

SHORT
COMMUNICATIONS

Thermolysis of 2-(*tert*-Alkylimino)-1,3-oxathiolanes as a New Route to *tert*-Alkyl Isocyanates

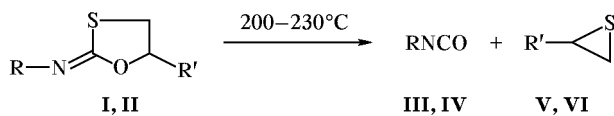
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1-Adamantyl isocyanate and *tert*-butyl isocyanate are typical members of the *tert*-alkyl isocyanate series which attract interest as starting compounds for the synthesis of biologically active compounds. They were previously obtained by conventional methods. For example, 1-adamantyl isocyanate was prepared by the Hoffmann [1] and Curtius rearrangements [2], as well as by the reaction of *N*-trimethylsilyl-1-aminoadamantane with carbon dioxide, followed by treatment with tetrachlorosilane, or by the reaction of the same compound with COCl₂ [3]. On the other hand, effective syntheses of isocyanates by decomposition of some heterocyclic compounds have been reported. Photolysis of 4-aryl-4,5-dihydro-3*H*-1,2,4-triazole-3,5-diones in acetonitrile or methylene chloride gives the corresponding aryl isocyanates [4], thermolysis of *N*-substituted 4-hydroxy-5,5-dimethyl-4-phenyloxazolidin-2-ones yields isocyanates [5], and thermal decomposition of 2*H*-[1,2,4]oxadiazolo-[2,3-*a*]pyridine-2-thiones and 2*H*-[1,2,4]oxadiazolo-[2,3-*a*]pyridazine-2-thiones also involves intermediate formation of isocyanates [6].

We have found that 1-adamantyl isocyanate (**III**) can readily be obtained by thermal decomposition of 2-(1-adamantylimino)-5-methyl-1,3-oxathiolane (**I**). Likewise, *tert*-butyl isocyanate (**IV**) is formed from 2-(*tert*-butylimino)-5-chloromethyl-1,3-oxathiolane (**II**). The other thermolysis product is 2-methylthiirane (**V**) (from compound **I**) and 2-chloromethylthiirane (**VI**) (from **II**). These data allowed us to presume the following reaction scheme:



I, III, R = 1-adamantyl; **II, IV**, R = *tert*-butyl;
I, V, R' = CH₃; **II, VI**, R = CH₂Cl.

Presumably, the reaction begins with heterolytic dissociation of the C²–S bond. The subsequent intramolecular attack by the sulfur atom on C⁵ leads to thiirane ring closure and formation of alkyl isothiocyanate. It is interesting that the reverse process has not been reported, although the synthesis of 2-imino-1,3-oxathiolanes by reaction of the coresponding isothiocyanates with oxiranes in the presence of lithium salts is well known [7].

1-Adamantyl isocyanate. A solution of 2 g (8 mmol) of 2-(1-adamantylimino)-5-methyl-1,3-oxathiolane, prepared by the procedure described in [8], in 10 ml of quinoline was heated for 30 min at 230°C. 2-Methylthiirane liberated during the process was collected in a cooled receiver; bp 72–75°C; published data [9]: bp 75–76°C; yield 0.16 g (27%). The mixture was cooled and poured with stirring to 50 ml of 10% hydrochloric acid, and the precipitate was filtered off, washed with water until neutral reaction, dried, and purified by chromatography on silica gel using cyclohexane as eluent. Yield 1.1 g (78%), mp 144–146°C; published data: mp 144–145°C [1], 143–145°C [2], 146.5–147.5°C [3]. IR spectrum, ν, cm^{−1}: 2258 (N=C=O). ¹H NMR spectrum (CDCl₃), δ, ppm: 1.60 m (6H), 1.81 m (6H), 2.02 m (2H). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 31.1 (Ad), 37.0 (Ad), 46.7 (Ad), 57.1 (Ad), 122.5 (NCO).

***tert*-Butyl isocyanate.** A solution of 2 g (10 mmol) of 2-(*tert*-butylimino)-5-chloromethyl-1,3-oxathiolane, prepared by the procedure described in [10], in 5 ml of freshly distilled quinoline was heated to 230°C. The product was collected in a receiver and was redistilled, a fraction with bp 84–86°C being collected; published data: bp 84–86°C [11]. Yield 0.78 g (81%). IR spectrum, ν, cm^{−1}: 2260 (N=C=O). The remaining material was distilled to obtain 2-chloromethylthiirane in a mixture with quinoline, bp 92–94°C (15 mm). The distillate was treated with 20 ml of 10% hydro-

chloric acid, the separated material was dissolved in 10 ml of cyclohexane, and the cyclohexane solution was filtered through a thin layer of silica gel and evaporated to obtain 0.13 g (12%) of 2-chloromethylthiirane which was identical to a sample prepared by the procedure reported in [12].

The IR spectra were recorded on Nicolet 5ZDX FT-IR and IKS-40 instruments from samples dispersed in mineral oil or prepared as thin film. The ^1H and ^{13}C NMR spectra were obtained on a JEOL EX90 spectrometer at 90 or 22 MHz, respectively, using the solvent signals as reference.

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