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A CONVENIENT REDUCTION OF DIALKYLATED TOSYLMETHYL ISOCYANIDE+

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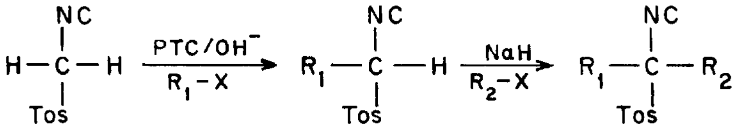
Dialkylated tosylmethyl isocyanides have been conveniently reduced to the corresponding hydrocarbons with lithium in liquid ammonia. This process has been successfully utilised in the synthesis of (Z)-9-tricosene - a sex pheromone of common house fly.

Tosylmethyl isocyanide[1] (TosMIC) has been shown to a useful reagent in organic synthesis, not only as a synthon for heterocyclic compounds[2] but in a variety of other synthetic transformation as well.[2,3] One interesting aspect of TosMIC reagent is its potential to serve as carbonyl anion equivalent.[4,5] For example, TosMIC (1) has been alkylated[4] sequentially with different bases (PTC/OH$^-$, NaH) to obtain 3 (equation 1) which has been converted with trace of acid into several symmetrical as well as unsymmetrical ketones (4). We now wish to report a new methodology for the synthesis of various substituted hydrocarbons by the reduction of the dialkylated TosMIC (3) with lithium in liquid ammonia.



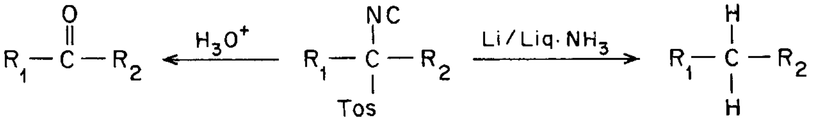
$$\mathrm{H}-\overset{\mathrm{NC}}{\underset{\mathrm{Tos}}{\mathrm{C}}}-\mathrm{H} \xrightarrow[R_1-X]{\mathrm{PTC/OH^-}} R_1-\overset{\mathrm{NC}}{\underset{\mathrm{Tos}}{\mathrm{C}}}-\mathrm{H} \xrightarrow[R_2-X]{\mathrm{NaH}} R_1-\overset{\mathrm{NC}}{\underset{\mathrm{Tos}}{\mathrm{C}}}-R_2$$

Eq.1

1 2 3

[+] Dedicated to Dr. Sukh Dev on the occasion of his 61st birthday.

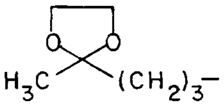
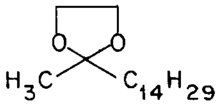
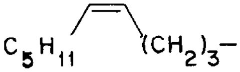
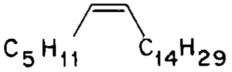
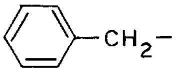
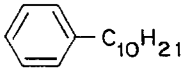
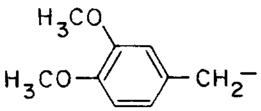
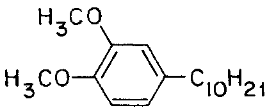
The ethereal solution of the dialkylated TosMIC (3) was treated[6] with lithium in liquid ammonia in presence of ethanol at -30 ± 3° for 2 hr to produce an excellent yield of the corresponding hydrocarbons (5) (Equation 2, Table 1).



4 3 5

Eq. 2

Table 1 Li/Liq·NH$_3$ Reduction of Dialkylated TosMIC[a] (3)

Entry	Dialkylated TosMIC (3)		Product (5)	Yield[b] % 5
	R_1	R_2		
1	$C_8H_{17}-$	$C_8H_{17}-$	$C_{17}H_{36}$	93
2	$C_{10}H_{21}-$			91
3	$C_{10}H_{21}-$			90
4	$C_8H_{17}-$	$C_8H_{17}-\equiv-(CH_2)_3-$	$C_8H_{17}-\equiv-C_{12}H_{25}$	90
5	$C_8H_{17}-$			95
6	$C_8H_{17}-$			95

a) All reactions were carried out with 10 molar equivalent of lithium in liq· NH$_3$ in presence of ethanol at -32° for 2 hr.

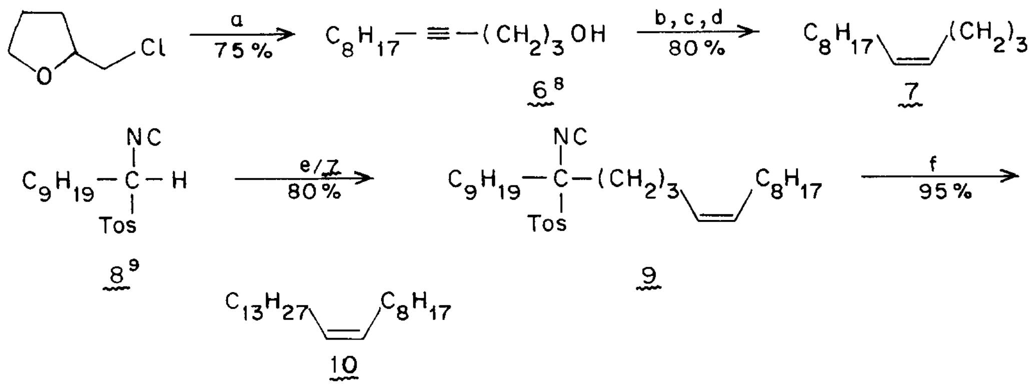
b) Isolated yield after distillation

It is pertinent to mention several advantages of this reduction process. For instance, the reaction is highly chemoselective as the triple bonds, aromatic rings etc. are unaffected under these reaction conditions (Table 1, entry 4-6). The reaction is very clean and offers no other side products. The byproducts arises from the reaction is minimal, highly soluble in water and could be removed easily. The reduction method described above appears to be a novel and general for conversion of dialkylated TosMIC to hydrocarbons.

A typical procedure is as follows: To a freshly distilled liquid ammonia at -33 ± 2° was added lithium (50 mg, 7 mmol) in one portion, followed by 3 ($R_1 = R_2 = C_8H_{17}$, 294 mg, 0.7 mmol) in ether (3 ml) and ethanol (0.12 ml, 2.1 mmol). After two hours, ammonia was allowed to evaporate by bringing it to room temperature. Then water was added and extracted with ether (5 x 10 ml). The organic layer was washed with water (20 ml), brine (20 ml), dried (Na_2SO_4) and concentrated. Distillation of the residue (pot temperature 125-135° at 1 mm) afforded heptadecane (156 mg, 93%) as colourless liquid.

In order to demonstrate the efficacy of this reduction procedure, (Z)-9-tricosene (10)[7], the sex pheromone of common house fly, was prepared (scheme 1). The dialkylated TosMIC (9) was conveniently reduced with lithium in liquid ammonia as described above.[10,11]

Scheme 1 Preparation of common House fly Pheromone 10



a) $LiNH_2$, liq$\cdot NH_3$, $C_8H_{17}Br$ b) H_2, $Pd-CaCO_3$, hexane c) MsCl, Et_3N, CH_2Cl_2, RT d) NaI, acetone reflux e) NaH, 1:1 DMSO-ether, RT f) Li, liq$\cdot NH_3$

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10. All new compounds were characterised by NMR, IR, mass spectrum and combustion analysis.

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