## TRIFLUOROMETHYL TRIFLUOROMETHANESULFONATE (CF<sub>3</sub>SO<sub>2</sub>OCF<sub>3</sub>)<sup>1</sup>

Yoshiro Kobayashi,\* Tsutomu Yoshida, and Itsumaro Kumadaki Tokyo College of Pharmacy, Horinouchi, Hachioji-shi, Tokyo 192-03, JAPAN

<u>Summary</u>. Trifluoromethyl trifluoromethanesulfonate (<u>1</u>) was synthesized by the reaction of silver trifluoromethanesulfonate with trifluoromethyl iodide in a benzene solution. Reaction of <u>1</u> with an enamine gave trifluoromethanesulfonyl compound. This is the first example of  $SO_2$ -O bond fission of alkyl trifluoromethanesulfonate.

Alkyl trifluoromethanesulfonates were found to be important synthetic intermediates in organic chemistry, and many applications were summarized in a review<sup>2</sup>).

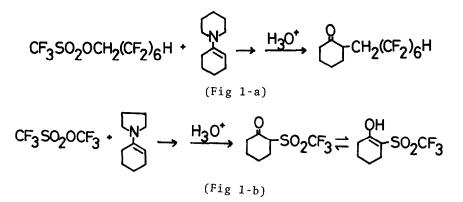
Therefore, we tried to use these synthetic reactions in the field of fluorine chemistry. Only two syntheses of trifluoromethyl trifluoromethane-sulfonate (<u>1</u>) were reported by Cady<sup>3</sup>) and Olah<sup>4</sup>, but the yield by both methods were poor. Further, in the former method, <u>1</u> was synthesized by explosion of  $(CF_3SO_3)_2$ , and in the latter, evolution of HF seems to be unfavorable for work in glassware. On the other hand, application of <u>1</u> to organic synthesis has hardly ever been examined.

We would like to report in this paper an easy synthesis of  $\underline{1}$  by the reaction of silver trifluoromethanesulfonate ( $\underline{2}$ ) with trifluoromethyl iodide ( $\underline{3}$ ), and the interesting reaction of 1 with enamine.

$$\begin{array}{c} CF_{3}SO_{3}Ag + CF_{3}I - \frac{200^{\circ}, 24h}{\ln C_{6}H_{6}} & CF_{3}SO_{2}OCF_{3} + AgI \\ \underline{2} & \underline{3} & \underline{1} \end{array}$$

Thus, a mixture of 2 (1g), 3 (1m1) and benzene (5m1) was sealed in Pyrex tube (15¢ x 150mm) under vacuum and heated at 200° for 24h. Trap-to-trap distillation of reaction mixture afforded 1 (730mg, 86% yield);<sup>19</sup>F nmr(CDC1<sub>3</sub>)  $\delta^{5}$ =+10.8 (q, J<sub>FF</sub>=3.8Hz), -10.8ppm (q, J<sub>FF</sub>=3.8Hz); ir (gas sample) v=1475, 1240, 1200, 1140, 955 cm<sup>-1</sup>; mass m/e=149(M<sup>+</sup>-CF<sub>3</sub>), 133(M<sup>+</sup>-OCF<sub>3</sub>). These data are comparable to those reported by Cady<sup>3</sup>.

In this reaction, trace of benzotrifluoride and iodine were detected. Benzene was indispensable as a solvent, because other solvents gave none or very low yield of <u>1</u>. Benzene was reported to form a complex with  $2^{6}$ . This might help to dissolve <u>2</u> and smooth reaction. Compound <u>1</u> reacted with enamine in an interesting manner; many alkyl trifluoromethanesulfonates react with enamine by cleavage of  $CF_3SO_2O$ -C bond (Fig 1-a),<sup>7</sup>) but in this case the bond cleavage occurred between  $CF_3SO_2$ - and  $-OCF_3$ , resulting in the formation of trifluoromethanesulfonyl compound (Fig 1-b)<sup>8</sup>.



This is the first case in the reaction of trifluoromethanesulfonates where the  $CF_3SO_2$ -OC bond was cleaved possibly due to high electronegativity of  $CF_3$  group.

## References and Notes

- 1) Presented at the 98th Annual Meeting of the Pharmaceutical Society of Japan, Okayama, Japan, April, 1978.
- 2) R. D. Howells and J. D. McCown, Chem. Rev., 77, 70 (1978).
- 3) R. E. Noftle and G. H. Cady, Inorg. Chem., 4, 1010 (1965).
- 4) G. A. Olah and T. Ohyama, Synthesis, 319 (1976).
- 5)  $C_6H_5CF_3 \delta 0.0$ ; + value means a high field.
- Y. Suzuki and T. Nakano, "The 3rd Symposium on Fluorine Chemistry (Japan)" abstract p. 34 (1975).
- 7) R. L. Hansen, U. S. Patent 3,419,595 (1968).
- 8) This compound is a mixture of keto-enol tautomers; keto-enol ratio is 5:7, yield 25%, bp 118-119°/40 torr. Spectral data; <sup>19</sup>F nmr (CDC1<sub>3</sub>)  $\delta^{5}$ =+11.4 (s, belong to keto form), -15.0 ppm (s, belong to enol form); <sup>1</sup>Hnmr (CDC1<sub>3</sub>)  $\delta^{=1.6-2.1}$  and 2.2-2.8 (8H), 4.2\*(t, J=6.2Hz, 5/12H, belong to keto form), 9.8 ppm\* (s, 7/12H, belong to enol form); ir (CC1<sub>4</sub>) v=3300, 2950, 2880, 1730, 1610, 1380, 1220, 1120 cm<sup>-1</sup>; mass m/e=230 (M<sup>+</sup>). \*) disappeared by treatment with D<sub>2</sub>O

(Received in Japan 23 June 1979)