methanol (10 mL) with stirring at room temperature under atmospheric pressure. After uptake of ca. 1 mmol of hydrogen, the reaction was stopped. The reaction mixture, exhibiting a strong odor of ammonia, was evaporated to dryness in vacuo and the residue was purified by short-path distillation under reduced pressure to give the parent quinoline which was characterized as its picrate.

From **8a** (144 mg): quinoline, 121 mg (94%).

From **8c** (158 mg): lepidine, 127 mg (89%).

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Registry No.—**6a,** 59046-19-4; **12a,** 55379-60-7; **12c,** 54507-51-6; **13a,** 59066-24-9; **13c,** 59066-25-0; **14a,** 59066-20-5; **14c,** 59066-21-6; **15a,** 59066-22-7; **15c,** 59066-23-8; **16a,** 59066-26-1; **16c,** 59066-27-2; **17a,** 59066-28-3; **17c,** 59066-29-4; **18a,** 61702-38-3; **18c,** 54507-52-7; **23a,** 580-22-3; **23c,** 27063-27-0; methyl chloroformate, 79-22-1.

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Amidrazones. 4.[1] Ylide Syntheses

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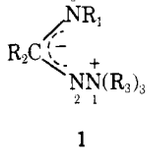
Aminimides derived from imidic acids (**3**) are conveniently prepared by the reaction of molar equivalents of a nitrile, 1,1,1-trimethylhydrazinium chloride (or tosylate), and KO-*t*-Bu in refluxing *t*-BuOH. Alkylation of 1,1,1-trimethyl-2-acetimidoylhydrazinium hydroxide inner salt (**3a**) with MeI and EtI gave N^3-alkylated salts which afforded N^3-substituted ylides (**6**) on neutralization. Reaction of 1,1,1-trimethyl-2-α-methoxybenzylidenehydrazinium tosylate (**11**) with either aniline or benzylamine gave 1,1-dimethyl-2-α-methoxybenzylidenehydrazine (**12**).

This paper summarizes the results of our study of preparative procedures for amidrazone ylides. These compounds, which may also be classified as aminimides[2] derived from imidic acids, are represented by the general structure **1**. The recommended[3] method for numbering the nitrogen atoms in amidrazones is also designated in structure **1** and is used throughout this paper.

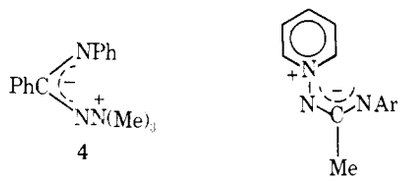


1

The preparation of ylides of type **1** has received scant attention. Appel and co-workers[4] have reported the preparation of 1,1,1-trimethyl-2-acetimidoylhydrazinium hydroxide inner salt (**3a**) by the addition of the *tert*-butyl alcohol complex of 1,1,1-trimethylhydrazinium hydroxide inner salt (**2**) to acetonitrile. We have previously reported[1] the preparation of ylide **4** by the reaction of **2** (generated in situ) with *N*-phenylbenzimidoyl chloride. Recently, Abramovitch and coworkers[5] obtained pyridinium ylides (**5**) by neutralization of the salts obtained by the reaction of 1-aminopyridinium fluoroborates with aryldiazonium fluoroborates in acetonitrile.

Subsequent to our communication describing the prepa-

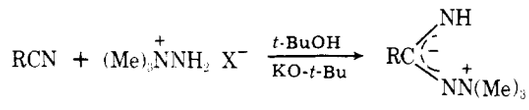
2 3a



4 5

ration and properties of **4**, a modified procedure was developed that resulted in a 72% yield of ylide. The improved procedure is described in the Experimental Section. Attempted preparation of the N^3-methyl analogue of this compound by reaction of *N*-methylbenzimidoyl chloride with **2** resulted in complex, tarry mixtures.

A serious disadvantage to the preparation of ylides of type **3** via Appel's[4] procedure is the difficulty encountered in the preparation of **2**, which is an extremely hygroscopic solid that requires rigorous exclusion of moisture for its successful preparation from 1,1,1-trimethylhydrazinium chloride and KO-*t*-Bu in THF containing *t*-BuOH. We have found that a variety of ylides of type **3** can be conveniently prepared by a procedure that generates **2** in situ. The modified procedure simply involves reaction of molar equivalents of a nitrile, 1,1,1-trimethylhydrazinium chloride (or tosylate), and KO-*t*-Bu in refluxing *t*-BuOH.



3

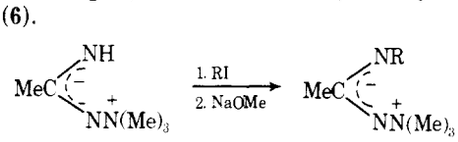
$X^- = Cl^-$ or TsO^-

a, R = Me	d, R = 4-ClC_6H_4
b, R = Et	e, R = 4-$MeOC_6H_4$
c, R = Ph	f, R = 3-pyridyl

The ylides prepared by the above procedure were obtained as extremely hygroscopic solids or oils that, with the exception of **3c**, could not be obtained analytically pure. However, all of the ylides displayed NMR spectra that support the assigned structures and were further characterized by conversion to picrate or hydrohalide salts.

The ylides are strongly basic compounds. Compound **3c** has $pK_b = 1.93$ (±0.03) and chloroform solutions of this compound darkened on standing and deposited the hydrochloride of **3c**. Apparently the basic ylide is capable of initiating α-elimination on chloroform.

Compound **3a** was alkylated in good yield with methyl and ethyl iodide to give, after neutralization, N^3-alkyl-substituted ylides (**6**).



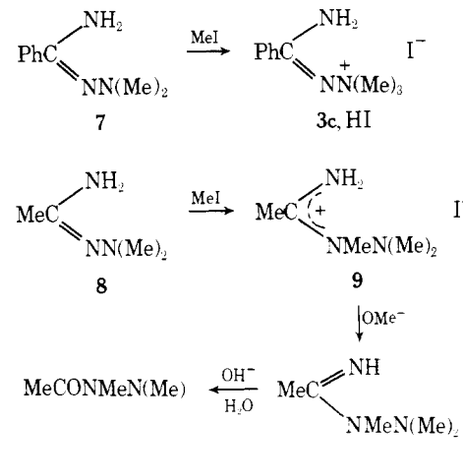
3a 6

a, R = Me; b, R = Et

Attempted alkylation of **3c** with methyl iodide and **3a** with *n*-propyl iodide and benzyl chloride resulted in the formation of mixtures from which, in each case, only the conjugate acid (hydrohalide) of the starting material could be isolated.

As an alternate approach to the synthesis of ylides of type **3**, we have examined the methylation of amidrazones **7** and **8** since alkylation of these compounds at N^1 would provide the conjugate acids of **3**. Although we have previously studied the alkylation of a variety of amidrazones,[6] our study did not include N^3-unsubstituted compounds. Treatment of **7** with methyl iodide resulted in a mixture from which the N^1-alkylated product (**3c** HI) was isolated in low yield. However **8** proved to be an unsuitable candidate for ylide synthesis since on treatment with methyl iodide the N^2-alkylated material (**9**) was produced in good yield. The structure of **9** was established by hydrolysis of the unstable free base (**10**) to 1,1,2-trimethyl-2-acetylhydrazine.

Scheme I

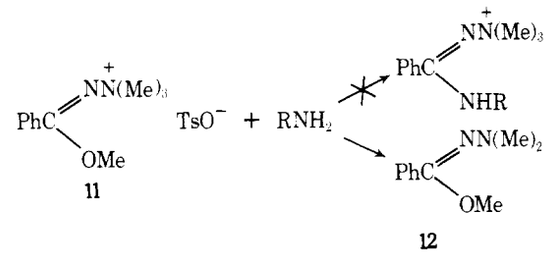


7 3c, HI

8 9

10

We have also attempted the preparation of the conjugate acids of amidrazone ylides by the reaction of 1,1,1-trimethyl-2-α-methoxybenzylidenehydrazinium tosylate (**11**)[7] with primary amines. However, instead of the desired displacement of the methoxyl group, the only reaction that was observed with aniline or benzylamine was nucleophilic displacement at a methyl group on the quaternary nitrogen to give the hydrazinic ester **12**. The structure of **12** was established by reconversion to **11** by reaction with methyl tosylate.



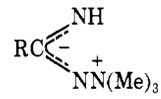
11 12

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. NMR spectra were determined on a Perkin-Elmer R-20 spectrometer utilizing hexamethyldisiloxane as an internal standard.

1,1,1-Trimethyl-2-(*N*-phenylbenzimidoyl)hydrazinium Hydroxide Inner Salt (4). A solution of KO-*t*-Bu was prepared from 4.0 g (0.1 mol) of potassium in 100 mL of dry *t*-BuOH. The solution was evaporated with a rotary evaporator and the residue heated at 100 °C at reduced pressure for 30 min. The resulting KO-*t*-Bu (containing *t*-BuOH) and 11.2 g (0.1 mol) of 1,1,1-trimethylhydrazinium chloride[8] were suspended in 150 mL of dry THF and vigorously stirred in a nitrogen atmosphere for 3 days. The suspension was rapidly filtered to remove KCl and transferred to a 500-mL three-necked flask equipped with a pressure-equalizing dropping funnel, nitrogen inlet tube, and magnetic stirrer. A solution of 10.5 g (0.05 mol) of *N*-phenylbenzimidoyl chloride[9] in 20 mL of anhydrous THF was added from the dropping funnel to the stirred, ice-cooled solution. Stirring was continued for 2 h at 0 °C. Filtration afforded a solid mixture (11.3 g) consisting of 1,1,1-trimethylhydrazinium chloride and the ylide. The ylide was separated from the salt by extraction with hot benzene and was precipitated with petroleum ether to give 5.90 g of product, mp 172–175 °C. An additional 3.3 g (mp 162–165 °C) was obtained

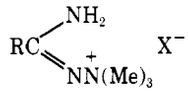
Table I. Ylides (3)



Compd	Formula	$(CH_3)_3\overset{+}{N}NH_2$ employed	Reaction time, h	Crude yield, %	Mp, °C	NMR ($CDCl_3$), δ
3a	$C_5H_{13}N_3$	Chloride	6	58	107–116[a]	3.45 (s, 9 H), 1.78 (s, 3 H), 7.48 (s, 1 H)
3a		Tosylate	6	86	105–117	
3b	$C_6H_{15}N_3$	Tosylate	6	67	83–93	3.45 (s, 9 H), 1.05 (t, 3 H, J = 9 Hz), 1.98 (q, 2 H, J = 9 Hz), 7.30 (s, 1 H)
3c	$C_{10}H_{15}N_3$	Chloride	15	66	140–141[b]	3.42 (s, 9 H), 7.1–7.5 (m, 6 H)
3c		Tosylate	14	70	138–141	
3d	$C_{10}H_{14}ClN_3$	Tosylate	23	62	Oil	3.54 (s), 7.1–7.6[c] (m)
3e	$C_{11}H_{17}N_3O$	Tosylate	6	48	Oil	3.45 (s, 9 H), 3.68 (s, 3 H), 6.6–7.6[d] (m)
3f	$C_9H_{14}N_4$	Tosylate	12	49[e]	117–120	3.53 (s, 9 H), 7.0–8.8 (m, 4 H), 5.1 (broad, 1 H)

[a] Reported[4] mp 124 °C. [b] Anal. Calcd for $C_{10}H_{15}N_3$: C, 67.76; H, 8.53. Found: C, 67.34; H, 8.43. [c] The spectrum indicated contamination with a small quantity of benzene. Aromatic AB at δ 7.15 and 7.49 (J = 9 Hz). [d] Contaminated with a small quantity of benzene. Aromatic AB at δ 6.72 and 7.50 (J = 9 Hz). [e] Yield of hygroscopic solid after recrystallization from acetone.

Table II. Ylide Salts



Compd	Mp, °C	Recrystn solvent	Formula	Calcd C	Calcd H	Found C	Found H
3a picrate	140–141[a]	EtOH	$C_{11}H_{16}N_6O_7$				
3a HCl	235–237	EtOH	$C_5H_{14}ClN_3$	39.60	9.30	39.47	9.20
3a HI	187–188	EtOH	$C_5H_{14}IN_3$	24.70	5.80	24.68	5.86
3b picrate	149–151	EtOH	$C_{12}H_{18}N_6O_7$	40.33	4.79	40.21	5.00
3c HCl	237–238	MeOH–ether	$C_{10}H_{16}ClN_3$	56.26	7.56	56.20	7.55
3c HI	212–213	EtOH	$C_{10}H_{16}IN_3$	39.36	5.29	39.27	5.40
3d picrate	220–222	DMF	$C_{16}H_{17}ClN_6O_7$	43.49	4.11	43.80	3.89
3e picrate	216–218	DMF	$C_{17}H_{20}N_6O_8$	46.78	4.61	46.73	4.42
3f dipicrate	227–228	DMF–EtOH	$C_{21}H_{20}N_{10}O_{14}$	39.67	3.01	39.58	3.06

[a] Reported[4] mp 144 °C.

by extraction of the residue remaining after evaporation of the THF filtrate with 50 mL of boiling benzene followed by precipitation with petroleum ether. The combined yield of crude ylide obtained by this procedure was 72%.

The analytical sample was obtained as white crystals, mp 174–175 °C dec, by recrystallization from benzene.

Anal. Calcd for $C_{16}H_{19}N_3$: C, 75.85; H, 7.56; N, 16.59. Found: C, 75.81; H, 7.84; N, 16.28.

Spectroscopic data and other properties of this compound have been previously reported.[1]

General Procedure for Preparation of Ylides (3). The nitrile (25 mmol) and 25 mmol of 1,1,1-trimethylhydrazinium chloride (or tosylate[6a]) were added to 40 mL of dry *t*-BuOH containing 25 mmol of KO-*t*-Bu (prepared from potassium). The reaction mixtures were heated and stirred for the times indicated in Table I. The solvent was removed in vacuo and the ylides were extracted from the inorganic material with several portions of boiling benzene. Evaporation of the combined extracts afforded the crude, hygroscopic products.

Alkylation of 1,1,1-Trimethyl-2-acetimidoylhydrazinium Hydroxide Inner Salt (3a). A. Methyl Iodide. Methyl iodide (15 mL) was cautiously added through a reflux condenser to a stirred solution containing 15 g (0.13 mol) of the ylide in 75 mL of dry acetonitrile. After the exothermic reaction had subsided, the reaction mixture was cooled and the product (**6a** HI) was filtered off as white crystals (21.5 g), mp 215–216 °C. Recrystallization from ethanol did not alter the melting point. NMR (Me_2SO-d_6) δ 3.32 (s, 9), 2.20 (s, 3), 2.50 (s, 3), 7.30 (broad NH, 1). When determined in D_2O, the NMR spectrum of **6a** HI displayed two sets of signals: δ 3.50, 3.52 [s, $(CH_3)_3N^+$], 2.08, 2.38, (s, CH_3C, rel intensity 1:1.7), 3.02, 2.72 (s, CH_3N, rel intensity 1:1.7). The intensities of these signals were found to be time independent. On heating the D_2O solution, the signals showed no tendency to coalesce, but at 70 °C, their intensities became equivalent.[10]

Anal. Calcd for $C_6H_{16}N_3I$: C, 28.03; H, 6.27. Found: C, 27.97; H, 6.16.

Attempted alkylation of **3a** with methyl iodide in refluxing ethanol afforded a 62% yield of **3a** HI and no detectable methylation.

The iodide (**6a** HI) (1.9 g), 0.55 g of sodium methoxide, and 50 mL of dry acetonitrile were heated under reflux and stirred for 3 h. The solvent was removed in vacuo and crude **1,1,1-trimethyl-2-(*N*-methylacetimidoyl)hydrazinium hydroxide inner salt (6a)** was separated from the solid residue by several extractions with boiling benzene. Evaporation afforded a quantitative yield of the ylide as a hygroscopic solid that was purified by vacuum sublimation as extremely hygroscopic white crystals: mp 67–71 °C; NMR (Me_2SO-d_6) δ 3.38 (s, 9), 1.50 (s, 3), 2.78 (s, 3).

Anal. Calcd for $C_6H_{15}N_3$ (anhydrous): C, 56.77; H, 11.70; N, 32.52. Calcd for $C_6H_{15}N_3$ containing 6.27% H_2O (calculated from oxygen content by difference): C, 52.28; H, 11.66; N, 30.45. Found: C, 52.30; H, 11.75; N, 30.38.

B. Ethyl Iodide. The ylide (2.7 g) was added to 4.5 mL of ethyl iodide. After briefly warming the solution on the steam bath, an exothermic reaction ensued and the reaction mixture solidified. The crude salt was filtered and washed with ether. Recrystallization from ethanol–ether gave 4.85 g (78%) of **6b** HI, mp 185–190 °C. The analytical sample was prepared by recrystallization from ethanol as white crystals: mp 193–194 °C, NMR (D_2O) δ 3.40 [s, 9 $(Me)_3N^+$], 0.85–1.19 (superimposed triplets, 3, CH_2CH_3), 1.88 and 2.15 [s (rel intensities 1:1.4), 3, CCH_3], 3.1 (m, 2, CH_2CH_3), NMR (Me_2SO-d_6) δ 3.41 [s, 9 $(Me)_3N^+$], 0.85–1.15 (superimposed triplets, 3, CH_2CH_3), 2.9 (m, 2 CH_2CH_3).[10]

Anal. Calcd for $C_7H_{18}IN_3$: C, 31.01; H, 6.69; N, 15.50. Found: C, 30.76; H, 6.42; N, 15.46.

Neutralization of the iodide by the procedure described above for **6a** HI gave 1,1,1-trimethyl-2-(*N*-ethylacetimidoyl)hydrazinium hydroxide inner salt (**6b**) as a hygroscopic oil: bp 81–91 °C (2.5 mm);

distilled yield 66%; NMR (neat) δ 3.24 (s, 9), 2.85 (q, 2, J = 7 Hz), 2.37 (s, 3), 0.85 (t, 3, J = 7 Hz).

Anal. Calcd for $C_7H_{17}N_3$ (anhydrous): C, 58.7; H, 12.0; N, 29.3. Calcd for $C_7H_{17}N_3$ containing 2.7% H_2O (calculated from oxygen content by difference): C, 57.1; H, 12.0; N, 28.5. Found: C, 57.2; H, 11.9; N, 28.5.

Acetamide Dimethylhydrazone (8). The hydriodide of this compound was prepared by reaction of S-methylthioacetamidium iodide[11] utilizing the procedure of Reynaud and co-workers.[12] The solution resulting from neutralization of the crude hydriodide with 2 N NaOH was saturated with Na_2SO_4 and extracted with several portions of chloroform. The dried chloroform extracts, on evaporation, gave the crude amidrazone in 82% yield, mp 71–76 °C (lit. mp[13] 79–80 °C).

Acetimidic Acid Trimethylhydrazide Hydriodide (9). Reaction of 2.12 g of **8** with 4.2 mL of methyl iodide resulted in an exothermic reaction. The crude solid was washed with ether and recrystallized from ethanol–ether to give 2.15 g of the iodide, mp 143–149 °C. The analytical sample was obtained by recrystallization from ethanol as white crystals: mp 154–156 °C; NMR (Me_2SO-d_6) δ 3.11 (s, 3), 2.48 (s, 6), 2.30 (s, 3), 8.8 (broad NH, exchangeable, 2).

Anal. Calcd for $C_5H_{14}IN_3$: C, 24.70; H, 5.80; N, 17.29. Found: C, 24.71; H, 5.53; N, 17.61.

The iodide was neutralized with 1 equiv of sodium methoxide in methanol. The free base (**10**) was obtained by benzene extraction of the residue remaining after removal of the solvent. Evaporation of the dried benzene extracts gave **10** as a dark oil: IR 1610 cm^{-1} (=NH); NMR ($CDCl_3$) δ 2.01 (s, 3), 2.36 (s, 6), 2.78 (s, 3), 5.49 (s, 1, NH). The base underwent extensive decomposition on attempted vacuum distillation.

Crude **10** (0.8 g), 5 mL of 6 N NaOH, and 5 mL of ethanol were heated under reflux for 1.5 h. The solution was concentrated to half volume, saturated with NaCl, and extracted with chloroform. Evaporation of the dried extracts gave 0.5 g of oily 1,1,2-trimethyl-2-acetylhydrazine which was identical (IR and NMR) with an authentic sample.[14]

Reaction of Benzamide Dimethylhydrazone (7) with Methyl Iodide. The amidrazone[12] (1.0 g) was treated with 2 mL of methyl iodide. After 24 h at room temperature, the solid product was filtered and washed with ether. Recrystallization from ethanol gave 0.34 g (19%) of **1,1,1-trimethyl-α-aminobenzylidenehydrazinium iodide (3c HI)**, mp 200–204 °C. The product was indentical (NMR, IR) with that obtained by reaction of hydriodic acid with **3a** (Table II). Evaporation of the filtrate afforded a syrupy mixture that could not be separated and displayed a complex NMR spectrum.

1,1-Dimethyl-2-α-methoxybenzylidenehydrazine (12). Benzylamine (10 mL) and 5.0 g of 1,1,1-trimethyl-α-methoxybenzylidenehydrazinium tosylate[7] (**11**) were heated at 170 °C for 2.5 h. The reaction mixture was diluted with ether to give 3.8 g of benzylammonium tosylate (by IR). The ether was evaporated and the residue dissolved in chloroform and extracted with four 20-mL portions of 3 N HCl. The acid extracts were saturated with salt and extracted with several portions of chloroform. The combined chloroform extracts were dried ($MgSO_4$) and evaporated to give 1.2 g (50%) of crude **12** as a semisolid. Kugelrohr distillation (120 °C, 0.50 mm) gave white crystals: mp 83–85 °C; NMR ($CDCl_3$) δ 2.34 (s, 6), 2.89 (s, 3), 6.9–7.6 (m, 5).

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.35; H, 7.91; N, 15.71. Found: C, 67.50; H, 7.91; N, 15.72.

Reaction of **11** with aniline at 175 °C gave low yields (<10%) of **12**.

Reconversion of **12** to **11** was accomplished by heating 0.3 g of **12** with 0.31 g of methyl tosylate at 120 °C for 4.5 h. Recrystallization of the ether-insoluble material from chloroform–ethyl acetate gave 0.11 g of **11**, mp 123–125 °C.

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Registry No.—**3a,** 13848-75-4; **3a** picrate, 13833-34-6; **3a** HCl, 61787-76-6; **3a** HI, 61787-77-7; **3b,** 61787-74-4; **3b** picrate, 61787-79-9; **3c,** 61787-75-5; **3c** HCl, 61787-80-2; **3c** HI, 61787-81-3; **3d,** 61787-82-4; **3d** picrate, 61827-41-6; **3e,** 61787-83-5; **3e** picrate, 61787-85-7; **3f,** 61787-86-8; **3f** dipicrate, 61787-89-1; **4,** 51283-81-9; **6a,** 61787-90-4; **6a** HI, 61787-91-5; **6b,** 61787-92-6; **6b** HI, 61787-93-7; **7,** 38706-49-9; **8,** 25430-77-7; **9,** 61787-94-8; **10,** 61787-95-9; **11,** 58426-21-4; **12,** 61787-96-0; acetonitrile, 75-05-8; propionitrile, 107-12-0; benzonitrile, 100-47-0; 4-chlorobenzonitrile, 623-03-0; 4-methoxybenzonitrile, 874-90-8; 3-pyridinecarbonitrile, 100-54-9; 1,1,1-trimethylhydrazinium chloride, 5675-48-9; N-phenylbenzimidoyl chloride, 4903-36-0; 1,1,1-trimethylhydrazinium tosylate 27808-77-1; methyl iodide, 74-88-4; ethyl iodide, 75-03-6.

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