Synthesis and Reaction of 5-Amino-3-trifluoromethylisoxazole and -pyrazole-4-carboxylic Acids

Kiyoshi Tanaka,* Takashi Suzuki, Seiji Maeno and Keiryo Mitsuhashi

Department of Industrial Chemistry, Seikei University, Musashino-shi, Tokyo 180, Japan

Received February 25, 1986

5-Amino-3-trifluoromethylisoxazole- and -pyrazole-4-carboxylic acids were prepared by the reactions of trifluoroacetonitrile oxide or -imines with cyanoacetic acid derivatives, respectively. The behavior of thus obtained aminoazole-4-carboxylic acids toward some electrophiles was examined. In acylation with acyl chlorides, the aminoisoxazole-4-carboxylate **2a** was diacylated to give the (diacylamino)isoxazole-4-carboxylate **7**, whereas the analogous aminopyrazole **5a** produced the cyclized pyrazolooxazinone **13**. Moreover, carbamoylation of **2a** with isocyanates gave the trifluoromethylisoxazolouracils **10**.

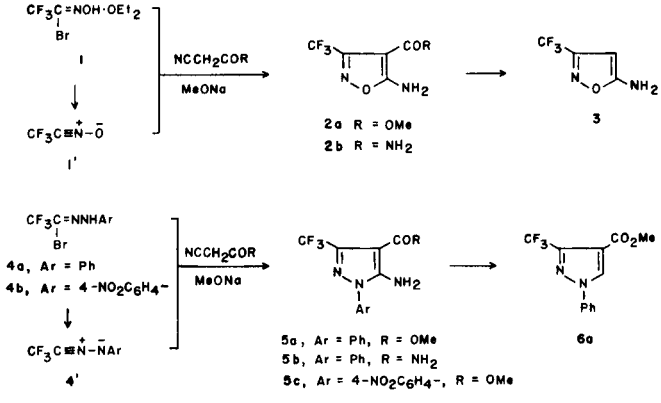
J. Heterocyclic Chem., **23**, 1535 (1986).

5-Aminoisoxazole- and -pyrazole-4-carboxylic acids or their amides are frequently applied as convenient sources of [5.6]fused systems such as isoxazolo[5,4-*b*]pyridines, -[5,4-*d*]pyrimidines [1], and pyrazolo[3,4-*d*]pyrimidines [2], respectively, some of which are reported to be biologically active [3]. Besides, certain 3-trifluoromethylisoxazoles are reported to have antimicrobial activity [4] and some of 3-trifluoromethylpyrazole derivatives are also known to be slightly effective as an amebicide or a trichomonacide [5]. In this connection, it is of interest to synthesize 5-aminoisoxazole- and -pyrazole-4-carboxylic acids bearing a trifluoromethyl group. We have demonstrated the synthetic utility of the fluorinated 1,3-dipolar compounds and, as a part of this research, we now wish to describe the synthesis of 5-amino-3-trifluoromethylisoxazole and -pyrazole-4-carboxylic acids from trifluoroacetonitrile oxide and -arylimines, respectively. The reactivities of thus obtained azole-4-carboxylic acids toward typical electrophiles such as acyl halides and isocyanates are also described [6].

Trifluoroacetohydroximoyl bromide etherate (**1**) reacted with methyl cyanoacetate in the presence of sodium methoxide to give methyl 5-amino-3-trifluoromethylisoxazole-4-carboxylate (**2a**) in a good yield. The isoxazole **2a** was hydrolyzed under alkaline conditions followed by decarboxylation, resulting in the formation of 5-amino-3-trifluoromethylisoxazole (**3**) in appreciable yield. The shielded methine proton (δ 5.34) in the ^{1}H nmr spectrum particularly supports the structure of **3** with no substituent at the 4-position of the isoxazole ring. From this chemical conversion, the structure of **2a** was confirmed. Similar treatment with cyanoacetamide produced in a moderate yield the isoxazole-4-carboxyamide **2b**, from which **3** was obtained. *N*-Phenyltrifluoroacetohydrazonoyl bromide (**4a**) was allowed to react with methyl cyanoacetate to give methyl 5-amino-1-phenyl-3-trifluoromethylpyrazole-4-carboxylate (**5a**) in a good yield. The structure of **5a** was also confirmed by chemical transformation such as deamination of **5a** giving methyl 1-phenyl-3-trifluoromethylpyrazole-4-carboxylate (**6a**). With cyanoacetamide, the pyrazole-4-carboxyamide **5b** was also obtained. Similarly, *N*-(4-nitrophenyl)trifluoroacetohydrazonoyl bromide (**4b**), under more drastic conditions, produced the corresponding pyrazole-4-carboxylate **5c** with methyl cyanoacetate.

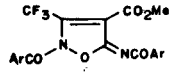
The aminoazole-4-carboxylic acids **2** or **5** can be formed *via* a direct concerted cycloaddition of the nitrile oxide **1′** or imine **4′** and the alternative stepwise path involving an electrophilic substitution of **1′** or **4′** is also possible [7].

Scheme 1



Acylation of the aminoisoxazole-4-carboxylate **2a** was first carried out using benzoyl chlorides in the presence of triethylamine to give methyl 5-(dibenzoylamino)-3-trifluoromethylisoxazole-4-carboxylate (**7**) in a fairly good yield (Table 2). The formation of the dibenzoylated isoxazoles **7** was so easy that the (monobenzoylamino)isoxazole **8** could not be detected during the reaction course. However, **8** was found to be easily prepared by hydrolysis of **7**. For the structure of **7**, the alternative structure **7′** can be anticipated and, however, it is ruled out from the absorption in the uv spectra, for example λ 249 nm (ϵ 30810) for **7a**, due to the isoxazole ring [8] and from the following chemical conversions: (a) The obtained **8a** was converted

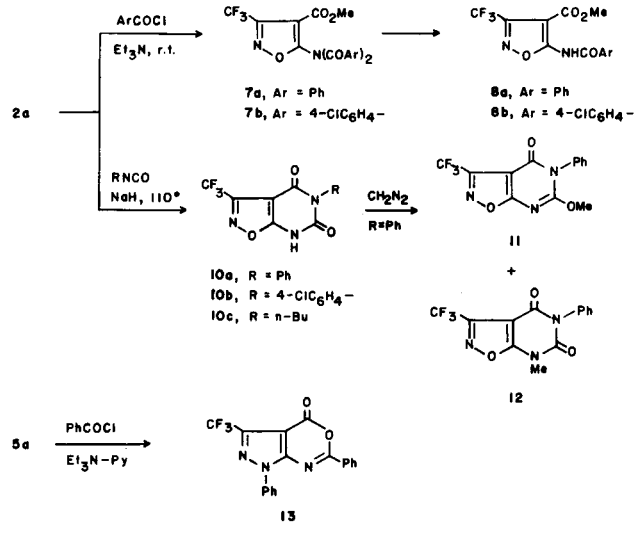
to **7a** on treatment with benzoyl chloride and (b) methyl 5-[benzoyl(4-chlorobenzoyl)amino]-3-trifluoromethylisoxazole-4-carboxylate (**9**) derived from **8a** and 4-chlorobenzoyl chloride is perfectly consistent with one from **8b** and benzoyl chloride. These results indicate both acylations take place on the amino group.



7'

Carbamoylation was performed under more drastic conditions. Phenyl, 4-chlorophenyl, or butylisocyanate re acted with **2a** in the presence of sodium hydride at 110° to give the corresponding cyclized trifluoromethylisoxazolouracil, 5-substituted 3-trifluoromethyl-5*H*,7*H*-isoxazolo[5,4-*d*]pyrimidine-4,6-dione (**10**) in a good yield, respectively (Table 2). Methylation of **10a** with diazomethane afforded a mixture of *O*-methylated **11** and *N*-methylated product **12** with preference for *N*-methylation, being in accordance with the behavior of the simple isoxazolouracils [9]. On the other hand, although carbamoylation of the analogous pyrazole **5a** under the similar conditions failed, recovering **5a** unchanged, benzoylation in triethylamine-pyridine occurred to result in cyclization, giving 1,6-diphenyl-3-trifluoromethylpyrazolo[3,4-*d*][1,3]-oxazin-4-one (**13**) in a good yield.

Scheme 2



The internal condensation giving **13** in the reaction of the pyrazole-4-carboxylate **5a** with benzoyl chloride is in contrast to dibenzoylation of the isoxazole-4-carboxylate **2a**. Such difference in the reaction course may be interpreted in terms of the difference in the reactivity of the anions **14a,b** of the initially formed monoamides. While the reactivity of **14b** is high enough to cyclize intramolecularly, **14a** is too stabilized to cyclize by the strong induc-

Table 1

Preparation of Isoxazoles **2,3,7,8**, and **9** and Pyrazoles **5**

Compound	Yield (%)	Mp (°C) [a]	Formula	Analysis, % Found/(Calcd.) C	H	N
2a	81	138-139	$C_6H_5F_3N_2O_3$	34.35 (34.30)	2.42 (2.40)	13.41 (13.33)
2b	30	122-123	$C_5H_4F_3N_3O_2$	30.86 (30.78)	2.10 (2.07)	21.62 (21.54)
3	41 [b], 41 [c]	51-52	$C_4H_3F_3N_2O$	31.36 (31.59)	1.79 (1.99)	18.34 (18.42)
5a	75	115-116	$C_{12}H_{10}F_3N_3O_2$	50.69 (50.53)	3.38 (3.53)	14.73 (14.73)
5b	53	170-172	$C_{11}H_9F_3N_4O$	49.18 (48.90)	3.60 (3.36)	20.76 (20.73)
5c	32	179-180	$C_{12}H_9F_3N_4O_4$	43.77 (43.65)	2.58 (2.75)	17.09 (16.97)
7a	71	98-99 [d]	$C_{20}H_{13}F_3N_2O_5$	57.58 (57.42)	3.21 (3.13)	6.72 (6.70)
7b	75	133-134 [d]	$C_{20}H_{11}Cl_2F_3N_2O_5$	49.27 (49.30)	2.19 (2.28)	5.53 (5.75)
8a	82	67-70	$C_{13}H_9F_3N_2O_4$	49.71 (49.69)	2.75 (2.89)	8.92 (8.92)
8b	83	139-140	$C_{13}H_8ClF_3N_2O_4$	44.43 (44.78)	2.29 (2.31)	8.13 (8.03)
9	76 [e], 78 [f]	118-119	$C_{20}H_{12}ClF_3N_2O_5$	53.37 (53.06)	2.66 (2.67)	5.94 (6.19)

[a] Recrystallized from hexane-chloroform unless otherwise noted. [b] Isolated yield from **2a**. [c] Yield based on ^{1}H nmr analysis from **2b**. [d] Recrystallized from hexane. [e] Yield from the reaction of **8a** with 4-chlorobenzoyl chloride. [f] Yield from the reaction of **8b** with benzoyl chloride.

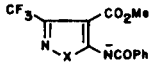
Table 2

Preparation of Fused Isoxazoles **10**, **11**, and **12** and Pyrazoles **13**

Compound	Yield (%)	Mp (°C) (Recrystallization Solvent)	Formula	Analysis, % Found/(Calcd.) C	H	N
10a	63	227-230 dec (toluene)	$C_{12}H_6F_3N_3O_3$	48.42 (48.50)	1.90 (2.03)	14.17 (14.14)
10b	38	231-232 dec (hexane-ethanol)	$C_{12}H_5ClF_3N_3O_3$	43.46 (43.46)	1.46 (1.52)	12.67 (12.67)
10c	56	115.5-116.5 (hexane-chloroform)	$C_{10}H_{10}F_3N_3O_3$	43.26 (43.33)	3.54 (3.64)	15.15 (15.16)
11	63 [a]	156-156.5 (hexane-chloroform)	$C_{13}H_8F_3N_3O_3$	50.38 (50.17)	2.38 (2.59)	13.50 (13.50)
12		130-134 (ethanol)	$C_{13}H_8F_3N_3O_3$	50.15 (50.17)	2.22 (2.59)	13.46 (13.50)
13	52	190-191 (hexane-chloroform)	$C_{18}H_{10}F_3N_3O_2$	60.44 (60.51)	2.49 (2.82)	11.67 (11.76)

[a] Total yield of **11** and **12**, ratio of which is 1/2.

tive effect of the isoxazole ring and reacts only with the more reactive benzoyl chloride.



14a X = O
14b X = NPh

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a JASCO A-100 spectrometer. Samples were run as potassium bromide pellets. The ^1H nmr spectra were measured with a JEOL JNM-PMX 60 spectrometer using tetramethylsilane as an internal standard, the chemical shifts being given in δ ppm downfield. Samples were prepared by dissolving in deuteriochloroform unless otherwise noted. The uv spectra were observed with a Hitachi 340 spectrometer.

The bromides **1** and **4** were prepared by bromination of trifluoroacetaldehyde oxime and -phenylhydrazone with *N*-bromosuccinimide (NBS), respectively, according to the methods reported in our previous papers [10]. The oxime and the hydrazone were both prepared from trifluoroacetaldehyde ethyl hemiacetal as follows.

To a mixture of the hemiacetal (50.0 g, 0.35 mole), hydroxylamine hydrochloride (24.3 g, 0.35 mole), 80 ml of methanol, and 160 ml of water was added dropwise 80.0 g of 50% aqueous sodium hydroxide. After stirring at room temperature for 6 hours, the mixture was adjusted to *p*H 6 with concentrated hydrochloric acid. Sodium chloride was added to the mixture and the separated upper layer was collected, dried over magnesium sulfate, and distilled to give 44.9 g of a mixture of the oxime and ethanol (boiling range 76-80°). The mixture thus obtained was treated with NBS to give **1** (41% yield based on the hemiacetal).

A mixture of the hemiacetal (25.0 g, 0.17 mole) and phenylhydrazine (18.8 g, 0.17 mole) was stirred at 100° for 1 hour. Diethyl ether was added to the mixture. The diethyl ether solution was washed with 5% hydrochloric acid and brine, dried over magnesium sulfate, and evaporated to leave a pale yellow solid (28.3 g, 87%) of the phenylhydrazone which was further purified by recrystallization from hexane, mp 69-73°.

Preparation of Methyl 5-Amino-3-trifluoromethylisoxazole-4-carboxylate (**2a**).

A solution of the bromide **1** (5.0 g, 18.8 mmoles) in 20 ml of methanol was added dropwise to a solution of methyl cyanoacetate (5.0 g, 50.5 mmoles) and sodium methoxide (2.5 g, 46.3 mmoles) in 15 ml of methanol. After stirring at room temperature for 1 hour, the mixture was evaporated to leave a residue. The residue was washed with dilute aqueous ammonia, dried at the pump, and recrystallized from hexane-chloroform to give 3.2 g (81%) of **2a**; ^1H nmr (deuteriochloroform-DMSO-d_6): δ 3.86 (s, 3H), 7.4 (br s, 2H); ir: 3488, 3300, 3260, 3200 (NH_2), 1710, 1655 cm^{-1} (C=O).

5-Amino-3-trifluoromethylisoxazole-4-carboxyamide (**2b**).

This compound was similarly prepared in 30% yield from **1** and cyanoacetamide; ^1H nmr (deuteriochloroform-DMSO-d_6): δ 6.0 (br s, 2H), 7.4 (br s, 2H); ir: 3530, 3400, 3270 (NH_2), 1678 cm^{-1} (C=O).

Preparation of 5-Amino-3-trifluoromethylisoxazole (**3**) from **2a** (Method A) or **2b** (Method B). Method A.

A mixture of **2a** (2.4 g, 11.4 mmoles) and 20 ml of 10% aqueous sodium bicarbonate was refluxed for 6 hours. The mixture was extracted with diethyl ether and the extracts were dried over magnesium sulfate and evaporated to leave a solid which was recrystallized from hexane-chloroform, giving 0.72 g (41%) of **3**; ^1H nmr: δ 5.0 (br s, 2H), 5.34 (s, 1H); ir: 3450, 3285, 3240, 3200 (NH_2), 1650, 1635 cm^{-1}.

Method B.

A mixture of **2b** (100 mg, 0.51 mmole), concentrated hydrochloric acid (5 ml), and acetic acid (10 ml) was refluxed for 3 hours. The mixture was evaporated to leave a residue to which 10 ml of 10% aqueous sodium bicarbonate was added. The following procedures are similar to the above and **3** was obtained in 41% yield, according to ^1H nmr analysis.

Preparation of Methyl 5-Amino-1-phenyl- and -1-(4-nitrophenyl)-3-trifluoromethylpyrazole-4-carboxylates **5a** and **5c** and 5-Amino-1-phenyl-3-trifluoromethylpyrazole-4-carboxyamide (**5b**). General Procedure.

A solution of the bromide **4a** (7.5 mmoles) in 10 ml of methanol was added dropwise to a mixture of sodium methoxide (15.0 mmoles) and methyl cyanoacetate or cyanoacetamide (22.5 mmoles) in 20 ml of methanol. After stirring at room temperature for 3 hours, the mixture was evaporated to leave a residue which was extracted with diethyl ether. The extracts were washed with water and brine, dried over magnesium sulfate, and evaporated to give a residue. The residue was chromatographed on silica gel to afford **5a** or **5b**, respectively. Each product was further purified by recrystallization; **5a**, ^1H nmr: δ 3.85 (s, 3H), 5.6 (br s, 2H), 7.5 (s, 5H); ir: 1679 cm^{-1} (C=O); **5b**, ^1H nmr (deuteriochloroform-

DMSO-d_6): δ 6.6 (br s, 4H), 7.3-7.8 (m, 5H); ir: 1638 cm^{-1} (C=O).

The similar reaction of **4b** and methyl cyanoacetate was performed at 65° for 12 hours to give **5c**; ^{1}H nmr: δ 3.90 (s, 3H), 5.7 (br s, 2H), 8.1 (A_2X_2, 4H); ir: 1683 cm^{-1} (C=O).

Deamination of **5a**.

A mixture of **5a** (1.00 g, 3.5 mmoles) in water and concentrated hydrochloric acid (30 ml each) was heated to boiling and then cooled to 10-13°. To the mixture was added a solution of 0.36 g (5.2 mmoles) in 1 ml of water and, after stirring at 0-5° for 20 minutes, 5 ml of 30% aqueous hypophosphorous acid was added. The mixture was stirred at 0-5° for 3 hours and then at room temperature for 10 hours and extracted with diethyl ether. The extracts were dried over magnesium sulfate and evaporated to leave a residue which was chromatographed on silica gel and eluted with hexane-ethyl acetate (4/1) to give 0.09 g (9%) of methyl 1-phenyl-3-trifluoromethylpyrazole-4-carboxylate (**6a**). The product was purified by recrystallization from hexane, mp 111-112° (lit 112° [11]). The spectral data of **6a** are consistent with those of our authentic sample.

Acylation of **2a**. General Procedure.

To a solution of **2a** (4.8 mmoles) and acyl chloride (14.3 mmoles) in 50 ml of toluene was added dropwise a solution of triethylamine (15.0 mmoles) in 10 ml of toluene. The mixture was stirred at room temperature for 15 hours, washed with water and brine, and dried over magnesium sulfate. The solvent was removed under reduced pressure, giving a solid which was purified by recrystallization to give methyl 5-(diacylamino)-3-trifluoromethylisoxazole-4-carboxylate (**7**); **7a** had ^{1}H nmr (carbon tetrachloride): δ 3.73 (s, 3H), 7.1-7.9 (m, 10H); ir: 1720 cm^{-1} (C=O); uv (ethanol): λ max 249 nm (ε 30810); **7b** had ^{1}H nmr (carbon tetrachloride): δ 3.85 (s, 3H), 7.6 (A_2X_2, 8H); ir: 1725 cm^{-1} (C=O).

Hydrolysis of **7a** and **7b**. General Procedure.

A mixture of **7** (1.6 mmoles) in water and ethanol (25 ml each) was refluxed for 15 hours and the solvent was removed to give a residue which was washed with hexane. The residual solid was recrystallized to afford methyl 5-(acylamino)-3-trifluoromethylisoxazole-4-carboxylate (**8**); **8a** had ^{1}H nmr: δ 3.97 (s, 3H), 7.4-8.1 (m, 5H), 10.9 (br s, 1H); ir: 3290 (NH), 1705 cm^{-1} (C=O); **8b** had ^{1}H nmr: δ 4.01 (s, 3H), 7.8 (A_2X_2, 4H), 10.9 (br s, 1H); ir: 3260 (NH), 1719, 1687 cm^{-1} (C=O).

Preparation of Methyl 5-[benzoyl(4-chlorobenzoyl)amino]-3-trifluoromethylisoxazole-4-carboxylate (**9**).

A solution of triethylamine (0.15 g, 1.5 mmoles) in 5 ml of toluene was added dropwise to a solution of **8a** (0.31 g, 1.0 mmole) and 4-chlorobenzoyl chloride (0.26 g, 1.5 mmoles) in 30 ml of toluene. The mixture was stirred at room temperature for 60 hours and the usual workup gave 0.34 g (76%) of **9**; ^{1}H nmr: δ 3.77 (s, 3H), 7.1-7.8 (m, 9H); ir: 1720 cm^{-1} (C=O).

From **8b** and benzoyl chloride, a similar procedure to the above was performed to give **9** in 78% yield.

Preparation of **7a** from **8a**.

By a similar procedure using **8a** and benzoyl chloride **7a** was produced in 67% yield. Its melting point and spectral data are consistent with those obtained above.

Carbamoylation of **2a**. General Procedure.

A mixture of **2a** (4.8 mmoles), sodium hydride (5.2 mmoles), and isocyanate (4.8 mmoles) in 25 ml of toluene was refluxed for 20 hours. A small amount of methanol was added to the mixture and the solvent was removed. The residue was dissolved in water and the mixture was washed with diethyl ether, acidified with concentrated hydrochloric acid, and extracted with diethyl ether. The extracts were dried over magnesium sulfate and evaporated to leave a solid of 3-trifluoromethyl-5*H*,7*H*-isoxazolo[5,4-*d*]pyrimidine-4,6-dione (**10**) which was further purified by recrystallization; **10a** had ^{1}H nmr (deuteriochloroform-DMSO-d_6): δ 7.1-7.6 (m, 5H), 13.1 (br s, 1H); ir: 3100 (NH), 1740 (C=O), 1680 (C=O), 1640 cm^{-1}; **10b** had ^{1}H nmr (deuteriochloroform-DMSO-d_6): δ 7.9 (br s, 1H), 7.4 (A_2X_2, 4H); ir: 3100 (NH), 1740 (C=O), 1680 (C=O), 1640 cm^{-1}; **10c** had ^{1}H nmr: δ 0.9 (t, 3H), 1.1-1.8 (m, 4H), 4.0 (t, 2H); ir: 2900 (NH), 1750 (C=O), 1680 cm^{-1} (C=O).

Methylation of **10a** with Diazomethane.

An excess of an ethereal solution of diazomethane was added dropwise to a solution of **10a** (0.80 g, 2.7 mmoles) in 40 ml of diethyl ether. After stirring at room temperature for 2 hours the solvent was removed to leave a residue which was passed through a short column (silica gel, hexane-chloroform) to give 0.53 g (63% overall yield) of a mixture of **11** and **12** in the ratio of 1/2, according to ^{1}H nmr analysis. Each product was separated by column chromatography (silica gel, hexane-chloroform, 2/3) and purified by recrystallization; **11** had ^{1}H nmr : δ 4.07 (s, 3H), 7.0-7.6 (m, 5H); ir: 1725 (C=O), 1640 cm^{-1} (C=N); **12** had ^{1}H nmr: δ 3.66 (s, 3H), 7.0-7.6 (m, 5H); ir: 1745 (C=O), 1700 cm^{-1} (C=O).

Benzoylation of **5a**.

Benzoyl chloride (4.92 g, 35.0 mmoles) was added to a solution of **5a** (2.00 g, 7.0 mmoles) and triethylamine (3.50 g, 35.0 mmoles) in 50 ml of pyridine and the mixture was stirred at 60° for 50 hours. The formed solid was filtered off and the filtrate was evaporated to leave a residue which was extracted with diethyl ether. The extracts were washed with water and brine and the solvent was removed. The residual solid was recrystallized from hexane-chloroform to give 1.30 g (52%) of 1,6-diphenyl-3-trifluoromethylpyrazolo[3,4-*d*][1,3]oxazin-4-one (**13**); ^{1}H nmr: δ 7.5-8.4 (m); ir: 1810 cm^{-1} (C=O).

Acknowledgment.

We gratefully thank Central Glass Co., Ltd. for their kind offer of the starting material, trifluoroacetaldehyde ethyl hemiacetal.

REFERENCES AND NOTES

[1] A. Camparini, F. Ponticelli and P. Tedeschi, *J. Heterocyclic Chem.*, **14**, 435 (1977); G. Desimoni, P. Gruenanger and P. Vita-Finzi, *Tetrahedron*, **23**, 687 (1967).

[2] P. Schmidt, K. Eichenberger and M. Wilhelm, *Helv. Chim. Acta.*, **45**, 1620 (1962); R. K. Robins, *J. Am. Chem. Soc.*, **78**, 784 (1956).

[3] T. Denzel and H. Hoehn, U. S. Patent 3,933,823 (1976); *Chem. Abstr.*, **84**, 135628 (1976); G. D. Snowling, J. M. Cox, R. A. Burrel and M. C. Shephard, German Patent 2,812,367 (1978); *Chem. Abstr.*, **90**, 82129u (1979).

[4] V. N. Pathak and V. Grover, *Pharmazie*, **34**, 568 (1979).

[5] H. V. Secor and J. F. De Bardeleben, *J. Med. Chem.*, **14**, 997 (1971).

[6] Part VIII in "Applications of the Fluorinated 1,3-Dipolar Compounds as Building Blocks of the Heterocycles with Fluorine Groups", Part VII; K. Tanaka, H. Masuda and K. Mitsuhashi, *Bull. Chem. Soc. Japan*, **58**, 2061 (1985).

[7] See ref [6] and K. Tanaka, S. Maeno and K. Mitsuhashi, *Bull. Chem. Soc. Japan*, **58**, 1841 (1985).

[8] G. Speroni, "The Physico-Chemical Properties of Isoxazole and Its Derivatives" in "The Chemistry of Heterocyclic Compounds", Vol **17**, A. Weissberger, ed, Interscience Publishers, New York, 1962, Chapter 5.

[9] G. Desimoni, P. Gruenanger and P. Vita-Finzi, *Tetrahedron*, **23**, 675 (1967).

[10] K. Tanaka, H. Masuda and K. Mitsuhashi, *Bull. Chem. Soc. Japan*, **57**, 2184 (1984); K. Tanaka, S. Maeno and K. Mitsuhashi, *J. Heterocyclic Chem.*, **22**, 565 (1985).

[11] K. Tanaka, S. Maeno and K. Mitsuhashi, *Chem. Letters*, 543 (1982).