pentane agreed with that appearing in the literature.[11]

Hydrolysis of *F*-Methoxycyclopentane. *F*-Methoxycyclopentane (0.321 g) was condensed onto an approximately equal volume of fuming sulfuric acid (30% SO_3) which had been degassed and vacuum stripped to remove the SO_3; the reaction tube was then sealed under vacuum and heated in a tube furnace at 360 °C for 24 h. The tube was then opened on the vacuum line and the reaction mixture fractionated through -131 and -196 °C cold traps, most of the material being collected in the -131 °C trap. Products from the -131 °C fraction were separated on the SE-52 column (temperature program: -10 °C, 5 min; 0.5 °C/min to 20 °C) and identified as *F*-cyclopentanone[11] (0.140 g) and unreacted *F*-methoxycyclopentane (0.103 g). The percent yield of *F*-cyclopentanone based on *F*-methoxycylopentane reacted was thus 89%, and the percent conversion for the reaction was 61%.

Aerosol Fluorination of Methoxycyclohexane. Methoxycyclohexane was prepared by the method of Vogel from cyclohexanol.[12] A pump speed corresponding to 3.8 mmol/h was established, and 3.30 mL (2.89 g, 25.3 mmol) of methoxycyclohexane was delivered over a 6.75-h period. From the 3.32 g of crude product collected 2.99 g (90%) of pure *F*-methoxycyclohexane was isolated (QF-1 program: 35 °C, 10 min; 4 °C/min to 100 °C, 100 °C/min; 50 °C/min to 180 °C) which correspond to a yield of 32% based on total methoxycyclohexane injected. The ^{19}F NMR spectrum of *F*-methoxycyclohexane was in agreement with the appearing in the literature.[11]

Hydrolysis of *F*-Methoxycyclohexane. *F*-Methoxycyclohexane (0.308 g) was treated with 100% sulfuric acid as described above and heated for 14 h at 340 °C. After a workup of the reaction mixture as for *F*-methoxycyclopentane, separation on the SE-52 column (0 °C, 10 min; 1 °C/min to 100 °C) yielded *F*-cyclohexanone[11] (0.066 g) and unreacted *F*-methoxycyclohexane (0.202 g). The percent yield of *F*-cyclohexanone based on the amount of *F*-methoxycyclohexane reacted was 82%, and the percent conversion to product for the reaction was 28%.

Aerosol Fluorination of 1,4-Dioxaspiro[4.4]nonane. 1,4-Dioxaspiro[4.4]nonane was prepared by the method of Daignault and Eliel from cyclopentanone.[13] A pump speed corresponding to 4.2 mmol/h was established, and 3.0 mL (3.21 g, 25.1 mmol) of 1,4-dioxaspiro[4.4]nonane was delivered over a 6-h period. Details of the aerosol fluorination parameters are available as supplementary materials. The crude product (1.65 g) was separated on the QF-1 column (30 °C, 5 min; 5 °C/min to 100 °C; 100 °C, 1 min; 50 °C/min to 180 °C) and yielded 1.22 g (74%) of pure *F*-1,4-dioxaspiro[4.4]nonane, corresponding to a 14% yield based on total 1,4-dioxaspiro[4.4]nonane injected. The ^{19}NMR consists of three singlets of equal intensity at φ -85.32, -130.36, and -131.69. Anal. Calcd for $C_7F_{12}O_2$: C, 24.44; F, 66.26. Found: C, 24.22; F, 66.25.

Hydrolysis of *F*-1,4-Dioxaspiro[4.4]nonane. *F*-1,4-Dioxaspiro[4.4]nonane (0.156 g) was treated with 100% sulfuric acid (as prepared previously) and was heated for 24 h at 450 °C. Separation of the products on the SE-52 column (-10 °C, 5 min; 0.5 °C/min to 50 °C) yielded 0.024 g of *F*-cyclopentanone (isolated as the monohydrate) and 0.07 g of unreacted *F*-1,4-dioxaspiro-[4.4]nonane. The percent yield of *F*-cyclopentanone based on the amount of *F*-1,4-dioxaspiro[4.4]nonane reacted was 45%, and the percent conversion to product for the reaction was 23%.

Aerosol Fluorination of 1,4-Dioxaspiro[4.5]decane. 1,4-Dioxaspiro[4.5]decane was prepared by the method of Daignault and Eliel from cyclohexanone.[13] A pump speed corresponding to 4.3 mmol/h was established and 3.0 mL (3.1 g, 21.5 mmol) of 1,4-dioxaspiro[4.5]decane was delivered over a 5-h period. The crude products (1.28 g) were separated on the QF-1 column (50 °C, 5 min; 2 °C/min to 100 °C; 100 °C, 1 min; 50 °C/min to 180 °C) and yielded 0.97 g (76%) pure *F*-1,4-doxaspiro[4.5]decane, corresponding to a percent yield of 12% based on total 1,4-dioxaspiro[4.5]decane injected. The *F*-1,4-dioxaspiro[4.5]decane ^{19}F NMR consisted of a singlet at ϕ -83.22 and a broad multiplet at ϕ -132.02 (4:10 relative intensity). Anal. Calcd for $C_8F_{14}O_2$: C, 24.38; F, 67.49. Found: C, 23.85; F, 66.78.

Hydrolysis of *F*-1,4-Dioxaspiro[4.5]decane. *F*-1,4-Dioxaspiro[4.5]decane (0.198 g) was treated with 100% sulfuric acid (as prepared previously) and was heated for 18 at 500 °C. Separation of the products on the SE-52 column (0 °C, 10 min; 1 °C/min to 100 °C) yielded 0.050 g *F*-cyclohexanone and 0.127 g unreacted *F*-1,4-dioxaspiro[4.5]decane, both identified from their infrared spectra. The percent yield of *F*-cyclohexanone based on *F*-1,4-dioxaspiro[4.5]decane reacted was 100%, and the percent conversion to products for the reaction was 36%.

Acknowledgment. This work was supported in part by the Office of Naval Research, whose support is gratefully acknowledged.

Registry No. Ia, 5614-37-9; Ib, 931-56-6; IIa, 788-40-9; IIb, 4943-06-0; IIIa, 376-66-9; IIIb, 1898-91-5; IVa, 176-32-9; IVb, 177-10-6; Va, 87901-77-7; Vb, 87901-78-8.

Supplementary Material Available: Characterization data for the products (IR, MS, ^{19}F NMR, aerosol parameters) (6 pages). Ordering information is given on any current masthead page.

(12) Vogel, A. I. *J. Chem. Soc.* **1948**, 1809.
(13) Daignault, R. A.; Eliel, E. L. *Org. Synth.* **1967**, *47*, 37.

Synthesis of 3-Nitro-5-acylpyridines by Condensation of Sodium Nitromalonaldehyde/Tosyl Chloride with 2-Amino-1-acyl Olefins. Evidence for the Intermediacy of 3-Chloro-2-nitroacrolein

Jacob M. Hoffman,* Brian T. Phillips, and David W. Cochran

Merck Sharp & Dohme Research Laboratories, West Point, Pennsylvania 19486

Received August 12, 1983

A search for a convenient synthesis of 3-nitro-5-acetylpyridine (**1a**) led to an investigation of the method developed by Fanta.[1] Ethyl 2-methyl-5-nitronicotinate (**1d**) was prepared in 35% yield by the condensation of sodium nitromalonaldehyde (**2**)[2] with ethyl 3-aminocrotonate, which was assumed to be generated in situ at -10 °C from ethyl acetoacetate and ammonia. However, with 4-amino-3-buten-2-one[3] or ethyl 3-aminocrotonate prepared by other methods,[4] the reaction with sodium nitromalonaldehyde gave only traces (~1%) of the respective nitropyridines **1a** and **1d**. Closer examination revealed that the solid intermediate formed in the Fanta procedure and assumed to be ethyl 3-aminocrotonate is, in fact, the ammonium salt of ethyl acetoacetate. When this solid is warmed to room temperature, ammonia gas is rapidly evolved, leaving a liquid residue identified as ethyl acetoacetate. Furthermore, when 1 equiv of ammonium hydroxide was added to a mixture of sodium nitromalonaldehyde and ethyl acetoacetate in water, the literature yield (34%) of **1d** was reproduced. These results coupled with literature precedent[6] would suggest that the formation of **1d** involved initial condensation of the anion of ethyl acetoacetate with sodium nitromalonaldehyde, amination of the dicarbonyl intermediate with ammonia, and subsequent ring closure. This approach was not ap-

(1) Fanta, P. E. *J. Am. Chem. Soc.* **1953**, *75*, 737.
(2) Fanta, P. E. "Organic Synthesis"; Wiley: New York, 1963; Collect. Vol. IV, p 844.
(3) Micheel, F.; Dralle, H. *Liebigs Ann. Chem.* **1963**, *670*, 57.
(4) Hope, E. *J. Chem. Soc.* **1922**, *121*, 2216; prepared most conveniently by the method in ref 5.
(5) Zymalkowski, F.; Rimek, H. *Arch. Pharm. (Weinheim, Ger.)* **1961**, *294*, 759.
(6) For a review, see: Fanta, P. E.; Stein, R. A. *Chem. Rev.* **1960**, *60*, 261. For a more recent reference, see: Kvitko, S. M.; Maksimov, Y. V.; Paperno, T. Y.; Perekalin, V. V. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 477 (*Zh. Org. Khim.* **1973**, *9*, 471).

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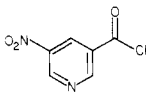
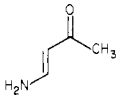
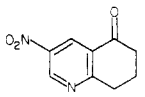
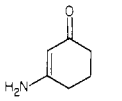
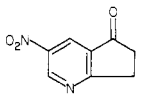
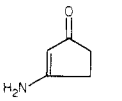
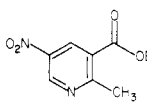
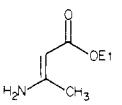
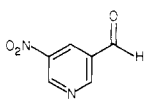
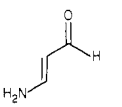
Table I. Formation of 3-Nitropyridines 1 from Sodium Nitromalonaldehyde/Tosyl Chloride

product	mp, °C	recrystn yield,[a] %	rctnt 3	(lit. ref)
 (1a)	84-86	53		(3)
 (1b)	120-121	54		(5)
 (1c)	158-160	10		(9)
 (1d)	63-64	61[b]		(4)
 (1e)	69-70	5		(10)

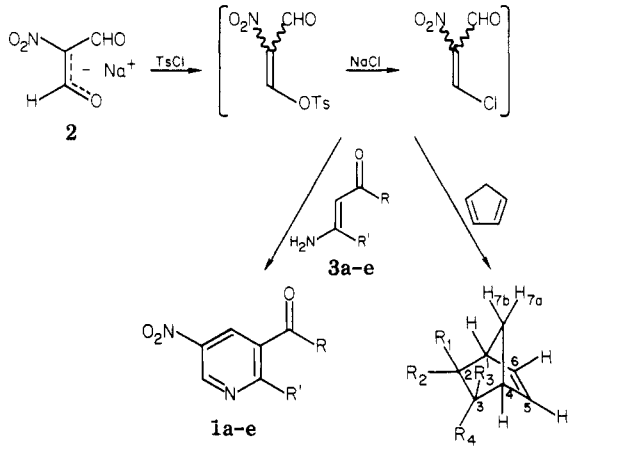
[a] All products crystallized from hexane/*n*-butyl chloride (6:1). [b] Lit.[1] mp 64-65 °C.

plicable to the synthesis of the desired 3-nitro-5-acetylpyridine (**1a**).

Early reports[6] indicated that nitromalonaldehyde and its sodium salt condensed with aniline and urea derivatives to form 3-(substituted imino)-2-nitropropionaldehydes. However, our lack of success in reactions involving vinylogous analogues prompted an investigation of methods to activate nitromalonaldehyde toward additions with 2-amino-1-acyl olefins such as 4-amino-3-buten-2-one. On the basis of the report[7] that sodium nitromalonaldehyde is readily acylated with acetic anhydride via the enolic hydroxy tautomer to give the acylal derivative of 3-acetoxy-2-nitroacrolein, 1,3,3-triacetoxy-2-nitro-1-propene, the tosylation of **2** would be expected to yield a very active Michael acceptor. Indeed, under anhydrous conditions tosyl chloride reacted with sodium nitromalonaldehyde (**2**) in dimethylformamide, followed by the addition of 4-amino-3-buten-2-one, to give a modest yield (29%) of 3-nitro-5-acetylpyridine (**1a**). Since base is expected to catalyze the final ring-closure step, addition of 4 equiv of pyridine to the dimethylformamide solvent resulted in the optimization of the yield of **1a** at 53%. Several novel 3-nitropyridines were prepared to evaluate the scope of this reaction. The results that are listed in Table I represent recrystallized product yields following complete disappearance of the aminoacyl olefins **3a–e**. The low yield of **1c** can be attributed to the increased ring strain during cyclization with the five-membered-ring aminoacyl olefin **3c**. The strong dipole of the aldehydic carbonyl group may decrease the nucleophilicity of **3e** sufficiently that the formation of **1e** is adversely affected. With crystalline ethyl 3-aminocrotonate the yield of ethyl 2-methyl-5-nitronicotinate (**1d**) was markedly improved (61%).

In an effort to characterize the initial intermediate generated from the reaction between sodium nitromalonaldehyde and tosyl chloride, cyclopentadiene was added to the reaction mixture to trap any dienophilic olefins generated. One major and two minor isomeric adducts

Scheme I



were isolated in 20% overall yield.[8] From an analysis of the NMR spectrum, it was evident that the adduct isolated lacked a tosyl group and in combination with the microanalysis of the (2,4-dinitrophenyl)hydrazone derivative was determined to be the chloro adduct **4a**, which would be derived from 3-chloro-2-nitroacrolein as indicated in Scheme I. The stereochemistry of the adduct **4a** was determined from detailed 360-MHz proton-decoupling experiments. The chloro group is exo to the norbornene double bond on the basis of the observation of a *W* coupling of 3.5 Hz between the H_3 and H_{7a} protons. The relative stereochemistry of the nitro and aldehydic groups could be assigned on the basis of known shielding effects.[11] Two minor isomeric adducts, **4b** and **4c**, were also formed that differed only in the relative configurations of the substituents about C_2 and C_3 of the norbornene ring.

In conclusion, a convenient synthesis of 3-nitro-5-acylpyridines from sodium nitromalonaldehyde/tosyl chloride and 2-amino-1-acyl olefins was developed, which obviated the need for elaborate functional group manipulations on the pyridine ring. In addition, the characterization of a Diels–Alder adduct **4a** suggests that 3-chloro-2-nitroacrolein is the intermediate formed from sodium nitromalonaldehyde and tosyl chloride.

Experimental Section

All routine proton NMR spectra were recorded on Varian Associates Model T-60 and EM-390 spectrometers. The detailed analyses of adducts **4a–c** were conducted on a Nicolet NT-360 spectrometer. All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

General Procedures. 5-Nitro-3-acetylpyridine (1a). A solution of sodium nitromalonaldehyde monohydrate[2] (0.79 g, 5.0 mmol) in dimethylformamide (3.4 mL) was dried over 4-Å sieves (1 g) for 2 h and filtered, and the sieves were washed with DMF (1 mL). Pyridine (1.6 mL, 20 mmol) was added to the filtrate, under N_2, and the red solution was cooled to −5 °C. A solution of *p*-toluenesulfonyl chloride (0.98 g, 5.0 mmol) in DMF (2 mL) was added dropwise, while the temperature was maintained below 0 °C. The solution became very viscous and was allowed to warm

(7) Kvitko, S. M.; Perekalin, V. V.; Maksimov, Y. V. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 2245 (*Zh. Org. Khim.* **1973**, *9*, 2228).

(8) A mixture of two minor isomeric adducts accounting for <5% of the adduct yield was characterized by NMR; see Experimental Section.

(9) Ruangsiyanand, C.; Rimek, H.-J.; Zymalkowski, F. *Chem. Ber.* **1920**, *103*, 2403; prepared by the method in ref 5.

(10) Thummel, R. P.; Kohli, D. K. *J. Org. Chem.* **1977**, *42*, 2742.

(11) Doerffel, V. K.; Kasper, H.; Zimmermann, G. *J. Prakt. Chem.* **1974**, *316*, 645.

to room temperature. A solution of 4-amino-3-buten-2-one[3] (0.42 g, 5.0 mmol) in DMF (4.0 mL) was added dropwise and the resultant homogeneous solution was stirred for 2 h. The solvent was removed under vacuum. The residue was dissolved in chloroform and washed with 5% Na_2CO_3 solution, and the chloroform layer was dried (Na_2SO_4), filtered, and evaporated. The crude material was chromatographed on silica gel, eluting with chloroform. The isolated product was crystallized from hexane/*n*-BuCl (6:1) to give 0.44 g (53%) of product: mp 84–86 °C; NMR ($CDCl_3$) δ 2.7 (s, 3 H), 9.0 (dd, J = 2, 3 Hz, H_4), 9.4 (d, J = 2 Hz, H_2), 9.6 (d, J = 3 Hz, H_6). Anal. Calcd for $C_7H_6N_2O_3$: C, 50.60; H, 3.64; N, 16.87. Found: C, 50.84; H, 3.36; N, 16.88.

3-Nitro-5,6,7,8-tetrahydroquinolin-5-one (1b): NMR ($CDCl_3$) δ 2.3 (m, 2 H_7), 2.8 (t, J = 6 Hz, 2 H_6), 3.3 (t, J = 8.9 Hz, 2 H_8), 8.9 (d, J = 3 Hz, H_4), 9.4 (d, J = 3 Hz, H_2). Anal. Calcd for $C_9H_8N_2O_3$: C, 56.25; H, 4.20; N, 14.58. Found: C, 56.38; H, 4.16; N, 14.36.

3-Nitro-5-oxo-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (1c): NMR ($CDCl_3$) δ 2.9 (m, 2 H_6), 3.4 (m, 2 H_7), 8.8 (d, J = 2 Hz, H_4), 9.6 (d, J = 2 Hz, H_2). Anal. Calcd for $C_8H_6N_2O_3$: C, 53.93; H, 3.39; N, 15.73. Found: C, 53.85; H, 3.41; N, 15.91.

5-Nitronicotinaldehyde (1e): NMR ($CDCl_3$) δ 8.9 (dd, J = 2 Hz, H_4), 9.4 (d, J = 2 Hz, H_2), 9.6 (d, J = 2 Hz, H_6), 10.3 (s, CHO). Anal. Calcd for $C_6H_4N_2O_3$: C, 47.37; H, 2.65; N, 18.42. Found: C, 47.38; H, 2.65; N, 18.59.

***endo*-2-Nitro-*exo*-3-chloro-5-norbornene-*exo*-2-carboxaldehyde (4a).** A solution of sodium nitromalonaldehyde monohydrate (3.14 g, 20 mmol) in DMF (18 mL) was dried over 4-Å sieves (4.0 g) for 2 h. The sieves were removed by filtration and washed with DMF (6 mL) and the combined filtrate was cooled to −5 °C. A solution of *p*-toluenesulfonyl chloride (3.81 g, 20 mmol) in DMF (18 mL) was added dropwise, while the temperature was maintained below 0 °C. After 15 min, a solution of freshly prepared cyclopentadiene (2.64 g, 40 mmol) in DMF (16 mL) was added and the solution was stirred overnight. The reaction mixture was diluted with diethyl ether (400 mL) and the precipitated sodium tosylate (2.0 g) removed by filtration. The filtrate was concentrated under high vacuum and the residue extracted with hot hexane followed by hot *n*-butyl chloride. The combined extracts were concentrated, and the residue was redissolved in diethyl ether, washed with water, dried (Na_2SO_4), and evaporated to give 1.87 g of a dark oil. This was chromatographed on E. Merck silica gel, eluting with hexane/*n*-butyl chloride (1:1), to give 0.76 g (19%) of solid product, which was recrystallized from hexane to give 0.60 g of product, which became gummy upon removal of solvent: NMR ($CDCl_3$) δ 2.03 (d, d, t, J = 10.5, 3.3, 1.6 Hz, H_{7a}), 2.37 (br d, J = 10.5 Hz, H_{7b}), 3.19 (m, H_4), 3.54 (m, H_1), 4.70 (d, d, J = 3.5, 0.5 Hz, H_3), 6.20 (d, d, J = 5.5, 3 Hz, H_5), 6.45 (d, d, J = 5.5, 3.5 Hz, H_6), 9.57 (s, CHO).

This adduct was analyzed as its (2,4-dinitrophenyl)hydrazone derivative, mp 158–161 °C. Anal. Calcd for $C_{14}H_{12}ClN_5O_6$: C, 44.04; H, 3.17; N, 18.35. Found: C, 44.21; H, 3.11; N, 18.19.

A mixture of two isomeric adducts (<5% yield) was obtained from the mother liquors of adduct **4a**. This was analyzed by NMR, and the stereochemistry as illustrated in Scheme I is based on the following assignments: adduct **4b**, δ 1.68 (br d, J = 10.5 Hz, H_{7b}), 1.98 (br d, J = 10.5 Hz, H_{7a}), 3.39 (m, H_4), 3.82 (m, H_1), 5.33 (d, J = 3.5 Hz, H_3), 6.52 (d, d, J = 5.5, 3 Hz, H_5), 6.55 (d, d, J = 5.5, 3 Hz, H_6), 9.23 (s, C*H*O); adduct **4c**, δ 2.11 (d, q, J = 10.5, 2 Hz, H_{7a}), 2.72 (br d, J = 10.5 Hz, H_{7b}), 3.18 (m, H_4), 3.60 (m, H_1), 4.58 (d, J = 3.5 Hz, H_3), 5.99 (d, d, J = 5.5, 2.8 Hz, H_6), 6.37 (obscured by overlap, H_5), 9.48 (s, CHO).

Acknowledgment. The encouragement of Dr. W. C. Lumma, Jr. during the course of this work was much appreciated. The authors are indebted to J. Stranick and J. P. Moreau for microanalytical determinations, J. S. Murphy for some spectroscopic data, and M. Banker for manuscript preparation.

Registry No. **1a**, 87883-17-8; **1b**, 87883-18-9; **1c**, 87883-19-0; **1d**, 51984-71-5; **1e**, 87883-20-3; **2**, 34461-00-2; **3a**, 2976-86-5; **3b**, 5220-49-5; **3c**, 28566-12-3; **3d**, 7318-00-5; **3e**, 25186-34-9; **4a**, 87883-21-4; **4a** 2,4-dinitrophenylhydrazone, 87883-22-5; **4b**, 87935-87-3; **4c**, 87935-88-4; tosyl chloride, 98-59-9; 3-chloro-2-nitroacrolein, 87883-23-6.

Addition-Rearrangement Reaction of 3,4-Dihydro-2*H*-pyrans and 3,4-Dihydro-2-methoxy-2*H*-pyrans with (4-Methylphenyl)sulfonyl Isocyanate[1]

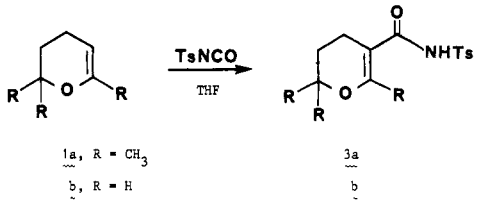
Joseph H. Chan[2] and Stan S. Hall*

Department of Chemistry, Olson Laboratories, Rutgers, The State University of New Jersey, Newark, New Jersey 07102

Received July 28, 1983

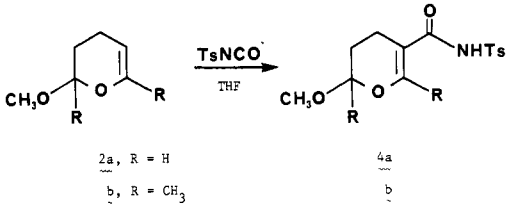
The cycloaddition and subsequent rearrangement reaction of alkyl vinyl ethers with (4-methylphenyl)sulfonyl isocyanate (TsNCO) has been extensively studied by Effenberger and his associates.[3] Herein we report the application of this reaction to a series of 3,4-dihydro-2*H*-pyrans (**1**) and 3,4-dihydro-2-methoxy-2*H*-pyrans (**2**) that results in the synthesis of a series of the corresponding 3,4-dihydro-*N*-[(4-methylphenyl)sulfonyl]-2*H*-pyran-5-carboxamides (**3**) and 3,4-dihydro-2-methoxy-*N*-[(4-methylphenyl)sulfonyl]-2*H*-pyran-5-carboxamides (**4**), respectively.

After a solution of dihydropyran **1a** and a slight excess of (4-methylphenyl)sulfonyl isocyanate in anhydrous tetrahydrofuran was stirred for 48 h, the solvent was removed and the residue crystallized to yield dihydropyran-5-carboxamide **3a** (88%). Similar treatment of dihydropyran **1b** formed dihydropyran-5-carboxamide **3b** in 83% yield.[4]



1a, R = CH_3 3a
b, R = H b

Analogous reactions with the 2-methoxydihydropyrans **2a** and **2b** yielded the corresponding 2-methoxydihydropyran-5-carboxamides **4a** and **4b** as the only condensation products in isolated yields of 74% and 58%, respectively.



2a, R = H 4a
b, R = CH_3 b

In contrast, treatment of 2-methoxy-6-methyldihydropyran (**2c**) with (4-methylphenyl)sulfonyl isocyanate in THF after 48 h yielded the expected 2-methoxy-6-methyldihydropyran-5-carboxamide **4c** (43%), as well as

(1) Part 9 in the series, "The Chemistry of 3,4-Dihydro-2-alkoxy-2*H*-pyrans". For part 8, see Weber, G. F.; Hall, S. S. *J. Org. Chem.* **1979**, *44*, 447–449.

(2) Taken in part from the Ph.D. thesis of J.H.C., Rutgers University, May 1982. Present address: Burroughs Wellcome Co., Research Triangle Park, NC 27709.

(3) (a) Effenberger, F.; Prossel, G.; Fischer, P. *Chem. Ber.* **1971**, *104*, 2002–2012. (b) Effenberger, F.; Fischer, P.; Prossel, G.; Gebhard, K. *Ibid.* **1971**, *104*, 1987–2001. (c) Effenberger, F. *Angew. Chem.* **1969**, *81*, 374–391. (d) Effenberger, F.; Kiefer, G. *Ibid.* **1967**, *79*, 936–937. (e) Effenberger, F.; Gleiter, R. *Chem. Ber.* **1964**, *97*, 1576–1583.

(4) This reaction with 3,4-dihydro-2*H*-pyran (**1b**) and TsNCO in Me_2SO and in refluxing benzene has been described in ref 3e. Analogous reactions with **1b** and trifluoroacetyl, (2,2,2-trichloroethyl)sulfonyl, and (2,2,2-trichloroethoxy)sulfonyl isocyanates [(a) Barrett, A. G. M.; Fenwick, A.; Bretts, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 299–301] and trichloroacetyl isocyanate [(b) Chitwood, J. L.; Gott, P. G.; Martin, J. C. *J. Org. Chem.* **1971**, *36*, 2228–2232; (c) Smith, L. R.; Speziale, A. J.; Fedder, J. E. *J. Org. Chem.* **1969**, *34*, 633–637] have also been reported.

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