Tetrahedron Letters,Vol 24,No.36,pp 3919-3920,1983
Printed in Great Britain

0040-4039/83 \$3.00 + .00

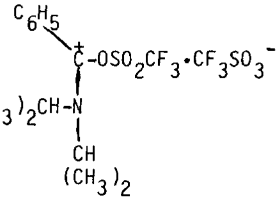
THE REACTION OF TRIFLUOROMETHANESULPHONIC ANHYDRIDE WITH CARBONYL COMPOUNDS

Thor Gramstad, Steinar Husebye and Johannes Sæbø
Department of Chemistry, University of Bergen
5014 Bergen-Univ., Norway

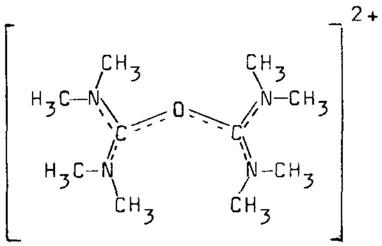
Abstract - Amides and ureas react with trifluoromethanesulphonic anhydride to give a new type of resonance stabilized dicarbonium salts, $R_1R_2\overset{+}{C}\text{-O-}\overset{+}{C}R_1R_2 \cdot 2CF_3SO_3^-$.

We have previously shown[1,2] that trifluoromethanesulphonic anhydride reacts with hexamethylphosphoramide and triphenylphosphine oxide to give $[(CH_3)_2N]_3\overset{+}{P}\text{-O-}\overset{+}{P}[N(CH_3)_2]_3 \cdot 2CF_3SO_3^-$ and $(C_6H_5)_3\overset{+}{P}\text{-O-}\overset{+}{P}(C_6H_5)_3 \cdot 2CF_3SO_3^-$, respectively. Similar reactions have now been carried out with ureas and amides and the present communication gives a potential route to a new type of stabilized dicarbonium salts, $R_1R_2\overset{+}{C}\text{-O-}\overset{+}{C}R_1R_2 \cdot 2CF_3SO_3^-$. So far the following salts have been prepared

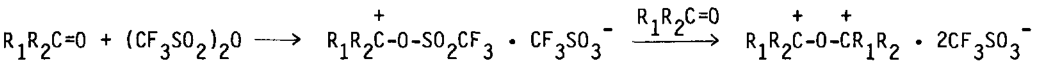
$$R_1R_2\overset{+}{C}\text{-O-}\overset{+}{C}R_1R_2 \cdot 2CF_3SO_3^-$$

	Calculated				Found				M	M
	C	H	S	O	C	H	S	O	calc.	found
(1) $R_1 = R_2 = NH_2$	11.94	2.00	15.94	27.84	12.03	2.35	15.59	27.94	402.2	406.4
(2) $R_1 = R_2 = N(CH_3)_2$	28.01	4.67	12.45	21.79	28.17	4.70	12.56	21.74	514.2	515.3
(3) $R_1 = CH_3$, $R_2 = N(CH_3)_2$	26.32	3.95	14.04	24.56	26.29	4 33	13.81	24.58	456.2	457.1
(4) $R_1 = C_6H_5, R_2 = NH_2$	36.65	2.69	12.23	21.36	37.01	3.09	11.97	22.03	524.4	526.3
(5) $R_1 = C_6H_5, R_2 = N(CH_3)_2$	41.38	3.82	11.04	19.29	41.41	4.06	11.39	19.53	580.5	581.6
(6) $R_1 = C_6H_5, R_2 = N(C_2H_5)_2$	45.28	4.78	10.07	17.59	45.15	4.84	10.11	17.76	636.6	639.1
(7) $R_1 = C_6H_5, R_2 = C_5H_{10}N$	47.27	4.58	9.71	16.95	46.98	4.99	10.00	17.35	660.6	663.7
(8) 	36.96	3.93	13 15	19.69	36.67	4.18	13.87	20.97	487.4	488.4

In a typical experiment trifluoromethanesulphonic anhydride (1.67 g., 5.9 mmoles) dissolved in dry CH_2Cl_2 (3ml) was added dropwise with stirring to a solution of tetramethylurea (1.39 g, 11.9 mmoles) in CH_2Cl_2 (6 ml) at 0 °C under dry nitrogen atmosphere. The reaction mixture was left overnight and the white crystals formed were filtered off and washed with dry CH_2Cl_2. The product (2.12 g, 69%) was found by x-ray crystallographic methods to be a dicarbonium salt and the resonance hybrid shown below will probably best describe the dicarbonium cation



The $\overset{+}{C}$-O-$\overset{+}{C}$ angle was found to be 122.4° and the N atoms were completely sp^2 hybridized. More details about the structure will be published elsewhere[3]. The salt was insoluble in CCl_4 and $CHCl_3$, but soluble in CH_3CN and $(CH_3)_2C=O$. The salt reacts very rapidly with water and the molecular weight was determined by titration with aqueous sodium hydroxide. The H NMR spectrum of the salt in CD_3CN at room temperature has only one peak at 3.75 ppm downfield from TMS. In the ^{13}C NMR spectrum of the cation there appeared two peaks at 156.45 (^{13}C-O-^{13}C) and at 41.41 ppm (N-$^{13}CH_3$) (downfield from TMS). On cooling the N-$^{13}CH_3$ peak broadened, (Tc = ca. -26 °C) and gave finally at -39 °C two sharp peaks with a separation of 40.81 Hz. In the IR spectrum there appeared a strong band at 1705 cm^{-1} (in Nujol) which is absent in the spectrum of tetramethylurea (C=O absorption at 1638 cm^{-1}, film). The following reaction mechanism is proposed for the reaction between trifluormethanesulphonic anhydride and ureas and amides



$$R_1R_2C{=}O + (CF_3SO_2)_2O \longrightarrow R_1R_2\overset{+}{C}\text{-}O\text{-}SO_2CF_3 \cdot CF_3SO_3^- \xrightarrow{R_1R_2C=O} R_1R_2\overset{+}{C}\text{-}O\text{-}\overset{+}{C}R_1R_2 \cdot 2CF_3SO_3^-$$

(a) (b)

We believe that the first step in the reaction is the formation of the monocarbonium salt (a) which is attacked by the carbonyl group of another molecule to give the dicarbonium salt (b). A support for this mechanism is that a monocarbonium salt (8) is formed when $(CF_3SO_2)_2O$ reacts with $C_6H_5C(O)N[CH(CH_3)]_2$. The formation of a monocarbonium salt is probably due to steric effects. NMR and IR studies and reactions of the dicarbonium salts are the subjects of a forthcoming paper.

REFERENCES

1. A. Aaberg, T. Gramstad and S Husebye, Tetrahedron lett., 24 2263 (1979).
2. A. Aaberg, T. Gramstad and S. Husebye, Acta Chem. Scand., A34 717 (1980).
3. T. Gramstad, S. Husebye, K. Maartmann-Moe and J. Sæbø, unpublished results.

(Received in UK 1 July 1983)