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NEW METHODS AND REAGENTS IN ORGANIC SYNTHESIS. 23.[1]
DIETHYL PHOSPHOROCYANIDATE(DEPC): A USEFUL REAGENT FOR AN UNPRECEDENTED TRANSFORMATION OF SULFINIC ACIDS TO THIOCYANATES

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Diethyl phosphorocyanidate(DEPC) can be efficiently used for a simple, one-step transformation of sulfinic acids to thiocyanates.

Our continued interest in the use of diethyl phosphorocyanidate(DEPC)[2] as a cyanation reagent[3] prompts us to report a simple, one-step procedure for the direct transformation of sulfinic acids to thiocyanates. We have found that sodium sulfinates react rapidly with DEPC in refluxing tetrahydrofuran to give thiocyanates in good yields. To our knowledge, this functional transformation has no precedent and will provide a novel and noteworthy addition to existing methodology for the thiocyanate synthesis.[4]

$$RSO_2Na \xrightarrow[\text{in THF}]{(C_2H_5O)_2P(O)CN} RSCN$$

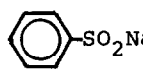
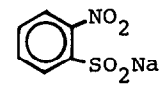
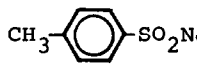
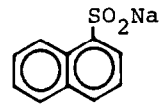
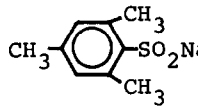
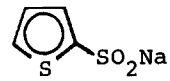
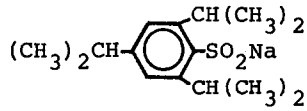
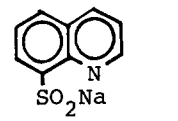
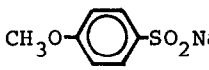
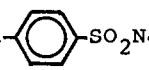
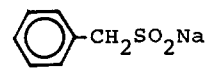
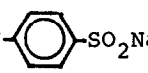
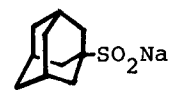
The scope of the novel transformation is summarized in Table. In general, aryl thiocyanates were obtained in preparatively satisfactory yields, except the sterically hindered case(run 4). Interestingly, sodium butanesulfinate did not give any thiocyanate under similar reaction conditions, while benzyl and adamantane sulfinates afforded the corresponding thiocyanates in moderate yields. In contrast to alkyl thiocyanates, aryl thiocyanates still require a good preparative method,[4] and hence our procedure will supply an alternative for the preparation of aryl thiocyanates. Although the mechanism of this interesting transformation is still under investigation, the intermediacy of sulfinyl cyanides has been well proved.

A general experimental procedure is as follows: DEPC(489 mg, 3 mM) in tetrahydrofuran(10 ml) was added to the sodium sulfinate(1 mM) and potassium carbonate (415 mg, 3 mM). The mixture was refluxed for 1 hr, and concentrated. After the addition of benzene-ethyl acetate(1:1, 50 ml) and water(10 ml), the organic layer was separated, and washed with water(10 ml x 2) and saturated aqueous sodium chloride(10 ml x 1). Drying over sodium sulfate followed by concentration gave the crude thiocyanate, which was purified by silica gel(Merck Art. 7734) column chromatography.

Potassium carbonate may not be necessary(runs 4,8,11, and 14), but it may be

effective to conduct the reaction smoothly in some case(run 2). Sodium sulfinates are better substrates than sulfinic acids themselves, lithium or potassium salts. Tetrahydrofuran seems to be a solvent of choice.

Table. A Novel Transformation of Sulfinic Acids to Thiocyanates[a)]

Run	RSO_2Na	Isolated yield of RSCN, % b)	Run	RSO_2Na	Isolated yield of RSCN, % b)
1		74	8		60 (66)[f)]
2		79 (52)[c)]	9		50
3		71	10		55
4		15 (13)[d)]	11		15 (36)[g)]
5		50, 70[e)]	12	$n\text{-}C_4H_9SO_2Na$	-
6		74	13		40
7		70	14		43 (44)[f)]

a) Unless otherwise stated, reactions were carried out as described in the text. b) Numbers in parentheses are yields when the reactions were carried out without potassium carbonate. c) reflux, 5 hr. d) room temp., 3 hr; reflux, 2 hr. e) reflux, 4 hr. f) reflux, 1 hr. g) reflux, 22 hr.

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References and Notes

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4 For reviews, see a) R.G. Guy, 'The Chemistry of Cyanates and Their Thio Derivatives,'(S. Patai, ed.), Chapter 18(1977), John Wiley & Sons; b) S. Harusawa and T. Shioiri, J. Synth. Org. Chem. Japan, 39, 741(1981).

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