May, 1981] © *1981 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***54***, *1579—1580 (1981)* 1579

N-Trifluoroacetylimidazoles as a Reagent for Converting Aldoximes into Nitriles under Mild Conditions

Takashi Keumi,* Takayoshi Yamamoto, Hiroshi Saga, and Hidehiko Kitajima
Department of Fiber and Color Chemistry, Faculty of Engineering, Fukui University, Bunkyo, Fukui 910

(Received October 29, 1980)

Synopsis. It was found that *N*-trifluoroacetylimidazole was an excellent reagent for the intramolecular dehydration of aldoximes to give nitriles uner mold conditions.

There are only a few examples of the use of *N*-trifluoroacetylimidazole (TFAI) as an organic synthetic reagent, though it seems to have a great potential. Thus far, it has only been used as trifluoroacetylating agent of amines or alcohols1) and as condensation agent of amino acids with *p*-nitrophenol.2) We have previously shown that TFAI is useful for the condensation of carboxylic acids with aromatic hydrocarbons to give aromatic ketones.3) In this paper, we wish to report that TFAI is also an excellent reagent for the intramolecular dehydration of aldoximes (**1**) to give nitriles (**4**).

Many methods are known for converting **1** into **4**, but some of them have disadvantages, such as needing vigorous reaction conditions or tedious work-up procedures, having unsatisfactory yields, or needing unusual reagents.4—6) For example, recently reported trifluoroacetic anhydride is very useful as the reagent;4) however, it requires at least two equivalents of a base to catalyze the reaction and to remove the acid generated.

TFAI converted **1** into **4** under practically neutral and mild conditions without any additives. The reac-

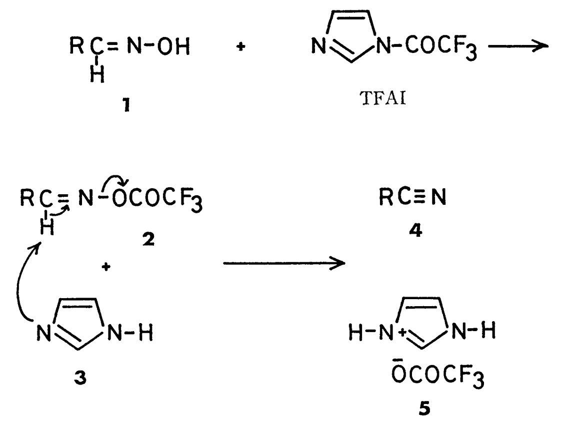

Table 1. Nitriles obtained from aldoximes by treatment with *N*-trifluoroacetylimidazole

	R of 4	Reaction time/h	Yielda) of 4/%	Bp/°C or [Mp/°C] Found	Reported	IR(ν/cm^{-1})	^{1}H-NMR(δ/ppm, CCl$_4$)
4a	Propyl	2c)	99b)	117—119	1178)	2220, 1450, 1060	0.9—1.3(m, 3H), 1.5—1.9(m, 2H), 2.2—2.4(m, 2H)
4b	Pentyl	2c)	90	160	1648)	2220, 1460, 1070	0.7—1.0(m, 3H), 1.2—1.9(m, 6H), 2.2—2.4(m, 2H)
4c	Hexyl	2	96	200	200.48)	2220, 1460, 1170	0.7—1.0(m, 3H), 1.1—1.7(m, 10H), 2.3—2.6(m, 2H)
4d	1-Ethylpentyl	2	95	187—190	98—1009) (50 Torr)	2210, 1460, 1170	0.7—1.1(m, 6H), 1.2—1.8(m, 8H), 2.4—2.8(m, 1H)
4e	1-Propenyl	3.5	77	118—122	1228)	2210, 1645, 1436	1.8—2.0(m, 3H), 5.3—5.6(m, 1H), 6.4—6.9(m, 1H)
4f	Phenyl	3.5	92	190	1917)	2220, 1600, 1490	7.2—7.7(m, 5H)
4g	*p*-Chlorophenyl	3.5	94	[90—91]	[94—96]7)	2210, 1590, 1480	7.3—7.8(m, 4H)
4h	*o*-Chlorophenyl	3.5	97	[45—46]	[43—44]10)	2210, 1583, 1465	7.3—7.8(m, 4H)
4i	*m*-Nitrophenyl	3.5	91	[113—114]	[117—118]11)	2210, 1530, 1355	7.7—8.0(m, 1H), 8.3(d, 1H, *J*=8 Hz), 8.54(d, 1H, *J*=8 Hz), 8.73(s, 1H)
4j	*p*-Tolyl	3.5	81	215—217	217.68)	2220, 1610, 1175	2.39(s, 3H), 7.23(d, 2H, *J*=8 Hz), 7.44(d, 2H, *J*=8 Hz)
4k	Styryl	3.5	95	254—255	253—25512)	2210, 1615, 970	5.80(d, 1H, *J*=16 Hz), 7.25(d, 1H, *J*=16 Hz), 7.33(m, 5H)
4l	2-Furyl	3.5	81	146—150	146—1488)	2220, 1465, 1225	6.5—6.6(m, 1H), 7.1—7.2(m, 1H), 7.55—7.65(m, 1H)

a) The isolated yield of **4**. b) Obtained by GLC. c) Ether was used as the solvent for this reaction. In the other reactions, THF was used as the solvent.

tion is carried out by heating a solution of **1** and TFAI (in a molar ratio of 1:1.1) in ether or tetrahydrofuran under reflux for 2—3.5 h. The results are summarized in Table 1. A wide variety of **1** substances, from the aliphatic or aromatic to the olefinic, are dehydrated by TFAI to give the corresponding **4** substances in satisfactory yields.

The dehydration of **1** is generally considered to proceed by means of a base-promoted bimolecular mechanism.[4] TFAI has a powerful trifluoroacetylating ability; in addition, as a result of the trifluoroacetylation, the reagent generates imidazole (**3**), which can act as a base. Therefore, in the above reaction it seems that the trifluoroacetylation of **1** by TFAI takes place first to give *O*-trifluoroacetyl aldoxime (**2**) and **3**, followed by the elimination of trifluoroacetic acid by the **3** thus yielded to afford **4** and imidazolium trifluoroacetate (**5**). Thus, the reaction system should be kept constantly neutral during the reaction. Further, conveniently, the by-product, **5**, can be easily removed from the product, **4**, by filtration, because it is hardly soluble in cold ether and tetrahydrofuran. TFAI is familiar in the field of the peptides chemistry[2] and is commercially available. Consequently, TFAI seems to be an efficient reagent for converting **1** into **4**.

Experimental

Materials and Measurements. TFAI was prepared from imidazole and trifluoroacetic anhydride accoridng to the procedure described in the literature.[1] The aldoximes were prepared by a general method. The solvents used for the reactions were dried and distillated over lithium aluminium hydride. The IR spectra were recorded on a Hitachi EPI-S2 Model spectrophotometer. The NMR spectra were measured as carbon tetrachloride solutions at 100 MHz with a JEOL Model PS-100 spectrometer, using tetramethylsilane as the internal standard.

General Procedure. A typical procedure will be described for the preparation of benzonitrile (**4f**): To a solution of benzaldehyde oxime (0.500 g, 4.1 mmol) in dried tetrahydrofuran (6 ml), TFAI (0.745 g, 4.5 mmol) in tetrahydrofuran (4 ml) was added, after which the mixture was heated under reflux for 3 h. After cooling, the resultant precipitates of imidazolium trifluoroacetate were removed off by filtration and washed with ether (about 30 ml). The combined filtrate was washed with water (about 30 ml×2) and dried over anhydrous sodium sulfate. The solvent was then evaporated to obtain **4f** (0.400 g, 94%). Bp 190 °C (lit,[7] Bp 191 °C).

References

1) H. A. Staab, G. Walther, and W. Rohl, *Chem. Ber.*, **95**, 2073 (1962).
2) H. D. Low, *J. Chem. Soc.*, **1965**, 3897.
3) T. Keumi, H. Saga, and H. Kitajima, *Bull. Chem. Soc. Jpn.* **53**, 638 (1980).
4) A. Carotti and F. Campagna, *Synthesis*, **1979**, 56.
5) G. A. Olah and T. Keumi, *Synthesis*, **1979**, 112.
6) G. Sosnovsky, J. A. Krog, and S. G. Umhoefer, *Synthesis*, **1979**, 722, and the references cited therein.
7) "Handbook of Chemistry & Physics," 57th ed, ed by R. C. Weast and M. J. Astle, Chemical Rubber Co., Cleveland, Ohio (1976).
8) "Handbook of Chemistry," 11th ed, ed by J. A. Dean, McGraw-Hill Co., New York (1973).
9) P. A. Levene and M. Kuna, *J. Biol. Chem.*, **140**, 259 (1941).
10) A. Korczynski and B. Fandrich, *C. R. Acad. Sci.*, **183**, 421 (1926); *Chem. Abstr.*, **14**, 2919 (1920).
11) "Dictionary of Organic Compounds," 4th ed, Eyre and Spottiswoode Publishers, London (1965).
12) T. L. Ho, *Synthesis*, **1975**, 401.