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Preparation of Trifluoronitrosomethane

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Synopsis. Trifluoronitrosomethane was prepared in a good yield by pyrolysis of nitrosyl trifluoroacetate in a flow of nitrogen monoxide at 190 °C using refluxed perfluorotributylamine as a diluent.

Trifluoronitrosomethane (**1**)[1] is an industrially important material for the preparation of nitroso rubber.[2] There have been many investigations on the preparation of **1**.[2-4] Pyrolysis of nitrosyl trifluoroacetate (**2**)[5] in refluxed perfluorotributylamine has been adopted as a preparative method in spite of the low yield of **1**.[2,4] In the kinetic studies on the gas-phase thermal decomposition of **2**, Haszeldine *et al.* examined the effects of additives such as propene, **1**, and nitrogen monoxide under reduced pressure (about 10 mmHg$=1.33\times10^3$ Pa) and showed that the presence of nitrogen monoxide enhanced the formation of **1** while the presence of propene or **1** inhibited it.[6] The pyrolysis of **2** under reduced pressure was undesirable for the mass production of **1** because a large reactor was necessary for pyrolysis and was difficult to operate.

During our investigation of the pyrolysis of **2**, we found that **1** was obtained in a good yield when **2** was pyrolyzed in a flow of nitrogen monoxide at 190 °C using refluxed perfluorotributylamine as a diluent. Nitrogen monoxide could easily be removed from the gaseous products by introduction of oxygen into a stream of the gaseous products followed by washing with aqueous alkaline solution and **1** condensed in liquid nitrogen-isopentane traps as blue liquid (Fig. 1).

$$\underset{\mathbf{2}}{CF_3COONO} \xrightarrow[\text{in a flow of NO}]{\Delta} \underset{\mathbf{1}}{CF_3NO} + CO_2$$

The influence of the flow rate of nitrogen monoxide on the yield of **1** was examined at a constant rate of addition of **2** (Table 1). The results show that the yield of **1** increases with an increase of the flow rate of nitrogen monoxide and reaches a maximum (77%) at the flow rate of 0.59 mmol/min. The decrease of the yield at the flow rates of more than 0.59 mmol/min is probably attributed to a shortage of the reaction time for **2** at such fast flow rates of nitrogen monoxide.

TABLE 1. PYROLYSIS OF **2** IN THE FLOW OF NITROGEN MONOXIDE

Run	Addition rate of **2** mmol/min	Flow rate of NO mmol/min	Yield of **1**/%
1	1.1	0.09	44
2	1.1	0.18	56
3	1.1	0.45	75
4	1.1	0.59	77
5	1.1	0.89	52
6	1.1	1.79	44

The pyrolysis of **2** in the flow of nitrogen monoxide depressed the formation of by-products condensed in Dry Ice–acetone traps, while that without nitrogen monoxide yielded a large amount of by-products containing trifluoronitromethane and *O*-nitroso-*N*,*N*-bis(trifluoromethyl)hydroxylamine as components.[2,4]

Our procedure provides an efficient process for the preparation of **1** because of good yields as well as a flow system desirable for mass production.

Experimental

Nitrosyl Trifluoroacetate (2).[3d] *Caution*: Nitrosyl trifluoroacetate decomposes explosively at temperatures higher than about 100 °C.[3c]

Method A: Trifluoroacetic anhydride (155 ml, 1.1 mol) was added dropwise to dinitrogen trioxide (84 g, 1.1 mol) at −30 °C for 5 min. After stirring at −30 °C for 30 min and then at −5 °C for 3 h, the reaction mixture was distilled under reduced pressure to give **2** (230 g, 74%): bp 42—43 °C/82 mmHg (lit,[3c] 47 °C/94 mmHg).

Method B: Nitrosyl chloride (100 g, 1.54 mol) was condensed into a flask containing finely powdered silver trifluoroacetate (188 g, 0.85 mol) at −70 °C. Then the mixture was allowed to stand for 2 h at −20 °C and gradually warmed to room temperature. The excess of nitrosyl chloride was

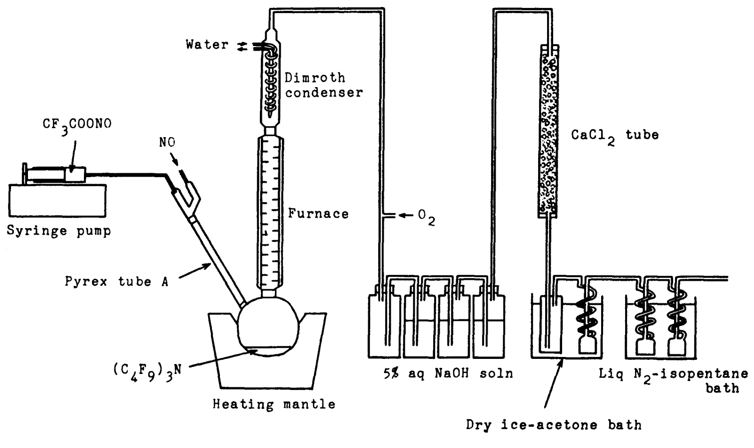

Fig. 1. Apparatus for pyrolysis of **2** in the flow of nitrogen monoxide.

removed and the residue distilled under reduced pressure to give **2** (87.7 g, 72%): bp 48 °C/92 mmHg.

Trifluoronitrosomethane (1). *Caution*: The pyrolysis must be carried out using a barricade in a hood for protection from a possible explosion hazard. The apparatus is shown in Fig. 1. The furnace is made of a Pyrex tube (2.5 cm × 50 cm, Vigreux tube) wrapped in an electrothermal heating tape controlled by a thermostat. The furnace was maintained at 190 °C. Trifluoroacetate **2** was added at a constant rate to a 500 ml-flask containing refluxed perfluorotributylamine (40 ml, bp 174 °C) through a Teflon tube by means of a syringe pump. A long Pyrex tube A (1.2 cm × 23 cm) is necessary to prevent an explosion of **2**. After the atmosphere in the furnace was replaced with nitrogen monoxide, the pyrolyses using 12.65 g of **2** were done under the conditions shown in Table 1. The results are summarized in Table 1. Oxygen was introduced to the apparatus at the same flow rate as that of nitrogen monoxide. The yields given in Table 1 are those of the product purified by distilling the blue liquid condensed in liquid nitrogen–isopentane traps. The properties of the product were in agreement with those of an authentic sample.

References

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5) An explosive compound. See Ref. 3c.

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