–lithium acetate as the source of nitrous acid. A slight excess (5–10%) of nitrous acid was used. Lithium acetate was added as a possible trapping agent to reactions run in benzene. Its use was continued in the other solvents. The reaction mixture was deaerated with N_2 and evacuated to 1 mm, and the deamination carried out at 50 ± 2 °C. The nitrous oxide formed was trapped with an efficiency of 80+%, and the yield was obtained from its absorbance in the IR[27] at 1300 cm^{-1}. The reactions run in alcoholic media were deaerated at 0 °C and those in benzene at room temperature. The yields of nitrous oxide for reactions run in benzene are comparable to or higher than those in the alcohols. This indicates that loss of nitrous oxide during deaeration is not a significant problem.



1, R = CH_3
2, R = t-C_4H_9
3, R = C_6H_5

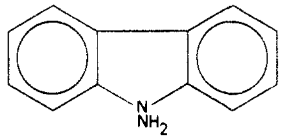


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Table I summarizes the products and the yields obtained in the deaminations studied. A comparison of the yields of secondary amine and nitrous oxide obtained in each reaction clearly demonstrates that most of the parent amines are formed in a reaction competitive with the process in eq 1. In the deamination of *N*-*tert*-butyl-*N*-phenylhydrazine, a small amount of phenyl azide was observed. It is proposed that the initially formed *N*-nitrosohydrazine decomposes not only to give an amine and nitrous oxide but also to give an *N*-diazonium ion. The products not accounted for in the process illustrated in eq 1 are derived from the decomposition of this species. The proposed *N*-diazonium ion can give a nitrenium ion and nitrogen or phenyl azide and a carbonium ion (Scheme I).

When the deamination of *N*-*tert*-butyl-*N*-phenylhydrazine was carried out in methanol, the *tert*-butyl carbonium ion fragment was trapped as the methyl ether. The formation of phenyl azide and methyl *tert*-butyl ether is evidence for the formation of an *N*-diazonium ion.

N-Diazonium ions[13] have been proposed as intermediates in the reactions of organic azides with strong acids[13] and alkylating[28] and arylating agents.[29] Tetraalkyl-2-tetrazenes undergo electrophilic attack and fragment to give an *N*-diazonium ion.[30] It has been proposed that this type of intermediate can decompose to give a nitrenium ion and nitrogen or that the loss of nitrogen is synchronous with either attack by a nucleophile or migration of a neighboring group.[13]

Cyclization of 2-azidobiphenyl-2′-diazonium tetrafluoroborate[29] is reported to give an *N*-diazonium ion; the same intermediate which we propose is formed during the deamination of 9-aminocarbazole (4). This intermediate then decomposes to give carbazole and nitrogen.[31] Nitrenium ions have been proposed as intermediates in the reactions of *N*-chloro-*N*-methylaniline[4] and *N*-chloro-*N*-*tert*-butylaniline[4,5] in methanol. Anisidines were obtained among the products. If the deamination of *N*-methyl-*N*-phenylhydrazine, *N*-*tert*-butyl-*N*-phenylhydrazine, and other hydrazines under study produced the same intermediates as in the above reaction, similar products should also be observed. A search was made for *N*-*tert*-butyl-*p*-anisidine under conditions where a 1% yield of this anisidine could be detected by VPC or NMR; none was found. The major or only organic product observed in each re-

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(31) The authors propose that carbazole is formed by hydride abstraction.

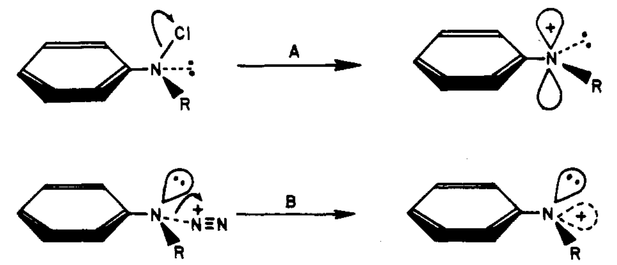

Figure 1. (a) Formation of a delocalized nitrenium ion from an *N*-chloroaniline. (b) Formation of a localized nitrenium ion from an *N*-diazonium ion. In the illustrated example the hybridization of nitrogen in both precursor and nitrenium ion is sp^3. In an actual example the hybridization would depend on the substituents present on the ring and on nitrogen [T. Axenrod, P. S. Pregosin, M. J. Wieder, E. D. Becker, R. B. Bradley, and G. W. A. Miline, *J. Am. Chem. Soc.*, **93**, 6536 (1971); M. P. Sibi and R. L. Lichter, *J. Org. Chem.*, 42, 2999 (1977); B. M. Lynch, *Tetrahedron Lett.*, 1357 (1969)].

action is an unsubstituted secondary amine. The reductive deamination of amines has been reported to occur by a radical mechanism.[32] Analogously, nitrogen radicals[33] could be formed in this study, and hydrogen atom abstraction would give the observed amines. The nitrogen-centered radicals which could be formed in this study have been previously reported.[34-37] These radicals couple, and mixtures of products are often formed.[34-38] When deamination of 2 was carried out in air, additional products were obtained. Analysis of the complex mixture by gas chromatography/mass spectroscopy indicated the presence of compounds containing more than one *N-tert*-butylaniline moiety. Similarly, in the deamination of 3 in air, a product was observed whose mass spectrum indicated it to be a diphenylamine dimer. If nitrogen radicals were formed in this study, the same type of product should have also been observed under nitrogen.[39] The failure to observe these products in an oxygen-free system eliminates neutral nitrogen radicals as intermediates. Cation radicals would also be expected to lead to coupling products[40] and can be eliminated as possible intermediates on the same basis as above.

The products obtained in this study indicate a difference in the nitrenium ions produced by deamination and those formed from similarly substituted *N*-chloroanilines. It is proposed that this is the result of the manner in which the positive charge develops on nitrogen. This is illustrated in Figure 1.

A process such as A in Figure 1 leads to a delocalized nitrenium ion, and a full positive charge never develops on nitrogen. This type of behavior has been observed in the reactions of para-substituted *N*-chloroanilines in methanol. In this study a ρ of -6.35 was found, indicative of considerable delocalization of the positive charge into the aromatic ring. Alternatively, the nitrenium ion can be formed with a full positive charge on nitrogen (Figure 1B). It is proposed that the nitrenium ion formed by the nitrous acid deamination reaction under study is formed in this manner.

Once formed, a localized nitrenium ion could react as follows: (a) trapping by a nucleophile to give ring-substituted product and/or *N*-substituted product; (b) hydride abstraction[5] to give an unsubstituted secondary amine;[29] (c) spin inversion[2] to the triplet state and subsequent hydrogen atom abstraction to give the same amine as in b. The N-substituted products expected from the deamination of *N-tert*-butyl-*N*-phenylhydrazine were prepared. No evidence was found for their formation.[41] It is not possible at present to distinguish between pathways b and c. It has been postulated as a possibility that concentration of the positive charge on nitrogen leads to enhanced spin inversion to the triplet state.[5] Our results support this hypothesis, and on the basis of the known behavior of the triplet nitrenium ion,[2] it appears at present to be the most plausible intermediate. Hydride abstraction is not explicitly ruled out by this study.

Figure 1 indicates that the formation of a localized nitrenium ion (Figure 1B) should be favored by a trigonal nitrogen and good leaving groups, whereas a delocalized nitrenium ion (Figure 1A) should be favored by a tetrahedral nitrogen and poorer leaving groups, with phenyl participation being more important.

The results of this study indicate that the nitrous acid deamination of phenylhydrazines occurs by more than one pathway and that the products derived from a nitrenium (anilenium) ion depend on the manner in which the positive charge develops on nitrogen.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer 236 spectrometer, NMR spectra on Varian A60-P and HA-100 spectrometers, and mass spectra on a Varian CH7 spectrograph. Quantitative analyses of reaction mixtures were done on a Hewlett-Packard 5750 gas chromatograph and a Varian 1520 Autoprep gas chromatograph. The Varian Autoprep was also used for preparative purposes. Melting points are uncorrected.

N-Methylaniline was distilled prior to use from zinc dust. Diphenylamine and carbazole were obtained commercially and used without further purification. *N-tert*-Butylaniline was prepared by the reaction of *tert*-butyl iodide with aniline.[42] *N-tert*-Butyl-*p*-anisidine was prepared by heating a mixture of *p*-anisidine hydrochloride and *tert*-butyl alcohol in a steel bomb for 24 h.[43] Literature procedures were used to convert *N*-methylaniline,[44] *N-tert*-butylaniline,[42] diphenylamine,[44] and carbazole[45] into their respective *N*-nitroso derivatives. *N*-

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[32] (a) K. V. Scherer and R. S. Lunt, *J. Am. Chem. Soc.*, **88**, 2860 (1966). (b) For a recent example see M. P. Doyle, J. F. Dellaria, B. Siegfried, and S. W. Bishop, *J. Org. Chem.*, **42**, 3494 (1977). (c) A review has appeared which discusses hydrodediazoniation of aromatic diazonium ions: H. Zollinger, *Angew. Chem., Int. Ed. Engl.*, 17, 141 (1978).

[33] See ref 26 and the following for a discussion of nitrenium ion vs. nitrogen radical processes for the reaction of *N*-chloro amines with Ag$^+$: O. E. Edwards, G. Bernath, J. Dixon, J. M. Paton, and D. Vocelle, *Can. J. Chem.*, **52**, 2123 (1974). See also P. G. Gassman, K. Uneyama, and J. L. Hahnfeld, *J. Am. Chem. Soc.*, **99**, 647 (1977).

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[38] In the following study the structure and yield of similar dimers have been worked out: R. F. Bridger, *J. Am. Chem. Soc.*, **94**, 3124 (1972).

[39] It is likely that in air the hydrazine is oxidized to the tetrazene which subsequently decomposes to give nitrogen radicals (see ref 6, footnote 25).

[40] R. F. Nelson in "Techniques of Chemistry", Vol V, N. L. Weinberg, Ed., Wiley, New York, 1974, Part 1, Chapter V.

[41] The *O*-methyl and *O*-acetyl derivatives of *N-tert*-butylphenylhydroxylamine were prepared. The *O*-acetyl derivative was stable (95% recovery) to the acid conditions, whereas under the same conditions there was an ca. 20% loss of the *O*-methyl compound. No formation of anisidine by the rearrangement of the *O*-methyl compound in acid was detected. The *O*-acetyl derivative was stable during VPC, and 1% yield could have been detected. The *O*-methyl derivative decomposed during VPC analysis, but by NMR it was possible to detect 1% of a methoxy-containing compound.

[42] W. J. Hickinbottom, *J. Chem. Soc.*, 946 (1933).

[43] W. W. Hartman and L. J. Roll, "Organic Syntheses", Collect. Vol. II, Wiley, New York, 1943, p 460.

[44] I. L. Kotlyarevskii, M. P. Terpugova, and A. A. Mituyshova, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Kim. Nauk.*, 151 (1965); *Chem. Abstr.*, **63**, 11402*h* (1965).

Nitroso-*N*-methylaniline,[43] *N*-nitrosodiphenylamine,[44] and *N*-nitrosocarbazole[45] were reduced with glacial acetic acid and zinc dust to their respective 1,1-disubstituted hydrazines.

***N*-*tert*-Butyl-*N*-phenylhydrazine.** A 4.0-g (0.023 mol) sample of *N*-nitroso-*N*-*tert*-butylaniline in 100 mL of anhydrous tetrahydrofuran was added slowly to 200 mL of gently refluxing tetrahydrofuran containing 1.7 g (0.045 mol) of lithium aluminum hydride, and the reaction mixture was refluxed for 16 h. The solvent was partially removed by evaporative distillation and excess lithum aluminum hydride destroyed by the careful addition of water. The reaction mixture was filtered and the solid residue washed with benzene. The benzene was removed by evaporative distillation, and the residue was distilled to give a 2.1-g (62%) yield of *N*-*tert*-butyl-*N*-phenylhydrazine: bp 91–93 °C (5.0 mm) [lit.[35] bp 47–48 °C (0.3 mm)]; NMR δ 1.12 (s, 9), 3.34 (s, 2), 7.10 (s, 5); IR (neat) 3325, 3050, 2960, 770, 700 cm^{-1}.

Deamination Procedure. The following is an example of the general procedure followed. Differences in the reaction times, acid used, and amount of added lithium acetate are noted in Table I. In a 250-mL flask there were combined 0.2196 g (1.80 mmol) of *N*-methyl-*N*-phenylhydrazine, 0.2391 g (1.94 mmol) of isoamyl nitrite (Eastman Yellow Label, 95% minimum purity), 0.20 g of lithium acetate, 0.68 mL (12.0 mmol) of glacial acetic acid, and 50.00 mL of benzene. The solution was deaerated by bubbling dry nitrogen through it for 5 min. The solution was frozen in a dry ice/2-propanol bath, evacuated to a pressure of 0.5–1.0 mm, and heated for 20 h at 50 ± 2 °C in an oil bath. Gaseous products were collected and analyzed as described in a following section. The mixture was then stirred with 2 g of sodium carbonate for 30–60 min. The benzene phase was decanted, and the sodium carbonate was dissolved in a small amount of water and extracted with two 25-mL portions of benzene. The benzene fractions were combined, and the volume was reduced to approximately 5 mL by distillation on a steam bath using a 10-cm column packed with glass helices. The internal standard was added and the mixture analyzed by gas chromatography. When an alcohol was used as the solvent, the mixture was first basified as above, the alcohol was decanted, and the sodium carbonate was washed twice with small volumes (10–20 mL) of alcohol. The alcohol fractions were combined, and 300 mL of water was added. The aqueous solution was extracted five times with 50-mL portions of benzene. The benzene phase was washed twice with an equal volume of water, reduced in volume, and analyzed by VPC.

Isolation and Analysis of Nitrous Oxide. Authentic nitrous oxide was obtained from Matheson. The identification and analysis of nitrous oxide were done by infrared spectroscopy. Nitrous oxide[27] has intense peaks at 1300 and 2250 cm^{-1}. These peaks were used for the quantitative determination of nitrous oxide. Spectra were taken of known volumes of nitrous oxide injected into an evacuated 10.0-cm gas cell with a gas-tight syringe. The gas cell was then brought to atmospheric pressure. Absorbance was plotted against volume.

Standard vacuum-line techniques were used to trap any gases formed which were condensible at liquid nitrogen temperature. The trapped gaseous material was transferred to a gas cell. From the known volumes of the gas cell and trap, the fraction of trapped gas transferred to the IR cell was calculated. The infrared spectrum was taken, and the calibration curve was used to determine the amount of nitrous oxide produced in the reaction. The trapping efficiency of the vacuum line was determined as follows. In a 250-mL flask were placed 50.00 mL of solvent and a magnetic stirring bar. The flask was covered with a septum, and a 10-mL, gas-tight syringe was used to bubble 5.0 mL of nitrous oxide through the solvent. The solution was frozen in a bath at −72 °C, connected to the vacuum line, and degassed, and an IR spectrum was taken of the condensed material. Nitrous oxide was recovered with an efficiency of 80–90% from benzene and of 90–100% from the alcohols.

Product Analysis. Vapor-phase chromatography was used to determine the yields of the products obtained in the deamination of *N*-methyl-*N*-phenylhydrazine, *N*-*tert*-butyl-*N*-phenylhydrazine, and 1,1-diphenylhydrazine. The *N*-methyl-*N*-phenylhydrazine and *N*-*tert*-butyl-*N*-phenylhydrazine reaction mixtures were analyzed on a column packed with 20% SE-30 on Diataport S. A column packed with 5% Carbowax 20M and 5% KOH on Chromosorb W(HP) was used to analyze the 1,1-diphenylhydrazine reaction mixtures.

The products obtained in the deamination of 9-aminocarbazole were isolated in the following manner. HCl gas was slowly bubbled through the benzene solution containing the products for 300 s whereupon a white solid precipitated. The hydrochloride salt was dissolved in 50 mL of water, and the benzene was separated and washed with 25 mL of water. The benzene containing the neutral material was concentrated to dryness under reduced pressure and the residue was sublimed at 60 °C and 0.1 mm. Material was obtained whose melting point and IR spectrum indicated it was carbazole. The aqueous solution was cooled in an ice–salt bath, basified with a concentrated sodium hydroxide solution, and extracted with two 25-mL portions of benzene. The benzene was removed under reduced pressure to give a crystalline residue whose melting point and infrared spectrum indicated it was unreacted 9-aminocarbazole.

All the products obtained in the deamination of the various 1,1-disubstituted hydrazines were isolated by preparative vapor-phase chromatography. The IR spectra of the isolated compounds were compared to those of authentic samples. Phenyl azide is unstable at high temperatures and decomposed on the VPC detector (300 °C). The peak with the same retention time as authentic phenyl azide[46] was collected and an infrared spectrum taken. The spectrum of the decomposed material was identical with that obtained from authentic phenyl azide which had been injected and collected under identical conditions. The reaction mixture obtained from the deamination of *N*-*tert*-butyl-*N*-phenylhydrazine in benzene was concentrated, and an infrared spectrum was taken of the residue. The spectrum contained a strong doublet at 2090 cm^{-1}. A peak in this region has been shown to be characteristic for azides.[47]

Isolation and Identification of Methyl *tert*-Butyl Ether. An authentic sample of this ether was prepared by following a literature procedure:[48] bp 54–56 °C (lit. bp 55 °C); NMR ($CDCl_3$) δ 1.15 (s, 9), 3.22 (s, 3); mass spectrum, *m*/*e* (relative intensity) 87 (2), 74 (2), 73 (40), 59 (4), 58 (1), 57 (25), 56 (4), 55 (5), 45 (15), 44 (2), 43 (48), 42 (10), 41 (100), 40 (6), 39 (35), 31 (18). The molecular ion (*m*/*e* 88) was of the same magnitude as the background noise.

The deamination of *N*-*tert*-butyl-*N*-phenylhydrazine was carried out in methanol and the solution basified with sodium carbonate. The yield of methyl *tert*-butyl ether was obtained by VPC and use of a calibration curve of weight vs. peak height. This solution was then distilled, 1–2 mL collected in a cooled flask, and the material analyzed on a Varian Aerograph Series 2700 gas chromatograph connected to a Varian CH7 mass spectrometer. A 5 ft × $^1/_8$ in. column packed with 5% Carbowax 20M and 5% KOH on Chromosorb P was used with the column temperature at 65 °C, the injection port at 95 °C, and the flow at 20 mL/min. The methanol solution contained two components: a major component with a retention time of 50 s and a minor component with a retention time of 80 s. The major component had the same retention time and mass spectrum as those of an authentic sample of methyl *tert*-butyl ether. There was not enough of the minor component to analyze in the mass spectrograph. The yield of methyl *tert*-butyl ether was 6%, and that of the phenyl azide was 5%. A control experiment indicated that the ether was stable to the reaction conditions (93% recovery).

***O*-Acetyl-*N*-*tert*-butyl-*N*-phenylhydroxylamine.** A mixture of 2.07 g (10.0 mmol) of *N*-*tert*-butyl-*N*-phenylhydroxylamine,[49] 0.83 mL (10.2 mmol) of pyridine, and 25 mL of absolute ether was cooled in an ice–water bath, and a similarly cooled solution of 0.72 mL (10.1 mmol) of acetyl chloride in 25 mL of absolute ether added to it. The reaction was kept at 0 °C for 48

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(45) H. Wieland, *Justus Liebigs Ann. Chem.*, **392**, 169 (1912).

(46) Authentic sample of phenyl azide courtesy of Dr. R. H. Odum, Brooklyn College, CUNY.

(47) K. Nakanishi, "Infrared Absorption Spectroscopy—Pratical", Holden-Day, San Francisco, 1962, p 28.

(48) J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.*, **54**, 2088 (1932).

(49) (a) B. Zeeh and H. Metzger in "Methoden der Organishen Chemie (Houben-Weyl)", Vol X, R. Stroh, Ed., 4th ed., Georg Thieme Verlag, Stuttgart, 1971, Part 1, p 1127. (b) A. K. Hoffman, A. M. Feidman, and E. Gelbaum, *J. Am. Chem. Soc.*, **86**, 646 (1964).

h. The reaction mixture was washed with two 50-mL portions of ice-cold 1 N hydrochloric acid solution and two 50-mL portions of ice-cold 10% sodium hydroxide solution. The acidic, aqueous solution was basified with 10% sodium hydroxide solution, and starting hydroxylamine precipitated out. This material was collected on a Büchner funnel, washed with water, and sucked dry to give 0.41 g (20%) of recovered starting material. The etheral solution was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to a dark oil. The oil was recrystallized by addition of 5 times its volume of petroleum ether, and the mixture was cooled in a dry ice/2-propanol bath, filtered, washed with cold petroleum ether, cooled to −72 °C, and sucked dry to give 0.89 g (54% yield) of *O*-acetyl compound: mp 35–37 °C; NMR (CDCl$_3$) δ 8.77 (s, 9), 7.90 (s, 3), 2.68 (br s, 5); IR (neat) 2960, 1790, 800, 695 cm^{-1}.

***O*-Methyl-*N*-*tert*-butyl-*N*-phenylhydroxylamine.** A 0.0756-g (0.63 mmol) sample of potassium hydride (33% oil dispersion) was placed in a sintered-glass funnel and washed with two 50-mL portions of dry hexane, sucked dry under an atmosphere of dry nitrogen, and transferred with 50 mL of dry methyl sulfoxide into a flask, and 0.0981 g (0.55 mmol) of *N*-*tert*-butyl-*N*-phenylhydroxylamine was added. To this oil-free solution there was added 0.17 mL (1.02 mmol) of dimethyl sulfate. Upon addition of the dimethyl sulfate, the reaction mixture turned red. The mixture was allowed to stand at room temperature for 30 min, diluted with 500 mL of water, and extracted with three 100-mL portions of ether. The combined ethereal extracts were extracted twice with 50-mL portions of ice-cold 1 N hydrochloric acid solution and twice with equal volumes of water, dried over anhydrous sodium carbonate, filtered, and concentrated under reduced pressure to give a red oil. The red oil was purified by molecular distillation at 0.10 mm and 20 °C to give 0.0357 g (36%) of a red liquid containing *O*-methyl-*N*-*tert*-butyl-*N*-phenylhydroxylamine: NMR (CDCl$_3$) δ 8.88 (s, 9), 6.55 (s, 3), 2.73 (br s, 5); IR (neat) 2970, 1205, 770, 700 cm^{-1}. The NMR spectrum indicated it was 90% pure.

Registry No. 1, 618-40-6; 2, 36171-18-3; 3, 530-50-7; 4, 17223-85-7; *N*-methylphenylamine, 26915-12-8; *N*-*tert*-butylaniline, 937-33-7; diphenylamine, 122-39-4; carbazole, 86-74-8; *N*-nitroso-*N*-*tert*-butylaniline, 24642-84-0; nitrous oxide, 10024-97-2; methyl *tert*-butyl ether, 1634-04-4; *O*-acetyl-*N*-*tert*-butyl-*N*-phenylhydroxylamine, 76599-72-9; *N*-*tert*-butyl-*N*-phenylhydroxylamine, 1127-42-0; *O*-methyl-*N*-*tert*-butyl-*N*-phenylhydroxylamine, 76599-73-0.

Nuclear Magnetic Resonance, Paramagnetic Ion Induced Relaxation Method to Differentiate between 1,3-Diketo and 1,3-Keto–Enol Isomers[1]

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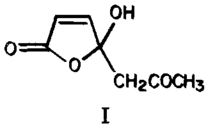
In aqueous solution manganous ion is shown to broaden the methyl ^{1}H resonance of the enol form of acetylacetone. Under the same conditions, where [Mn(II)] $\ll$ [keto–enol] and $\ll$ [1,3-diketone], the methyl of the diketo form is affected to a smaller degree. This is primarily due to the more favorable association constant of Mn(II) with the keto–enol than with the diketo form. This diagnostic is used to differentiate between resonances due to diketo and keto–enol forms of the substrate for maleylacetone cis–trans isomerase and is proposed for use in elucidating NMR spectra of other diketo/keto–enol mixtures.

Several years ago we reported the synthesis of maleylacetone ((*Z*)-4,6-dioxo-2-heptenoic acid),[2a] a substrate for the cis–trans isomerizing enzyme isolated from Vibrio 01 bacteria.[2b,e] The low-wavelength ultraviolet absorption maximum (195 nm) of the acid suggested that it exists in the cyclic form I, but at pH 7, strong absorption at 312 nm (ϵ 9300) indicated that the 4-hydroxy-6-oxo-2,4-heptadienoate ion (IIa and/or IIb) was present. Absorption at 212 nm (ϵ ~4000) and 243 (~4000) suggested that the (*Z*)-4,6-dioxo-2-heptenoate ion (IIc) may also be present at neutral pH.[2a] Of the two enol forms, (2*Z*,4*E*)-4-hydroxy-6-oxo-2,4-heptadienoate ion (IIa) and (2*Z*,4*Z*)-4-hydroxy-6-oxo-2,4-heptadienoate ion (IIb), the presence of IIa might be thought to be more probable because of the intramolecular hydrogen bond. In solvent water, however, intermolecular hydrogen bonding may compensate for the loss of the intramolecular bond. Moreover, the presence of IIb was postulated, for it was seen to have a mechanistic role in the silver ion catalyzed cis–trans isomerization about the C-2,C-3 bond of II.[2c,d]



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Although the presence of three species has been mentioned, it was known early that only two ^{1}H NMR methyl singlets of about equal intensities are exhibited by II in D$_2$O,[2a] even at 360 MHz. The two singlets are 0.08 ppm apart and are about equally intense. Two limiting interpretations are possible. The first is that one methyl singlet is due to the keto form IIc and one to a rapidly equilibrating mixture of IIa, IIb, and perhaps other enol isomers. This would mean that the molar extinction coefficient for the mixture of enol isomers at 312 nm would be unusually large (ϵ ~18 500). Moreover, interconversion of IIa and IIb would have to be more rapid than the conversion of either one to IIc. That is to say that a lower energy path than that shown in eq 1 is required to convert IIa to IIb.

The second possible interpretation is that IIc is present in very small quantity. Then one methyl singlet represents IIa and the other IIb, and the methyl resonance of IIc is undetectable or isochronous with one of the other resonances. Interconversion could occur according to eq 1 and

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[1] Research carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences and by the National Institutes of Health (Grant GM 27636).

[2] (a) Fowler, J.; Seltzer, S. *J. Org. Chem.* **1970**, *35*, 3529. (b) Seltzer, S. *J. Biol. Chem.* **1973**, *248*, 215. (c) Johnson, R. A.; Seltzer, S. *J. Am. Chem. Soc.* **1972**, *94*, 4755. (d) Johnson, R. A.; Seltzer, S. *Ibid.* **1973**, *95*, 5700. (e) Seltzer, S.; Lin, M. *Ibid.* **1979**, *101*, 3091.

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