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Preparation and Reactions of Sulfonimidoyl Fluorides

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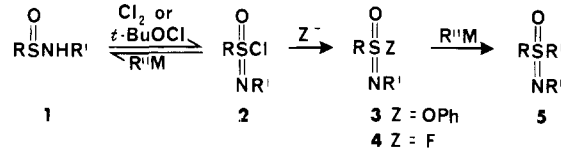
Sulfonimidoyl fluorides have been prepared for the first time by treatment of sulfonimidoyl chlorides with various sources of fluoride ion. Sulfonimidoyl chlorides are reduced to sulfinamides with alkyllithium reagents; however, the corresponding fluorides are converted in high yield to sulfoximines upon treatment with primary alkyllithiums. In the presence of Lewis acids, *N*-methylbenzenesulfonimidoyl fluoride was shown to react with anisole in a Friedel–Crafts manner and with silyl enol ethers to produce β-keto sulfoximines.

Sulfonimidoyl chlorides **2** have been prepared by oxidation of sulfinamides **1** with various chlorinating agents. Chlorine is the preferred reagent for the oxidation of *N*-alkyl sulfinamides.[1] The reaction of chlorine with *N*-aryl sulfinamides is sometimes violent, and *tert*-butyl hypochlorite is the reagent of choice for these substances.[2] Substitution of the chloride of sulfonimidoyl chlorides by a variety of nucleophiles is successful except for their reactions with organometallic reagents which generally result in reductions to sulfinamides rather than substitution to yield sulfoximines.[1] We have shown that this problem can be circumvented by prior conversion of the sulfonimidoyl chlorides to the phenyl esters **3** (Scheme I).[3]

The successful substitution reactions by organometallic reagents on sulfonyl fluorides[4] suggested that sulfonimidoyl fluorides would be useful reagents for sulfoximine synthesis. In this paper we describe the preparation of this new class of compounds and the advantages of their use in sulfoximine synthesis.

Treatment of sulfonimidoyl chlorides with fluoride ion (sodium fluoride in acetonitrile, tetrabutylammonium fluoride in acetonitrile, or potassium fluoride in acetonitrile containing catalytic 18-crown-6) resulted in good to excellent yields of the corresponding sulfonimidoyl fluorides (Table I). The progress of the exchange reaction could be monitored by thin-layer chromatography (the fluorides were considerably more mobile on silica gel than the chlorides) or by ^{1}H NMR [for example, the *N*-methyl group of *N*-methylbenzenesulfonimidoyl chloride appears as a singlet at δ 3.23 whereas that of the corresponding fluoride appears as a doublet at δ 3.0 (J_{HF} = 9 Hz)]. In some cases the sulfonimidoyl fluorides were used directly

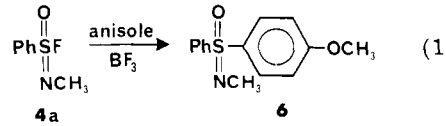
Scheme I



without purification, but, when desirable, purification was accomplished by flash chromatography.

Treatment of sulfonimidoyl fluorides with methyl- or butyllithium afforded the corresponding sulfoximines in high yield with little or no sulfinamide byproduct. The reaction of phenyllithium with *N*-methylbenzenesulfonimidoyl fluoride (**4a**) resulted in a mixture of sulfoximine **5j** and sulfinamide. *tert*-Butyllithium failed to react with *N*-(4-chlorophenyl)-benzenesulfonimidoyl fluoride. These results suggest that the reaction is moderately sensitive to steric crowding in the transition state. The reactions of sulfonimidoyl fluorides with Grignard reagents resulted in mixtures of sulfoximines and sulfinamides.

Sulfonimidoyl fluorides were also found to be useful in Friedel–Crafts reactions. Treatment of equimolar quantities of *N*-methylbenzenesulfonimidoyl fluorides and anisole with excess gaseous boron trifluoride afforded sulfoximine **6** in 63% yield (eq 1). In comparison, the alu-



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minum chloride catalyzed reaction of the corresponding sulfonimidoyl chloride with anisole afforded sulfoximine in 36% yield.[2] The Lewis acid catalyzed reaction of *N*-methylbenzenesulfonimidoyl fluoride with silyl enol ethers[6]

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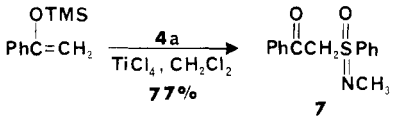
Table I. Preparation of Sulfonimidoyl Fluorides and Their Conversion to Sulfoximines

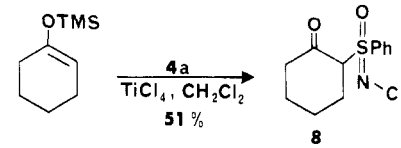
compd	R	R'	R''	method[a]	% yield: sulfonimidoyl fluoride 4	% yield: sulfoximine 5
a	Ph	Me	Me	A	89	100
b	Ph	4-ClC_6H_4	Me	B	71	79
c	Ph	4-$MeOC_6H_4$	Me	B	27	84
d	Ph	2-pyridyl	Me	B	75	84
e	Ph	Ph	Me	B	76	95
f	1-naphthyl	Me	Me	B	88	95
g	Ph	$CH_3CH(Ph)$	Me	A	70[b]	45 (A), 34 (B)
h	Ph	(1-naphthyl)ethyl	Me	C	86[b]	48 (A), 31 (B)
i	Ph	Me	*n*-Bu	A	89	100
j	Ph	Me	Ph	A	89	54

[a] See Experimental Section. [b] Mixture of diastereomers. Letters refer to diastereomers.

was also investigated; β-oxo sulfoximines were produced in good to moderate yield (eq 2 and 3).



(2)



(3)

Experimental Section

Preparation of Sulfonimidoyl Fluorides. Method A. The corresponding sulfonimidoyl chloride (35 mmol) was dissolved in acetonitrile (10 mL) and added to a stirring slurry of sodium fluoride (7.35 g, 175 mmol) in acetonitrile (90 mL). The mixture was stirred for 2 h at room temperature then diethyl ether was added to precipitate salts. The mixture was filtered and the filtrate concentrated under vacuum to provide the sulfonimidoyl fluoride.

Method B. The sulfinamide (26 mmol) was dissolved in carbon tetrachloride (165 mL) and cooled to 0 °C. *tert*-Butyl hypochlorite (3.5 g, 32 mmol) was added dropwise to the vigorously stirred mixture. After 15 min at 0 °C, the solvent was removed under vacuum and the reaction flask flushed with argon. Acetonitrile (80 mL), potassium fluoride (3.0 g, 52 mmol), and 18-crown-6 (0.07 g, 0.26 mmol) were added, and the mixture was stirred at room temperature until thin-layer chromatography on silica gel with hexane/EtOAc indicated complete reaction. The acetonitrile was removed by rotary evaporation, and the product was purified by flash chromatography[5] on silica gel with hexane/EtOAc.

Method C. The sulfinamide was oxidized with *tert*-butyl hypochlorite by the method described above. The crude sulfonimidoyl chloride was dissolved in acetonitrile (ca. 1 mmol/10 mL). To this was added 1.2 equiv of a 1 M solution of tetrabutylammonium fluoride (Aldrich) in THF. The mixture was stirred for 1 h at room temperature, the solvents were removed by rotary evaporation, and the crude sulfonimidoyl fluoride was purified by chromatography.

Reaction of Sulfonimidoyl Fluorides with Alkyllithiums. The sulfonimidoyl fluoride (4 mmol) was dissolved in THF (ca. 20 mL), and the solution was cooled to −78 °C. The alkyllithium (2 equiv) in ether or hexane was added dropwise, and the mixture was stirred for 15 min before being poured into an equivalent volume of saturated aqueous ammonium chloride. The organic layer was separated, and the aqueous layer was extracted several times with dichloromethane. The combined organic layers were dried over $MgSO_4$, and the solvents were removed. The residue was chromatographed on silica gel with hexane/EtOAc.

***N*-Methylbenzenesulfonimidoyl Fluoride (4a).** *N*-Methylbenzenesulfonimidoyl chloride[1] was converted to **4a**: an oil; IR (neat) 1458 (s), 1340 (s), 1220 (s), 1104 (m), 880 (s), 760 (s), 742 (s), 726 (m), 690 (s), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.23–7.33 (m, 5, Ar H), 3.10 (d, $^4J_{H-F}$ = 9.6 Hz, 3). The fluoride was further characterized by conversion to sulfoximines **5a**,[1] **5i**,[1] and **5j** which were compared with authentic samples.

***N*-(4-Chlorophenyl)benzenesulfonimidoyl Fluoride (4b).** *N*-(4-Chlorophenyl)benzenesulfinamide[6] was converted to the fluoride **4b**: mp 31–32.5 °C; IR (film) 3300 (w), 2910 (w), 1590 (m), 1490 (s), 1450 (m), 1360 (s), 1260 (s), 1120 (m), 1090 (m), 1065 (m), 827 (m), 735 (m), 670 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.4–8.2 (m, 2), 7.6–7.4 (m, 3), 7.4–7.2 (s, 4). Anal. Calcd for $C_{12}H_9ClFNOS$: C, 53.43; H, 3.37. Found: C, 53.53; H, 3.36.

***N*-(4-Chlorophenyl)-*S*-methyl-*S*-phenylsulfoximine (5b)**: mp 85–86 °C; IR ($CHCl_3$) 1580 (w), 1480 (s), 1290 (s), 1090 (m), 830 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.1–7.8 (m, 2 H), 7.7–7.3 (m, 3 H), 7.0 (q, 4 H), 3.2 (s, 3 H). Anal. Calcd for $C_{13}H_{12}ClNOS$: C, 58.75; H, 4.56. Found: C, 58.93; H, 4.61.

***N*-(4-Methoxyphenyl)benzenesulfonimidoyl fluoride (4c)** was prepared from *N*-(4-methoxyphenyl)benzenesulfinamide:[6] mp 70–71 °C; IR 3100–2900 (w), 1500 (m), 1380–1350 (s), 1280 (s), 1260–1240 (s), 1180 (m), 1120 (m), 1065 (m), 1030 (m), 825 (s), 650–670 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.4–8.0 (m, 2), 7.8–7.4 (m, 3), 7.5–6.7 (q, 4). Anal. Calcd for $C_{13}H_{12}FNO_2S$: C, 58.85; H, 4.57. Found: C, 58.82; H, 4.63.

***N*-(4-Methoxyphenyl)-*S*-methyl-*S*-phenylsulfoximine (5c)**: oil; IR (film) 3100–2800 (w), 1500 (s), 1445 (m), 1260 (s), 1235 (s), 1198 (s), 1091 (m), 1039 (s), 828 (m), 738 (m), 680 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2–7.9 (m, 2), 7.7–7.3 (m, 3), 7.2–6.5 (q, 5), 3.7 (s, 3), 3.2 (s, 3). Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.33; H, 5.80. Found: C, 63.88; H, 5.97.

***N*-(2-Pyridyl)benzenesulfonimidoyl Fluoride (4d).** *N*-(2-Pyridyl)benzenesulfinamide (mp 121–123 °C) was prepared from benzenesulfinyl chloride and 2-aminopyridine and converted to **4d**: mp 64–66.5 °C; IR ($CHCl_3$), 3000–2900 (w), 1590 (m), 1470 (s), 1435 (s), 1260 (m), 650 (m) cm^{-1}; ^1H NMR ($CHCl_3$) δ 8.7–8.2 (m, 3), 8.0–7.5 (m, 5), 7.4–7.0 (m, 2). Anal. Calcd for $C_{11}H_{19}FN_2OS$: C, 55.91; H, 3.85. Found: C, 55.99; H, 3.81.

***S*-Methyl-*S*-phenyl-*N*-(2-pyridyl)sulfoximine (5d)**: mp 131–132 °C (from carbon tetrachloride–ethyl acetate); IR ($CHCl_3$) 3100–2900 (w), 1590 (s), 1460 (s), 1420 (m), 1330–1280 (s), 1205 (s), 1101 (m), 1090 (m), 1045 (m), 1010 (m), 770–670 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.3–7.9 (m, 3), 8.7–7.3 (m, 5), 7.0–6.8 (m, 2), 3.3 (s, 3). Anal. Calcd for $C_{12}H_{12}N_2OS$: C, 62.04; H, 5.22. Found: C, 62.24; H, 5.35.

***N*-Phenylbenzenesulfonimidoyl fluoride (4e)** was prepared from *N*-phenylbenzenesulfinamide:[6] mp 36–37 °C; IR 3040–3000 (w), 1597 (m), 1495 (s), 1458 (m), 1370 (s), 1260 (s), 1122 (s), 1072 (m), 670 (s), 620 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.4–8.1 (m, 2), 8.4–7.8 (m, 3), 7.4–7.0 (m, 5). Anal. Calcd for $C_{12}H_{10}FNOS$: C, 61.27; H, 4.25. Found: C, 60.98; H, 4.30.

***S*-Methyl-*N*,*S*-diphenylsulfoximine (5e)**: mp 95–96 °C; IR 3100–2980 (m), 1600 (m), 1490 (s), 1450 (w), 1290–1260 (s), 1190 (s), 1080 (m), 1040 (m), 1020 (m), 970 (m), 680 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.1–7.8 (m, 2), 8.5–7.3 (m, 3), 7.2–6.5 (m, 5), 3.2 (s, 3). Anal. Calcd for $C_{13}H_{13}NOS$: C, 67.49; H, 5.68. Found: C, 67.58; H, 5.81.

***N*-Methyl-1-naphthalenesulfonimidoyl fluoride (4f)** was obtained from *N*-methyl-1-naphthalenesulfinamide: mp 95–96 °C; an oil; IR 3090 (m), 2940 (s), 2860 (m), 1600 (m), 1520 (s),

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1465 (s), 1350 (s), 1225 (s), 1050 (m), 1000 (m), 900 (s), 850 (s), 830 (s), 800 (s), 760 (s), 720 (s), 700 (s), 650 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.5–7.2 (m, 7), 3.3 (s, 3), 3.2 (s, 3).

***N,S*-Dimethyl-*S*-(1-naphthyl)sulfoximine (5f)**: mp 50–55 °C; IR 3200–2800 (s), 1750 (s), 1390 (s), 1240 (s), 1170 (m), 1100 (m), 1000 (m), 870 (m), 823 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.5–7.4 (m, 7), 3.2 (s, 3), 2.6 (s, 3). Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.75; H, 5.94. Found: C, 65.42; H, 5.66.

***N*-(1-Phenylethyl)benzenesulfonimidoyl Fluoride (4g).** *N*-(1-Phenylethyl)benzenesulfinamide was obtained as a colorless oil which was a mixture of diastereomers (methyl doublets at δ 1.5 and 1.6) from benzenesulfinyl chloride and (–)-1-phenylethylamine (Aldrich). Oxidation of the sulfinamide mixture with chlorine and treatment of the crude sulfonimidoyl chlorides with sodium fluoride in acetonitrile gave **4g** (a mixture of diastereomers) as an oil: IR (film) 3050 (w), 2970 (w), 1450 (s), 1200 (s), 1100 (s), 750 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2–7.0 (m, 10), 5.1 (m, 1), 1.8–1.5 (m, 3).

***S*-Methyl-*S*-phenyl-*N*-(1-phenylethyl)sulfoximines (5g).** The above fluoride was treated with methyllithium to give sulfoximines **5g** which could be separated by medium-pressure liquid chromatography on silica gel with hexane/EtOAc. The faster moving diastereomer, **diastereomer A**, was a colorless oil: bp 87–92 °C, (0.1 torr); IR (film) 3050 (m), 2950 (m), 1450 (s), 1250 (s), 1150 (s), 990 (s), 750 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.1 (m, 10), 4.2 (q, 1), 3.0 (s, 3), 1.5 (d, 3); $[\alpha]^{25}_D$ –14.2° (*c* 0.5, $CHCl_3$). Anal. Calcd for $C_{15}H_{17}NOS$: C, 69.52; H, 6.56. Found: C, 69.78; H, 6.84.

Diastereomer B: bp 93–95 °C (0.1 torr); IR similar to that of diastereomer A; ^1H NMR ($CDCl_3$) δ 8.2–7.2 (m, 10), 4.4 (q, 1), 3.0 (s, 3), 1.4 (d, 3); $[\alpha]^{25}_D$ –194.5° (*c* 0.7, $CHCl_3$).

***N*-(1-Naphthylethyl)-*S*-methyl-*S*-phenylsulfoximines (5h).** Optically pure (–)-1-naphthylethylamine (Norse) was treated sequentially with benzenesulfinyl chloride, *tert*-butyl hypochlorite, and tetrabutylammonium fluoride to yield **4h** which was treated with methyllithium to give **5h** as a mixture of diastereomers. The diastereomers were separated by medium-pressure liquid chromatography on silica gel with hexane/EtOAc. The faster eluting diastereomer, **diastereomer A**, was isolated as a white solid: mp 108–109 °C; $[\alpha]_D$ +81.6° (*c* 1.0, $CHCl_3$); IR 3400–3100, 2980 (s), 1585 (w), 1445 (s), 1250 (br), 1165 (br), 975 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6 (m, 12), 5.1 (q, 1), 3.1 (s, 3), 1.7 (d, 3).

Diastereomer B was also a white solid: mp 88–89 °C; $[\alpha]_D$ –132.8° (*c* 1.0, $CHCl_3$); IR 3500–3150, 2995 (s), 2490 (w), 1615 (s), 1480 (s), 1465 (s), 1245 (br), 1185 (s), 1140 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6 (m, 2), 5.2 (q, 1), 3.0 (s, 3), 1.6 (d, 3). Anal. Calcd for $C_{19}H_{19}NOS$: C, 72.73; H, 6.40. Found: C, 72.80; H, 6.26.

2-(*N*-Methylphenylsulfonimidoyl)-1-phenylethanone (7). Titanium tetrachloride (5 drops) was added to a stirred solution of *N*-methylbenzenesulfonimidoyl fluoride (173 mg, 1 mmol) and 1-phenyl-1-(trimethylsiloxy)ethene (212 mg, 1.1 mmol) in dichloromethane at –78 °C. After 30 min the reaction mixture was diluted with water and extracted with dichloromethane. The combined extracts were dried over sodium sulfate and reduced in vacuo. The residue was chromatographed (50% ether/hexane) to afford the sulfoximine (77%) identical chromatographically and spectroscopically with an authentic sample.[7]

***S*-(4-Methoxyphenyl)-*N*-methyl-*S*-phenylsulfoximine (6).** An excess of gaseous boron trifluoride was bubbled through a stirred solution of *N*-methylbenzenesulfonimidoyl fluoride (**4a**; 250 mg, 1.45 mmol) and anisole (56 mg, 1.45 mmol) in dichloromethane (10 mL) at 0 °C. After 15 min the reaction mixture was allowed to warm to room temperature before being diluted with dichloromethane (10 mL) and 2 M sodium hydroxide (10 mL). The organic phase was separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic phases were dried over sodium sulfate and concentrated to an oil which was chromatographed (ether/hexane) to yield sulfoximine (240 mg, 63%), which was chromatographically and spectroscopically identical with an authentic sample.[2]

2-(*N*-Methylphenylsulfonimidoyl)cyclohexanone (8). Titanium tetrachloride (0.5 mL, 4.54 mmol) was added dropwise to a stirred solution of *N*-methylbenzenesulfonimidoyl fluoride (**4a**; 500 mg, 2.9 mmol) and 1-(trimethylsiloxy)cyclohexene (600 mg, 3.53 mmol) in dichloromethane (25 mL) at –78 °C. After 15 min the reaction mixture was poured into saturated aqueous sodium hydrogen carbonate and extracted with dichloromethane. The combined extracts were dried over sodium sulfate and concentrated. The residue was chromatographed (hexane/ether) to afford the product: 370 mg (51%); mp 88–89 °C (needles from hexane–dichloromethane); IR ($CHCl_3$) 1715 (w), 1635 (s, C=C of enol form), 1250, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.2 (m, 5), 2.63 (s, 3), 2.56–1.13 (m, 8). Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.15; H, 6.77. Found: C, 61.88; H, 6.77.

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Registry No. **1b**, 14934-02-2; **1c**, 14934-04-4; **1d**, 83706-17-6; **1e**, 14933-97-2; **1f**, 83706-18-7; **1g** (isomer 1), 83706-19-8; **1g** (isomer 2), 83706-20-1; **1h** (isomer 1), 83706-21-2; **1h** (isomer 2), 83706-22-3; **2a**, 15934-21-1; **2g** (isomer 1), 83706-23-4; **2g** (isomer 2), 83706-24-5; **2h** (isomer 1), 83706-25-6; **2h** (isomer 2), 83706-26-7; **4a**, 83706-27-8; **4b**, 83706-28-9; **4c**, 83706-29-0; **4d**, 83706-30-3; **4e**, 83706-31-4; **4f**, 83706-32-5; **4g** (isomer 1), 83706-33-6; **4g** (isomer 2), 83706-34-7; **4h** (isomer 1), 83706-35-8; **4h** (isomer 2), 83706-36-9; **5a**, 30004-67-2; **5b**, 56158-15-7; **5c**, 83706-37-0; **5d**, 83706-38-1; **5e**, 83706-39-2; **5f**, 83706-40-5; **5g** (isomer 1), 83706-41-6; **5g** (isomer 2), 83706-42-7; **5h** (isomer 1), 83706-43-8; **5h** (isomer 2), 83706-44-9; **5i**, 67087-36-9; **5j**, 54755-72-5; **6**, 69726-38-1; **7**, 83706-45-0; **8**, 83706-46-1; benzenesulfinyl chloride, 4972-29-6; 2-aminopyridine, 504-29-0; (–)-1-phenylethylamine, 2627-86-3; methyllithium, 917-54-4; (–)-1-naphthylethylamine, 10420-89-0; 1-phenyl-1-(trimethylsiloxy)ethene, 13735-81-4; anisole, 100-66-3; 1-(trimethylsiloxy)-cyclohexene, 6651-36-1; butyllithium, 109-72-8; phenyllithium, 591-51-5.

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Translocative Rearrangements. Generality of the Formamidine-Induced Rearrangement of 4-Substituted 5-Amino-4-cyano-4*H*-imidazoles

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The generality of two different courses of cyclization reactions for 4-substituted 5-amino-4-cyano-4*H*-imidazoles (**5**) is demonstrated. One results from treatment of **5** with formamidine in a "translocative rearrangement" that leads to 8-substituted 4-aminoimidazo[1,5-*a*]-1,3,5-triazines (**7**). The other results from treatment with dimethyl acetylenedicarboxylate, without rearrangement, that leads to 8-substituted 8-cyano-8*H*-imidazo[1,5-*a*]pyrimidin-4-ones (**10**).

In the course of our investigation of rearrangement reactions best explained by the transient intermediacy of 5-substituted 5*H*-purines,[1-3] we discovered one reaction sequence in which the overall result is to remove a C≡N

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