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An Efficient Synthesis of 1,1-Disubstituted Hydrazines[1]

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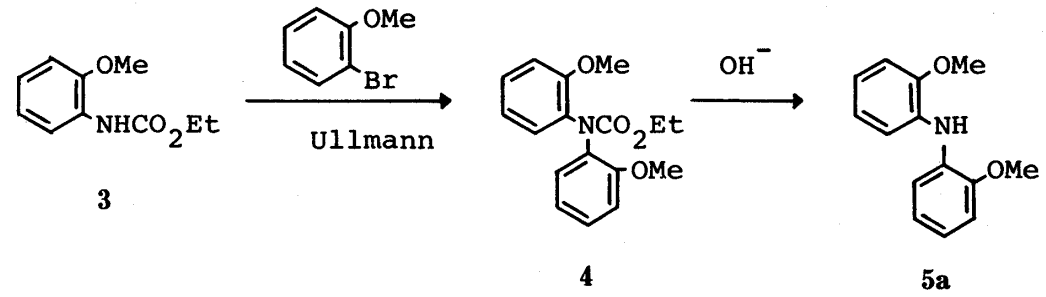
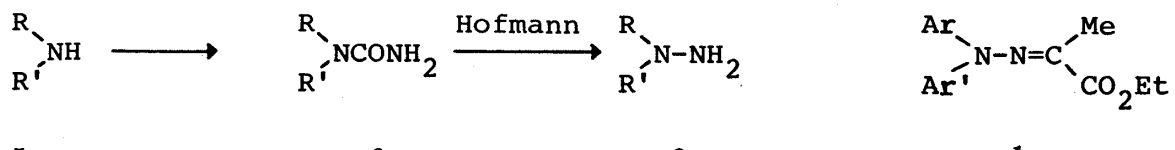
1,1-Disubstituted hydrazines were prepared from the corresponding 1,1-disubstituted ureas by means of the Hofmann rearrangement reaction. The yields were fairly good, except from the ureas susceptible to oxidation, and thus the present method represents an additional and efficient procedure for the synthesis of 1,1-disubstituted hydrazines.

Keywords——urea; hydrazine; Hofmann rearrangement; sodium hypochlorite

Representative synthetic methods[2] for 1,1-disubstituted hydrazines include i) reduction of the corresponding nitrosamine and ii) amination of a secondary amine with a suitable reagent.[3] Several years ago we wanted[4] to carry out Fischer indolization of 1,1-diarylhydrazone (**1**) for studies on abnormal Fischer indolization. The key intermediates, 1,1-diarylhydrazines (**2**), for the synthesis of most hydrazones (**1**) were satisfactorily prepared *via* a nitrosamine method. However, synthesis of some hydrazines (**2**) gave very poor results, especially for 1,1-di(*o*-methoxyphenyl)hydrazine (**2a**), because the N–N bond was easily cleaved by reduction. It is well known[5] that the N–N bond of 1,1-diarylhydrazines is liable to reductive





a: R=R'=*o*-methoxyphenyl
b: R=R'=phenyl
c: R=*o*-nitrophenyl, R'=phenyl
d: R=1-naphthyl, R'=phenyl
e: R=2-naphthyl, R'=phenyl
f: R=*m*-chlorophenyl, R'=phenyl
g: R, R'=piperidine
h: R=cyclohexyl, R'=phenyl
i: R=benzyl, R'=phenyl
j: R=methyl, R'=phenyl
k: R, R'=9-tetrahydrocarbazolyl

Chart 1

cleavage. Amination was also unsuccessful for preparing **2a**. Therefore we investigated alternative methods. In this paper, we report the successful outcome.

We examined non-reductive methods, since the N–N bond is susceptible to reduction. O'Conner[5] reported the preparation of 1,1-diphenylhydrazine (**2b**) by Curtius rearrangement of the corresponding carbamoyl azide. However this method involves the usage of hazardous phosgene and proceeds *via* the unstable carbamoyl azide. Thus we examined the use of the Hofmann rearrangement reaction.[6] The Hofmann rearrangement of urea itself and some substituted ureas[6,7] has been reported in a few papers or patents. Systematic conversion of 1,1-disubstituted (especially 1,1-diaryl) ureas to the corresponding hydrazines has not been reported.

Our first target was the preparation of the 1,1-di(*o*-methoxyphenyl) hydrazine (**2a**) from the corresponding urea (**6a**), the preparation of the latter (**6a**) being started from 2-methoxycarbanilate (**3**) (Chart 1). The amine (**5a**) was treated with sodium cyanate and trifluoroacetic acid according to the method of Durant[8] to give the urea (**6a**). The urea (**6a**) thus obtained was allowed to react under Hofmann rearrangement conditions. Treatment of **6a** in EtOH with NaOCl/NaOH aq., followed by acidification and then basification gave the hydrazine (**2a**) as a solid. A small amount of the amine (**5a**) was obtained as a by-product by extraction of the first basic solution. As it was difficult to recrystallize, the hydrazine (**2a**) was immediately allowed to react with ethyl pyruvate to give the desired hydrazone (**1a**, 85% from **6a**). The identification data are given in the experimental section.

The success of this approach led us to apply our method to 1,1-diarylureas and then other kinds of 1,1-disubstituted ureas.

TABLE I. The Preparation of Ureas (**6**)

Starting materal (**5**)	Method	Product (**6**)	
		Yield (%)	mp (lit. mp) (°C)
a (R=R′=*o*-methoxyphenyl)	A	78.9	188.5—190
b (R=R′=phenyl)	A	66.9	196—197 (191—192[8])
c (R=*o*-nitrophenyl, R′=phenyl)	A	6.2	186.5—188
	B	66.4	
d (R=1-naphthyl, R′=phenyl)	A	50.3	185—186.5 (180—181.5[8])
e (R=2-naphthyl, R′=phenyl)	A	67.6	190.5—192.5 (188—191[8])
f (R=*m*-chorophenyl, R′=phenyl)	A	84.0	112—115
g (R, R′=piperidine)	C	82.5	105—106 (125[9])
h (R=cyclohexyl, R′=phenyl)	A	93.8	179
i (R=benzyl, R′=phenyl)	A	82.3	113.5—114.5 (105[10])
j (R=methyl, R′=phenyl)	B	44.5	79.5—80.0 (79[12])
k (R, R′=9-tetrahydrocarbazolyl)	B	43.9	246—249 (244—245[13])

A : $NaOCN/CF_3CO_2H$,[8] B : $ClSO_2NCO$,[11] C) $Si(NCO)_4$.[9]

Urea derivatives (**6**) were generally prepared with $NaOCN/CF_3CO_2H$[8] (method A). However, some ureas(**6**) which were difficult to prepare by method A were prepared with chlorosulfonyl isocyanate ($ClSO_2NCO$)[11] (method B) or with $Si(NCO)_4$[9] (method C). The results are listed in Table I. The ureas(**6**) thus obtained were subjected to the Hofmann reaction as mentioned above. The reaction conditions were optimized as will be described in the experimental section, that is, 5 eq mol of NaOH and 1.2 eq mol of NaOCl to 1.0 eq mol of a urea (**6**). In the optimization process, *N*-chlorosuccinimide (NCS) or *tert*-BuOCl as a chlorination reagent, Et_3N or 1,8-diazabicyclo[5.4.0]undecene-7(DBU) as a base, and chloroform as a solvent were examined, but did not give good results. The results are listed in Table II. The yields were generally good or moderate, indicating that this procedure is a practical syntheic method for 1,1-disubstituted hydrazines. The reason why 2-naphthylurea (**6e**) did not give a good result is presumably that an active α-position would be attacked by the

TABLE II. Synthesis of Hydrazines (**2**) from the Ureas (**6**)

Starting material (**6**)	Reaction temperature	Product (**2**) Yield (%)	Identified form	mp (°C)
a (R=R′=*o*-methoxyphenyl)	r. t.	85.0	*a*)	89—91
b (R=R′=phenyl)	r. t.	62.0	*b*)	196—198
c (R=*o*-nitrophenyl, R′=phenyl)	70—80°C	73.1	*b*)	180—181
d (R=1-naphthyl, R′=phenyl)	r. t.	65.0	*b*)	173—174.5
e (R=2-naphthyl, R′=phenyl)	Reflux	8.1	*b*)	192—195
f (R=*m*-chlorophenyl, R′=phenyl)	r. t.	51.5	*b*)	186—188
g (R, R′=piperidine)	r. t.	50.2	*b*)	106—109
h (R=cyclohexyl, R′=phenyl)	r. t.	55.2	*b*)	206—209
i (R=benzyl, R′=phenyl)	r. t.	67.8	*b*)	179—180
j (R=methyl, R′=phenyl)	r. t.	64.2	*c*)	82—84
k (R, R′=9-tetrahydrocarbazolyl)	Reflux	6.9	*c*)	122—124

r. t.: room temperature.
a) Hydrazone with ethyl pyruvate.
b) Salt with TsOH.
c) Hydrazone with piperonal.

oxidative reagent (NaOCl). As for 1,2,3,4-tetrahydrocarbazole urea (**6k**), hydrolysis of the urea would occur in preference to the rearrangement at elevated temperature, which was used because of the poor solubility of the urea (**6k**) (**4k** was recovered in 66.3 % yield).

The Hofmann rearrangement of urea derivatives presumably proceeds in the same manner as usual Hofmann rearrangement,[5,12] as shown in Chart 2. As the reaction stops at the stage of alkali-soluble sodium carbamate (D), extraction with solvent at this stage (D) can conveniently be used to remove unchanged starting urea (**6**) and a by-product amine (**3**) formed by hydrolysis of the urea (**6**). The subsequent acidification causes decarboxylation and gives a hydrazine (**2**).

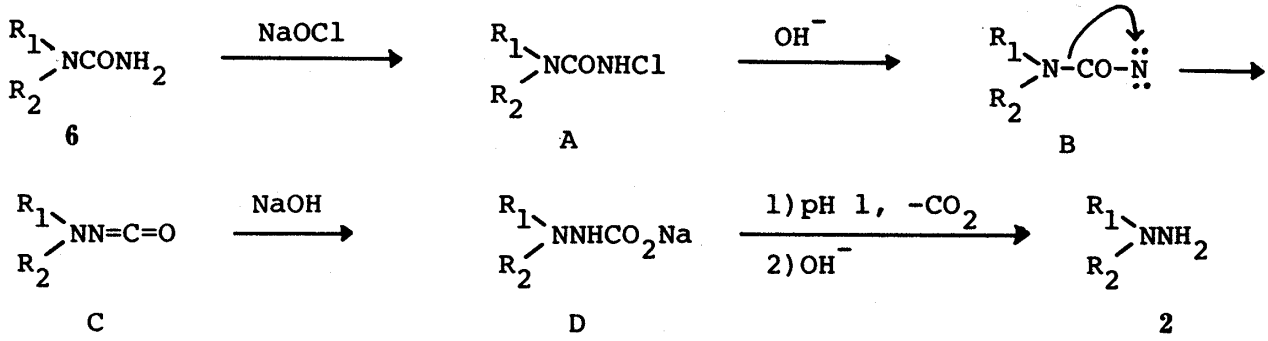


Chart 2

In conclusion, the present Hofmann reaction of 1,1-disubstituted ureas is a useful synthetic tool for the preparation of various kinds of 1,1-disubstituted hydrazines, except from ureas susceptible to oxidation, and is an important supplement to the usual synthetic method for 1,1-disubstituted hydrazines, that is, reduction of nitrosamines, because the former involves oxidative conditions, while the latter involves reductive conditions. Therefore the nitro urea (**4c**) can be converted to the corresponding nitro hydrazine without affecting the nitro group. It is noteworthy that nitrosamines are potentially carcinogenic while urea derivatives are not.

Experimental

All melting points were measured on a micro melting point hot stage (Yanagimoto) and are uncorrected. Infrared (IR), ^{1}H-nuclear magnetic resonance (NMR) and mass spectra (MS) were obtained with Shimadzu IR-400, Hitachi R-24B (60 MHz), and JEOL JMS-01-SG-2 spectrometers, respectively. In the NMR

spectra,chemical shifts are given in δ-values referred to internal tetramethylsilane (TMS), and the assignments of all NH and OH signals were confirmed by observing the disappearance of their signals after addition of D_2O. MS were measured by the direct inlet system. For column chromatography, Kieselgel 60 (70—230 mesh), Merck, and for thin-layer chromatography (TLC), Kieselgel GF_{254}, Merck, were used. The abbreviations used are as follows: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet; dif, diffused; sh, shoulder; br, broad. All starting materials were commercial products unless otherwise stated. The reaction temperatures given were those measured in the bath.

Ethyl 2-Methoxy-*N*-(2-methoxyphenyl)carbanilate (4)———A mixture of ethyl 2-methoxycarbanilate[13] (**3**) (1.95 g), *o*-bromoanisole (3.74 g), anhyd. K_2CO_3 (2.07 g), and CuBr (200 mg) in nitrobenzene (10 ml) was heated with stirring at 180—190 °C for 3.5 h. The reaction mixture was poured into H_2O and extracted with Et_2O. The extract was dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The residue was chromatographed over silica gel with benzene–AcOEt(3 :1) to give a solid (1.255 g, 41.7%), which was recrystallized from benzene–hexane as colorless needles, mp 128.5—130.5 °C. *Anal.* Calcd for $C_{17}H_{19}NO_4$; C, 67.76; H, 6.36; N, 4.65. Found: C, 67.66; H, 6.41; N, 4.89. IR ν_{max}^{Nujol} cm^{-1}: 1705 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.16 (3H, t, J=7.0 Hz, $CH_2\underline{CH_3}$), 3.86 (6H, s, 2×OCH_3), 4.16 (2H, q, J=7.0 Hz, $O\underline{CH_2}CH_3$), 6.68—7.40 (8H, m, arom H).

2,2′-Dimethoxydiphenylamine (5a)———KOH (1.0 g) was added to a solutin of the carbanilate (**4**) (250 mg) in ethylene glycol (5 ml) and the mixture was heated at 150—160 °C with stirring for 2 h. The reaction mixture was poured into H_2O and extracted with Et_2O. The extract was dried over anhyd. K_2CO_3, and evaporated to dryness *in vacuo*. The residue (175 mg) was chromatographed over silica gel with benzene to give a solid (174 mg, 91.5%). Recrystallization of the product from pentane gave colorless needles, mp 30 °C [lit.,[14] bp 150 °C (1.5 mmHg)]. *Anal.* Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.14; H, 6.85; N, 6.14. IR ν_{max}^{Nujol} cm^{-1}: 3420 (NH).

General Procedure for Preparation of Urea (6) from Corresponding Amine (5)———i) With $NaOCN/CF_3CO_2H$ (method A)[8]:. NaOCN (66 mmol) was added to a solution of an amine (**5**) (33 mmol) in benzene (75 ml). CF_3CO_2H (66 mmol) was added to the above suspension over a period of 5 min, and the whole was stirred at room temperature. After 2 h, further NaOCN (33 mmol) and then CF_3CO_2H (33 mmol) were added. The reaction mixture was stirred for a further 3 h then poured into H_2O. Precipitates were extracted with an appropriate solvent or collected by filtration, and recrystallized.

1,1-Di(2-methoxyphenyl)urea (**6a**): Colorless fine prisms from EtOH–AcOEt–hexane, mp 188.5—190 °C. *Anal.* Calcd for $C_{15}H_{16}N_2O_3$; C, 66.16; H, 5.92; N, 10.29. Found: C, 65.91; H, 6.01; N, 10.35. IR ν_{max}^{Nujol} cm^{-1}: 3475, 3360 (NH), 1685, 1645 (C=O). MS m/z: 272 (M^+), 229 (base peak).

1-(*m*-Chlorophenyl)-1-phenylurea (**6f**): Colorless needles from benzene–hexane, mp 112—115 °C. *Anal.* Calcd for $C_{13}H_{11}ClN_2O$: C, 63.30; H, 4.49; N, 11.36. Found: C, 63.33; H, 4.21; N, 11.28. IR ν_{max}^{Nujol} cm^{-1}: 3450, 3280 (NH), 1690 (C=O). MS m/z: 248 (M^++2, 40% intensity of M^+), 246(M^+), 203 (base peak).

1-Cyclohexyl-1-phenylurea (**6h**): Colorless needles from benzene, mp 179 °C. *Anal.* Calcd for $C_{13}H_{18}N_2O$: C, 71.52; H, 8.31; N, 12.83. Found: C, 71.50; H, 8.41; N, 12.62. IR ν_{max}^{Nujol} cm^{-1}: 3475, 3180 (NH), 1660 (C=O). MS m/z: 218 (M^+), 93 (base peak).

1,1-Diphenylurea (**6b**): Colorless needles from EtOH, mp 196—197 °C (lit.,[8] mp 191—192 °C). IR ν_{max}^{Nujol} cm^{-1}: 3460, 3330 (NH), 1650 (C=O).

1-(1-Naphthyl)-1-phenylurea (**6d**): Colorless needles from EtOH, mp 185—186.5 °C (lit.,[8] mp 180—181.5 °C). *Anal.* Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.66; H, 5.37; N, 10.43. IR ν_{max}^{Nujol} cm^{-1}: 3450 (NH), 1670 (C=O).

1-(2-Naphthyl)-1-phenylurea (**6e**): Colorless needles from $CHCl_3$, mp 190.5—192.5 °C (lit.,[8] mp 188—191 °C). IR ν_{max}^{Nujol} cm^{-1}: 3450, 3300 (NH), 1640 (C=O). MS m/z: 262 (M^+), 219 (base peak).

1-Benzyl-1-phenylurea (**6i**): Colorless plates from benzene–hexane, mp 113.5—114.5 °C (lit.,[10] mp 105 °C). *Anal.* Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.14; H, 6.28; N, 12.44. IR ν_{max}^{Nujol} cm^{-1}: 3450, 3150 (NH), 1670 (C=O). MS m/z: 226 (M^+), 91 (base peak).

ii) With $ClSO_2NCO$ (Method B)[11] [The Preparation of 1-(*o*-Nitrophenyl)-1-phenylurea (**6c**) is Described as a Typical Case]: A solution of the amine (5) (30 mmol) in dry benzene (60 ml) was treated with $ClSO_2NCO$ (30 mmol) with ice-cooling under an Ar atmosphere. After being stirred for 0.5 h at the same temperature, the reaction mixture was warmed to room temperature and stirred for a further 1 h. Yellowish-green precipitates (an intermediate) were collected by filtration. The filtrate was diluted with AcOEt, washed with sat. NaCl, and dried over $MgSO_4$. Evaporation of the solution to dryness *in vacuo* gave the recovered amine. The collected precipitate (the intermediate) was dissolved in CH_3CN (190 ml), and the solution was adjusted to pH 8 with 5 % $NaHCO_3$ aq., then stirred at room temperature for 2 h. The reaction mixture was concentrated *in vacuo* to half the initial volume, and the crude urea precipitate was collected by filtration. The filtrate was diluted with AcOEt, washed with sat. NaCl, and dried over $MgSO_4$. The residue obtained by evaporation of the solvent was combined with the precipitate of the crude urea. The combined crude urea was suspended in benzene and shaken for several minutes. The insoluble material was collected by filtration and recrystallized to give the pure urea (**6c**). Recrystallization from EtOH gave yellow prisms, mp 186—188 °C. *Anal.* Calcd for $C_{13}H_{11}N_2O_3$: C, 60.69; H, 4.31; N, 16.34. Found: C, 60.63; H, 4.28; N, 16.20. IR ν_{max}^{Nujol} cm^{-1}: 3475 (NH), 1680 (C=O).

1-Methyl-1-phenylurea (**6j**): Colorless plates from AcOEt–hexane, mp 79.5—80.0 °C (lit.,[15] mp 79 °C). *Anal.* Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.05; H, 6.65; N, 18.38. IR ν_{max}^{Nujol} cm^{-1}: 3370, 3185 (NH), 1635 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 3.26 (3H, s, $-NCH_3$), 4.75 (2H, br s, NH_2), 7.35 (5H, s, arom H).

1,2,3,4-Tetrahydrocarbazole-9-carboxamide (**6k**): Colorless needles from AcOEt, mp 246—249 °C (lit.,[16] mp 244—245 °C). *Anal.* Calcd for $C_{13}H_{14}N_2O$: C, 72.89; H, 6.54; N, 13.08. Found: C, 72.87; H, 6.65; N, 12.97. IR ν_{max}^{Nujol} cm^{-1}: 3340, 3180 (NH), 1670 (C=O). MS *m/z*: 214(M^+).

iii) With $Si(NCO)_4$ (Method C).[9] Piperidine-1-carboxamide (**6g**): A solution of $Si(NCO)_4$ (0.88 g, 4.5 mmol) in dry benzene (36 ml) was slowly added to a slution of piperidine (**5g**) (1.76 ml, 18 mmol) in dry benzene (6 ml) with ice-cooling under an N_2 atmosphere. The mixture was refluxed for 3 h, forming a clear solution. The residue was obtained by evaporation of the benzene *in vacuo*, iso-PrOH (27 ml) and H_2O (3 ml) were added, and the mixture was refluxed for 2 h. The precipitate was filtered off and washed with acetone. The combined filtrate and washings were evaporated to dryness *in vacuo* to give a solid. Recrystallization of this product from AcOEt–hexane gave colorless leaflets (1.90 g, 82.5%), mp 105—106 °C. *Anal.* Calcd for $C_6H_{12}N_2O$: C, 56.22; H, 9.44; N, 21.86. Found: C, 56.38; H, 9.62; N, 21.87. IR ν_{max}^{Nujol} cm^{-1}: 3360, 3175 (NH), 1650 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.57 (6H, br s, C_3, C_4 and C_5-H), 3.33 (4H, m, C_2 and C_6-H), 4.80 (2H, br s, NH_2).

General Procedure for Synthesis of the Hydrazine (2) from the Corresponding Urea (6)——A mixture of 14% NaOH aq. (1.5 ml) and NaOCl (0.86 ml) containing 10.2% active chlorine was slowly added to an ice-cooled solution of a urea (**6**, 1.0 mmol) in EtOH (5 ml). The resulting suspension (or solution) was stirred for 1 to 2 h at room temperature. When the reaction was complete, the reaction mixture was diluted with H_2O, and then extracted with an appropriate solvent to remove the amine (**5**) formed as a by-product. The aqueous layer was acidified with dil. HCl, then basified with K_2CO_3 aq., and extracted with an appropriate solvent. The organic layer was dried over anhyd. K_2CO_3 and evaporated to dryness *in vacuo* to give a crude hydrazine. The hydrazine (**2**) thus obtained was converted to a salt with TsOH or a hydrazone of ethyl pyruvate or piperonal for characterization.

Preparation of Hydrazone: A hydrazine (**2**) was added to a solution of an equivalent amount of ethyl pyruvate or piperonal in EtOH. The mixture was refluxed for several minutes then evaporated to dryness *in vacuo*. The residue of the desired hydrazone was purified by recrystallization from an appropriate solvent or by chromatography.

Preparation of the Tosylate: A solution of TsOH (1.75 mmol) in amyl alcohol (2 ml) was mixed with Et_2O–benzene (1 : 1 v/v) (4 ml). To this solution was added a solution of a hydrazine [prepared from the corresponding urea (1.0 mmol)] in Et_2O–benzene (1 : 1 v/v) (20 ml). The precipitate of the tosylate was collected by filtration and recrystallized from an appropriate solvent.

1,1-Di(*o*-methoxyphenyl)hydrazine (**2a**): Ethyl pyruvate 2-[di-(*o*-methoxyphenyl)hydrazone]: Pale yellow needles from benzene–hexane, mp 89—91 °C. *Anal.* Calcd for $C_{19}H_{22}N_2O_4$: C,66.65; H, 6.48; N, 8.18. Found: C, 66.45; H, 6.51; N, 8.33. IR ν_{max}^{Nujol} cm^{-1}: 1695. ^{1}H-NMR ($CDCl_3$) δ: 1.28 (3H, t, J=7.0 Hz, $CH_2\underline{CH_3}$), 1.60 (3H, s, C-CH_3), 3.70 (6H, s, 2×OCH_3), 4.25 (2H, q, J=7.0 Hz, $O\underline{CH_2}CH_3$), 6.63—7.28 (8H, m, arom H). MS *m/z*: 342 (M^+).

1,1-Diphenylhydrazine (**2b**): Tosylate: Colorless feathers from EtOH, mp 196—198 °C. *Anal.* Calcd for $C_{19}H_{20}N_2O_3S$: C, 64.03; H, 5.66; N, 7.86. Found: C, 64.17; H, 5.51; N, 7.88. IR ν_{max}^{Nujol} cm^{-1}: 2660 (NH_3^+).

1-(*o*-Nitrophenyl)-1-phenylhydrazine (**2c**): Tosylate: Yellow needles from EtOH, mp 180—181 °C. *Anal.* Calcd for $C_{19}H_{19}N_3O_5S$: C, 56.85; H, 4.77; N, 10.47. Found: C, 56.66; H, 4.80; N, 10.09. IR ν_{max}^{Nujol} cm^{-1}: 2650 (NH_3^+).

1-(1-Naphthyl)-1-phenylhydrazine (**2d**): Tosylate: Pale brown needles from EtOH, mp 173—174.5 °C. *Anal.* Calcd for $C_{23}H_{22}N_2O_3S$: C, 67.95; H, 5.46; N, 6.89. Found: C, 67.66; H, 5.43; N, 6.82. IR ν_{max}^{Nujol} cm^{-1}: 2660 (NH_3^+).

1-(2-Naphthyl)-1-phenylhydrazine (**2e**): Tosylate: Pale purple needles from EtOH, mp 192—195 °C. IR ν_{max}^{Nujol} cm^{-1}: 2680 (NH_3^+).

1-(3-Chlorophenyl)-1-phenylhydrazine (**2f**): Tosylate: Colorless feathers from EtOH, mp 186—188 °C. *Anal.* Calcd for $C_{19}H_{19}ClN_2O_3S$: C, 58.38; H, 4.90; N, 7.17. Found: C, 58.18; H, 4.74; N, 6.83. IR ν_{max}^{Nujol} cm^{-1}: 2700 (NH_3^+).

1-Aminopiperidine (**2g**): Tosylate: Colorless fine needles from AcOEt–hexane, mp 106—109 °C. *Anal.* Calcd for $C_{12}H_{20}N_2O_3S$: C, 52.91; H, 7.40; N, 10.28. Found: C, 52.94; H, 7.53; N, 10.05. IR ν_{max}^{Nujol} cm^{-1}: 3280,3180.

1-Cyclohexyl-1-phenylhydrazine (**2h**): Tosylate: Colorless needles from EtOH–AcOEt, mp 206—209 °C. *Anal.* Calcd for $C_{19}H_{26}N_2O_3S$: C, 62.96; H, 6.23; N, 7.73. Found: C, 62.60; H, 7.14; N, 7.54. IR ν_{max}^{Nujol} cm^{-1}: 2700 (NH_3^+). Hydrazone of piperonal: Colorless plates from hexane, mp 73 °C. *Anal.* Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.12; H, 7.11; N, 8.66. IR ν_{max}^{Nujol} cm^{-1}: 1570 (C=N). ^{1}H-NMR ($CDCl_3$) δ: 0.90—2.40 (10H, m, aliphatic H), 3.47 (1H, br s, N–CH), 5.85 (2H, s, OCH_2O), 6.68 (1H, s, N=CH), 6.95—7.60 (8H, m, aromatic H). MS *m/z*: 322 (M^+).

1-Benzyl-1-phenylhydrazine (**2i**): Tosylate: Colorless feathers from EtOH–hexane, mp 179—180 °C. *Anal.* Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.85; H, 5.99; N, 7.56. Found: C, 64.59; H, 5.97; N, 7.29. IR ν_{max}^{Nujol} cm^{-1}:

2690 (NH_3^+).

1-Methyl-1-phenylhydrazine (**2j**): Hydrazone of piperonal: Pale yellow rods from hexane, mp 82—84 °C. *Anal.* Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.46; H, 5.36; N, 10.94. IR ν_{max}^{Nujol} cm^{-1}: 1605 (C=N). ^{1}H-NMR ($CDCl_3$) δ: 3.36 (3H, s, NCH_3), 5.94 (2H, s, OCH_2O), 6.68—7.50 (9H, m, arom H and N=CH). MS *m/z*: 254 (M^+).

9-Amino-(1,2,3,4-tetrahydrocarbazole) (**2k**): Hydrazone of piperonal: Colorless rods from hexane–benzene, mp 122—124 °C. IR ν_{max}^{Nujol} cm^{-1}: 1610 (C=N). ^{1}H-NMR ($CDCl_3$) δ: 1.45—2.20 (4H, m, C_2- and C_3-H), 2.40—3.05 (4H, m, C_1- and C_4-H), 5.92 (2H, s, OCH_2O), 6.65—7.70 (7H, m, arom H), 8.53 (1H, s, N=CH). MS *m/z*: 318 (M^+).

References and Notes

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