evaporator. All operations that required exclusion of moisture were carried under dry N_2, using standard syringe-septum techniques.

Tricyclo[4.2.2.0^{2,5}]deca-3,7-dien-9-one (I).[4,10] To a solution of lithium diisopropylamide [6 mmol, prepared by adding 5 mL of 1.6 M *n*-butyllithium in hexane to a stirred solution of diisopropylamine (605 mg, 6 mmol) in 5 mL of dry THF at -78 °C] was added 9-cyanotricyclo[4.2.2.0^{2,5}]deca-3,7-diene (630 mg, 4 mmol)[5] in 5 mL of dry THF at -78 °C. Dry oxygen gas was bubbled at a moderate flow rate into the lithionitrile solution for 30 min at the same temperature. The reaction was quenched with 12 mL of 1 M stannous chloride in 2 M HCl and stirred for 1 h at ice temperature. The reaction mixture was diluted with water (50 mL) and extracted with ether (3 × 25 mL). Washing of the ether extract with 1 M NaOH (3 × 20 mL) and concentration yielded (600 mg) of an oily residue. Filtration through a silica gel (20 g) column and direct bulb-to-bulb distillation, bp 90 °C (bath) (8 mm), afforded 450 mg (77%) of I as a low-melting solid: IR (neat) 1720 cm^{-1} (carbonyl); ^{1}H NMR (100 MHz, $CDCl_3$) δ 5.7–6.3 (m, 4 H), 2.6–3.15 (m, 4 H), 2.1 (dd, 1 H, J_1 = 16 Hz, J_2 = 4 Hz), 1.75 (dd, 1 H, J_1 = 16 Hz, J_2 = 2 Hz).

3,4-Dibromo-9-chloro-9-cyanotricyclo[4.2.2.0^{2,5}]dec-7-ene (IX). Dibromocyclooctatetraene (9.25 g, 0.035 mol),[11] α-chloroacrylonitrile (9.25 g, 0.105 mol), and 2,6-di-*tert*-butylphenol (0.1 g) were heated in a sealed glass tube (3.5 × 12 cm, N_2 atmosphere) to 105 °C for 8 h. The sealed tube was cooled and carefully opened and its contents were filtered through a silica gel (100 g) column, using 20% benzene in petroleum ether as eluant. Crystallization of appropriate fractions from carbon tetrachloride furnished 7.5 g (61%) of IX: mp 181–182 °C; IR (KBr) 2250 cm^{-1} (cyano); ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.3–6.9 (m, 2 H), 4,6–5.0 (m, 1 H), 4.1–4.4 (m, 1 H), 2.8–3.9 (m, 4 H), 2.0–2.6 (m, 2 H). Anal. Calcd for $C_{11}H_{10}Br_2ClN$: C, 37.55; H, 2.84; N, 3.98. Found: C, 37.58; H, 3.04; N, 4.04.

3-(or 4-)-Bromotricyclo[4.2.2.0^{2,5}]deca-3,7-dien-9-one (II).[4,5] To a solution of the adduct IX (3.52 g, 10 mmol) in 12 mL of Me_2SO was added a hot solution of 1.5 g of KOH (assay 85%) in 1 mL of water. After being stirred at room temperature for 13 h, the reaction mixture was poured in ice-water (40 mL) and extracted with hexane (3 × 25 mL). The organic extract was washed well with water (3 × 25 mL) and concentrated. Direct sublimation of the residue afforded 1.95 g (86%) of II. The product appeared to be a regioisomeric mixture of two bromides from which the major bromide (II) crystallized from hexane: mp 83–84 °C; IR (KBr) 1730 cm^{-1} (carbonyl); ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.9–6.5 (m, 3 H, olefinic), 2.7–3.3 (m, 4 H, ring CH), 1.5–2.25 (dq, 2 H, $CH_2C{=}O$); ^{13}C NMR (22.64 MHz, $CFCl_3$) δ 139.4, 134.1, 127.0, 119.0 (all olefinic), 53.5, 50.0, 46.7, 37.4, 35.7 (carbonyl carbon not seen). Anal. Calcd for $C_{10}H_9BrO$: C, 53.33; H, 4.0. Found: C, 53.58; H, 3.79.

Schmidt Fragmentation of Tricyclo[4.2.2.0^{2,5}]deca-3,7-dien-9-one (I). To a stirred ice-cold solution of I (90 mg, 0.615 mmol) and methanesulfonic acid (1 mL) in dry dichloromethane (5 mL) was added sodium azide (41 mg, 0.615 mmol) in small portions. After being stirred for 5 min more, the solution was quenched in aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (2 × 15 mL). TLC examination (silica gel plates, solvent system 40% ethyl acetate in benzene) indicated the presence of two components. The reaction mixture was charged on a silica gel (10 g) column and eluted with 20% ethyl acetate in benzene to furnish the cyano mesylate (IV, 80 mg, 55%). Bulb-to-bulb distillation [165 °C (0.6 mm)] and crystallization from carbon tetrachloride yielded the crystalline compound: mp 65–66 °C; IR (KBr) 2250 (cyano), 1360 and 1180 cm^{-1} (mesylate ester); ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.25 (dd, 1 H, J_1 = 6 Hz, J_2 = 3 Hz), 5.75–6.15 (m, 2 H), 5.64 ($^1/_2$AB, 1 H, J = 10 Hz), 5.05 (t, 1 H, J = 5 Hz), 3.02 (s, 3 H, OSO_2CH_3), 2.85–3.05 (m, 1 H), 2.2–2.8 (m, 4 H); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 139.0 (d), 129.5 (d), 128.1 (d), and 127.5 (d) (olefinic), 118.6 (s, CN), 78.4 (d, COMs), 42.3 (d) and 40.3 (d) (bridge head C's), 38.6 (q, SO_3CH_3), 33.5 (d, allylic), 21.2 (t, CH_2CN). Anal. Calcd for $C_{11}H_{13}O_3SN$: C, 55.23; H, 5.48; N, 5.85. Found: C, 55.25; H, 5.21; N, 5.76.

Further elution of the column with 50% ethyl acetate in benzene yielded 22 mg (22%) of 7-azatricyclo[4.3.2.0^{2,5}]undeca-3,11-dien-8-one (V): mp 178 °C (crystallized from ether); IR (CH_2Cl_2) 3410, 1665 cm^{-1} (lactam); ^{1}H NMR (100 MHz, $CDCl_3$) δ 5.6–6.45 (m, 5 H, olefinic and NH), 3.3–3.6 (m, 3 H), 2.95–3.3 (m, 2 H), 2.55 (m, 1 H). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.42; H, 6.99; N, 8.75.

Schmidt Fragmentation of 3-(or 4-)-Bromotricyclo[4.2.2.0^{2,5}]deca-3,7-dien-9-one (II). Reaction of bromo ketone II (100 mg, 0.44 mmol) with sodium azide (29 mg, 0.45 mmol) in methanesulfonic acid–methylene chloride as described above resulted in 120 mg of crude mixture. Filtration through a silica gel (10 g) column, using 20% ethyl acetate in benzene as eluant, yielded 100 mg of the cyano mesylate VIII (70%): mp 110 °C (white needles from dichloromethane–petroleum ether); IR (KBr) 2255 (cyano), 1595 (olefinic), 1360, 1180 cm^{-1} (mesylate ester); ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.0–6.25 (m, 2 H), 5.8 ($^1/_2$AB, 1 H, J = 8 Hz), 5.18 (t, 1 H, J = 5 Hz), 3.05 (s, 3 H), 3.0–3.2 (m, 1 H), 2.3–2.9 (m, 4 H); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 129.0, 128.7, 128.0, and 126.3 (olefinic), 118.3 (CN), 76.2 (COMs), 47.1 and 43.8 (bridgehead C's), 38.5 (CH_3SO_3), 32.8 (allylic), 20.2 (CH_2CN). Anal. Calcd for $C_{11}H_{12}O_3NSBr$: C, 41.5; H, 3.71; N, 4.48. Found: C, 41.32; H, 3.71; N, 4.34.

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Registry No. I, 16282-05-6; II, 73382-94-2; III, 73395-57-0; IV, 76446-95-2; V, 76447-09-1; VIII, 76447-08-0; IX, 73374-41-1; α-chloroacrylonitrile, 920-37-6; dibromocyclooctatetraene, 76447-10-4.

(10) Selikson, S. J.; Watt, D. S. *J. Org. Chem.* **1975**, *40*, 267.
(11) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1.

Ethyl *N*-[(Trifluoromethanesulfonyl)oxy]carbamate: A New Reagent for the Synthesis of *N*-(Ethoxycarbonyl)sulfilimines

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Despite current interest in the chemistry of sulfilimines,[1] there are no general methods available for the synthesis of *N*-(alkoxycarbonyl)sulfilimines. The most useful procedures involve direct amination of sulfides of *N*-chlorocarbamates[2] and (alkoxycarbonyl)nitrenes (generated from azidoformates[3,4] or *N*-[(arenesulfonyl)oxy]carbamates),[5] but all of them suffer from limited applications. We now introduce ethyl *N*-[(trifluoromethanesulfonyl)oxy]carbamate (1)[6] as a new reactive aminating reagent of sulfides.

The reagent 1 was prepared in 72% overall yield by the reaction of the thallium salt[7] of ethyl *N*-hydroxycarbamate with trifluoromethanesulfonic anhydride[8] in methylene chloride at -30 to -40 °C (eq 1). The use of the sodium

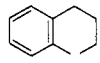
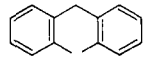
$$\mathrm{HONHCO_2Et} \xrightarrow[\text{2. } Tf_2O]{\text{1. TlOEt or NaOEt}} \underset{1}{\mathrm{TfONHCO_2Et}} \quad (1)$$

$$Tf = CF_3SO_2$$

(1) Gilchrist, T. L.; Moody, C. J. *Chem. Rev.* **1977**, *77*, 409.
(2) Whitfield, G. F.; Beilan, H. S.; Saika, D.; Swern, D. *J. Org. Chem.* **1974**, *39*, 2148.
(3) Ando, W.; Ogino, N.; Migita, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2278.
(4) Appleton, D. C.; Bull, D. C.; McKenna, J.; McKenna, J. M.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 385.
(5) Okahara, M.; Swern, D. *Tetrahedron Lett.* **1969**, 3301.
(6) For a review of trifluoromethanesulfonic acid derivatives, see: Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.
(7) Chapman, T. M.; Freedman, E. A. *Synthesis* **1971**, 591.
(8) Burdon, J.; Farazmand, I.; Stacey, M.; Tatlow, J. C. *J. Chem. Soc.* **1957**, 2574.

0022-3263/81/1946-1732$01.25/0

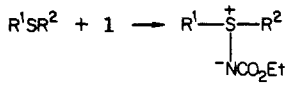
Table I. Preparation of *N*-(Ethoxycarbonyl)sulfilimines 2

compd	R^1	R^2	yield, %
2a	Et	Et	84
2b	$PhCH_2$	$PhCH_2$	79
2c	Ph	Me	94
2d	Ph	n-C_4H_9	97
2e	Ph	$(CH_2)_3CO_2Et$	61
2f			63
2g	Ph	Ph	62 (76[a])
2h			67

[a] The reaction was carried out in the presence of a small amount of trifluoroacetic acid.

salt in place of the thallium salt also gave 1 but in lower yield. This compound is a stable colorless oil which could be distilled at 80–81 °C (0.3 mmHg).

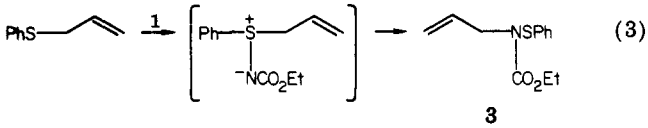
S-Amination was effected by treating a sulfide (1 mmol) with 1 (1.3 mmol) in methylene chloride at room temperature for 4–6 h. Treatment of the reaction mixture with sodium bicarbonate gave the sulfilimine 2 (eq 2). The


(2)

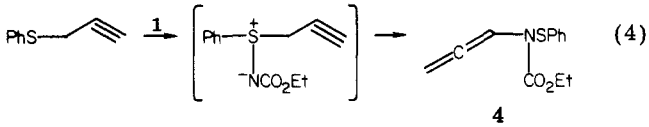
2

results are summarized in Table I. It is interesting to note that the reaction was catalyzed by acid. Thus, the reaction with diphenyl sulfide in the presence of a small amount of trifluoroacetic acid was complete within 6 h, while the starting material did not disappear in the absence of the acid. The structures of the sulfilimines were apparent from their spectroscopic data (see Experimental Section).

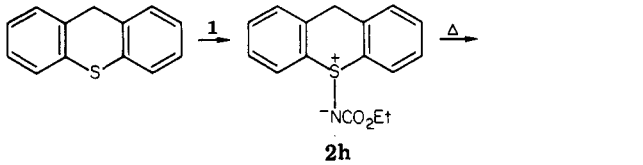
Application of this procedure to phenyl allyl sulfide and phenyl propargyl sulfide gave the sulfenamides 3 and 4 (eq 3 and 4) in 77% and 84% yields, respectively, which arose


(3)

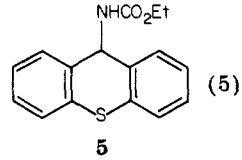
3


(4)

4



2h


(5)

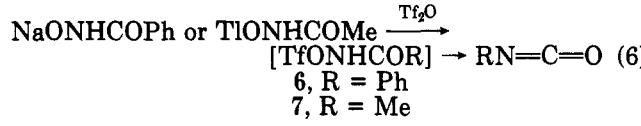
5

via [2,3] sigmatropic rearrangement of the intermediary sulfilimines. Similar rearrangements have been observed previously with the related sulfilimines.[9-11] Thioxanthene gave the corresponding *N*-(ethoxycarbonyl)sulfilimine **2h** in 67% yield, which, during attempted recrystallization from refluxing ethyl acetate, underwent rearrangement to 9-[(ethoxycarbonyl)amino]thioxanthene (5) in quantitative yield.[12]

This new procedure for the synthesis of the *N*-(ethoxycarbonyl)sulfilimines has several advantages over the previously known methods: (i) the yield is high; (ii) the scope is wide; (iii) a large excess of the sulfide is not required.

This reagent can also aminate triphenylphosphine to give *N*-(ethoxycarbonyl)triphenylphosphinimine in 61% yield. However, the reaction with tertiary amines such as pyridine or triethylamine did not give the expected N-aminated products, presumably because proton abstraction from the reagent takes place prior to nucleophilic substitution.

An attempt to prepare *N*-[(trifluoromethanesulfonyl)oxy]benzamide (6) and -acetamide (7) by a similar procedure to that used for the preparation of 1 resulted in the formation of phenyl and methyl isocyanates, respectively (eq 6), which arose via a Lossen rearrangement of 6 and 7.


(6)

6, R = Ph
7, R = Me

Experimental Section

Ethyl *N*-[(Trifluoromethanesulfonyl)oxy]carbamate (1).[13] To a solution of ethyl *N*-hydroxycarbamate (1.05 g, 10 mmol) in acetone (30 mL) was added thallium ethoxide (2.49 g, 10 mmol) at 0 °C. The mixture was stirred at 0 °C for 20 min, and the precipitated white solid was collected and dried to give the thallium salt (2.93 g, 95%). The crude material (1.33 g, 4.3 mmol) was suspended in methylene chloride (50 mL), and trifluoromethanesulfonic anhydride (1.18 g, 4.4 mmol) was added at −30 to −40 °C with stirring. After the reaction mixture was stirred at the same temperature for 2 h, the precipitated thallium trifluoromethanesulfonate was filtered off. The filtrate was concentrated and distilled to give 1 as a colorless oil: bp 80–81 °C (0.3 mm); IR ($CHCl_3$) 3360, 1770, 1750, 1430, 1130 cm^{-1}; NMR ($CDCl_3$) δ 9.1 (1, br s), 4.34 (2 q, J = 7 Hz), 1.35 (3, t, J = 7 Hz).

Anal. Calcd for $C_4H_6F_3NO_5S$: C, 20.26; H, 2.55; N, 5.91. Found: C, 20.32; H, 2.55; N, 6.25.

The use of sodium ethoxide in place of thallium ethoxide gave the sodium salt of ethyl *N*-hydroxycarbamate in 66% yield which, upon treatment with trifluoromethanesulfonic anhydride, afforded 1 in 50% yield.

General Procedure for *N*-(Ethoxycarbonyl)sulfilimines (2). To a solution of the sulfide (1 mmol) in methylene chloride (10 mL) was added 1 (1.3 mmol). The mixture was stirred at room temperature for 4–6 h, washed with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated. The residue was purified either by recrystallization or by column chromatography on silica gel (AcOEt as eluant).

***S,S*-Diethyl-*N*-(ethoxycarbonyl)sulfilimine (2a):** an oil;[2] IR ($CHCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$) δ 4.09 (2, q, J = 7 Hz), 2.98 (4, q, J = 7 Hz), 1.37 (6, t, J = 7 Hz), 1.25 (3, t, J = 7 Hz).

***S,S*-Dibenzyl-*N*-(ethoxycarbonyl)sulfilimine (2b):** mp 106–107 °C (from isopropyl ether); IR ($CHCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.27 (10, s), 4.28, 4.05 (2 each, AB q, J = 14 Hz), 4.07 (2, q, J = 7 Hz), 1.24 (3, t, J = 7 Hz); mass spectrum, m/e (relative

(9) Ash, A. S. F.; Challenger, F.; Stevens, T. S.; Dunn, J. L. *J. Chem. Soc.* **1952**, 2792.

(10) Atkinson, R. S.; Awad, S. B. *J. Chem. Soc., Perkin Trans. 1* **1977**, 346.

(11) Tamura, Y.; Matsushima, H.; Ikeda, M.; Sumoto, K. *Tetrahedron* **1976**, *32*, 431.

(12) Tamura, Y.; Mukai, C.; Nakajima, N.; Ikeda, M. *J. Org. Chem.* **1980**, *45*, 2972 and references cited therein.

(13) Melting points are uncorrected. NMR spectra were determined with a Hitachi R-22 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded with a JASCO IRA-1 spectrophotometer. Low- and high-resolution mass spectra were obtained with a JMS-D-300 instrument with a direct-inlet system operating at 70 eV.

intensity) 301 (M^+, 0.6), 246 (1.5), 214 (4.6), 91 (100).

Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.70; H, 6.34; N, 4.70.

S-Methyl-S-phenyl-N-(ethoxycarbonyl)sulfilimine (2c): mp 77-78 °C (from isopropyl ether); IR ($CHCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.4-7.9 (5, m), 4.09 (2, q, J = 7 Hz), 2.82 (3, s), 1.27 (3, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 211 (M^+, 7.9), 168 (40.9), 138 (9.9), 124 (100).

Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.84; H, 6.20; N, 6.63. Found: C, 56.90; H, 6.19; N, 6.61.

S-n-Butyl-S-phenyl-N-(ethoxycarbonyl)sulfilimine (2d): an oil; IR ($CHCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.4-7.9 (5, m), 4.10 (2, q, J = 7 Hz), 3.3-2.6 (2, m), 1.28 (3, t, J = 7 Hz), 1.9-0.7 (7, m); mass spectrum, m/e (relative intensity) 254 (M^+ + 1, 0.8), 253 (M^+, 0.1), 208 (15.9), 197 (100).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{13}H_{20}NO_2S$ (M^+ + 1 ion) m/e 254.1213, found m/e 254.1208.

S-[3-(Ethoxycarbonyl)propyl]-S-phenyl-N-(ethoxycarbonyl)sulfilimine (2e): an oil; IR ($CHCl_3$) 1720, 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.4-8.0 (5, m), 4.11 (4, q, J = 7 Hz), 3.2-3.0 (2, m), 2.65-1.85 (4, m), 1.27 (3, t, J = 7 Hz), 1.23 (3, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 312 (M^+ + 1, 0.1), 311 (M^+, 0.1), 266 (9.9), 224 (8.6), 197 (80.3), 115 (100).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{15}H_{21}NO_4S$, m/e 311.1190; found, m/e 311.1190.

Thiochroman-N-(ethoxycarbonyl)sulfilimine (2f): an oil; IR ($CHCl_3$) 1620 cm^{-1}; NMR ($CDCl_3$) δ 7.1-8.0 (4, m), 4.09 (2, q, J = 7 Hz), 3.6-1.9 (6, m), 1.26 (3, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 237 (M^+, 4.8), 192 (10.6), 149 (100).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{12}H_{15}NO_2S$, m/e 237.0821; found, m/e 237.0818.

S,S-Diphenyl-N-(ethoxycarbonyl)sulfilimine (2g): mp 88.5-89 °C (from isopropyl ether) (lit.[14] mp 88.5-89 °C).

Thioxanthene-N-(ethoxycarbonyl)sulfilimine (2h): thermally unstable crystals; IR ($CHCl_3$) 1640 cm^{-1}; NMR ($CDCl_3$) δ 7.1-8.0 (8, m), 4.47, 3.92 (1 each, AB q, J = 17 Hz), 4.18 (2, q, J = 7 Hz), 1.30 (3, t, J = 7 Hz).

Ethyl N-Allyl-N-phenylthiocarbamate (3). By use of a procedure similar to that described for **2**, **3** was obtained from allyl phenyl sulfide (50 mg) and **1** (100 mg) in a 77% yield as an oil: IR ($CHCl_3$) 1690 cm^{-1}; NMR ($CDCl_3$) δ 7.22 (5, s), 6.4-4.9 (3, m), 4.23 (2, q, J = 7 Hz), 4.19 (2, dd, J = 6, 1 Hz), 1.28 (3, t, J = 7 Hz).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{12}H_{15}NO_2S$, m/e 237.0822; found, m/e 237.0817.

Ethyl N-Allenyl-N-phenylthiocarbamate (4). By use of a procedure similar to that described for **2**, **4** was obtained from phenyl propargyl sulfide (100 mg) and **1** (192 mg) in 86% as an oil: IR ($CHCl_3$) 1970, 1700 cm^{-1}; NMR ($CDCl_3$) δ 7.4-7.0 (6, m), 5.31 (2, d, J = 6 Hz), 4.24 (2, q, J = 7 Hz), 1.29 (3, t, J = 7 Hz).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{12}H_{13}NO_2S$, m/e 235.0664; found, m/e 235.0665.

9-[(Ethoxycarbonyl)amino]thioxanthene (5). A solution of **2h** (100 mg) in ethyl acetate (4 mL) was refluxed for 3 min and concentrated to give **5**: 100 mg; mp 175-176 °C (from AcOEt); IR ($CHCl_3$) 3420, 1700 cm^{-1}; NMR ($CDCl_3$) δ 7.7-7.0 (8, m), 5.88 (1, d, J = 10 Hz), 5.5-5.1 (1, br), 4.09 (2, q, J = 7 Hz), 1.20 (3, t, J = 7 Hz).

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.10; H, 5.40; N, 4.86. Found: C, 67.34; H, 5.30; N, 4.91.

N-(Ethoxycarbonyl)triphenylphosphinimine. To a solution of triphenylphosphine (100 mg, 0.38 mmol) in methylene chloride (5 mL) was added **1** (130 mg, 0.55 mmol), and the mixture was stirred at room temperature for 30 min. The reaction mixture was washed with $NaHCO_3$, dried ($MgSO_4$), and concentrated to give crystals of N-(ethoxycarbonyl)triphenylphosphinimine: 92 mg (61%); mp 135-136.5 °C (from ether) (lit.[2] mp 135-136 °C).

Attempted Preparation of N-[(Trifluoromethanesulfonyl)oxy]benzamide (6). To a suspension of sodium benzohydroxamate (318 mg, 2 mmol) in methylene chloride (10 mL) was added with stirring a solution of trifluoromethanesulfonic anhydride (584 mg, 2 mmol) in methylene chloride (5 mL) at -40 °C. The mixture was stirred at room temperature for 3 h. The precipitate was filtered off, and the filtrate was concentrated. The residue was diluted with ether, filtered, and concentrated to give phenyl isocyanate (124 mg, 52%), which was identified by IR spectral comparison with an authentic sample and by its conversion to N,N'-diphenylurea [mp 233-235 °C (lit.[15] mp 235 °C)] by treatment with aniline.

Attempted Preparation of N-[(Trifluoromethanesulfonyl)oxy]acetamide (7). To a solution of acetohydroxamic acid (300 mg, 4 mmol) in acetone (15 mL) was added dropwise thallium ethoxide (998 mg, 4 mmol), and the mixture was stirred at room temperature for 3 h. The precipitated white thallium salt was collected, washed with acetone, and dried. The thallium salt (1.08 g, 3.88 mmol) was suspended in methylene chloride (15 mL), and solution of trifluoromethanesulfonic anhydride (1.09 g, 3.88 mmol) in methylene chloride (10 mL) was added dropwise at -40 to -50 °C. The mixture was stirred at room temperature for 3 h. The precipitate was filtered off. The filtrate was concentrated under reduced pressure below 25 °C. The residue was an intractable mixture. The distillate was collected in a trap cooled at -78 °C and treated with aniline to give diphenylurea (18 mg, 2%) and N-methyl-N'-phenylurea: 21 mg (3.5%); mp 148-150 °C (lit.[16] mp 151-152 °C).

Registry No. 1, 76447-86-4; **2a**, 37939-75-6; **2b**, 76447-87-5; **2c**, 59742-66-4; **2d**, 76447-88-6; **2e**, 76447-89-7; **2f**, 76447-90-0; **2g**, 39149-62-7; **2h**, 76447-91-1; **3**, 76447-92-2; **4**, 76447-93-3; **5**, 35707-41-6; ethyl N-hydroxycarbamate, 589-41-3; ethyl N-hydroxycarbamate thallium salt, 76447-94-4; ethyl N-hydroxycarbamate sodium salt, 54149-38-1; allyl phenyl sulfide, 5296-64-0; phenyl propargyl sulfide, 5651-88-7; N-(ethoxycarbonyl)triphenylphosphinimine, 17437-51-3; triphenylphosphine, 603-35-0; sodium benzohydroxamate, 22513-32-2; acetohydroxamic acid, 546-88-3; acetohydroxamic acid thallium salt, 76447-95-5; diphenylurea, 102-07-8; N-methyl-N'-phenylurea, 1007-36-9; ethyl sulfide, 352-93-2; benzyl sulfide, 538-74-9; methyl phenyl sulfide, 100-68-5; butyl phenyl sulfide, 1126-80-3; ethyl 4-(phenylthio)butanoate, 29193-72-4; thiochroman, 2054-35-5; phenyl sulfide, 139-66-2; thioxanthene, 261-31-4.

(14) Tamura, Y.; Sumoto, K.; Matsushima, H.; Taniguchi, H.; Ikeda, M. *J. Org. Chem.* **1973**, *38*, 4324.

(15) Sonn, A. *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 2437.

(16) Scholl, R.; Holdermann, K. *Justus Liebigs Ann. Chem.* **1906**, *345*, 376.

Preparation of Vinylene Diacetate

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Recently, (Z)-vinylene diacetate (**1a**) has been shown to be useful as a 1,2-ethylenediol species for the photochemical cycloaddition with 1,3-diacetoxy-2-propanone; the adduct was converted to a branched-chain sugar, DL-apiose.[1] However, **1** was obtained in only 14% yield[2] by pyrolysis of 1,1,2-triacetoxyethane (**2**),[3] which was prepared in 38% yield from vinyl acetate through addition of bromine followed by acetoxylation.[3] In order to make **1** a more promising material for photochemical reactions, we examined some preparative routes to **1**.

First we attempted enolacetylation of acetoxyacetaldehyde (**3**); **3**[4] was prepared from (E)-1,4-diacetoxy-2-

(1) Y. Araki, J. Nagasawa, and Y. Ishido, *J. Chem. Soc., Perkin Trans. 1*, 12-23 (1981).

(2) Several attempts at the pyrolysis of **2** carried out in our laboratory resulted in formation of **1** in yields of less than 5%.

(3) M. F. Shostakovskii, N. V. Kuznetsov, and C.-M. Yang, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 710-716 (1962).

0022-3263/81/1946-1734$01.25/0