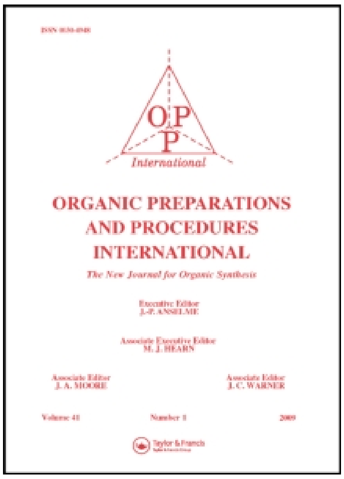

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A SIMPLE REDUCTION OF ARALKYL KETONES TO ALCOHOLS

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the reaction was monitored by ^{1}H-NMR. The reaction mixture was filtered through a pad of Celite and the aqueous filtrate was treated with potassium hydroxide, concentrated to 200 ml under reduced pressure, acidified with conc. HCl and extracted with dichloromethane (5 x 400 ml). After drying on sodium sulfate, the solvent was evaporated and the crude oil distilled to yield the pure lactone 1 (6.54 g, 60%), bp. 140°/16 mmHg; ^{1}H-NMR ($CDCl_3$): δ 1.2 (d, 3H), 2.0-3.0 (m, 3H), 3.8-4.9 (m, 2H); $[\alpha]_D$-23° (c = 4, MeOH).

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A SIMPLE REDUCTION OF ARALKYL KETONES TO ALCOHOLS

Submitted by (06/08/87)
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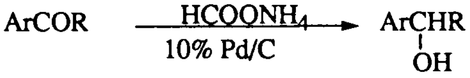
Catalytic transfer hydrogenation has been widely studied in the past three decades.[1] Palladium-catalysed ammonium formate reduction of aromatic halides,[2] nitriles,[3] nitro compounds[2,4] and α,β-unsaturated carbonyl compounds[5] has been reported. Aromatic ketones are reduced to the corresponding aromatic hydrocarbons using Pd/C-formic acid in refluxing ethanol;[6] aromatic aldehydes and ketones are also reduced to the hydrocarbons using palladium-carbon/cyclohexene or limonene.[7] The hitherto undescribed reduction of aralkyl ketones to alcohols using palladium-carbon-ammonium formate is now reported to proceed in high yields at room temperature. The completion of reductions was followed by TLC. Aromatic aldehydes failed to give the alcohols under the same conditions.



$$ArCOR \xrightarrow[10\%\ Pd/C]{HCOONH_4} ArCH(OH)R$$

EXPERIMENTAL SECTION

General Procedure.- To a stirred suspension of an appropriate ketone (20 mmol) and 10% Pd/C (1.5-1.6 g) in dry methanol (25 ml), anhydrous ammonium formate was added (50 mmol) in a single portion. The resulting reaction mixture (slight exotherm and effervescence) was stirred at room temperature for 4 hrs. under N_2. The catalyst was then removed by filtration through Celite and washed with methanol (20 ml). The filtrate was evaporated under reduced pressure. The resulting residue was diluted with water (50 ml) and the product extracted with chloroform and the solution was dried over Na_2SO_4. Distillation of the solvent gave the pure alcohol.

TABLE. Reduction of Aralkyl Ketones to Alcohols[a]

Ketones	Yield (%)	bp.	lit. bp.	n_D^{20}
$C_6H_5COCH_3$	90	98-100°/20mm	98-99°/20mm[b]	1.524
p-$MeOC_6H_4COCH_3$	85	138-140°/2mm	310/760mm[b]	1.518
p-i-$BuC_6H_4COCH_3$	90	103-105°/2mm	93-95°/1mm[c]	1.509
p-i-$BuC_6H_4COCH_2CH_3$	91	118-120°/3mm	118-120°/3mm[d]	1.505
p-t-$BuC_6H_4COCH_2CH_3$	87	112-114°/3mm	112-114°/3mm[d]	1.508

a) Products were characterised by comparison with authentic samples (IR, ^{1}H-NMR, TLC and bp.), prepared by reduction of ketones with sodium borohydride. Isolated yields are based on a single experiment and are not optimized. All reactions were carried out for 4 hrs.

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A CONVENIENT SYNTHESIS OF TOSYLLACTONITRILE AND ITS REACTION WITH BENZENE

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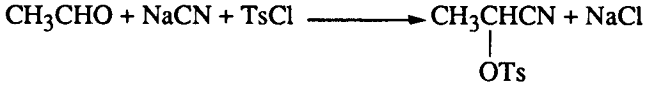
Tosyllactonitrile constitutes an important three carbon synthon with a nitrile functionality that can be converted to other useful groups. It can be used to introduce a three carbon chain directly into an aromatic nucleus via the Friedel-Crafts reaction which would lead to biologically important compounds such as ibuprofen, naproxen and hydratropic acid.

$$\mathrm{ArH} + \mathrm{CH_3}\overset{\mathrm{OTs}}{\overset{|}{\mathrm{C}}}\mathrm{HCN} \longrightarrow \mathrm{Ar}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCN} \longrightarrow \mathrm{Ar}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HCOOH}$$

Tosyllactonitrile is generally prepared by a two-step synthesis. Acetaldehyde is reacted with hydrogen cyanide (HCN) under carefully controlled conditions to give lactonitrile[1] which is isolated and then tosylated using pyridine/tosylchloride.[2] Since lactonitrile is reported to be a very toxic compound,[3] we now report here a simple one-pot synthesis of tosyllactonitrile which has the merit of eliminating the need to use HCN. The method consists of treating a mixture of aqueous acetaldehyde and tosylchloride with sodium cyanide.



$$\mathrm{CH_3CHO + NaCN + TsCl} \longrightarrow \mathrm{CH_3}\underset{\mathrm{OTs}}{\underset{|}{\mathrm{C}}}\mathrm{HCN + NaCl}$$

Tosyllactonitrile thus prepared has been successfully reacted with benzene to get hydratroponitrile in high yield. The reactions of tosyllactonitrile with other aromatic compounds are now being investigated in our laboratories.