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A NEW ROUTE TO MONOALKYLHYDRAZINES

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Abstract: Electrophilic amination of primary amines with N-(diethoxyphosphoroyl)-O-(p-nitrophenylsulfonyl)-hydroxylamine **1**, followed by dephosphorylation of the phosphorohydrazidate **2** with p-toluenesulfonic acid monohydrate in ethanol, represents a novel approach to monoalkylhydrazines.

Monoalkylhydrazines, important starting materials for the preparation of various heterocyclic compounds containing N-N bonds[1], have been so far available by two general methods - alkylation of hydrazine[2-4] or its protected derivatives[5,6] and electrophilic amination of primary amines by means of chloroamine [7-9] or hydroxylamine-O-sulfonic acid[10]. Electrophilic amination, although widely and conveniently used for preparing N-amine salts from a variety of tertiary amines[11], is of limited synthetic value when applied to primary amines. Transformation of the latter into the corresponding hydrazines by the treatment with

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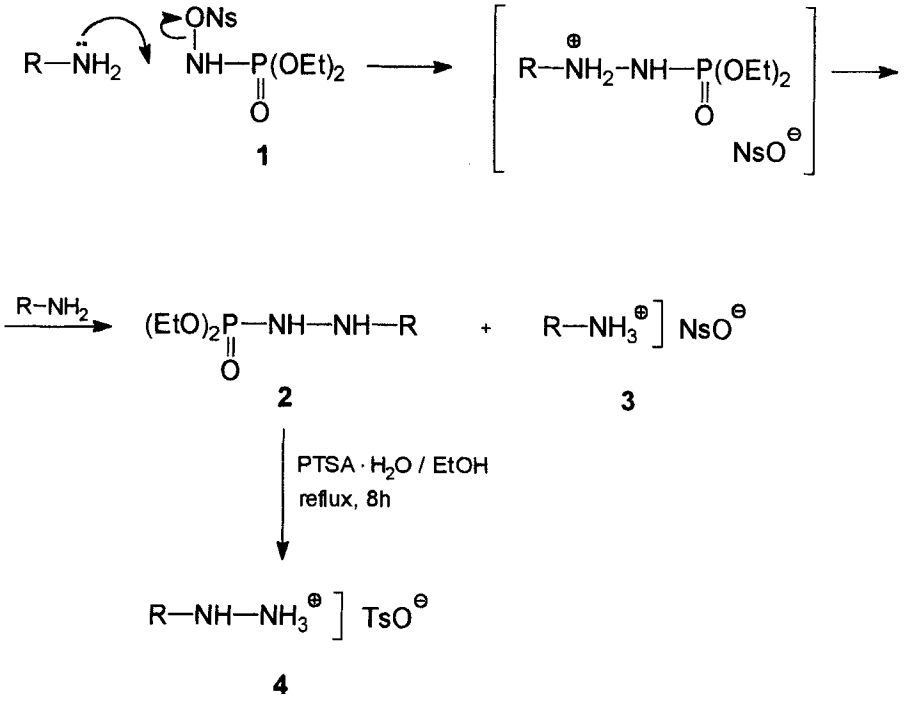
hydroxylamine-O-sulfonic acid in the presence of alkali demands a large excess of an amine (5-6 moles per mole of the aminating agent) and does not secure high yields of alkylhydrazine oxalates[10]. Tedious preparative procedure can be also considered as an essential disadvantage of this approach.

In the course of our current studies on the preparative potential of N-(diethoxyphosphoroyl)-O-(p-nitrophenylsulfonyl)-hydroxylamine **1** as a reagent for electrophilic amination we have recently found that **1** can be conveniently used for transforming primary alkylamines into the corresponding monoalkylhydrazines. Herein we wish to present an expedient procedure describing this transformation. When two moles of primary amine are treated with one mole of the nosylate **1** in dichloromethane solution at ambient temperature a slightly exothermic reaction takes place leading to the formation of N-alkyl-N'-(diethoxyphosphoroyl)-hydrazine **2** and the amine nosylate **3**. The proposed reaction pathway is presented on the Scheme. In contrast to electrophilic amination with hydroxylamine-O-sulfonic acid[10] the use of large excess of an amine is neither necessary nor desirable. The amine nosylate **3** can be separated from phosphorohydrazidate **2** by washing with water. Crude amination product **2**, although contaminated with two unidentified phosphorus compounds (see Table), does not need to be purified, but can be directly subjected to dephosphorylation by refluxing

Scheme



Ns = p-NO_2-C_6H_4-SO_2

Ts = p-CH_3-C_6H_4-SO_2

2 (4)	a	b	c	d	e	f
R	Pr	Bu	i-Bu	C_6H_{13}	$PhCH_2$	$PhCH_2CH_2$

TABLE

Preparation of Monoalkylhydrazine p-Toluenesulfonates **4**

Compound No.	R	Yield of **4**[a] (%)	% of pure **2** in the crude amination product[b]	^{31}P-NMR of **2** δ (ppm)	m.p. of **4** (°C)	Lit.[6] m.p. of **4** (°C)
2 (4) a	Pr	46	52	8.10	111-113	-
2 (4) b	Bu	67	70	8,34	115-117	116-118
2 (4) c	i-Bu	63	68	8.10	126-130[c]	126-130
2 (4) d	C_6H_{13}	40	62	8.16	98-112[d]	111-115
2 (4) e	Ph-CH_2	51	61	7.98	138-141[c]	143-144
2 (4) f	Ph-CH_2CH_2	60	63	8.16	135-139	-

[a] Yield (1→4) of isolated, crude **4**. [b] Calculation from ^{31}P-NMR spectrum of crude **2**. [c] M.p. of crude **4**.

[d] As determined by ^{1}H-NMR crystallized sample of **4** contains ~27% of hexylamine nosylate.

with equimolar amount of p-toluenesulfonic acid monohydrate in ethanol (Scheme). Evaporation of the solvent followed by precipitation of the product with ether affords monoalkylhydrazine p-toluenesulfonate **4** as crystalline solid. Analytically pure samples of **4** obtained by dissolving the crude salts in warm ethanol and reprecipitation with ether have m.p.'s and also mixed m.p.'s (Table) identical with those of the specimens prepared by an independent procedure[6]. New compounds **4a** and **4f** have been satisfactorily analysed and characterized spectroscopically.

Owing to its simplicity and mild reaction conditions the procedure reported herein may serve in our opinion as a useful alternative to the existing methods of preparing monoalkylhydrazines.

EXPERIMENTAL

All solvents and reagents were of reagent grade. Melting points were determined in open capillaries and are uncorrected. IR spectra were measured using a Specord M 80 (C.Zeiss) instrument.

^{1}H-NMR spectra were recorded at 80 MHz with a Tesla 587 FT spectrometer. ^{31}P-NMR spectra were taken at 36.43 MHz with a Bruker HFX-90 spectrometer. Positive chemical shifts are downfield from 85% H_3PO_4. FAB/MS were measured on a APO Electron (Ukraine) Modell MI

12001 E mass spectrometer equipped with a FAB ion source (thioglycerol matrix).

N-(Diethoxyphosphoroyl)-O-(p-nitrophenylsulfonyl)-hydroxylamine1 was obtained according to the previously published procedure[12].

Preparation of monoalkylhydrazine p-toluenesulfonates 4a-f. General Procedure:

Primary alkylamine (0.15 mol) was added dropwise with stirring to the solution of N-(diethoxyphosphoroyl)-O-(p-nitrophenylsulfonyl)--hydroxylamine **1** (2.65 g, 0.0075 mol) in dichloromethane (25 mL) at ambient temperature (18-20°). The slight exothermic effect was observed. Stirring was continued for 2 h at room temperature, the solvent was then evaporated and the residue was diluted with ether (40 mL) and left overnight at 0-5°. The precipitated amine nosylate **3** was filtered off. Ether was evaporated from the filtrate, the residue was taken into dichloromethane (50 mL), and washed with water (5 mL) in order to remove the residual amounts of **3**. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated in vacuo to give crude N-alkyl-N'-(diethoxyphosphoroyl)-hydrazine **2** as an oil, contaminated (^{31}P-NMR) with two unidentified phosphorus compounds. The approximate amount of pure **2** in this mixture was calculated by integration the respective signals in ^{31}P-NMR spectrum of crude material (see Table).

Crude **2** was then dissolved in ethanol (10 mL), one molar equivalant of p-toluenesulfonic acid monohydrate, and water (0.1 mL) were added and the mixture was refluxed for 8 h. It was then cooled to room temperature, evaporated under reduced pressure, and treated with ether (50 mL). Monoalkylhydrazine p-toluenesulfonates **4** crystallized overnight in a refrigerator. They were filtered off, washed with ether, and recrystallized by dissolving in warm ethanol and reprecipitation with ether. Yields and m.p.'s of the tosylates **4a-f** are compiled in the Table.

Propylhydrazine p-toluenesulfonate 4a:

Yield: 46%, m.p. 111-113°.

$C_{10}H_{18}N_2O_3S$ calc. C,48,76%; H,7.37%; N,11.37%.

(246.3) found C,49.02%; H,7.50%; N,11.55%.

IR (KBr): $\upsilon = 3328$ (NH), 1598 (NH_3^+), 1176,1124,1036,1012, 684 cm^{-1}.

^{1}H-NMR (D_2O/DSS): $\delta = 0.95$ (t,3H,J = 7.35); 1.77 (qt,2H,J = 7.5); 2.37 (s,3H); 3.10 (t,2H,J = 7.5); 7.29-7.74 (m,4H).

MS (m/z): 75 (M - TsO).

2-Phenylethylhydrazine p-toluenesulfonate 4f:

Yield: 60%, m.p. 135-139°.

$C_{15}H_{20}N_2O_3S$ calc. C, 58.42%; H,6.54%; N,9.08%.

(308.4) found C,58.75%; H,6.70%; N,9.30%.

IR(KBr): $\upsilon = 3325$(NH),1600 (NH_3^+),1180,1126,1036,1012,814,688cm^{-1}.

^{1}H-NMR (D_2O/DSS): δ=2.37 (s,3H); 2.89-3.47 (m,4H); 7.36 (s,5H); 7.20-7.86 (m,4H).

MS (m/z): 137 (M-TsO).

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