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ISOMERIZATION OF TRIFLUOROACETIMIDOYL CHLORIDES AND THEIR 1,3-DIPOLAR CYCLOADDITIONS WITH ELECTRON-DEFICIENT OLEFINS

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N-Arylmethyltrifluoroacetimidoyl chlorides isomerize to N-(arylmethylene)-1-chloro-2,2,2-trifluoroethylamines in the presence of triethylamine at room temperature and to the corresponding N-trifluoroethylbenzimidoyl chlorides under more drastic conditions. The reactions of the trifluoroacetimidoyl chlorides with methyl acrylate and acrylonitrile give the corresponding 1,3-dipolar cycloadducts.

Isomerization of imidoyl chlorides is an interesting problem in connection with the formation of nitrile ylides but that has not been fully investigated because of the low stability of the intermediates.[1] As a part of research on applications of the fluorinated 1,3-dipolar compounds as building blocks of the heterocycles with fluorine groups,[2] we now wish to report the isomerization of N-arylmethyltrifluoroacetimidoyl chlorides (1) to N-(arylmethylene)-1-chloro-2,2,2-trifluoroethylamines (2) and reactions of the chlorides 1 with electron-deficient olefins which give trifluoromethylpyrrolines.

The chlorides 1a-c were prepared by chlorination of the corresponding trifluoroacetamides with phosphorus pentachloride in 71, 68, and 76% yields, respectively.[3]

Treatment of 1 with triethylamine in toluene at room temperature for 12 h gave the chlorides 2 in good yields which were isolated by distillation and stored under nitrogen atmosphere (Table 1).[4,5] Refluxing of 1 in toluene, however, resulted in the formation of the benzimidoyl chlorides 3, which were also obtained from the isolated 2 under similar conditions (Table 1). The reverse conversion from 3 to 2 or 1 did not occur at all. The exclusive formation and the unusual stability of 2 may be ascribed to the strong electron-withdrawing effect of the trifluoromethyl group which stabilizes the carbanion 2' derived from the initially formed carbanion 1' and interferes the formation of 3' leading to 3.

1,3-Dipolar cycloadditions of the trifluoroacetonitrile ylide, generated in situ by the removal of chloride ion from 1a' or 2a' under isomerization-conditions, with electron-deficient olefins were next investigated. Thus, the reaction with an excess of methyl acrylate at room temperature for 7 days yielded 34% of the epimeric isomers of 4-methoxycarbonyl-5-phenyl-2-trifluoromethyl-Δ^1-pyrrolines (4a and 4b) in the ratio of 3/1, according to GC analysis. The isomer 4a was epimerized in the presence of potassium t-butoxide to the more stable 4b

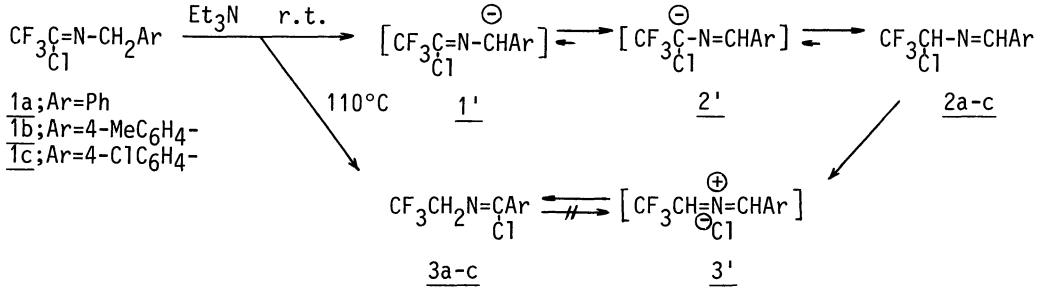
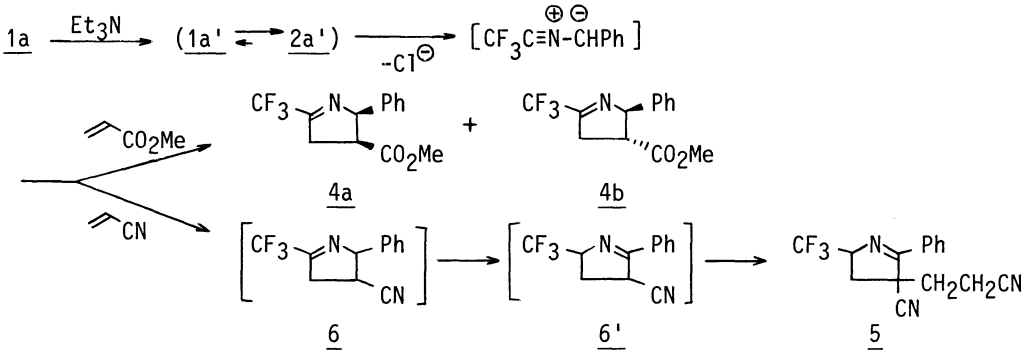


Table 1. Preparations and Spectral Data of 2 and 3

	Yield/%[a]	Bp θ_m/°C(mmHg)	IR(film) $\nu_{C=N}$/cm^{-1}	^{1}H NMR($CDCl_3$) δ
2a[b]	76	91-93(8)	1665	6.13(qd, J=5.0, 2.0 Hz, 1H), 7.3-7.9(m,5H), 8.5(br, 1H)
2b	60	85-88(5)	1665	2.37(s, 3H), 6.15(qd, J=5.0, 2.0 Hz, 1H), 7.15-7.75 (A$_2$X$_2$,4H), 8.5(br, 1H)
2c	51	88-90(3)	1670	6.22(qd, J=5.0, 2.5 Hz, 1H), 7.4-7.9(A$_2$X$_2$, 4H), 8.6(br, 1H)
3a	78[c](78)[d]	77-78(7)	1670	4.12(q, J=9.0 Hz, 2H), 7.2-8.1(m, 5H)
3b	49[c]	85(9-6)	1670	2.40(s, 3H), 4.17(q, J=9.0 Hz, 2H), 7.2-8.0(A$_2$X$_2$, 4H)
3c	50[c](69)[d]	86-87(4)	1675	4.07(q, J=9.0 Hz, 2H), 7.2-7.9(A$_2$X$_2$, 4H)

a) Isolated yields. b) MS(m/e), 221 and 223(M^+). c) Yields from 1. d) Yields from 2.

(equilibrium ratio 4a/4b = 1/7). Unexpectedly, a similar reaction of 3a did not proceed at all and 3a was recovered unchanged. On the other hand, the reaction of 1a with acrylonitrile was more complicated and gave the pyrroline 5 in 20% yield; 5 may be formed via the base-catalyzed proton-shift from the cycloadduct 6 to 6' followed by Michael-type addition of 6' to acrylonitrile.[6] The structure of 4 and 5 was established by their elemental analyses and spectral data.[7]



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2) Part II on "Applications of the fluorinated 1,3-dipolar compounds as building blocks of the heterocycles with fluorine groups." Part I: K. Tanaka, S. Maeno, and K. Mitsuhashi, Chem. Lett., 1982, 543.

3) W. P. Norris and H. B. Jonassen, J. Org. Chem., 27, 1449 (1962).

4) K. Bunge, R. Huisgen. and R. Raab, Chem. Ber., 105, 1296 (1972).

5) The chlorides 2 were easily hydrolyzed to afford the corresponding benzaldehydes.

6) K. Burger, J. Albanbauer, and F. Manz, Chem. Ber., 107, 1823 (1974).

7) The chemical shifts for ^{1}H, ^{19}F, and ^{13}C NMR are all given in δppm downfield from internal tetramethylsilane, external trifluoroacetic acid, and tetramethylsilane, respectively. 4a; IR(KBr) 1740(C=O) and 1677 cm^{-1}(C=N), ^{1}H NMR(CCl_4) δ2.7-3.8(m, 3H), 3.07(s, 3H), 5.57(dm, J=9 Hz, 1H), and 6.9-7.4(m, 5H), ^{19}F NMR(CCl_4) δ8.4(s). 4b; IR(film) 1740(C=O) and 1675 cm^{-1} (C=N), ^{1}H NMR(CCl_4) δ3.0-3.6(m, 3H), 3.70(s, 3H), 5.48(m, 1H), and 7.1-7.4(m, 5H). 5; IR(KBr) 2220(C≡N) and 1609 cm^{-1}(C=N), ^{1}H NMR($CDCl_3$) δ1.8-2.8(m, 4H), 2.70(d, J=7.5 Hz, 2H), 4.78(qt, J=7.5 and 7.5 Hz, 1H), and 7.4-8.2(m, 5H), ^{19}F NMR($CDCl_3$) δ4.0(d), ^{13}C NMR($CDCl_3$) δ14.1(t), 31.8(t), 35.9(t), 50.3(s), 68.5(d), 70.6(d), 72.6(d), 96.7, 115.3(s), 117.4(s), 118.7(s), 128.7(d), 129.3(d), 129.8(d), 132.8(d), 133.9, and 171.4(s), J_{CF}=279.3 Hz and J_{CCF}=29.3 Hz.

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