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Reactive Triflate Alkylating Agents

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Trifluoromethanesulfonate esters of α-hydroxycarbonyl compounds, several derivatives of allyl alcohol, formaldehyde cyanohydrin, and propargyl alcohol have been prepared. In most cases, the triflates can be isolated by distillation or crystallization. All of the triflates prepared are reactive toward sulfides and can be used for convenient synthesis of substituted sulfonium salts. The allylic triflates are exceptionally reactive and attack a variety of S-, P-, N-, or O-containing molecules. The triflate of 2-ethoxyprop-2-en-1-ol has been characterized by formation of the corresponding triphenylphosphonium salt. The latter is a source of 2-ethoxyallylidenetriphenylphosphorane.

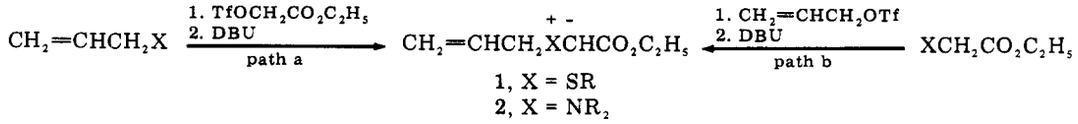
Synthetic projects under way in our laboratory require the conversion of highly functionalized allylic sulfides or amines into carbonyl-stabilized ylides. We had hoped to prepare ylides such as **1** or **2** by alkylation of the appropriate sulfide or amine using ethyl bromoacetate, followed by deprotonation with base. However, it quickly became apparent that ethyl bromoacetate is not sufficiently reactive for this purpose. Alkylation of α-branched sulfides and amines requires heating the reactants and complex product mixtures are formed in typical cases. To avoid high-temperature alkylations, we have prepared several trifluoromethanesulfonates (triflates) of α-hydroxy esters, ketones, and nitriles. As expected,[1] these reagents are far more reactive than the analogous bromides. Alkylation of branched sulfides and amines with the triflate reagents becomes a routine operation and the corresponding ylides can be obtained easily (path a, below).[2] We have also prepared and isolated several substituted allyl triflates which allow synthesis of **1** and **2** from α-thiomethyl or α-dialkylamino carbonyl compounds (path b). Not surprisingly, the allyl triflates are extremely reactive alkylating agents toward a variety of sulfur-, nitrogen-, phosphorus, or oxygen-containing molecules.

The trifluoromethanesulfonate ester (**3**) of ethyl glycolate is representative of triflates derived from α-hydroxycarbonyl compounds. This reagent is most conveniently prepared by slow addition of ethyl diazoacetate to trifluoromethanesulfonic acid in liquid sulfur dioxide at −78 °C. Wentrup and Dahm have used a similar method to prepare the analogous fluorosulfonate ester.[3] Under optimized conditions, **3** can be isolated in 73% yield as an air-stable, easily crystallized (mp 22 °C), and mildly lachrymatory liquid. Ether can be substituted for the sulfur dioxide solvent, but the yield of triflate is only 30–40%. Several related triflates have been prepared similarly from the diazo compounds in liquid SO_2, as summarized in Table I.

Table II lists triflates which have been prepared from alcohols and trifluoromethanesulfonic anhydride. This method appears suited for α-hydroxycarbonyl compounds (entries VII–X), although it is less convenient (and more expensive) than the diazo ester procedure for preparation of **3**. In several cases (notably, entries VIII and X) we have found that a 5% excess of pyridine is essential for good yields. Accordingly, a stoichiometry of 1:1.05 m of anhydride/pyridine per 0.8–1.0 mol of alcohol has been adopted as the standard procedure using inert solvents such as liquid sulfur dioxide or halogenated hydrocarbons.

As indicated in Table II, it is possible to prepare exceedingly reactive allylic triflates. The propenyl and propargyl derivatives **8** and **9** have been reported previously, although neither triflate was isolated in pure form.[4] We have found that trifluoromethanesulfonates **8–11** can be purified by distillation if a sufficiently low-boiling solvent is used for the experiment. Thus, allyl triflate **8** can be prepared in methyl chloride solution, and solvent removal followed by product distillation affords **8** as a colorless liquid. The most reactive triflates **8–12** all decompose if stored at room temperature. In one instance, a neat sample of **8** which had been placed in a sealed ampule exploded upon reaching ambient temperature. It is essential to store purified samples of **8–12** at −78 °C, and to exercise precautions during distillation of the triflates.

All of the allylic triflates are extremely reactive toward typical compounds containing covalent oxygen, nitrogen,



1, X = SR
2, X = NR_2

Table I. Triflates from Diazo Esters, Ketones, and Nitriles

Entry	Starting diazo comp	Registry no.	Triflate	Registry no.	Isolated yield, %
I	$C_2H_5O_2CCHN_2$	623-73-4	$C_2H_5O_2CCH_2OTf$ (3)	61836-02-0	73
II	$C_6H_5COCHN_2$[15]	3282-32-4	$C_6H_5COCH_2OTf$ (4)	62861-51-2	75
III	$NCCHN_2$[8]	13138-21-1	$NCCH_2OTf$ (5)	62861-52-3	23
IV	CH_3COCHN_2[15]	2684-62-0	CH_3COCH_2OTf (6)	62861-53-4	37
V	$Cl_3CCOCHN_2$[9]	20485-55-6	Cl_3CCOCH_2OTf (7)	62861-54-5	36

Table II. Triflates from Alcohols and Trifluoromethanesulfonic Anhydride–Pyridine

Entry	Starting alcohol	Registry no.	Triflate	Registry no.	Yield, %
I	$CH_2{=}CHCH_2OH$	107-18-6	8	41029-45-2	69[a]
II	$CH{\equiv}CCH_2OH$	107-19-7	9	41029-46-3	28[a]
III	$CH_2{=}C(Cl)CH_2OH$	5976-47-6	10	62861-56-7	79[a]
IV	$Me_3SiCH{=}CHCH_2OH$		11	62905-84-4	72[a]
V	$CH_3O_2CCH{=}CHCH_2OH$	4508-99-0	12	62861-57-8	80[d]
VI	$CH_2{=}C(OC_2H_5)CH_2OH$	62861-55-6	13	62905-85-5	60[b]
VII	$C_2H_5O_2CCH_2OH$	623-50-7	3		77[a]
VIII	$C_6H_5C(=O)CH(OH)C_3H_7$	20907-23-7	14	62905-86-6	44[a,c]
IX	$CH_3O_2CCH(OH)C_5H_{11}$	54340-91-9	15	62861-58-9	89[a]
X	$C_2H_5C(=O)CH(OH)CH_3$	5704-20-1	16	62861-64-7	75[a]

[a] Isolated yield of purified triflate. [b] Yield based on salt formation with triphenylphosphine. [c] Initial yield 75% by NMR; partial decomposition during isolation. [d] Yield of oil after solvent removal, pure by NMR.

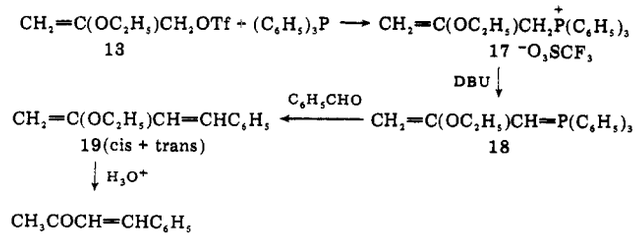
Table III. Half-Lives for Diphenyl Sulfide Alkylation by Triflates[a]

Triflate	$T_{1/2}$	Triflate	$T_{1/2}$
$TfOCH_2CO_2C_2H_5$	5 h	$TfOCH_2CN$	8 h
$TfOCH_2COCH_3$	8 h	$TfOCH_2CH{=}CHCO_2CH_3$	<5 min
$TfOCH_2COC_6H_5$	2 h	$TfOCH(C_5H_{11})CO_2CH_3$	4.5 days
$TfOCH_2COCCl_3$	0.7 h	$TfOCH(CH_3)COC_2H_5$	12 h

[a] Experiments performed in CD_3CN: half-life indicates disappearance of one-half of triflate at 25 °C according to NMR integration; sixfold excess diphenyl sulfide (~1 M).

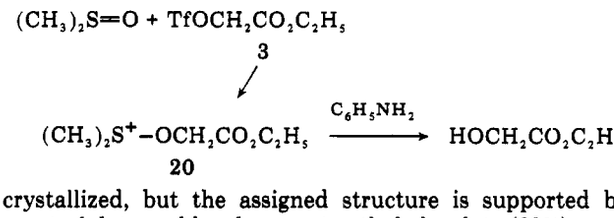
sulfur, or phosphorus. Only the α,β-unsaturated ester derivative **12** has a sufficient lifetime in acetonitrile at 20 °C to allow use of this solvent for preparation of sulfonium salts from the triflate. The other allylic triflates attack acetonitrile within minutes at room temperature, and react violently with solvents such as Me_2SO or DMF. Typical sulfides are alkylated with considerable evolution of heat using any of the reagents **8–11**, and even diphenyl sulfide is completely alkylated after 1–2 min at room temperature in chloroform.

Entry VI, Table II, refers to the trifluoromethanesulfonate ester **13** of 2-ethoxyprop-2-en-1-ol. This triflate is too unstable for isolation by the usual distillation procedure and decomposes in methylene chloride solution above −20 °C. In order to characterize the triflate, we have treated filtered solutions of **13** with nucleophiles at −40 °C. Noncrystalline salts are formed with diphenyl sulfide, thioanisole, or pyridine, but the triphenylphosphonium salt **17** is easily obtained as the pure solid in 61% yield. The structure of **17** is based on spectral and



analytical data, as well as on Wittig condensation with benzaldehyde in the presence of DBU to form the dienyl ether **19**. Acid hydrolysis of **18** affords the enone in good yield. Prior to our work, the ethoxyallylidenetriphenylphosphorane (**18**) had not been described in the literature. However, we have recently learned that Martin and Desai have generated the same phosphorus ylide from a different precursor.[6]

The trifluoromethanesulfonate esters of α-hydroxycarbonyl compounds are considerably less reactive than the allylic reagents, but the triflates are far more effective alkylating agents than the α-bromocarbonyl analogues. For example, tetrahydrothiophene is alkylated rapidly at −20 °C by the triflate **3** derived from ethyl glycolate, while the corresponding reaction with ethyl bromoacetate requires several hours at 25 °C. The triflate **3** does not alkylate acetonitrile or dimethylformamide to an appreciable extent at 25 °C after 24 h, but extensive decomposition of **3** occurs in these solvents at 40 °C. Dimethyl sulfoxide is O-alkylated cleanly at room temperature. The moisture-sensitive alkoxysulfonium salt **20** could not be



crystallized, but the assigned structure is supported by spectral data and by cleavage to ethyl glycolate (89%) upon treatment with aniline.

Table III compares the relative reactivity of representative triflates toward diphenyl sulfide. Qualitative half-lives are listed for disappearance of starting triflate in the presence of a sixfold excess of diphenyl sulfide (deuterioacetonitrile, NMR analysis). To a first approximation, alkylation rates increase with increasing electron demand from substituents and decrease with increased substitution at the triflate α carbon. These observations are compatible with S_N2 attack by sulfide on triflates derived from hydroxy esters, ketones, or nitriles.

The triflate reagents described in Tables I and II provide easy access to a variety of stabilized sulfur or nitrogen ylides. We have already published some examples of the utility of

triflate 3 for synthesis of ester-stabilized ylides, which undergo facile fragmentation to alkenes.[2] By comparison, the carbenoid decomposition of ethyl diazoacetate in the presence of sulfide or amine gives poor yields of ylide-derived products and numerous side products in several cases that we have examined. Other synthetic applications of the triflate reagents involving ring expansion by repeatable 2,3-sigmatropic shifts will be described elsewhere.

Experimental Section

Preparation and Purification of Starting Materials. Trifluoromethanesulfonic acid was obtained from 3M Company, distilled, and kept in a flask equipped with a three-way stopcock under N_2 atmosphere. Trifluoromethanesulfonic anhydride was prepared according to the method of Burdon, Sarazmand, Stacy, and Tatlow[7] from trifluoromethanesulfonic acid and P_2O_5. Ethyl diazoacetate was obtained from the Aldrich Chemical Co. and was used without further purification.

Methylene chloride was distilled from P_2O_5 and stored over 4A molecular sieves.

Carboethoxymethyl Trifluoromethanesulfonate (3). Procedure A. To a solution of trifluoromethanesulfonic acid (6.0 g, 40 mmol) in sulfur dioxide (SO_2) (100 mL) at −78 °C was slowly added ethyl diazoacetate (4.56 g, 40 mmol) over a 20-min period. The mixture was stirred for 1 h at −78 °C and then the solvent was evaporated by removing the dry ice bath. The residue was cooled to 0 °C and ice water (15 mL) was added. The mixture was extracted with hexane (three 40-mL portions) and the combined hexane extracts were dried over Na_2SO_4. Norit (~100 mg) was added and the hexane solution was passed through a thin silica gel plug (1.5 cm). More hexane (50 mL) was used to further wash the silica gel plug. The hexane solution was then cooled in the freezer overnight and the hexane decanted from the colorless crystals (6.9 g, 73%): mp 22–23 °C; NMR ($CDCl_3$, δ) 1.35 (3 H, t, J = 7.0 Hz), 4.34 (2 H, q, J = 7.0 Hz), 4.98 (2 H, s); IR (cm^{-1}, film) 2990 (m), 2950 (w), 1769 (s), 1418 (s), 1385 (m), 1304 (m), 202 (s), 1145 (s), 930 (w), 864 (m), 813 (s), 760 (m), 610 (s).

Procedure B. Pyridine (166 mg, 2.1 mmol) in methylene chloride (7 mL) was cooled to −22 °C and trifluoromethanesulfonic anhydride (564 mg, 2.0 mmol) was added. After 5 min, ethyl glycolate (208 mg, 2.0 mmol) was added and the mixture was warmed to ambient temperature with a 22 °C water bath. The mixture was then filtered, the solvent evaporated, and the residue passed through a silica gel plug (~2 cm) with hexane. Evaporation of the solvent and crystallization from hexane at 0 °C gave a colorless liquid (364 mg, 77%), identical with material prepared previously.

Phenacyl Trifluoromethanesulfonate (4). Trifluoromethanesulfonic acid (900 mg, 6.0 mmol) was dissolved in SO_2 (20 mL) at −78 °C. diazoacetophenone[15] (877 mg, 6.0 mmol) was added slowly to the colorless acid solution. The yellow diazoacetophenone upon addition quickly dissolved and N_2 evolution was apparent. The reaction was stirred for 20 min at −78 °C and then warmed to 0 °C to evaporate the solvent. The residue was extracted with hexane, and Norit treatment followed by evaporation of solvent gave phenacyl trifluoromethanesulfonate. The product was recrystallized from hexane to give fine white needles (1.207 g, 75%): mp 55.5–56 °C; NMR (CDCl, δ) 5.7 (2 H, s), 7.5–9.0 (5 H, m); IR (cm^{-1}, CHCl) 3042 (w), 2961 (w), 1715 (s), 1601 (m), 1588 (w), 1455 (m), 1419 (s), 1372 (m), 1238 (s), 1145 (s), 1049 (s), 1020 (m), 960 (s), 829 (m), 687 (m).

Cyanomethyl Trifluoromethanesulfonate (5). A methylene chloride solution of diazoacetonitrile was prepared according to the procedure of Curtius[8] from aminoacetonitrile hydrochloride (1.296 g, 14 mmol), sodium acetate trihydrate (21.4 mg, 0.17 mmol), sodium nitrite (1.47 g, 21.2 mmol), and 10% H_2SO_4 (0.464 mL). The methylene chloride extracts were combined and dried over Na_2SO_4. After filtering, the solution was concentrated to about one-third of the original volume. (CAUTION: Neat diazoacetonitrile is extremely explosive.) The crude reaction mixture was added dropwise to trifluoromethanesulfonic acid (1.80 g, 12 mmol) in SO_2 (20 mL) at −78 °C. After 20 min at −78 °C, the mixture was warmed to 0 °C and then quenched with ice water (10 mL). Extraction of the reaction mixture with ether (three 15-mL portions) gave a yellow oil after combining extracts, drying over Na_2SO_4, and evaporating. The oil was taken up as much as possible in hexane (two 15-mL portions) and the combined hexane washings were cooled to −78 °C. The triflate crystallized and the hexane was decanted at 0 °C. The crystals quickly melt when removed from a 0 °C ice bath. A colorless liquid (522 mg, 23%) was obtained; NMR ($CDCl_3$, δ) 5.10 (2 H, s); IR (film, cm^{-1}) 2260 (w), 1750 (w), 1420 (s), 1200–1250 (s), 1130 (s), 980 (s), 800 (w), 750 (m), 610 (s).

2-Oxopropyl Trifluoromethanesulfonate (6). This triflate was prepared from trifluoromethanesulfonic acid (2.37 g, 1.55 mmol) and 1-diazo-2-propanone[15] according to procedure A described for the preparation of carboethoxymethyl trifluoromethanesulfonate. The usual workup gave a yellow oil which was crystallized from hexane at −78 °C. The material crystallized as fine white needles (1.22 g, 37%): NMR ($CDCl_3$, δ) 2.21 (3 H, s), 4.90 (2 H, s); IR (cm^{-1}, CHCl) 3040 (w), 2979 (w), 1755 (s), 1736 (sh), 1420 (s), 1370 (w), 1252 (s), 1232 (s), 1146 (s), 1024 (s), 984 (s), 810 (m), 610 (s); mp 43.5–45 °C.

3,3,3-Trichloro-2-oxopropyl Trifluoromethanesulfonate (7). Trifluoromethanesulfonic acid (800 mg, 5.32 mmol) was dissolved in SO_2 (10 mL) at −78 °C. To this solution was added 1-diazo-3,3,3-trichloro-2-propanone[9] (1.00 g, 5.32 mmol). The diazo compound was instantly decolorized and N_2 evolution was apparent. The mixture was stirred for another 20 min at −78 °C and then warmed to 0 °C. The usual workup followed by several recrystallizations from hexane gave 3,3,3-trichloro-2-oxopropyl trifluoromethanesulfonate (450 mg, 36%); mp 36–38 °C; NMR ($CDCl_3$, δ) 5.70 (2 H, s); IR ($CHCl_3$, cm^{-1}) 2985 (w), 1780 (s), 1430 (s), 1370 (w), 1410 (s), 1215 (s), 1140 (s), 1020 (s), 885 (w), 825 (w), 760 (m), 610 (s).

Prop-2-enyl Trifluoromethanesulfonate (8). Freshly distilled trifluoromethanesulfonic anhydride (14.1 g, 50.0 mmol) was dripped slowly into a mechanically stirred solution of dry pyridine (4.05 mL, 50.0 mmol) in refluxing chloromethane (70 mL, Matheson, unpurified) under a slight positive N_2 pressure (dry ice condenser). Neat 2-propen-1-ol (3.40 mL, 50.0 mmol) was then added dropwise to the white, viscous suspension over a 10-min period. The solvent was then allowed to boil away and the stirring apparatus replaced by a short-path distillation head. The triflate was distilled (ambient temperature, safety shield) and the product was trapped into a cooled (dry ice–EtOH) receiver (6.54 g, 69%, density 1.47 g/mL at 20 °C). The colorless oil must be stored at −78 °C in a vented flask. CAUTION: an explosion occurred on accidental warming of sealed ampules. Care should be exercised to avoid contact with or inhalation of this volatile, extremely reactive alkylating agent. The neat reagent has a half-life of ~10 min at room temperature: IR (neat, cm^{-1}) 2970 (w), 1413 (m), 1281 (s), 1248 (s), 1194 (s), 1149 (m), 913 (m); NMR (CCl_4, δ) 5.8–6.2 (1 H, m), 5.4–5.6 (2 H, m), 4.95 (2 H, d, J = 6 Hz).

Prop-2-ynyl Trifluoromethanesulfonate (9). Freshly distilled trifluoromethanesulfonic anhydride (2.82 g, 10.0 mmol) was dripped slowly into a mechanically stirred solution of dry pyridine (791 mg, 10.0 mmol) in methylene chloride (20 mL) at −23 °C (dry ice-CCl_4) under positive nitrogen pressure. Neat propargyl alcohol (449 mg, 8.0 mmol) was added dropwise over a 10-min period. The suspension was allowed to warm and was quickly filtered and evaporated under the aspirator. The resultant oil was extracted with hexane (three 20-mL portions) and the hexane was quickly removed under the aspirator (20 °C). The residue was immediately distilled (ambient temperature, 0.1 mm) through a short-path apparatus and the volatile product was trapped in a cooled (dry ice–EtOH) receiver (0.80 g, 53%). The colorless oil must be stored at −78 °C in a vented flask: IR (CCl_4, cm^{-1}) 3330 (m), 2970 (w), 2142 (w), 1430 (s), 1251 (m), 1220 (s), 1148 (s), 1008 (w), 981 (m), 945 (s); NMR (CCl_4, δ) 5.06 (2 H, d, J = 2 Hz), 2.76 (1 H, t, J = 2 Hz).

2-Chloroprop-2-enyl Trifluoromethanesulfonate (10). This triflate was prepared according to the method described for the preparation of **8**, using 2-chloroprop-2-en-1-ol (184 mg, 2.0 mmol, Chemical Samples Co.), trifluoromethanesulfonic anhydride (593 mg, 2.1 mmol), and pyridine (174 mg, 2.2 mmol) in methyl chloride solution. The solvent was removed at 0 °C by a stream of dry N_2 and the residue was distilled through a short-path distillation apparatus. A colorless liquid (354 mg, 79%) was trapped in a dry ice–ethanol cooled flask; NMR ($CDCl_3$, δ) 5.01 (2 H, s), 5.64 (1 H, d, J = 2.2 Hz), 5.70 (2 H, d, J = 2.2 Hz); IR (cm^{-1}, $CHCl_3$) 2987 (w), 1639 (m), 1415 (s), 1250 (s), 1211 (s), 1142 (s), 1005 (m), 975 (m), 950 (s), 928 (s), 848 (m), 818 (m), 763 (m), 618 (s); bp <22 °C [bath temperature 22 °C (0.25 mm)].

(*E*)-3-Trimethylsilylprop-2-enyl Trifluoromethanesulfonate (11). This material was prepared using a procedure identical with that for allyl triflate (**8**). Thus, the combination of trifluorosulfonic anhydride (2.82 g, 10.0 mmol), pyridine (791 mg, 10.0 mmol), and 3-trimethylsilylprop-2-enol[10] in methylene chloride (40 mL) yielded **11** (1.50 g, 57%) after distillation [34 °C (0.25 mm)]: NMR (δ, CCl_4) 6.2 (2 H, m), 5.1 (2 H, m), 0.13 (9 H, s); IR (cm^{-1}, neat) 2970 (w), 1620 (w), 1410 (m), 1280 (s), 1248 (s), 1190 (s), 995 (w). The product was stored at −78 °C in a vented flask, and turned dark within an hour at 20 °C.

(*E*)-3-Trimethylsilylprop-2-enol.[10] According to a procedure provided by Professor Stork, 3-trimethylsilylprop-2-ynol (50 mmol) was dripped into a suspension of $LiAlH_4$ (57.5 mmol) and sodium

methoxide (105 mmol) in THF (95 mL) at reflux. Freshly opened $LiAlH_4$ gave 61% of *E* alcohol (>90% *E*) using the recommended 3 h reaction time and workup with water (20 °C, careful addition), followed by 15% aqueous sodium hydroxide and distillation [bp 34 °C (0.1 mm)]. Our first attempts using the conventional procedure of dripping the alcohol into an ether–lithium aluminum hydride suspension (2:1 molar ratio, $LiAlH_4$-alcohol) at varying temperatures gave mixtures of what appear to be the *Z* and the *E* alcohols (2–3:1, *Z*/*E*) in reasonable yield (60–70%). Our evidence for the identity of the "*Z*" product consists only of the following data extracted from an NMR spectrum of the mixture [NMR (δ, $CDCl_3$) 6.31 (1 H, d of t, J = 14, 6 Hz), 5.53 (1 H, d, J = 14 Hz), 4.07 (2 H, d, J = 6 Hz), 2.8 (1 H, s), 0.12 (9 H, s)], which is to be compared with the NMR spectrum of the *E* isomer [NMR (δ, $CDCl_3$) 6.03 (1 H, d, J = 19 Hz), 5.85 (1 H, d of t, J = 19, 3 Hz), 4.02 (2 H, d, J = 3 Hz), 3.20 (1 H, s), 0.03 (9 H, s).

(3-Carbomethoxy)prop-2-enyl Trifluoromethanesulfonate (12). A solution of pyridine (1.22 mL, 15.0 mmol) in methylene chloride (25 mL) was treated with trifluoromethanesulfonic anhydride (3.95 g, 14.0 mmol) at −23 °C (dry ice–CCl_4) with vigorous mechanical stirring under a slight nitrogen pressure. Methyl (3-hydroxy)but-2-enoate[14] (1.39 g, 12.0 mmol) dissolved in methylene chloride (5 mL) was slowly dripped into the white suspension. The reaction was then allowed to warm to 20 °C and quickly filtered. The filtrate was evaporated and the yellow oil was extracted with hexane (two 15-mL portions). The washings were then evaporated, leaving **12** as a pale yellow oil which appeared pure by NMR (2.23 g ~80%). Attempted distillation (<0.1 mm) resulted in decomposition and attempts at crystallization failed: IR (CCl_4, cm^{-1}) 2960 (w), 2850 (w), 1729 (s), 1671 (w), 1648 (w), 1421 (s), 1244 (s), 1219 (s), 1205 (s), 1144 (s), 933 (m); NMR (CCl_4, δ) 6.92 (1 H, dt, J = 16, 5 Hz), 6.17 (1 H, dm, J = 16 Hz), 5.12 (2 H, dm, J = 5 Hz), 3.78 (3 H, s).

2-Ethoxyprop-2-en-1-ol. Ethyl 2-ethoxypropenoate[11] (3.0 g, 20.8 mmol) in ether (5 mL) was slowly added to lithium aluminum hydride (780 mg, 20.8 mmol) in refluxing ether (100 mL). After refluxing the mixture for 18 h and cooling to ambient temperature, Glauber's salt (Na_2SO_4, 10 H_2O) was continuously added to decompose the excess $LiAlH_4$. An excess of Glauber's salt was used and the mixture was stirred for 2 hr before filtering. The filtrate was concentrated and distilled to give a colorless oil (1.80 g, 86%); bp 30–35 °C (0.5 mm); NMR ($CDCl_3$, δ) 1.28 (3 H, t, J = 7.0 Hz), 3.5 (1 H, broad OH), 3.75 (2 H, q, J = 7.0 Hz), 3.94 (2 H, s), 3.99 (1 H, d, J = 2 Hz), 4.13 (1 H, d, J = 2 Hz); IR (cm^{-1}, film) 3360 (s), 2975 (s), 2922 (m), 1662 (s), 1625 (m), 1442 (m), 1378 (m), 1294 (s), 1256 (s), 1090 (s), 1030 (s), 970 (w), 808 (s); exact mass determined, 102.068 08; calcd for $C_5H_{10}O_2$, 102.06820.

Preparation and Trapping of 2-Ethoxyprop-2-enyl Trifluoromethanesulfonate 13 with Pyridine. Pyridine (166 mg, 2.1 mmol) in dichloromethane (7 mL) was cooled to −22 °C and trifluoromethanesulfonic anhydride (564 mg, 2.0 mmol) was added to form the crystalline pyridinium adduct at −22 °C. The solution was cooled to −42 °C and 2-ethoxyprop-2-en-1-ol (204 mg, 2.0 mmol) was added slowly with vigorous stirring. The mixture was stirred for 10 min after the addition was complete and during this time most of the precipitate had dissolved. Dry hexane (8 mL) was slowly added via syringe to precipitate the dissolved salts. The solution was filtered through a sintered glass frit built into the reaction vessel directly into a solution of pyridine (158 mg, 2.0 mmol) in dry methylene chloride (1 mL) at 0 °C and the mixture was stirred for 20 min at 0 °C. After warming to ambient temperature and removing the solvents, the residue was washed with ether to remove neutral materials and pumped dry under vacuum (0.25 mm). A pyridinium salt (523 mg, 81%) was obtained which failed to crystallize; NMR ($CDCl_3$, δ) 1.20 (3 H, t, J = 7.6 Hz), 3.74 (2 H, q, J = 7.6 Hz), 4.30 (1 H, d, J = 3.1 Hz), 4.65 (1 H, d, J = 3.1 Hz), 5.24 (2 H, s), 8.15 (2 H, m), 8.62 (1 H, m), 8.94 (2 H, d, J = 6.2 Hz); IR (cm^{-1}, $CHCl_3$) 3070 (m), 2985 (w), 1640 (s), 1580 (w), 1489 (s), 1444 (m), 1438 (m), 1270 (s), 1225 (s), 1160 (s), 1074 (m), 1030 (s), 984 (w), 822 (w), 772 (m), 752 (m), 688 (m), 634 (s).

Preparation and Trapping of 2-Ethoxyprop-2-enyl Trifluoromethanesulfonate 13 with Thioanisole. Following the above procedure the sulfonium salt was prepared from pyridine (166 mg, 2.1 mmol), trifluoromethanesulfonic anhydride (564 mg, 2.01 mmol), 2-ethoxyprop-2-en-1-ol (204 mg, 2.0 mmol), and thioanisole (248 mg, 2.0 mmol). The salt (494 mg, 76%) was an oil which failed to crystallize; NMR ($CDCl_3$, δ) 1.2 (3 H, t, J = 6.8 Hz), 3.4 (3 H, s), 3.65 (2 H, m), 4.28 (1 H, d, J = 3 Hz, 4.44 (1 H, d, J = 3 Hz), 4.50 (2 H, AB, J = 12.0 Hz), 7.7 (3 H, m), 8.0 (2 H, m); IR (cm^{-1}, $CHCl_3$) 2970 (m), 1645 (s), 1570 (w), 1450 (m), 1405 (m), 1280 (s), 1150 (s), 1035 (s), 980 (w), 750 (m), 695 (m), 638 (s).

Preparation of 2-Ethoxyprop-2-enyltriphenylphosphonium Trifluoromethanesulfonate (17). 2-Ethoxyprop-2-enyl trifluoromethanesulfonate was prepared as above from 2-ethoxyprop-2-en-1-ol (204 mg, 2.0 mmol), pyridine (166 mg, 2.1 mmol), and trifluoromethanesulfonic anhydride (564 mg, 2.0 mmol). The hexane–dichloromethane solution of the triflate at −42 °C was filtered through a frit in the side arm of the flask directly into a solution of triphenylphosphine (470 mg, 1.8 mmol) in dry dichloromethane (1 mL) at −42 °C. During the addition the phosphonium salt precipitates out. The mixture was stirred at −42 °C for 10 min and warmed to ambient temperature (30 min). After solvent removal and recrystallization from THF–ether, colorless, fine needles (541 mg, 61% based on triphenylphosphine) were obtained: mp 87–88.5 °C; NMR ($CDCl_3$, δ) 0.88 (3 H, t, J = 7.0 Hz), 3.45 (2 H, q, J = 7.0 Hz), 4.10 (1 H, m), 4.38 (1 H, m), 4.30 (2 H, d, J = 14.4 Hz), 7.7 (15 H, m); IR (cm^{-1}, $CHCl_3$) 3010 (m), 1630 (m), 1586 (w), 1484 (w), 1440 (m), 1382 (w), 1272 (s), 1220 (m), 1156 (m), 1108 (m), 1055 (w), 1029 (s), 995 (w), 866 (w), 680 (m), 632 (s). Anal. Calcd for $C_{24}H_{24}F_3PO_4S$: C, 58.05; H, 4.88; S, 6.44. Found: C, 58.06; H, 4.83; S, 6.50.

Preparation of (*E*)- and (*Z*)-(3-Ethoxybutadienyl)benzene (19) and Hydrolysis to 4-Phenylbut-3-en-2-one. (2-Ethoxyprop-2-enyl)triphenylphosphonium trifluoromethanesulfonate (17) (124 mg, 0.25 mmol) was dissolved in THF (3 mL) and cooled to −78 °C, and DBU (24 mg, 0.25 mmol) was added. With the addition of base the solution turned from colorless to deep yellow. Benzaldehyde (27 mg, 0.25 mmol) was added and the mixture was stirred at −78 °C for 15 min, at 0 °C for 1 h, and then overnight. After refluxing for 6 h, the mixture was diluted with water (5 mL) and extracted with hexane (three 20-mL portions). The hexane extracts were combined, dried over Na_2SO_4, and evaporated. PLC of the residue on silica gel using 40% ether in hexane gave a pale yellow oil, R_f 0.6 (28 mg, 64%): NMR ($CDCl_3$, δ) [mixture of *E*/*Z* isomers 7.6:1 based on NMR integration] *E* isomer 1.37 (3 H, t, J = 7 Hz), 3.85 (2 H, q, J = 7 Hz), 4.2 (2 H, s), 6.50 (1 H, d, J = 17 Hz), 6.93 (1 H, d, J = 17 Hz), 7.2 (5 H, m); *Z* isomer 1.05 (3 H, t, J = 7 Hz), 3.70 (2 H, q, J = 7 Hz), 4.12 (2 H, s), 5.95 (1 H, d, J = 13 Hz), 6.45 (1 H, d, J = 13 Hz), 7.2 (5 H, m); IR (cm^{-1}, film) 2980 (m), 1640 (w), 1595 (m), 1580 (m), 1490 (m), 1445 (m), 1373 (w), 1310 (s), 688 (s); exact mass determined, 174.104 46; calcd for $C_{12}H_{14}O$, 174.104 43. Treatment of the diene in methanol (2 mL) and water (1 mL) with 10% HCl (2 drops) for 4 h at ambient temperature gave 4-phenylbut-3-en-2-one, identical with authentic material.

1-(1-Phenylcarbonyl)butyl Trifluoromethanesulfonate (14). Pyridine (41 mg, 0.52 mmol) in dry CH_2Cl_2 (1.8 mL) was cooled to −22 °C and trifluoromethanesulfonic anhydride (144 mg, 0.51 mmol) was added. A white pyridinium salt immediately precipitated. After stirring the mixture for 5 min, 2-hydroxy-1-phenylpentan-1-one[11] (89 mg, 0.5 mmol) in CH_2Cl_2 (0.5 mL) was added. Stirring was continued for 10 min and then the reaction mixture was brought to ambient temperature with a water bath (~22 °C). The mixture was quickly filtered and the white precipitate was washed with CH_2Cl_2 (2 mL). The solvent was evaporated and the crude oil which remained was extracted with hexane. After concentrating the hexane extracts to 5 mL, the solution was left in the freezer overnight to give fine white crystals (71 mg, 44%); mp 46–47.5 °C; NMR ($CDCl_3$, δ) 1.1 (3 H, t, J = 8.0 Hz), 1.65 (2 H, m), 2.02 (2 H, m), 6.00 (1 H, t, J = 6.0 Hz), 7.3–7.7 (3 H, m), 7.95 (2 H, dd, J = 2.0, 8.0 Hz); IR (cm^{-1}, $CHCl_3$) 3080 (w), 2050 (w), 2980 (m), 2970 (m), 2890 (m), 1708 (s), 1601 (m), 1586 (w), 1456 (m), 1461 (s), 1250 (s), 1215 (s), 1156 (s), 1008 (w), 938 (s), 764 (s), 699 (s), 668 (m).

1-(1-Carbomethoxy)hexyl Trifluoromethanesulfonate (15). To a solution of pyridine (181 mg, 2.3 mmol, distilled from BaO and stored over KOH) in CH_2Cl_2 (6.6 mL) at −22 °C was slowly added freshly distilled trifluoromethanesulfonic anhydride (586 mg, 2.2 mmol). The white suspension which formed was stirred vigorously for 5 min and then methyl 2-hydroxyheptanoate (320 mg, 2.0 mmol) in CH_2Cl_2 (1 mL) was slowly added. Stirring was continued for 15 min at −22 °C. A 20 °C water bath was used to warm the reaction mixture quickly to ambient temperature. The reaction turned light tan at this point and the precipitate was filtered and washed with more dichloromethane (two 3-mL portions). After evaporating the combined filtrates, the residue was extracted with hexane (three 15-mL portions), dried over Na_2SO_4, and passed through a silica gel plug (1.5 cm). The plug was thoroughly washed with more hexane (20 mL). Evaporation of the solvent gave a colorless liquid (522 mg, 89%): NMR ($CDCl_3$, δ) 0.91 (3 H, t, J = 7.1 Hz), 1.40 (6 H, m); IR (cm^{-1}, film) 2972 (m), 2948 (m), 1770 (s), 1435 (m), 1425 (s), 1362 (w), 1295 (w), 1250 (s), 1215 (s), 1149 (s), 1011 (w), 948 (s), 875 (w), 620 (s).

3-Oxo-pent-2-yl Trifluoromethanesulfonate (16). A solution of pyridine (2.02 mL, 25 mmol) in CH_2Cl_2 (50 mL) was treated with trifluoromethanesulfonic anhydride (7.04 g, 25 mmol) at −23 °C (CCl_4–dry ice) under slight N_2 pressure with mechanical stirring. Freshly distilled 2-hydroxy-3-pentanone[13] (2.00 g, 19.6 mmol) was dripped in over a 5-min period and the reaction immediately allowed

Table IV. Crystalline Diphenylsulfonium Derivatives of Triflate Reagents

Triflate	Solvent for alkylation	Mp of salt, °C	Chemical shift of HCS^+Ph_2, ppm	Registry no.
4	CH_3CN	168–169.5	6.52 (CD_3COCD_3)	62861-59-0
6	CH_3CN	119–120	5.97 (CD_3COCD_3)	62861-61-4
7	CH_3CN	163–165.5	5.18 ($CDCl_3$)	62861-66-9
9	$CHCl_3$	118–120	5.12 (CD_3CN)	62861-63-6
10	$CHCl_3$	104–105	5.35 ($CDCl_3$)	62861-68-1

Table V. Crystalline Triphenylphosphonium Salts from Triflates

Triflate	Solvent for alkylation	Mp of salt, °C	Chemical shift of HCP^+Ph_3, ppm	Registry no.
8	$CHCl_3$	131–133	4.21 ($CDCl_3$)	62861-69-2
12	$CHCl_3$	150–153	4.55 ($CDCl_3$)	62861-70-5
16	$CHCl_3$	137–139	5.87 ($CDCl_3$)	62861-72-7

to warm to 20 °C. The red oil resulting from evaporation of the methylene chloride was extracted with three 10-mL portions of 10% ether–hexane. Evaporation and distillation [bp 35 °C (0.8 mm), 3.43 g, 75%] of the combined extracts yielded a colorless oil which crystallized on standing in a freezer. These crystals melt at approximately 5 °C: IR (CCl_4, cm^{-1}) 2995 (w), 2955 (w), 1731 (m), 1422 (s), 1248 (m), 1215 (s), 1148 (s), 940 (m), 915 (s); NMR (CCl_4, δ) 5.14 (1 H, q, J = 5 Hz), 2.61 (2 H, q, J = 6 Hz), 1.65 (2 H, d, J = 5 Hz), 1.12 (3 H, t, J = 6 Hz).

General Method for Preparation of Diphenylsulfonium Salts from Trifluoromethanesulfonates. Preparation of (Carboethoxymethyl)diphenylsulfonium Trifluoromethanesulfonate. To carboethoxymethyl trifluoromethanesulfonate (**3**) (472 mg, 2.0 mmol) in dry acetonitrile (4 mL) was added diphenyl sulfide (558 mg, 3.0 mmol). This mixture was stored at room temperature, in the dark, and under a static nitrogen atmosphere for 2 days. The solvent was evaporated and the residue washed with hexane (two 5-mL portions) to remove excess sulfide. The residue was taken up in a minimum amount of THF and then ether was slowly added until the mixture became cloudy. At this point, the triflate crystallized. The mixture was left in the freezer overnight and then the salt was filtered and recrystallized from THF–ether (490 mg, 58%): mp 120.5–121 °C; NMR ($CDCl_3$, δ) 1.20 (3 H, t, J = 7.1 Hz), 4.20 (2 H, q, J = 7.1 Hz), 5.40 (2 H, s), 7.71 (6 H, s), 8.08 (4 H, m); IR (cm^{-1}, $CHCl_3$) 3030 (m), 1735 (s), 1580 (w), 1480 (m), 1448 (m), 1400 (w), 1372 (m), 1315 (m), 1255 (s), 1215 (s), 1165 (m), 1035 (s), 750 (s), 660 (m), 635 (m). Anal. Calcd for $C_{17}H_{17}O_5S_2F_3$: C, 48.45; H, 4.06; S, 15.15. Found: C, 48.48; H, 4.08; S, 15.23.

The same method was used to prepare crystalline diphenylsulfonium salts for additional characterization of triflates **4, 6,** and **7** (Table IV). The more reactive triflates **9** and **10** also gave crystalline diphenylsulfonium salts, but the reaction could not be performed in acetonitrile due to solvent alkylation. Chloroform was used for these alkylations. The diphenylsulfonium salts from **5, 8, 11, 12, 15,** and **16** did not crystallize. Characterization of **8, 12,** and **16** by way of the crystalline triphenylphosphonium salts was successful (Table V). Thus, 0.25 mmol of triflate was added to 0.28 mmol of triphenylphosphine in 1–2 mL of dry chloroform. After 1 h, the residual oil after solvent removal and ether trituration was crystallized from tetrahydrofuran–ether.

Alkylation of Dimethyl Sulfoxide with Carboethoxymethyl Trifluoromethanesulfonate (3) and Proof of O-Alkylation. Dimethyl sulfoxide (78 mg, 1.0 mmol) was dissolved in dry acetonitrile (1.6 mL) and carboethoxymethyl trifluoromethanesulfonate (236 mg, 1.0 mmol) (**3**) was added. The mixture was stirred overnight and the solvent was evaporated. A colorless oil (301 mg, 96%) which failed to crystallize was obtained after washing with hexane: NMR ($CDCl_3$, δ) 1.30 (3 H, t, J = 7.1 Hz), 3.48 (6 H, s), 4.30 (2 H, q, J = 7.1 Hz), 4.95 (2 H, s); ^{13}C NMR ($CDCl_3$, ppm) 168.157 (C=O), 71.05 (OCH_2), 62.888 (CH_2C=O), 35.608 (CH_2=CH_3), 13.912 (Me_2S^+); IR (cm^{-1}, film) 3470 (m), 3030 (m), 2940 (m), 1735 (s), 1435 (w), 1387 (m), 1260 (s), 1230 (s), 1169 (s), 1100 (m), 1055 (m), 1034 (s), 980 (m), 870 (w), 760 (w), 640 (s).

The colorless oil (314 mg, 1.0 mmol) was dissolved in dry chloroform and freshly distilled aniline (75 mg, 0.95 mmol) was added. The reaction mixture quickly turned yellow and within a few minutes a white precipitate formed. After 15 min, ether was added until cloudy and the precipitate was filtered and washed with more ether. The filtrate was passed through a silica gel plug and the solvent was evaporated. PLC of the residue on silica gel using 50% ether in hexane gave a colorless oil (92 mg, 89%) identified as ethyl glycolate.

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Registry No.—**13** pyridinium salt, 62861-74-9; **13** thioanisole salt, 62861-76-1; **17,** 62861-78-3; (*E*)-**19,** 1902-98-3; (*Z*)-**19,** 1981-43-7; **20,** 62861-79-4; trifluoromethanesulfonic acid, 1493-13-6; trifluoromethanesulfonic anhydride, 358-23-6; 3-trimethylsilylprop-2-ynol, 5272-36-6; (*Z*)-3-trimethylsilylprop-2-enol, 62861-80-7; (*E*)-3-trimethylsilylprop-2-enol, 59376-64-6; ethyl 2-ethoxypropenoate, 22121-86-4; pyridine, 110-86-1; thioanisole, 100-53-8; triphenylphosphine, 603-35-0; (carboethoxymethyl)diphenylsulfonium trifluoromethanesulfonate, 62861-81-8; diphenyl sulfide, 139-66-2; dimethyl sulfoxide, 67-68-5.

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