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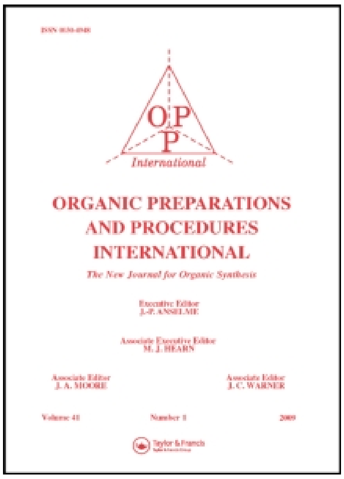

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^{13}C-LABELLED ALIPHATIC NITRILES AND KETONES

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chloroform. The solution was then stirred for 1 hr. at room temperature and 10 g. of basic alumina (chromatographic grade) was added and the mixture evaporated to dryness (rotary evaporator). The powder was then added to the top of a 12" x 0.5" alumina column; elution with 3:1 benzene-chloroform (v/v) gave II as an oil. Addition of ether followed by slow concentration gave 1.10-1.22 g. (50-55%) of pure II, mp. 59-61°, lit.[4] 58.5-59.5°.

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^{13}C-LABELLED ALIPHATIC NITRILES AND KETONES

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^{13}C-Labelled aliphatic nitriles and ketones have been prepared as shown.

$$R\text{-}X + K^{13}CN \longrightarrow R^{13}CN \xrightarrow{MeMgI} \xrightarrow{H_2O,\ H^+} R^{13}COCH_3$$

EXPERIMENTAL

Aliphatic Nitriles. General Procedure.- In a 10 ml flask, equipped with a reflux condenser and a drying tube, the $K^{13}CN$[1] was dissolved in 5 ml dry, freshly distilled triethylenglycol at 20°; this solution was then frozen with the aid of liquid nitrogen and the corresponding alkyl halide was added at once. Upon slowly warming to room temperature, the reaction started immediately and was again cooled in ice-water. Then the reaction mixture was heated to reflux at 70° for 3-5 hrs. After cooling, the resulting nitrile was isolated by lyophilisation on the manifold (10^{-4} Torr). In the case of the octane carboxylic acid nitrile the whole reaction mixture was transferred into a "Fischer-Spaltrohr" column MMS 200[2] and fractionated.

$CH_3{}^{13}CN$ from 1 g. of $K^{13}CN$, 1.5 ml. of CH_3I, 3 hrs, yield 0.68 ml (84%).
$CH_3{}^{13}C^{15}N$ from 0.5 g. of $K^{13}C^{15}N$, 0.75 ml. of CH_3I, 3 hrs, yield 0.35 ml. (87%).
$CH_3CH_2CH_2{}^{13}CN$ from 1 g. of $K^{13}CN$, 1.35 ml. of *n*-propyl bromide, 3 hrs, yield 1.2 ml. (77%).
$CH_3(CH_2)_6{}^{13}CN$ from 1.5 g. of $K^{13}CN$, 3.6 ml. of *n*-heptyl bromide, 5 hrs, yield 2.9 ml. (82%); distillation: bath temperature, 150-160°; bottom temperature, 140°; column head, 100-102°/12 mm.

Preparation of 2-Pentanone-2-^{13}C. Typical Procedure.- With stirring and cooling, 3.2 g methyl iodide was added dropwise to a suspension of 570 mg Mg in 30 ml dry ether under a N_2 atmosphere. To the resulting Grignard solution, 1.7 ml butyronitrile-1-^{13}C in 2 ml dry ether, was added slowly with vigorous stirring. Stirring was continued for 3 hrs. The reaction mixture was cooled to -20° (acetone/liquid N_2 mixture) and 20 ml of a 20% aqueous ammonium chloride solution and finally 5 ml of 6 N HCl were added. After being stirred for 1 hr at 20°, the ethereal phase was separated, the water phase extracted with more ether and the combined ethereal solution was dried over Na_2SO_4. Then 1,2,3-trimethylbenzene (bp. 165°, 1.5 ml) was added as a displacing agent and the whole was fractionated using a "Fischer-Spaltrohr" column MMS 200[2] (bath temp. 170°, bottom tem. 150°, column head 100-101°) to yield 0.7 g., (42%) of ketone.

2-Nonanone-2-^{13}C was similarly obtained in 42% yield, bp. 75-78°/20 mm.

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AN EFFICIENT SYNTHESIS OF 5-SULFOSALICYLALDEHYDE SODIUM SALT

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Because of several recent reports in which 5-sulfosalicylaldehyde is prepared either by protection of the aldehyde group prior to sulfonation[1-4] or by catalytic oxidation of 3-(hydroxymethyl)-4-hydroxybenzenesulfonic acid,[5] a more direct preparation seems worth reporting. Although it is well documented that aromatic aldehydes are easily oxidized to the corresponding carboxylic acids in sulfuric acid,[6,7] it has been recognized for a long time that the carbonyl group of benzaldehyde is stable in concentrated sulfuric acid at low temperatures.[8] Using this basic knowledge, we developed a direct synthesis of 5-sulfosalicylaldehyde by sulfonation of salicylaldehyde in sulfuric acid at 40°.