Aminimides. III. A convenient synthesis of isopropenyl isocyanate[1]

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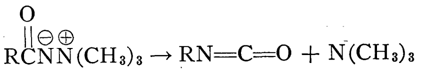
Vinyl isocyanates, especially vinyl and isopropenyl isocyanate, have been known for some time (1–9). The general method of synthesis has been to treat an α,β-unsaturated acyl chloride with sodium azide to form the acyl azide, which is subsequently converted into the isocyanate by the Curtius rearrangement (1–4). Many derivatives have been made and polymerized, as well as the isocyanates themselves (5–9). The polymers and copolymers are reported to be of a high molecular weight and to possess interesting properties (4, 6, 7, 9). However, the synthesis of the isocyanates has not become commercial, probably because of the potential danger of working with azides and the expense of using acyl halides.

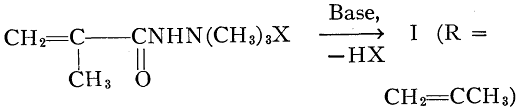
We have discovered a new process for synthesizing one such unsaturated isocyanate in high yields. Recent work by three research groups (10–12) has shown that pyrolysis of trimethylaminimide I gives isocyanate II and trimethylamine.



$$\underset{\text{I}}{R\overset{O}{\overset{\|}{C}}\overset{\ominus}{N}\overset{\oplus}{N}(CH_3)_3} \rightarrow \underset{\text{II}}{RN{=}C{=}O} + \ddot{N}(CH_3)_3$$

These aminimides may be synthesized by alkylating hydrazides (13) or by treating an ester with an unsymmetrically trisubstituted hydrazinium quaternary salt and base in an appropriate solvent (14, 15). Our process involves the use of the latter method.

We have been able to react methyl methacrylate, trimethylhydrazinium chloride, and sodium methoxide in t-butanol to provide aminimide I ($R = CH_2{=}CCH_3$) in up to a 91% yield. This aminimide has been reported recently (16), but was made by dehydrohalogenation of trimethylhydrazinium iodide III ($X = I$), which was in turn made by alkylating the N,N-dimethylhydrazide (prepared from unsymmetrical dimethylhydrazine and methacrylyl chloride) with methyl iodide. We have also used

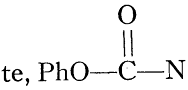


$$\underset{\text{III}}{CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}\underset{\underset{O}{\|}}{C}NHN(CH_3)_3X} \xrightarrow[-HX]{\text{Base,}} \text{I } (R = CH_2{=}CCH_3)$$

a similar method ($X = OTs$) and have found it to be very inefficient, because of the low yield of the dimethyl hydrazide from unsymmetrical dimethylhydrazine and methacrylyl chloride (17) and also because of the many steps involved. Our overall yield for this method was only 52%.

Pyrolysis of trimethylamine methacrylimide (I, $R = CH_2{=}CCH_3$) either at atmospheric or at reduced pressure has given isopropenyl isocyanate in yields of up to 86%. This means that, starting from methyl methacrylate, we are able to synthesize the isocyanate in two steps by a safe method in an overall yield of 78%.

Several derivatives of isopropenyl isocyanate were made. One was the adduct with α-naphthylamine, which has previously been reported by Coffman (1b). A second was the phenol adduct, phenyl-N-isopropenyl carbamate. By "capping" the isocyanate with phenol, we felt that the monomer could be handled more easily and also that the isocyanate functionality could be regenerated on demand by pyrolysis. However, the latter was not obtained experimentally. In fact, the carbamate was quite unstable, hydrolyzing on a silica gel chromatographic column to phenyl aminoformate, $PhO{-}\overset{O}{\overset{\|}{C}}{-}NH_2$. A third derivative



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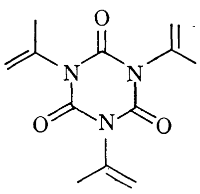
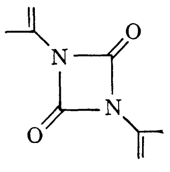
was the bisulfite addition product, synthesized by the method of Schulz (18), who made the corresponding adduct with vinyl isocyanate. Pyrolysis of the adduct did not yield free isopropenyl isocyanate.

There always seems to be some trimethylamine present in the isolated isopropenyl isocyanate. When the product is stored in the freezer at −20° for several days, a solid precipitates. An infrared spectrum shows bands at 1 790 (w), 1 710, and 760 cm^{-1}, among others. Recrystallization of the solid provided a white crystalline material possessing the latter two bands but not the band at 1 790 cm^{-1}. Further identification of this material by elemental analysis and nuclear magnetic resonance (n.m.r.) spectroscopy has shown it to be triisopropenyl isocyanate (IV). The band at 1 790 cm^{-1} in the crude mixture is probably attributable to the dimer or 1,3-diisopropenyl-1,3-diazacyclobutane-2,4-dione (V). The carbonyl band for phenyl isocyanate dimer appears at 1 776 cm^{-1} (19). Unfortunately our material was present in only small amounts and we were not able to isolate it.



IV



V

We have also made trimethylamine acrylimide (I, R = $CH_2{=}CH$) from both acrylyl chloride (26%) (the long method) and methyl acrylate (40%) (the short method). However, pyrolysis of the aminimide did not yield vinyl isocyanate, but gave what is believed to be a mixture of polymer and trivinyl isocyanurate (19). This is not surprising, since Overberger has recently reported (20) the polymerization of vinyl isocyanate through both the vinyl and the isocyanate groups at or below room temperature.

EXPERIMENTAL

All melting points are corrected, and boiling points are not. The infrared spectra were obtained on a Perkin–Elmer 237B grating spectrophotometer, and the n.m.r. spectra (τ scale) on a Varian A-60A spectrometer with tetramethylsilane as an internal standard. The elemental analyses were performed either by Huffman Laboratories, Inc., Wheatridge, Colorado, or by Mr. Clifford Glowacki of these laboratories on an F & M carbon, hydrogen, and nitrogen analyzer, model 185.

Trimethylamine Methacrylimide (Long Method)

To a stirred solution of 264 g (4.3 moles) of unsymmetrical dimethylhydrazine in 2 l of benzene at 8–12° was added 208 g (2.0 moles) of methacrylyl chloride during 2 h. After the reaction mixture was allowed to warm to room temperature, the precipitate was removed by filtration. The solid was extracted four times with 1 l portions of warm benzene. The extracts were combined with the filtrate and then evaporated *in vacuo* to give 137.4 g (53%) of a white solid, m.p. 67–70°. Recrystallization from hexane gave 1,1-dimethyl-2-methacrylylhydrazine, m.p. 73° (lit. (21) m.p. 71–71.5°).

Next, 20.0 g (0.154 mole) of 1,1-dimethyl-2-methacrylylhydrazine and 28.6 g (0.154 mole) of methyl *p*-toluenesulfonate were refluxed in 225 ml of acetonitrile for 6 h. When the mixture was cooled to room temperature, a white solid crystallized, m.p. 150–151°. Evaporation of the solvent *in vacuo* gave more product, the total yield of 1,1,1-trimethyl-2-methacrylylhydrazinium *p*-toluenesulfonate being 99%. The infrared spectrum (halocarbon mull) showed the expected absorption at 3 150, 3 040, 1 690, 1 630, and 1 565 cm^{-1}. To 20 g (0.63 mole) of this salt in 100 ml of distilled water was added 10% aqueous sodium hydroxide until a phenolphthalein end point was reached. Evaporation of the water *in vacuo* gave a white solid, which was then extracted with warm chloroform. Evaporation of the chloroform extracts provided 9.0 g of a white solid. Recrystallization from benzene gave m.p. 149–50° (lit. (16) m.p. 146–147°). The infrared spectrum (halocarbon mull) exhibited double-bond absorption at 3 040 and 1 645 cm^{-1} and the expected aminimide band at 1 565 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) showed a singlet at 6.55 p.p.m. and multiplets at 8.05, 4.85, and 4.25 p.p.m. in the expected ratio of 9:3:1:1, respectively.

Anal. Calcd. for $C_7H_{14}N_2O$: C, 59.12; H, 9.92; N, 19.70. Found: C, 59.24; H, 9.89; N, 19.54.

Trimethylamine Methacrylimide (Short Method)

A stirred mixture of 11.0 g (0.1 mole) of 1,1,1-trimethylhydrazinium chloride, 10.0 g (0.1 mole) of methyl methacrylate (10 p.p.m. *p*-methoxyphenol), and 5.4 g (0.1 mole) of sodium methoxide in 75 ml of *t*-butanol was heated at 48° for 6 h. While still warm, the reaction mixture was filtered under pressure. Evaporation of the filtrate gave 12.9 g (91%) of a white solid. Recrystallization from benzene gave m.p. 149–150°. The mixture melting point with authentic trimethylamine methacrylimide (previous experiment) was not depressed.

Isopropenyl Isocyanate

Trimethylamine methacrylimide (2.0 g, 0.014 mole) was pyrolyzed at 50 mm pressure by gradually increasing the pot temperature from 135 to 160°. A water-white liquid (1.0 g, 86%) was "trapped out" at −25°. Redistillation gave b.p. 60–61° (lit. (1) b.p. 62–63°). The infrared spectrum (neat) showed the expected absorption at 2 270 and 1 655 cm^{-1}. Trimethylamine was collected in a second trap at −78° and identified by its boiling point and infrared spectrum. The isocyanate was further identified by its adduct with α-naphthylamine, m.p. 226–229° (lit. (1*b*) m.p. 228°).

When the isopropenyl isocyanate was left in a freezer at −20° for several days, a yellow solid precipitated. The solid, showing absorption at both 1 790 and 1 710 cm^{-1} in the infrared, was collected by filtration and recrystallized from hexane – carbon tetrachloride to give a white crystalline material, m.p. 182–183°. The infrared spectrum (halocarbon mull) no longer exhibited the 1 790 cm^{-1} peak, but did show a strong doublet at 1 710 cm^{-1} (carbonyl) and singlets at 1 670 (C═C) and 760 cm^{-1} (isocyanurate ring) (19). The n.m.r. spectrum ($CDCl_3$) showed singlets at 7.95, 4.85, and 4.57 (broad) p.p.m.

Anal. Calcd. for $(C_4H_5NO)_3$: C, 57.82; H, 6.06; N, 16.85. Found: C, 57.55; H, 5.99; N, 16.70.

Phenol – Isopropenyl Isocyanate Adduct

A mixture of 2.0 g (0.024 mole) of isopropenyl isocyanate and 2.0 g (0.021 mole) of phenol was stirred for 15 min. The excess isocyanate was removed *in vacuo* at 40°, yielding 3.2 g (86%) of a yellow solid, m.p. 48–56°. The infrared spectrum (halocarbon mull) showed the expected absorption at 3 340 cm^{-1} (NH), a split peak centered at 1 745 cm^{-1} (carbonyl), and a singlet at 1 655 cm^{-1} (C═C). We were unable to purify the material by recrystallization. The crude adduct sublimed at 36° and 0.05 mm. However, the sublimate possessed a melting point of 50–60° and a strong odor of phenol. As a final attempt at purification, the crude adduct was chromatographed on silica gel, with chloroform as eluent. A white crystalline solid was obtained, m.p. 149–150°. The infrared spectrum (halocarbon mull) showed significant absorption at 3 420, 3 340, 3 190, 1 710, 1 620, and 1 600 cm^{-1}. The n.m.r. spectrum (acetone-d_6) exhibited multiplets at 3.83 and 2.83 p.p.m. in an area ratio of 2:5, respectively; no vinyl protons were observed. This evidence, along with the elemental analysis, suggests that the phenol adduct hydrolyzed on the column to give phenyl aminoformate.

Anal. Calcd. for $C_7H_7NO_2$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.51; H, 5.15; N, 10.21.

Pyrolysis of the crude adduct, between 180–230° at 150 mm, did not give isocyanate but only a brown polymeric residue.

Bisulfite – Isopropenyl Isocyanate Adduct

A mixture of 12.3 g (0.149 mole) of isopropenyl isocyanate and a small amount of trimethylamine in 25 ml of acetone was added to a mixture of 10.0 g (0.1 mole) of sodium bisulfite and 35 ml of distilled water. The resulting mixture was stirred for 1.5 h at 24°. The volatile solvent was evaporated *in vacuo* at 24° and the remaining product freeze dried to give 18.1 g of a white solid. The solid was dried over phosphorus pentoxide *in vacuo*. The infrared spectrum (halocarbon mull) showed significant absorption at 3 390, 3 320, 3 075, 1 695, and 1 630 cm^{-1}. Pyrolysis at 130° gave an unidentified liquid and no isopropenyl isocyanate.

The adduct was dissolved in water, along with a catalytic amount of ammonium persulfate, and the mixture was stirred for 16 h at 24°. The reaction mixture was then poured into methanol and the resulting precipitate removed by filtration. The filtrate was evaporated *in vacuo* and then freeze dried to give the white solid homopolymer, which was dried over phosphorus pentoxide *in vacuo*. The infrared spectrum (halocarbon mull) showed significant absorption at 3 390, 3 320, 3 075, and 1 695 cm^{-1}; the 1 630 cm^{-1} absorption found in the monomer was no longer present.

Anal. Calcd. for $C_4H_6NNaO_4S$: C, 25.67; H, 3.22; N, 7.48. Found: C, 24.09; H, 5.85; N, 9.37.

Trimethylamine Acrylimide (Long Method)

To a stirred solution of 264 g (4.3 moles) of unsymmetrical dimethylhydrazine in 2 l of benzene at 8–12° was added 181 g (2.0 moles) of acrylyl chloride during 4 h. In a work-up similar to that used for the trimethylamine methacrylimide example, 27.5 g of a white solid was obtained. Recrystallization from hexane gave m.p. 86–87°. The infrared spectrum (halocarbon mull) showed significant absorption at 3 200, 3 040, 1 670, 1 650, 1 620, and 1 600 cm^{-1}, indicating that the compound was 1,1-dimethyl-2-acrylylhydrazine.

Anal. Calcd. for $C_5H_{10}N_2O$: C, 52.65; H, 8.77; N, 24.55. Found: C, 52.41; H, 8.58; N, 24.28.

Next, 31.0 g (0.22 mole) of iodomethane was added to 25 g (0.22 mole) of 1,1-dimethyl-2-acrylylhydrazine in 170 g of acetonitrile. The resulting solution was refluxed for 3 h. The solvent was removed *in vacuo* to give 54.8 g (98%) of a pale-yellow solid, m.p. 128–133°. The infrared spectrum (halocarbon mull) showed significant absorption at 3 090, 3 040, and 1 680 cm^{-1}. Of this 1,1,1-trimethyl-2-acrylylhydrazinium iodide, 50 g (0.19 mole) was dissolved in 80 ml of water and titrated with 10% aqueous sodium hydroxide to a phenolphthalein end point. Evaporation of the water gave a gummy solid, which was subsequently extracted in a Soxhlet apparatus with chloroform. Evaporation of the chloroform gave 23.9 g (95%) of a yellow solid, m.p. 49–78°. The solid was sublimed three times to give a white crystalline product, m.p. 102–104° (sealed tube). The infrared spectrum (halocarbon mull) showed significant absorption at 3 040, 1 630, and 1 570 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) exhibited a singlet at 6.55 p.p.m. and multiplets at 4.7 and 3.9 p.p.m. in a ratio of 9:1:2, respectively, as expected for trimethylamine acrylimide.

Anal. Calcd. for $C_6H_{12}N_2O$: C, 56.27; H, 9.37; N, 21.86. Found: C, 56.10; H, 9.53; N, 21.28.

Trimethylamine Acrylimide (Short Method)

A stirred mixture of 8.6 g (0.1 mole) of methyl acrylate (15 p.p.m. *p*-methoxyphenol), 11.0 g (0.1

mole) of 1,1,1-trimethylhydrazinium chloride, and 5.4 g (0.1 mole) of sodium methoxide in 75 ml of *t*-butanol was heated at 45° for 7 h. While still warm, the reaction mixture was filtered under pressure. Evaporation of the filtrate gave 11.4 g of a viscous yellow liquid, which crystallized when left. Vacuum sublimation gave 4.5 g of a white solid which, on resublimation, showed no depression in the mixture melting point with authentic trimethylamine acrylimide.

Pyrolysis of Trimethylamine Acrylimide

Several grams of trimethylamine acrylimide was pyrolyzed by gradually increasing the pot temperature of a short-path still from 125 to 200°. A small amount of yellow oil was collected in the receiver; this oil solidified when left. The dry ice trap contained only trimethylamine, as identified by its infrared spectrum and boiling point. The rest of the material stayed in the pot as a dark intractable tar. The solidified oil proved to be a mixture of several components, but did give an infrared spectrum showing bands at 3 045, 1 700, 1 645, 1 545, and 765 cm^{-1}, corresponding to known trivinyl isocyanurate (19).

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Alkylation of 1,2-dimethylindole with allyl bromide

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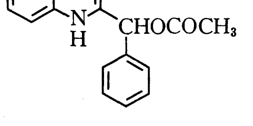
It was recently demonstrated that indole and substituted indoles can be alkylated in aqueous acidic solution with reactive benzyl or phenylindolylmethyl derivatives such as I, obtained through ring cleavage of tetrahydrocarbolines (1).



I

Although this alkylation of the indole nucleus, in the case of 2,3-disubstituted indoles such as carbolines, gives poor yields because of the less-nucleophilic character of the 5 or 6 positions, it proceeds with great ease when the 2 or 3 positions are available for susbstitution.

This note describes the substitution of 1,2-dimethylindole with allyl bromide by the same technique, namely, refluxing the components in acetic acid and 2 *N* phosphoric acid.

Whereas many examples for the condensation of indoles in aqueous acidic solution

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