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DISSOLVING METAL REDUCTION WITH CROWN ETHER ---REDUCTIVE REMOVAL OF ISOCYANO GROUPS

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Summary: Toluene radical anion generated from K metal and toluene with the assistance of crown ether has been proven effective for reductive removal of aliphatic isocyano groups.

Crown ether enables the generation of such uncommon chemical species as potassium anion from K metal or toluene radical anion from K metal and toluene.[1] There is high expectation that these species provide a new aspect in the field of dissolving metal reduction. During studies on the application of these chemical species to reductions of various functional groups,[2] we found the high reactivity of a potassium anion in etheric solvents for reductive cleavage of sulfonamides,[2b] and the unusually high ability of a toluene radical anion in reductive defluorination and decyanation.[2a,c]

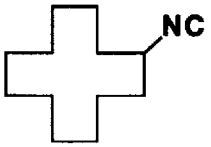
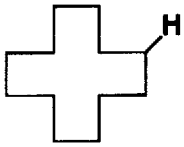
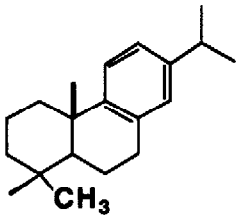
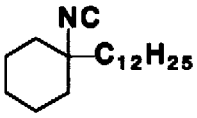
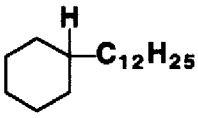
In the present paper, we wish to report that reduction with this particular radical anion was successfully extended to the reductive removal of isocyano groups.

General reduction conditions are as follows: A solution of isocyanide (0.5 mmol) and dicyclohexano-18-crown-6 (1.0 mmol) in toluene (20 ml) is agitated with excess potassium metal in nitrogen at ambient temperature for several hours. After treatment with isopropanol, removal of the solvent, extraction with n-hexane and column chromatography on silica gel, hydrocarbon is obtained as the sole product.

The results in Table 1 clearly show that the toluene radical anion generated with the assistance of crown ether is effective for reductive removal of primary, secondary or tertiary aliphatic isocyano groups. It should be noted that the isolated olefin and the aromatic ring remained totally unaffected.

Isocyanides, the substrates(entry 1-4) for the present study, were synthesized in high yields from the corresponding amine hydrochlorides through trans-formylation followed by dehydration.[3] This overall reaction path as shown below therefore provides an alternative method for reductive deamination of aliphatic primary amines.[4]

Table 1 Reductive Removal of Isocyano Groups with Toluene Radical Anion

Entry	Isonitrile	Product	Yield, %
1	$nC_{18}H_{37}$-NC	$nC_{18}H_{38}$	99
2	$nC_8H_{17}CH{=}CHC_8H_{16}$-NC	$nC_8H_{17}CH{=}CHC_8H_{17}$	96
3			90
4			97
5			99

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