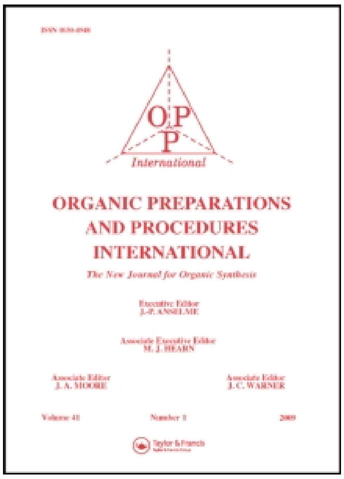

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A FACILE SYNTHESIS OF BENZYL ISOTHIOCYANATES BY USE OF 18-CROWN-6 ETHER

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This paper is dedicated to Professor Cal Y. Meyers on the occasion of his 60th birthday.

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5. Sodium borohydride (purchased from Aldrich or Fisher Chemical Co.) bearing different lot numbers often led to incomplete reaction, which required more sodium borohydride (added in small portions). In some cases, but not all, an additional 16 g of sodium borohydride led to completion.

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A FACILE SYNTHESIS OF BENZYL ISOTHIOCYANATES BY USE OF 18-CROWN-6 ETHER

Submitted by
(12/21/87)

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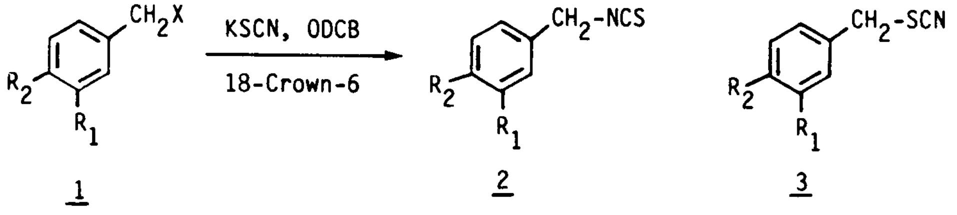
The reaction of alkyl halides with potassium thiocyanate invariably results in the formation of alkyl thiocyanates.[1,2] Benzyl halides (1) on treatment with KSCN have been reported to give benzyl isothiocyanates (2) in 90-96% yields; however, we obtained only benzyl thiocyanate in 80% yield from benzyl chloride under the conditions reported (30°, 4 hrs, DMF).[2] We now report here the information of benzyl isothiocyanate (2) in 50-66% yields, by the use of crown ether at sufficiently high temperature (180°) in o-dichlorobenzene (ODCB); at 100°, even in the presence of the crown ether, benzyl thiocyanate was obtained. The thiocyanates (3) were prepared in over 70% yields in acetone under reflux for 1 hr.

A 40:1 ratio of benzyl chloride to crown ether required 2.5 hrs reaction time whereas 80:1 ratio needed 6 hrs to effect the reaction. The isolated yield of benzyl isothiocyanate was generally 50%, based on 10 and 50 g scales. The thiocyanates showed a sharp peak at 2160 cm^{-1} whereas the isothiocyanates showed a broad peak around 2100 cm^{-1}. The methylene hydrogens of the isothiocyanates appeared at d 4.4 whereas thiocyanates exhibited singlets at δ

4.0.

When the reaction was carried out in ODCB in the absence of the crown ether, benzyl chloride furnished benzyl isothiocyanate and benzyl thiocyanate in a ratio of 1:3, as dertermined by PMR data; the reaction of the α-bromoxylenes (1b,c) gave only the respective thiocyanates (3). To study the possible interconvertion,[3,4] a solution of the thiocyanate (3) in ODCB was refluxed in the presence of crown ether, wherein no change was observed. This finding somewhat contradicts the observation that under slightly different conditions, i.e. in the presence of laurylpyridinium bromide, rearrangement of thiocyanate to isothiocyanate was observed.[4]



a) $R_1 = R_2 = H, X = Cl$ b) $R_1 = CH_3, R_2 = H, X = Br$
c) $R_1 = H, R_2 = CH_3, X = Br$

EXPERIMENTAL SECTION

Benzyl Isothiocyanate (2a).- A mixture of benzyl chloride (2.5 g, 20 mmol), 18- crown-6-ether (0.15 g, 0.57 mmol) and potassium thiocyanate (2.5 g, 25 mmol) in o-dichlorobenzene (10 ml) was heated under reflux for 2 hrs. The reaction mixture was filtered to remove any precipitated salts, and these were washed with chloroform. The combined filtrates were washed with water and dried over anhyd. $MgSO_4$. After distillation of the chloroform, the residue was chromatographed over a column of silica gel. Elution with hexane gave ODCB. Further elution with a benzene-hexane mixture (1:1) furnished 1.5 g (50%) of benzyl isothiocyanate. On large scale runs, the ODCB may be distilled off and the product isolated by distillation in which case slightly higher yields are obtained.

3-Methylbenzyl isothiocyanate (2b)[5] and 4-methylbenzyl isothiocyanate (2c)[5] were similarly prepared in 66% and 57% yields, respectively, from the corresponding α-bromoxylenes (1b,1c).

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A NEW METHOD FOR THE CONVERSION OF ALDOXIMES INTO NITRILES WITH ZEOLITES[†]

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(03/08/88)

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Recently we reported a convenient method for the synthesis of nitriles from the corresponding carboxamides using zeolite as catalyst.[1] The conversion of aldehydes into nitriles via aldoximes also represents an important reaction.[2] Several methods using a wide reagents have been reported[2] for the dehydration of aldoximes. Many of the reagents, however, are expensive and are consumed during the reaction and thus are not amenable to scale up, especially for industrial large scale continuous operations. We now report a facile and commercially feasible process for the conversion of aldoximes into nitriles using zeolite as a catalyst.

$$\underset{\mathbf{1}}{\mathrm{RCH{=}NOH}} \xrightarrow[350^{\circ}]{\text{Cs - X Zeolite}} \underset{\mathbf{2}}{\mathrm{RC{\equiv}N}}$$

Zeolites have received much attention recently in a wide range of contexts, particularly in catalysis.[3] However, little attention has been given to the possibility of employing zeolites in the synthesis of nitriles. The HZSM-5 zeolite, which we reported for the dehydration of carboxamides,[1] was less effective in the conversion of aldoximes into nitriles because of its acidic nature. As the dehydration of aldoximes is base-catalyzed,[4] a basic zeolite is more suitable for the conversion.

The acid and base properites of zeolite can be easily modified by exchanging the cations involved in the zeolite.[5] Onaka et al.[6] applied various cation-exchanged zeolites to liquid phase