Tosylhydrazines by the Reduction of Tosylhydrazones with Triethylsilane in Trifluoroacetic Acid

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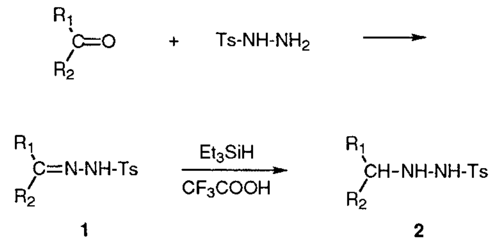
Received 1 June 1995

Tosylhydrazines were easily prepared by the reduction of tosylhydrazones with triethylsilane in the presence of trifluoroacetic acid.

Tosylhydrazines are synthetically useful in the conversion of carbonyl compounds to the corresponding alkanes;[1] which offers an alternative method to the Wolff–Kishner and Clemmensen reductions. In addition, the oxidation of tosylhydrazines provides hydroperoxides,[2] tosylazaalkanes,[3] or iodides.[4] Since tosylhydrazines are sometimes prepared by the direct alkylation of 4-toluenesulfonohydrazide (tosylhydrazine)[5] or more often by the reduction of tosylhydrazones with sodium cyanoborohydride,[6] sodium borohydride,[7] bis(acyloxy)borane,[8] catecholborane[9] and pyridineborane,[10] there are still some synthetic limits. In continuing our interest in the triethylsilane reductions,[11] the reaction of tosylhydrazones with triethylsilane in the presence of trifluoroacetic acid successfully provided a mild and convenient alternative to the method for the preparation of tosylhydrazines.

A variety of tosylhydrazones **1a**—**1n**, readily prepared from the reaction between carbonyl compounds and 4-toluenesulfonohydrazide by modification of Bertz's method,[12] was added to trifluoroacetic acid followed by the addition of triethylsilane. After stirring at 0 °C for 1 hour, the resulting mixture was subjected to acid/base extraction to give tosylhydrazine **2** as the sole product. Tosylhydrazones are known to be unstable under the conditions of a polar solvent and heat[12] and were usually used for the following reduction without further purification. However, tosylhydrazines are also unstable. For this reason, their elemental analyses and melting points should be considered as approximate. FAB-MS and HRFAB-MS spectroscopic measurements were taken for elemental identification. However, if purification is necessary, two methods are available: fast chromatography on silica gel or recrystallization from CH_2Cl_2/hexane. The physical and spectroscopic data of compounds **1** and **2** are summarized in Tables 1 and 2, respectively.



	R_1	R_2		R_1	R_2
a	H	*n*-C_6H_{13}	**h**	CH_3	CH_3
b	H	*c*-C_6H_{11}	**i**	CH_3	C_2H_5
c	H	Ph	**j**	$-(CH_2)_5-$	
d	H	*m*-methoxyphenyl	**k**	CH_3	Ph
e	H	*p*-cyanophenyl	**l**	CH_3	*i*-Pr
f	H	3-cyclohexenyl	**m**	*i*-Pr	*i*-Pr
g	H	2-ethoxycarbonyl-cyclopropyl	**n**	Ph	Ph

As revealed in Table 2, the reduction of tosylhydrazones to tosylhydrazines with triethylsilane in trifluoroacetic acid worked well for aldehyde and most ketone tosylhydrazones. It occurred without the concurrent reduction of the carboxylate ester, cyano, and double bond functional group (entries **1g**, **1e** and **1f**). Furthermore, the reduction of acetophenone and 3-methylbutan-2-one tosylhydrazones (**1k** and **1l**) gave moderate yields whereas 2,4-dimethylpentan-3-one and benzophenone tosylhydrazones (**1m** and **1n**) failed to react under the same reduction conditions. When subjected to more vigorous reaction conditions under reflux, **1n** afforded a little hydrolysis and elimination products, benzophenone and diphenylmethane, respectively. A limitation of this method was disclosed by the resistance of diphenyl and diisopropyl ketone tosylhydrazones to reduction. The resistance of the diphenyl and diisopropyl ketone tosylhydrazones to reduction suggests that this method is limited to hydrazones lacking bulky substituents adjacent to the imino carbon. This is reasonable considering the steric interactions that develop as the central carbon approaches a tetrahedral geometry. In addition, the triethylsilane reagent is, itself, bulky and its approach to the imino carbon should be impeded by adjacent substituents. From either point of view, these triethylsilane reductions are expected to be sensitive to the steric environment of the imino carbon.

In recent years silane reductions have been the focus of increased interest in organic synthesis and mechanistic studies.[13] The reaction has been studied extensitively and in detail by Doyle et al.[14] After replacing trifluoroacetic acid with deuterated trifluoroacetic acid, the ^1H NMR analysis of the reaction mixture indicated that the deuterium was not incorporated into the imine carbon. This mechanistic study was in accordance with the usual proposal[15] that the reduction mechanism proceeds with initial protonation of the tosylhydrazone to form an iminium cation followed by hydride transfer instead of the tautomerization-then-reduction route as was seen for the sodium cyanoborohydride reduction.[16] It can be a useful method for the preparation of regiospecifically labeled molecules.

In summary, we have developed an effective route for the reduction of tosylhydrazones into tosylhydrazines with triethylsilane in trifluoroacetic acid.

Melting points were recorded on a Büchi 535 melting-point apparatus and are uncorrected. IR spectra were recorded on a Nicolet Magna FT-IR spectrometer as either thin films or solid dispersions in KBr. NMR spectra were recorded on a Bruker AC-200 FT-NMR

Table 1. Selected Physical and Spectroscopic Data of Tosylhydrazones **1**

Product[a]	Yield (%)	mp[b] (°C)	IR ν (cm^{-1})	^{1}H NMR ($\mathrm{CDCl_3}$) δ, J (Hz)	^{13}C NMR ($\mathrm{CDCl_3}$) δ, J (Hz)	FAB-MS m/z (%)
1a	93	75–77[c]	3200, 1360, 1170	0.83 (t, 3 H, $\mathrm{C}H_3\mathrm{CH_2}$, $J = 7$), 1.1–2.2 (m, 10 H, 5 $\mathrm{CH_2}$), 2.40 (s, 3 H, $\mathrm{CH_3}$), 6.68 and 7.17 (t, 1 H, CH=N of *syn* and *anti* isomers, $J = 5$ and 6), 7.28 and 7.79 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$), 8.1–8.8 (br, 1 H, TsNH)	13.91, 21.47, 22.37, 25.92, 28.48, 31.36, 32.15, 127.77, 129.46, 135.16, 143.86, 153.09	283 (100, MH$^+$), 157 (8), 139 (11), 127 (18), 91 (7)
1b	91	97–98[d]	3210, 1320, 1170	1.1–2.3 (m, 11 H, *c*-$\mathrm{C_6H_{11}}$), 2.43 (s, 3 H, $\mathrm{CH_3}$), 7.04 (d, 1 H, CH=N, $J = 5$ Hz), 7.31 and 7.80 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$), 7.2 – 7.4 (br, 1 H, TsNH)	21.36, 25.04, 25.57, 29.52, 40.36, 127.65, 129.29, 135.06, 143.68, 156.60	281 (100, MH$^+$), 157 (4), 139 (5), 125 (11), 95 (12)
1c	85	126–127[e]	3230, 1330, 1170	2.38 (s, 3 H, $\mathrm{CH_3}$), 7.2–8.0 (m, 9 H, $\mathrm{C_6H_4}$ and $\mathrm{C_6H_5}$), 7.80 (s, 1 H, CH=N), 8.5–8.6 (br, 1 H, TsNH)	21.51, 127.28, 127.84, 128.51, 129.63, 130.28, 133.15, 135.16, 144.18, 147.94	275 (100, MH$^+$), 154 (4), 139 (5), 119 (13), 91 (13)
1d	81	104–105	3160, 1330, 1170	2.34 (s, 3 H, $\mathrm{CH_3}$), 3.75 (s, 3 H, $\mathrm{OCH_3}$), 6.8– 7.2 (m, 4 H, $\mathrm{C_6H_4}$), 7.25 and 7.90 (d, 2 H each, $\mathrm{C_6H_4}$ of Ts, $J = 8$), 7.80 (s, 1 H, CH=N), 8.94 (br s, 1 H, TsNH)	21.37, 55.14, 111.24, 116.49, 120.31, 127.73, 129.41, 129.54, 134.47, 135.02, 144.10, 147.95, 159.48	305 (100, MH$^+$), 149 (14), 120 (11), 91 (9)
1e	81	155–156	3170, 1370, 1170	2.39 (s, 3 H, $\mathrm{CH_3}$), 7.31 and 7.86 (d, 2 H, each, $\mathrm{C_6H_4}$ of Ts, $J = 8$), 7.55 and 7.65 (m, 4 H, $\mathrm{C_6H_4}$), 7.80 (s, 1 H, CH=N), 9.05 (br s, 1 H, TsNH)	21.54, 113.14, 118.36, 127.50, 127.78, 129.76, 132.30, 134.90, 137.43, 144.58, 144.87	300 (100, MH$^+$), 154 (32), 136 (29), 91 (11)
1f	92	81–82	3210, 1320, 1160	1.3–2.1 (m, 7 H, 3 $\mathrm{CH_2}$ and CH), 2.41 (s, 3 H, $\mathrm{CH_3}$), 5.61 (br s, 2 H, CH=CH), 7.15 (d, 1 H, CH=N, $J = 5$), 7.29 and 7.79 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$), 8.0–8.2 (br, 1 H, TsNH)	21.51, 23.94, 25.64, 27.97, 36.47 124.93, 126.81, 127.80, 129.44, 135.07, 143.93, 155.75	279 (100, MH$^+$), 157 (4), 139 (7), 91 (9)
1g	94	liq	3200, 1330, 1170	1.18 (t, 3 H, $\mathrm{C}H_3\mathrm{CH_2}$, $J = 7$), 1.0–1.4 (m, 2 H, $\mathrm{CH_2}$), 1.7–1.8 and 2.0–2.1 (m, 1 H each, 2 CH), 2.36 (s, 3 H, $\mathrm{CH_3}$), 4.04 (q, 2 H, $\mathrm{CH_2O}$, $J = 7$), 6.84 (d, 1 H, CH=N, $J = 7$), 7.25 and 7.73 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$), 8.75 (br s, 1 H, TsNH)	13.93, 14.34, 21.14, 21.36, 23.16, 60.78, 127.62, 129.42, 134.94, 143.92, 150.63, 172.09	311 (100, MH$^+$), 155 (75), 139 (55), 91 (89)
1h	92	154–155[f]	3230, 1330, 1160	1.84 and 1.98 (s, 3 H each, 2 $\mathrm{CH_3}$), 2.42 (s, 3 H, $\mathrm{CH_3}$), 7.31 and 7.85 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$)	16.93, 21.46, 25.16, 127.86, 129.39, 135.33, 143.78, 156.29	227 (100, MH$^+$), 157 (5), 139 (5), 91 (3), 71 (14)
1i	92	122–123	3210, 1330, 1160	0.99 (t, 3 H, $\mathrm{C}H_3\mathrm{CH_2}$, $J = 7$), 1.76 (s, 3 H, $\mathrm{C}H_3\mathrm{C{=}N}$), 2.20 (q, 2 H, $\mathrm{CH_3C}H_2$, $J = 7$), 2.42 (s, 3 H, $\mathrm{CH_3}$ of Ts), 7.30 and 7.85 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$), 7.0–8.0 (br 1 H, TsNH)	10.32, 15.51, 21.53, 31.89, 128.02, 129.35, 135.34, 143.81, 159.62	241 (100, MH$^+$), 157 (3), 139 (4), 85 (12)
1j	91	155–156[g]	3250, 1340, 1170	1.4–2.3 (m, 10 H, 5 $\mathrm{CH_2}$), 2.39 (s, 3 H, $\mathrm{CH_3}$), 7.27 and 7.82 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$), 7.2–8.5 (br, 1 H, TsNH)	21.42, 25.16, 25.52, 26.60, 26.86, 35.07, 127.85, 129.29, 135.30, 143.60, 162.64	267 (100, MH$^+$), 154 (7), 136. (6), 111 (20)
1k	91	142–143[h]	3220, 1340, 1170	2.17 (s, 3 H, $\mathrm{CH_3C{=}N}$), 2.39 (s, 3 H, $\mathrm{CH_3}$), 7.2 – 8.0 (br m, 10 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$ and TsNH)	13.48, 21.49, 126.16, 127.98, 128.17, 129.39, 129.49, 135.30, 137.20, 144.01, 152.73	289 (100, NH$^+$), 154 (6), 133 (17), 104 (12), 91 (4)
1l	89	119–120	3230, 1330, 1170	0.97 (d, 6 H, 2 $\mathrm{C}H_3\mathrm{CH}$, $J = 7$), 1.72 (s, 3 H, $\mathrm{CH_3C{=}N}$), 2.3–2.5 (m, 1 H CH), 2.40 (s, 3 H, $\mathrm{CH_3}$), 7.27 and 7.84 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$), 7.5–8.3 (br, 1 H, TsNH)	13.42, 19.44, 21.45, 36.66, 127.94, 129.23, 135.30, 143.68, 162.50	255 (100, MH$^+$), 157 (3), 139 (4)
1m	90	65–67	3200, 1330, 1160	0.98 and 1.01 (d, 6 H each, 4 $\mathrm{CH_3}$, $J = 7$), 2.41 (s, 3 H, $\mathrm{CH_3}$ of Ts), 2.51 and 2.75 (septet, 1 H each, 2 CH, $J = 7$), 7.28 and 7.83 (d, 2 H each, $\mathrm{C_6H_4}$, $J = 8$), 7.5–7.8 (br, 1 H, TsNH)	18.57, 21.46, 21.61, 28.16, 30.42, 127.98, 129.12, 135.26, 143.57, 169.11	283 (100, MH$^+$), 139 (6), 91 (3)
1n	75	187–189	3200, 1350, 1170	2.44 (s, 3 H, $\mathrm{CH_3}$), 7.1–7.9 (m, 15 H, $\mathrm{C_6H_4}$, 2 $\mathrm{C_6H_5}$ and TsNH)	21.55, 127.52, 127.83, 128.14, 128.19, 129.61, 129.71, 129.80, 130.04, 131.03, 135.44, 136.34, 144.09, 154.20	351 (100, MH$^+$), 154 (41), 136 (28), 77 (12)

[a] All compounds were analyzed for C, H and N, and results agreed to ± 0.4 % of the theoretical values or by high resolution FAB mass spectroscopic measurements, and results agreed to 5 mmu of the theoretical values.

[b] Satisfactory mp data even without crystallization due to the easy decomposition.

[c] Lit.[12] mp 72–73 °C.

[d] Lit.[12] mp 92–94 °C; Lit.[17] mp 99–100 °C.

[e] Lit.[18] mp 126–127 °C.

[f] Lit.[19] mp 149 °C.

[g] Lit.[20] mp 152–153 °C.

[h] Lit.[18] mp 145–146 °C; Lit.[9] mp 141–143 °C.

Table 2. Selected Physical and Spectroscopic Data of Tosylhydrazines **2**

Product[a]	Yield (%)	mp[b] (°C)	IR ν (cm^{-1})	^{1}H NMR (CDCl$_3$) δ, J (Hz)	^{13}C NMR (CDCl$_3$) δ, J (Hz)	FAB-MS m/z (%)
2a	75	57–58[c]	3190, 1330, 1160	0.85 (t, 3H, $\mathrm{C}H_3\mathrm{CH}_2$, $J = 7$), 1.1–1.4 (m, 10H, 5CH$_2$), 2.42 (s, 3H, CH$_3$), 2.64 (t, 2H, CH$_2$N, $J = 7$), 2.7–3.5 (br, 1H, NH), 7.30 and 7.81 (d, 2H each, C$_6$H$_4$, $J = 8$), 7.0–7.7 (br, 1H, TsNH)	14.01, 21.53, 22.52, 26.67, 27.46, 28.95, 31.64, 51.78, 128.06, 129.52, 135.48, 143.88	285 (89, MH$^+$), 157 (62), 139 (37), 129 (100), 91 (16)
2b	76	90–92	3320, 3250, 1310, 1150	0.8–1.9 (m, 11H, c-C$_6$H$_{11}$), 2.42 (s, 3H, CH$_3$), 2.48 (d, 2H, CH$_2$N, $J = 7$), 3.0–4.0 (br, 1H, NH), 7.30 and 7.81 (d, 2H each, C$_6$H$_4$, $J = 8$), 7.5–7.8 (br, 1H, TsNH)	21.51, 25.73, 26.38, 30.88, 35.71, 58.33, 128.10, 129.45, 135.36, 143.82	283 (92, MH$^+$), 157 (28), 139 (16), 127 (100), 97 (21), 91 (9)
2c	82	97–99	3300, 1320, 1150	2.41 (s, 3H, CH$_3$), 3.2–4.0 (br, 1H, NH), 3.78 (s, 2H, CH$_2$N), 5.0–7.0 (br, 1H, TsNH), 7.1–7.3 (m, 5H, C$_6$H$_5$), 7.31 and 7.82 (d, 2H each, C$_6$H$_4$, $J = 8$)	21.53, 55.64, 127.77, 128.07, 128.61, 128.69, 129.57, 135.40, 136.41, 143.97	277 (77, MH$^+$), 157 (17), 91 (100)
2d	81	104–106	3240, 1330, 1160	2.43 (s, 3H, CH$_3$), 3.3–3.9 (br, 1H, NH), 3.74 (s, 2H, CH$_2$N), 3.76 (s, 3H, OCH$_3$), 5.6–6.5 (br, 1H, TsNH), 6.7–7.2 (m, 4H, C$_6$H$_4$), 7.30 and 7.81 (d, 2H each, C$_6$H$_4$ of Ts, $J = 8$)	21.43, 55.02, 55.45, 113.17, 114.01, 120.73, 127.95, 129.46, 129.52, 135.28, 137.93, 143.85, 159.63	307 (52, MH$^+$), 151 (77), 121 (100), 91 (11)
2e	76	136–137[d]	3270, 3200, 1300, 1150	2.42 (s, 3H, CH$_3$), 3.99 (s, 2H, CH$_2$N), 4.3–5.2 (br, 1H, NH), 7.36, 7.47, 7.65 and 7.76 (d, 2H each, 2C$_6$H$_4$, $J = 8$), 7.5–7.9 (br, 1H, TsNH)[e]	21.37, 55.88, 111.45, 119.36, 128.83, 130.12, 130.31, 132.64, 137.32, 144.16, 145.02	302 (37, MH$^+$), 154 (100), 136 (71), 91 (14)
2f	82	87–88	3320, 3250, 1320, 1160	1.0–2.1 (m, 7H, 3CH$_2$ and CH), 2.39 (s, 3H, CH$_3$), 2.55 (d, 2H, CH$_2$N, $J = 6$), 3.3–4.0 (br, 1H, NH), 5.55 (br, s, 2H, CH=CH), 6.2–6.9 (br, 1H, TsNH), 7.27 and 7.78 (d, 2H each, C$_6$H$_4$, $J = 8$)	21.40, 24.32, 26.21, 29.28, 31.54, 57.28, 125.63, 126.77, 128.01, 129.34, 135.15, 143.68	281 (90, MH$^+$), 157 (27), 139 (15), 125 (100), 95 (23)
2g	84	liq	3310, 3240, 1330, 1160	1.24 (t, 3H, $\mathrm{C}H_3\mathrm{CH}_2$, $J = 7$), 0.7–1.6 (m 4H, CH$_2$ and 2CH), 2.43 (s, 3H, CH$_3$), 2.66 (d, 2H, CH$_2$N, $J = 7$), 2.3–3.1 (br, 1H, NH), 4.14 (q, 2H, CH$_2$O, $J = 7$), 5.8–6.8 (br, 1H, TsNH), 7.31 and 7.80 (d, 2H each, C$_6$H$_4$, $J = 8$)	13.46, 14.17, 18.78, 20.23, 21.56, 54.49, 60.63, 128.04, 129.62, 135.17, 144.07, 173.55	313 (19, MH$^+$), 157 (46), 136 (52), 91 (55), 55 (100)
2h	80	104–105	3290, 3240, 1320, 1160	0.93 (d, 6H, 2CH$_3$, $J = 6$), 1.8–2.5 (br, 1H, NH), 2.44 (s, 3H, CH$_3$), 2.96 (septet, 1H, CHN, $J = 6$), 7.32 and 7.81 (d, 2H each, C$_6$H$_4$, $J = 8$)	20.47, 21.46, 50.74, 127.97, 129.39, 135.33, 143.70	229 (100, MH$^+$), 157 (25), 139 (10), 73 (95)
2i	79	75–76	3320, 3260, 1320, 1160	0.74 (t, 3H, $\mathrm{C}H_3\mathrm{CH}_2$, $J = 7$), 0.87 (d, 3H, $\mathrm{C}H_3\mathrm{CH}$, $J = 6$), 1.1–1.5 (m, 2H, $\mathrm{CH_3C}H_2$), 2.38 (s, 3H, CH$_3$ of Ts), 2.66 (sextet, 1H, $\mathrm{CH_3C}H$, $J = 6$), 2.9–4.0 (br, 1H, NH), 6.0–7.0 (br, 1H, TsNH), 7.26 and 7.78 (d, 2H each, C$_6$H$_4$, $J = 8$)	9.81, 17.72, 21.39, 26.99, 56.51, 127.99, 129.30, 135.25, 143.59	243 (100, MH$^+$), 157 (18), 139 (8), 87 (77), 57 (14)
2j	89	114–115[f]	3300, 1320, 1160	0.8–1.8 (m, 10H, 5CH$_2$), 2.39 (s, 3H, CH$_3$), 2.4–2.6 (m, 1H, CHN), 2.8–4.0 (br, 1H, NH), 5.5–7.5 (br, 1H, TsNH) 7.26 and 7.77 (d, 2H each, C$_6$H$_4$, $J = 8$)	21.39, 24.18, 25.68, 30.89, 58.21, 127.93, 129.27, 135.25, 143.53	269 (78, MH$^+$), 157 (13), 139 (8), 113 (100), 83 (22), 55 (11)
2k	51	113–114[g]	3300, 3250, 1310, 1160	1.23 (d, 3H, $\mathrm{C}H_3\mathrm{CH}$, $J = 7$), 1.0–2.0 (br, 1H, NH), 2.45 (s, 3H, CH$_3$), 3.78 (q, 1H, CHN, $J = 7$), 5.63 (s, 1H, TsNH), 7.1–7.3 (m, 5H, C$_6$H$_5$), 7.31 and 7.79 (d, 2H each, C$_6$H$_4$, $J = 8$)	20.54, 21.59, 55.46, 126.76, 127.83, 128.07, 128.76, 129.55, 135.60, 141.61, 143.94	291 (28, MH$^+$), 129 (12), 154 (10), 135 (27), 105 (100), 91 (8)
2l	30	73–74	3300, 3250, 1320, 1150	0.73, 0.78 and 0.82 (d, 3H each, 3CH$_3$, $J = 7$), 1.5–1.7 (m, 1H, CH), 2.42 (s, 3H, CH$_3$ of Ts), 2.5–2.7 (m, 1H, CHN), 3.0–5.0 (br, 1H, NH), 6.8–7.5 (br, 1H, TsNH), 7.29 and 7.80 (d, 2H each, C$_6$H$_4$, $J = 8$)	13.88, 16.72, 19.09, 21.52, 30.04, 60.15, 128.12, 129.41, 135.32, 143.79	257 (100, MH$^+$), 157 (18), 139 (9)

[a] All compounds were analyzed for C, H and N, and results agreed to ±0.4% of the theoretical values or by high resolution FAB mass spectroscopic measurements, and results agreed to 5 mmu of the theoretical values.

[b] Recrystallization from CH$_2$Cl$_2$/hexane.

[c] Lit.[21] mp 71–72 °C.

[d] Lit.[10] mp 122 °C.

[e] This ^{1}H NMR spectrum was measured in acetone-d_6.

[f] Lit.[10] mp 105–107 °C.

[g] Lit.[22] mp 108–110 °C.

spectrometer; all chemical shifts are reported in ppm from TMS as an internal standard. MS and HRMS spectra were recorded on a VG 70-250S spectrometer. Elemental analyses were performed on a Heraeus CHN-RAPID elemental analyzer. Column chromatography was carried out using silica gel. All reactions were carried out under an atmosphere of dry N$_2$.

Tosylhydrazones 1a–1l; General Procedure:

4-Toluenesulfonohydrazide (2 mmol) was added to a hexane solution (10 mL) containing a suitable carbonyl compound (3 mmol). The mixture was stirred at r.t. for 2 h. For benzaldehyde, 3-methoxybenzaldehyde, 4-cyanobenzaldehyde, acetophenone and 3-methylbutan-2-one, the reaction was allowed to proceed at 50 °C for

2 h. During this time the resulting tosylhydrazones may precipitate. The crystallized solid was filtered and washed with hexane (3 x 10 mL).

Tosylhydrazones **1a–1l** were obtained as white solids and used for the following reduction without further purification. However pure tosylhydrazone **1g** was obtained as colorless liquid by chromatography (silica gel; hexane/EtOAc, 3:1). The physical and spectroscopic data are given in Table 1.

Tosylhydrazones 1m and 1n; General Procedure:
4-Toluenesulfonohydrazide (2 mmol) was added to an abs EtOH solution (10 mL) containing the appropriate carbonyl compound (2.2 mmol). The resulting mixture was stirred under reflux for 1 d.[12] The solvent was evaporated and the crystallized solid was filtered and washed with hexane or Et_2O (3 x 10 mL). Tosylhydrazones **1m** and **1n** were obtained and used for the following reduction without further purification. The physical and spectroscopic data are given in Table 1.

Reduction of Tosylhydrazones 1 to Tosylhydrazines 2; General Procedure:
To a solution of hydrazone **1** (1 mmol) in trifluoroacetic acid (10 mmol), Et_3SiH (2 mmol) was added. The resulting solution was stirred at 0 °C for 1 h. The mixture was acidified with 10% aq HCl (15 mL) and washed with hexane (2 x 15 mL). The aqueous layer, after carefully rebasification with KOH pellets, was extracted with CH_2Cl_2 (4 x 20 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated to give a basic product. Tosylhydrazines **2** were obtained as pure products by recrystallization from CH_2Cl_2/hexane. The physical and spectroscopic data are given in Table 2.

We thank the National Science Council, R.O.C., for support of this research (NSC 85-2113-M006-004).

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