Mild Reduction of *N*,*N'*-Mercurio-bis-tosylhydrazones with Sodium Cyanoborohydride. Synthesis of *N*-Aroyl-*N'*-tosylhydrazines and Deoxygenation of Aromatic Ketones

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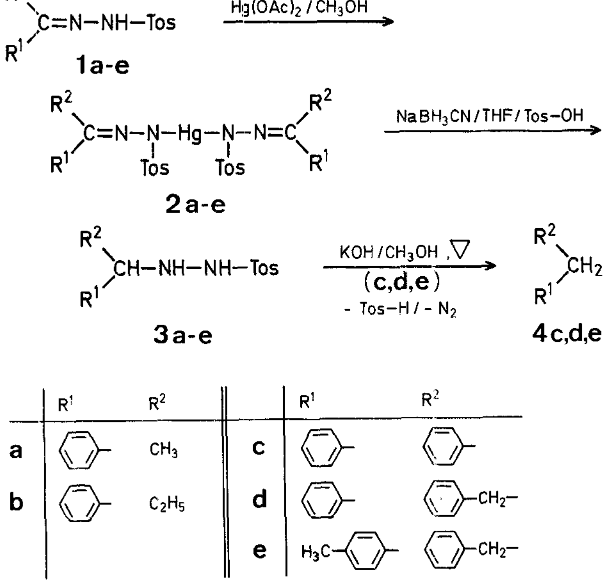
The reduction of aliphatic ketone and aldehyde tosylhydrazones with sodium borohydride in refluxing methanol or dioxan[1], or with sodium cyanoborohydride in acidic dimethylformamide/sulfolane (1:1)[2] at 100–105° provide mild, selective, and high-yield alternatives to the Wolff-Kishner and Clemmensen reductions. However, arylcarbonyl compounds proved to be quite resistant to reduction by these methods regardless of the procedure used. This limitation has been ascribed to a decrease in electrophilicity of the iminium C-atom in such compounds.

We have recently found that the iminium C-atom can be easily activated with respect to nucleophilic hydride attack by converting aryl ketone tosylhydrazones (**1**) into the corresponding *N*,*N'*-mercurio-bis-tosylhydrazones (**2**) by reaction with equimolar quantities of mercury(II) acetate in methanol



at 40–45° for a few minutes. In fact, when a solution of *p*-toluenesulfonic acid (8 equiv) in tetrahydrofuran is slowly added to a stirred solution of the mercurated tosylhydrazones **2** (1 equiv) and sodium cyanoborohydride (10 equiv) in tetrahydrofuran at room temperature, *N*-aroyl-*N'*-tosylhydrazines (**3**) are produced which can be isolated without difficulty in nearly quantitative yields (Table 2). Several other solvent systems including dimethylformamide, sulfolane, dioxane, and hexamethylphosphoric triamide were also tried and gave nearly the same results. Hydrochloric acid (6 *M*) can be used instead of *p*-toluenesulfonic acid.

The conversion of the tosylhydrazines **3c, d, e** into the hydrocarbons **4d, c, e** is effected by heating compounds **3** with methanolic potassium hydroxide. Diphenylmethane (**4c**), 1,2-diphenylethane (**4d**), and 1-(4-methylphenyl)-2-phenylethane (**4e**) may thus be obtained in yields of 85–90%.

Table 1. *N,N'*-Mercurio-bis-tosylhydrazones (**2**) from Tosylhydrazones (**1**) and Mercury(II) Acetate

2	Yield [%]	m.p. (dec)	I.R. (KBr) ν_{SO} [cm^{-1}]	Molecular formula[a]
a	92	144–146°	1260, 1125	$C_{30}H_{30}HgN_4O_4S_2$ (775.2)
b	95	118–120°	1260, 1140	$C_{32}H_{34}HgN_4O_4S_2$ (801.2)
c	94	167–169°	1310, 1145	$C_{40}H_{32}HgN_4O_4S_2$ (897.3)
d	98	122–123°	1300, 1140	$C_{42}H_{38}HgN_4O_4S_2$ (927.4)
e	87	163–165°	1290, 1135	$C_{44}H_{42}HgN_4O_4S_2$ (955.4)

[a] The elemental analyses were in satisfactory agreement with the calculated values: C, ±0.08 (except for **2e**: −0.19); H, ±0.16; N, ±0.12; Hg, ±0.52.

Preparation of Tosylhydrazones; General Procedure:

The tosylhydrazones **1a–e** are prepared in good yields from the corresponding carbonyl compounds by addition of equimolar quantities of tosylhydrazine in methanol at temperatures not exceeding 50° (1–2 h). The tosylhydrazones crystallize from the solution after cooling; they are isolated by filtration, dried in vacuo, and used in the next step without further purification. They all show I.R. absorptions (KBr) at $\nu \approx 3230$, 1600, 1360, 1170, and 820 cm^{-1}.

Preparation of *N,N'*-Mercurio-bis-tosylhydrazones (2a–e); General Procedure:

The tosylhydrazone **1** (10 mmol) is dissolved in boiling methanol and the solution cooled to 30°. To this solution, mercury(II) acetate (3.19 g, 10 mmol) is added with stirring. After a few minutes, the mercurio derivative **2** precipitates from the solution. It is isolated by filtration, washed with ether, and dried in vacuo.

Preparation of *N*-Aroyl-*N'*-tosylhydrazines (3a–e); General Procedure:

A solution or suspension of sodium cyanoborohydride (1.356 g, 20 mmol) and the *N,N'*-mercurio-bis-tosylhydrazone **1a–e** (2 mmol) in dry tetrahydrofuran (100 ml) is stirred under nitrogen in a three-necked flask. A solution of *p*-toluenesulfonic acid (3.04 g; 16 mmol) in tetrahydrofuran (30 ml) is slowly added at room temperature. The mixture becomes grey. Stirring is continued for a further 10 min and the reaction is then quenched by the addition of saturated aqueous sodium carbonate. The mixture is extracted three times with ether, the extract is washed twice with water, dried with sodium sulfate, and concentrated in vacuo using a rotary evaporator. The crude tosylhydrazines are recrystallized from dichloromethane/hexane.

Decomposition of the Tosylhydrazines 3c, d, e to the Hydrocarbons 4c, d, e:

A mixture of the *N*-aroyl-*N'*-tosylhydrazine **3c, d, e** (4 mmol) and 1 *N* methanolic sodium hydroxide (100 ml) is refluxed for 1 h. The resultant mixture is extracted with hexane, and the organic layer is dried with sodium sulfate and filtered. The solvent is evaporated under reduced pressure and the crude product **4** is purified by chromatography on a silica-gel column (hexane as eluent); yield: 85–90%.

Table 2. *N*-Aroyl-*N'*-tosylhydrazines (**3**) from *N,N'*-Mercurio-bis-tosylhydrazones (**2**) by Reduction with Sodium Cyanoborohydride

3	Yield[a] [%]	m.p. (dec)	I.R. (KBr) [cm^{-1}] ν_{NH}	ν_{SO_2}	^{1}H-N.M.R. (CDCl$_3$) δ [ppm]	Molecular formula[b]
a	95	108–110°	3290 3240	1320 1150	7.7–6.8 (m, 9H); 5.65 (bs, 1H)[c]; 3.6 (bs, 1H)[d]; 3.7 (q, J=7.0 Hz, 1H); 2.40 (s, 3H); 1.2 (d, J=7.0 Hz, 3H).	$C_{15}H_{18}N_2O_2S$ (290.3)
b	93	113°	3290 3240	1320 1150	7.8–6.8 (m, 9H); 5.62 (bs, 1H)[c]; 3.64 (bs, 1H)[d]; 3.45 (t, J=7.5 Hz, 1H); 2.45 (s, 3H); 1.9–1.25 (m, 2H); 0.72 (t, 3H).	$C_{16}H_{20}N_2O_2S$ (304.3)
c	87	115°	3285 3220	1330 1160	7.9–6.95 (m, 14H); 5.7 (bs, 1H)[c]; 4.87 (s, 1H); 7.45 (bs, 1H)[d]; 2.42 (s, 3H).	$C_{20}H_{20}N_2O_2S$ (352.4)
d	96	114–116°	3305 3240	1325 1150	7.6–6.75 (m, 14H); 5.57 (bs, 1H)[c]; 3.42 (bs, 1H)[d]; 3.93 (t, J=7.5 Hz, 1H); 2.80 (d, J=7.5 Hz, 2H); 2.4 (s, 3H).	$C_{21}H_{22}N_2O_2S$ (366.4)
e	93	123–125°	3280 3245	1310 1150	7.55–6.7 (m, 13H); 5.5 (bs, 1H)[c]; 3.82 (bs, 1H)[d]; 3.82 (t, J=8.0 Hz, 1H); 2.75 (d, J=8.0 Hz, 2H); 2.38 (s, 3H); 2.27 (s, 3H).	$C_{22}H_{24}N_2O_2S$ (380.4)

[a] Yield refer to products recrystallized from dichloromethane/hexane.

[b] The elemental analyses were in good agreement with the calculated values: C, ±0.07; H, ±0.06; N, ±0.08.

[c] D_2O exchange, Tos—N$\underline{H}$—NH—R.

[d] D_2O exchange, Tos—NH—N$\underline{H}$—R.

Compounds **4** were identified by comparison with authentic samples (I.R., ^{1}H-N.M.R., mass spectra).

Table 3. Hydrocarbons (**4**) by Cleavage of *N*-Aroyl-*N'*-tosylhydrazines (**3**) with Methanolic Potassium Hydroxide

4	Yield [%]	m.p.	m.p. (Lit.)
c	90	25–26°	26–27°[3]
d	87	51–52°	52°[4]
e	85	26–27°	27°[5]

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