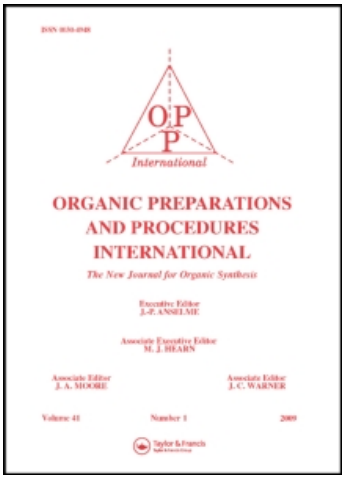


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## INTRODUCTION

The sulfonyl group has unusually versatile reactivity, functioning both as an electrophile and as a nucleophile or leaving group.[1] These properties are enhanced in the trifluoromethanesulfonyl group ($CF_3\overset{O}{\overset{\|}{S}}\overset{}{\underset{O}{\|}}-$, abbreviated as "trifyl" ≡ Tf) one of the strongest electron-withdrawing groups known. This review explores the practical aspects of its use in organic synthesis when attached to carbon (triflones), nitrogen (triflamides), or oxygen (triflates). The chief source of this functionality is triflic acid ($CF_3SO_2OH$, bp 162°) an extremely strong, non-oxidizing acid available as an anhydrous reagent.[2]

## SOURCES OF THE TRIFYL GROUP

The primary electrophilic source of the trifyl group

($CF_3SO_2$-) is the very reactive triflic anhydride[$(CF_3SO_2)_2O$, bp 82-83°] obtained by dehydration of $CF_3SO_2OH$ with $P_2O_5$ (Prep. 1). It is a colorless liquid stable indefinitely if stored under nitrogen at room temperature. Three other trifyl electrophiles have found use: trifyl chloride ($CF_3SO_2Cl$, bp 30-32°) made from reaction of $Zn(OSO_2CF_3)_2$ and $PCl_5/ZnCl_2$ (Prep. 2),[2] N-trifyl imidazolide [$CF_3SO_2C_3H_3N_2$, bp 38-40° (10 mm)] (Prep. 3),[4] and N-phenyl triflimide [$PhN(SO_2CF_3)_2$, mp 95-96°] (Prep. 4).[5] The latter two reagents are made by reaction of $(CF_3SO_2)_2O$ with imidazole and aniline respectively. Trifyl fluoride has also been used but is not readily available.[2]

The main nucleophilic source of trifyl is triflinate anion ($CF_3SO_2^-$). Potassium triflinate ($KSO_2CF_3$) is available from iodide reduction of $CF_3SO_2Cl$ or in anhydrous form from reaction of N-phenacyl-N-phenyl triflamide and anhydrous $K_2CO_3$ (Eq. 1, Prep. 5);[7] the salt is quite soluble in various solvents (e.g. $CH_3CN$, DMF, HMPA, and mixtures of these with various other solvents). Unfortunately $KSO_2CF_3$ is

$$\begin{array}{ccc} PhNH_2 + (CF_3SO_2)_2O & \xrightarrow[-78°]{NEt_3,\ CH_2Cl_2} & PhNHSO_2CF_3 \\ & & \Big\downarrow \text{PhCOCH}_2\text{Br},\ K_2CO_3 \\ PhN{=}CHCOPh + KSO_2CF_3 & \xleftarrow[\text{acetone}]{K_2CO_3} & PhN(SO_2CF_3)CH_2COPh \end{array} \qquad (1)$$

quite hygroscopic and is best used immediately after preparation. Alternatively sodium triflinate ($NaSO_2CF_3$) can be prepared by pyrolysis of the corresponding sodium salt of N-trifyl-t-butyl carbazate (Eq. 2, Prep. 6).[8] This salt is non-hygroscopic and therefore easily stored so that anhydrous triflinate can be generated in situ on demand without manipulation.[23]

$$Na^+CF_3SO_2\bar{N}\text{-}NH\text{-}COO\text{-}t\text{-}Bu \xrightarrow[\text{neat or in xylene}]{140^\circ} NaSO_2CF_3 + [N_2H_2] + CO_2 + \rangle\!= \quad (2)$$

TRIFLONES ($CF_3SO_2$-C)

The trifyl group can be attached to carbon either as electrophile or nucleophile. Its primary synthetic functions are to act as an effective stabilizing group for carbanions, readily formed at the α-carbon with bases, and as a superior electron-withdrawing group to promote nucleophilic addition or cycloaddition to conjugated double bonds. Removal of the trifyl group may be effected reductively, isohypsically or oxidatively.

A. Formation of Triflones

Three main ways exist to prepare triflones, all of them restricted to the formation of primary triflones ($RCH_2SO_2CF_3$). The nucleophilic triflinate anion S-alkylates to form triflones on treatment with primary alkyl halides in refluxing $CH_3CN$ and KI catalysis (Eq. 3, Prep. 7).[6] The reaction is

slow, requiring up to 7 days for completion but proceeds cleanly and in good yield.

$$RCH_2Br + KSO_2CF_3 \xrightarrow[CH_3CN,\ \Delta]{\text{cat. KI}} RCH_2\overset{O}{\overset{\|}{S}}CF_3 + KBr \qquad (3)$$

$$\overset{O}{\overset{\|}{S}}$$

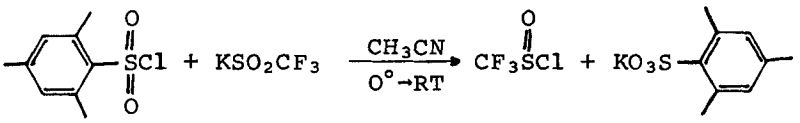
(6 hr.-7 days)

(R=Ar, ArCO, R, COOR) (70-95%)

Rate enhancement with silver ion, or simple displacements of sulfonate esters, lead to O-akylation, yielding triflinate esters $R\text{-}O\overset{O}{\overset{\|}{S}}CF_3$.[7] These esters are more easily formed from alcohols by reaction with triflinyl chloride ($CF_3SOCl$) and pyridine at RT (Eq. 4, Prep. 8).[7] $CF_3SOCl$ is made *in situ* by the reaction of mesitylene sulfonyl chloride with $KSO_2CF_3$ (Eq. 5, Prep. 8).[7]

$$RCH_2OH + CF_3\overset{O}{\overset{\|}{S}}Cl \xrightarrow[C_5H_5N]{CH_3CN,\ RT} RCH_2O\overset{O}{\overset{\|}{S}}CF_3 \qquad (4)$$

(R=1°, 2°, allyl) (68-78%)




(5)

Primary triflinate esters can be converted to the thermodynamically more stable triflones by heating to 145° in dipolar aprotic solvents (HMPA preferred), but allylic triflinates proceed at much lower temperatures in $CH_3CN$ (Eq. 6, Prep. 8).[7] Unless allylic, secondary (and tertiary) triflinates only result in elimination (to triflinic acid, $CF_3SO_2H$) on heating. The procedure, however is often

valuable in allowing direct conversion of the usually more

$$ROSCF_3 \xrightarrow{\Delta} RSO_2CF_3 \quad (6)$$

25-95%

available alcohols as starting materials for triflones.

The third method for the preparation of triflones employs the reaction of primary or secondary alkyllithium reagents with the mild electrophile $PhN(SO_2CF_3)_2$ in ether. The use of organocopperlithium reagents gave the highest yields (Eq. 7, Prep. 9).[9]

$$RLi + PhN(SO_2CF_3)_2 \xrightarrow[78^\circ]{Et_2O} R\text{-}SO_2CF_3 + PhNHSO_2CF_3 \quad (7)$$

(or $R_2CuLi$; R=Et, n-Bu, s-Bu) 67-92%

This method is unsatisfactory for methyl or aryl triflones. Some mildly activated arenes can be converted to aryl triflones by Friedel-Crafts acylation with $(CF_3SO_2)_2O$ using $AlCl_3$ as the catalyst (Eq. 8, Prep. 10).[9] Methyl triflone has been prepared by Grignard reaction of $CF_3SO_2F$ with

$$ArH + (CF_3SO_2)_2O \xrightarrow[RT/18\ hr.]{AlCl_3} ArSO_2CF_3 \quad (8)$$

10-62%

$CH_3MgI$[2,10] but with the fluoride not readily available is more conveniently prepared by pyrolysis of t-butyl-trifylacetate (Eq. 9, Prep. 11).[7]

$$BrCH_2COO\text{-}\underline{t}\text{-}Bu + KSO_2CF_3 \xrightarrow[\Delta]{CH_3CN} [CF_3SO_2CH_2COO\text{-}\underline{t}\text{-}Bu] \xrightarrow{\Delta\ (140°)} CH_3SO_2CF_3 + CO_2 + (CH_3)_2C{=}CH_2 \quad (9)$$

(62%)

B. α-Alkylations of Triflones

The stabilized α-carbanions of triflones are readily formed with NaH in glyme [or THF/HMPA (4:1)] and their solutions may be alkylated directly (Eq. 10, Prep. 12).[6,7] Dialkylation is not observed so that successive alkylations with different alkyl halides may be smoothly carried out, even on

$$RR'CHSO_2CF_3 \xrightarrow[RT]{NaH} Na^+RR'C^-SO_2CF_3 \xrightarrow[RT,\ 2\text{-}18\ hr.]{R''X} RR'R''CSO_2CF_3 \quad (10)$$

(R,R′=alkyl,aryl,H) (60-95%)

methyl triflone. The use of alkoxide bases often results in haloform reaction products (e.g. $RSO_2OR'$). When DMF is used as the solvent, formylation of α-trifyl anion can compete. α-Alkylation also occurs using $K_2CO_3$ as the base in refluxing $CH_3CN$ (16-36 hr./70-95%). Intramolecular alkylation has been used to form 3- and 5-membered rings. An example of this is the synthesis of cyclopropyl triflone (Eq. 11, Prep. 13), which also illustrates the availability of triflinate as a leaving group.

$$CF_3SO_2CH_2CH_2CH_2SO_2CF_3 \xrightarrow[\Delta,\ 4\ hr.]{NaH/glyme} \triangleright CHSO_2CF_3 \quad (11)$$

(69%)

Reaction of the triflone α-carbanion with aldehydes and ketones give β-hydroxytriflones which may be dehydrated to unsaturated triflones, and the same conversion has been done with amine bases (analogous to the Mannich reaction).[6,11,12] Acylations of triflone carbanions have been studied less but methyl triflone has been acylated with both HCOOEt and DMF.[7] A cyclic β-keto triflone has also been formed by an internal acylation.[7] β-Ketotriflone anions appear generally to O-alkylate, yielding trifyl enol ethers.[7]

α-Alkylation of triflones by conjugate addition is facile, occurring with only mild base catalysis in unhindered cases (Eq. 12).[6]

$$PhCH_2SO_2CF_3 + CH_2{=}CHCOCH_3 \xrightarrow[\Delta,\ 30\ hr.]{NEt_3} \begin{matrix} Ph \\ \diagdown \\ \quad CHCH_2CH_2COCH_2 \\ \diagup \\ SO_2CF_3 \end{matrix} \quad (12)$$

C. Addition to Vinyl Triflones

Conjugate addition to unsaturated triflones appears to be a general reaction with a variety of nucleophiles such as secondary amines, thiols, cyanide and malonate anions (Eq. 13 & 14).[6,13] Organocuprate nucleophiles add without complication (Eq. 15)[7] but other organometallic reagents are not usually successful.

$$PhCH{=}C(Ph)SO_2CF_3 \xrightarrow[H_2O/EtOH/Et_2O]{KCN/NH_4Cl} [Ph(CN)CHCH(Ph)SO_2CF_3]$$

$$40°/12\ hr. \rightarrow \begin{matrix} Ph \\ \diagdown \\ CN \end{matrix}{=}CHPh + KSO_2CF_3 \quad (75\%) \quad (13)$$

$$CH_2{=}C(SO_2CF_3)Ph + CH_2(COOEt)_2 \xrightarrow[EtOH]{NEt_3}$$

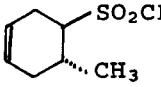
$$Ph(SO_2CF_3)CHCH_2CH(COOEt)_2 + (Ph(SO_2CF_3)CCH_2)_2C(COOEt)_2$$

1:2 (88%) (14)

$$(CH_3)_2CuLi + CH_3CH{=}CHSO_2CF_3 \xrightarrow[-50°]{Et_2O} (CH_3)_2CHCH_2SO_2CF_3$$

(78%) (15)

Diels-Alder reactions of vinyl triflones with butadiene occur readily (25°-100°),[6] in Eq. 16.

$$CH_2{=}CHCH{=}CH_2 + CH_3CH{=}CHSO_2CF_3 \xrightarrow[100°]{10\ days}$$  (16)



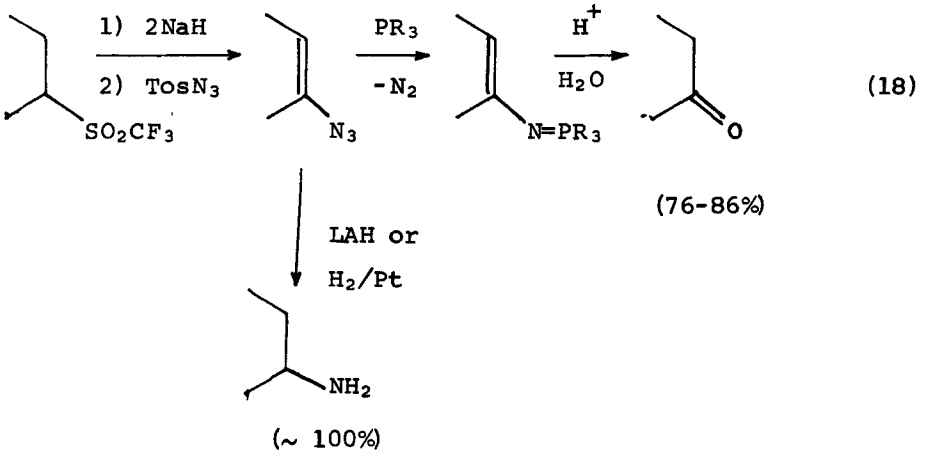
D. Removal of the Trifyl Group from Carbon

In general the trifyl group may be removed in a number of different ways. When β- to electron-withdrawing groups it is readily eliminated by mild bases such as $K_2CO_3$ (see also Eq. 13), leaving the stable triflinate anion. Secondary and tertiary triflones also undergo smooth thermal elimination (< 200°). Although stable to $NaBH_4$, Al-amalgam reduction, or Pt-catalyzed hydrogenolysis (unless benzylic), triflones are reduced to thiols by LAH and completely and quantitatively removed by Raney nickel.[6] α-Trifyl ketones and esters are also quickly and quantitatively reduced by zinc in alcohol (Eq. 17).

$$\begin{matrix} R \\ RO \end{matrix}\Big\rangle COCHR' \xrightarrow[\text{cat. HOAc}]{\text{Zn/EtOH}} \begin{matrix} R \\ RO \end{matrix}\Big\rangle COCH_2R' + Zn(SO_2CF_3)_2 \qquad (17)$$

$SO_2CF_3$ 1 min, 25° (100%)

Oxidative removal of triflones with both α- and β-hydrogens occurs on treatment of the α-carbanion with $TosN_3$. The vinyl azide rapidly formed in good yield, may be converted to the corresponding amine by treatment with LAH or by catalytic reduction,[7] or to the corresponding ketone or aldehyde (at the trifyl site) by treatment with $P(OEt)_3$ followed by dilute aqueous acid. The entire procedure is done without isolation of the vinyl azide intermediate (Eq. 18, Prep. 14).[15]




(18)

TRIFLAMIDES ($CF_3SO_2$-N)

Triflamides are readily formed from amines or their salts by reaction with one equivalent of $(CF_3SO_2)_2O$ in $CH_2Cl_2$ and $NEt_3$ at -78° (Eq. 19, Prep. 15).[5,16]

$$\left.\begin{matrix}RNH_2\\RR'NH\end{matrix}\right\} + (CF_3SO_2)_2O + NEt_3 \xrightarrow[-78^\circ]{CH_2Cl_2} \left\{\begin{matrix}RNHSO_2CF_3\\RR'NSO_2CF_3\end{matrix}\right. + Et_3\overset{+}{N}H\ \overset{-}{O}SO_2CF_3 \quad (19)$$

If two equivalents of $(CF_3SO_2)_2O$ are used, triflimides are formed (Prep. 4) [$PhN(SO_2CF_3)$ is a mild triflating agent (Eq. 7, Prep. 9].[5,16] Amides may also be triflated in a similar manner but with NaH as the base to give N-trifylamide (N-acyl triflamides) or by the acylation of triflamides (Eq. 20, Prep. 16).[5] These compounds are stable and crystalline and serve as mild acylating agents for amines but not alcohols (Eq. 20, Prep. 17).[5,16]

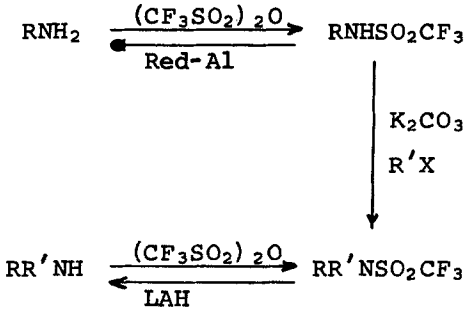
$$\begin{matrix}RCONHR' & \xrightarrow[2)\ (CF_3SO_2)_2O/5^\circ]{1)\ NaH/PhH} & \\ & & \rightarrow RCON(SO_2CF_3)R' \quad (19)\\ R'NHSO_2CF_3 & \xrightarrow[NEt_3/25^\circ]{RCOCl/CH_2Cl_2} & \end{matrix} \qquad (> 90\%)$$

$$PhCON(SO_2CF_3)Ph + PhNH_2 + NEt_3 \xrightarrow[0^\circ]{CH_2Cl_2} PhCONHPh \quad (98\%) \qquad (19)$$

$$Et_3\overset{+}{N}H \qquad PhN\overset{-}{S}O_2CF_3$$

In general primary triflamides are quite acidic ($Pk_a$ = 5-9). They are soluble in alkali and readily mono-alkylated using $K_2CO_3$ as the base (Eq. 20, Prep. 18).[5,16,17] Like other sulfonamides, triflamides are generally stable to most reaction conditions, but with two useful exceptions. They may be removed by either hydride reduction or by base-cataly-

zed elimination if activated β-hydrogens are available. The trifyl group therefore can serve as a useful amine protecting group which can be easily removed after the desired reaction has occurred.[5,16] The sequence for synthesis, mono-alkylation, and deprotection of triflamides is shown below (Eq. 20). Secondary triflamides are rapidly reduced with LAH to the corresponding amine in excellent yield (Prep. 19)[5,16] but



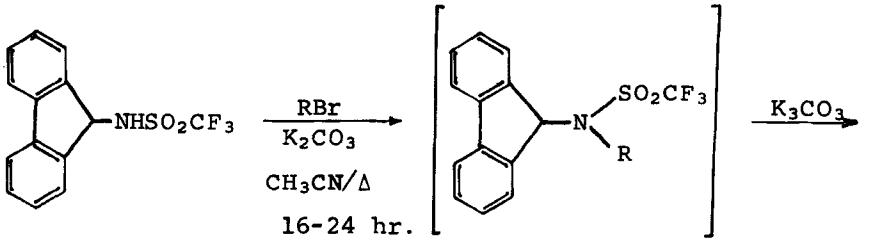

(20)

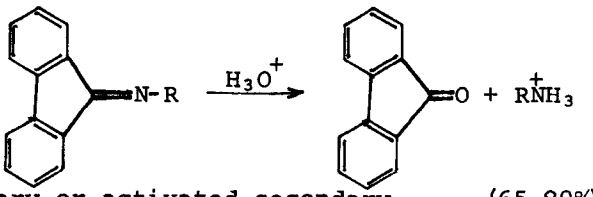
primary triflamides form only stable salts. These triflamides, however, are readily reduced to primary amines (again in high yields) by treatment with Red-Al [$NaAlH_2(OCH_2CH_2OCH_3)_2$] in refluxing benzene (Prep. 20).[5,16]

A. Gabriel Synthesis of Primary Amines

The ready elimination of triflinate from various triflamides was adapted to create an alternative Gabriel synthesis of primary amines.[17,18] In this procedure a triflamide is first alkylated and the trifyl group eliminated to give an imine which upon hydrolysis gives a primary amine. The best reagent for this purpose is 9-fluorenyl triflamide (Prep. 15).[18] Elimination of $KSO_2CF_3$ occurs under the

alkylation conditions and the resulting imine is hydrolyzed directly by mild acid work-up (Eq. 21, Prep. 21.[18]



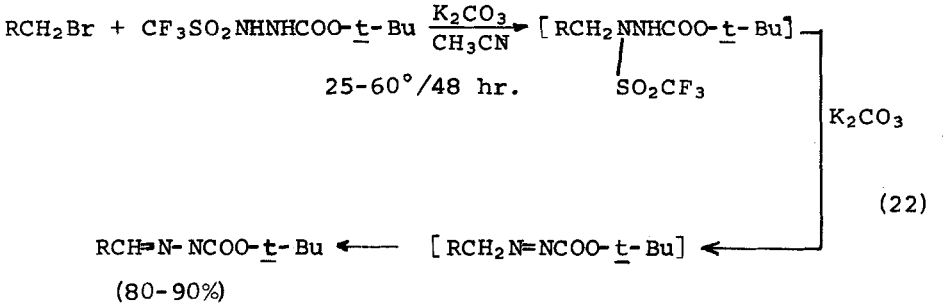

(21)

(R = Primary or activated secondary bromide) (65-80%)

B. Oxidation of Primary Halides to Aldehyde Hydrazones

A second adaptation of triflinate elimination affords an overall oxidation of a primary halide to an aldehyde oxidation state without using a conventional oxidant. This can occur if the imine, formed by N-alkylation followed by triflinate elimination, can further tautomerize. Such a reaction occurs with triflated acyl hydrazine reagents (Eq. 22, Prep. 22).[19] Although the trifyl derivative of benzoyl hydrazide has been used with equal success, the t-butoxycarbonyl hydrazide derivative is shown in Eq. 22 and felt to be the more useful since the urethane formed in the reaction is readily removed with acid to give the parent hydrazone of the product alde-

hyde. The latter can be hydrolyzed when required to give the corresponding aldehyde under very mild conditions.[20]




(22)

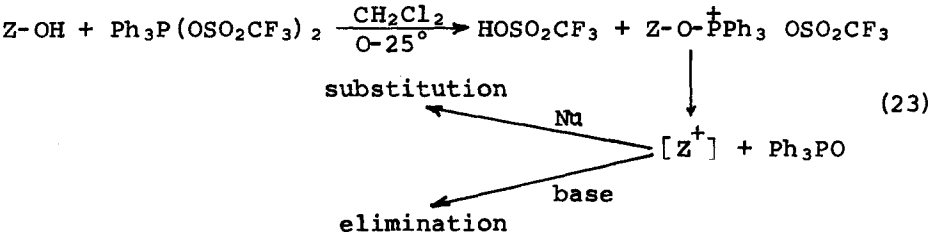
TRIFLATES ($CF_3SO_2$-O)

The triflate ion ($CF_3SO_3^-$) is exceedingly stable; it is accordingly a very inactive nucleophile but a superb leaving group, with solvolysis rates of $10^5$-$10^7$ times greater than the corresponding halides or tosylates. Cleavage of the trifyl-oxygen bond is very difficult and examples are rare. Triflates may be prepared by reaction of any oxygen source (e.g. alcohol, enol, etc.) with $(CF_3SO_2)_2O$, $CF_3SO_2C_3H_3N_2$ or $PhN(SO_2CF_3)_2$. The effectiveness of triflate as leaving group has been exploited by converting phosphorus and sulfur oxides to triflates to serve as leaving groups from those atoms.

A. Phosphine Ditriflates for Dehydration

Triphenylphosphine oxide reacts with $(CF_3SO_2)_2O$ in $CH_2Cl_2$ at 0° to give triphenylphosphine ditriflate

$[Ph_3P(OSO_2CF_3)_2$, mp 74-75°]. Although this reagent can be isolated and stored, it is usually prepared and used in situ.[21] This reagent reacts instantly with -OH groups to form an oxyphosphonium triflate with no other nucleophile present except triflate ion (Eq. 23). Accordingly, added bases or nucleophiles can now cause either elimination or substitution; with alcohols, however, mild warming usually suffices for elimination (Eq. 23).[21]



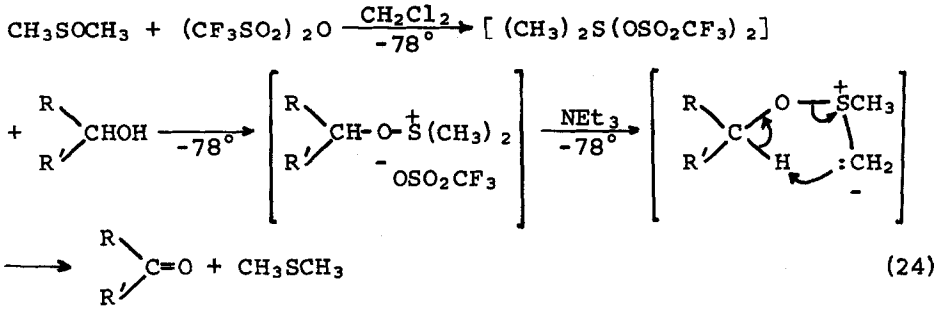

(23)

The reagent dehydrates alcohols, activates carboxylic acids for substitution, dehydrates amides (Prep. 23),[21] effects amide cyclodehydration, and is undoubtably more widely useful as an oxygen activator than the few examples mentioned here.

B. Sulfide Ditriflates

Reaction of $(CH_3)_2SO$ with $(CF_3SO_2)_2O$ gives the less stable dimethylsulfide ditriflate, $(CH_3)_2S(OSO_2CF_3)_2$, a white solid again made and used in situ.[22] Analogous to the phosphine, alcohols react at sulfur displacing triflate as before. When base is added the alcohol derivative is oxi-

dized to the ketone (Eq. 24, Prep. 24).[22]



(24)

## SUMMARY

In view of both the massive electron-withdrawing power of the trifyl group and its general tendency to retain its structural integrity in reactions, there is every reason to suppose that trifyl activation will be even more broadly applied than in these examples and will have wide application in organic synthesis. The examples given already show the practical ease and high yields typical of its use. The preparation and reactions of the several standard reagents given are meant to serve as a guide as well as a temptation for others to apply these useful tools in their own work.

## PREPARATIONS

General Comments. -- The best yields in these reactions are obtained if dry solvents are used. In addition, these reactions are best run protected by a drying tube. Although not always stated it is generally advisable to run these

reactions under a dry nitrogen atmosphere.

Preparation 1. Triflic Anhydride. - Triflic acid (400 g, 2.67 mol) and $P_2O_5$ (420 g, 2.95 mol) were placed in a 2 $\ell$ round bottom flask. After vigorous shaking (3 min) the mixture was allowed to stand for 1 hr. The flask was then warmed slowly to the distillation temperature. After discarding the first 5 ml on distillation, a total of 340 g (90%) of $(CF_3SO_2)_2O$ was collected, bp 82-83°. Stored in a sealed flask under $N_2$, this reagent is stable indefinitely. The density of $(CF_3SO_2)_2O$ is 1.81. A syringe was used in smaller reactions to measure the correct amount of reagent rather than direct weighing.

Preparation 2. Trifyl Chloride.

A. Zinc Triflate. - A solution of $CF_3SO_2OH$ (300 g, 2 mol) in 200 ml of $H_2O$ was cooled (0°) and added to solid $Ca(OH)_2$ (74.1 g, 1 mol) over 1 hr. (reaction temperature was kept below 50°). Powdered, solid $CO_2$ (25 g) was added to the solution. After stirring for 30 min an additional 1000 ml of $H_2O$ was added to the milky solution; it was then filtered through a coarse sintered glass funnel. Addition of more $CO_2$ (2 g) gave no more precipitate. To the clear solution was added solid $ZnSO_4 \cdot 7H_2O$ (288 g, 1 mol). The mixture was then warmed to 50° and stirred for 30 min. The warm solution was filtered through a coarse sintered glass funnel and

then through Whatman's #1 Filter paper. The final volume of clear, colorless liquid was 1000 ml. The solution was concentrated to 300 ml by heating. The remainder of the water was removed under reduced pressure to give 441 g of wet $Zn(OSO_2CF_3)_2$. Drying overnight (50 μ) gave 287 g (80%) of pure product.

B. Trifyl Chloride. - To hot molten anhydrous $ZnCl_2$ (544 g, 4 mol) previously melted in a 2 ℓ round bottom flask with a Fisher burner, was added $PCl_5$ (416 g, 2 mol) in 10 portions while the reaction mixture was stirred by hand. The molten salt mixture became much more fluid as more $PCl_5$ was added. The mixture was allowed to cool slightly and solid $Zn(OSO_2CF_3)_2$ (219 g, 0.6 mol) was added to the flask. The mixture was then heated strongly with a Fisher burner for 4 hr. The product distilling over was collected in a chilled receiver (salt-ice). The crude yellow liquid (a mixture of $CF_3SO_2Cl$ and $POCl_3$) was redistilled through a Vigreux column, the fraction boiling between 26-30° being collected. The final yield of product was 120 g (43%).

Preparation 3. N-Trifyl Imidazolide. - Triflic anhydride, $(CF_3SO_2)_2O$ (56.4 g, 0.2 mol) was dissolved in 50 ml of dry $Et_2O$. This was added dropwise over 30 min to a solution of imidazole (36.1 g, 0.53 mol) in 500 ml of dry $CH_2Cl_2$. The reaction mixture was then placed in a refrigerator (-20°) for

12 hr. The yellow solution was filtered through Celite and concentrated on a steam bath to give 60 g of yellow liquid. This was fractionally distilled and the portion boiling between 38-41° (10 mm) taken. The yield of pure colorless reagent was 299 g (75%).

Preparation 4. N-Phenyl Triflimide. - A solution of aniline (23.3 g, 0.25 mol) and $NEt_3$ (54.6 g, 0.54 mol) in 1500 ml of dry $CH_2Cl_2$ was cooled to -78°. To this was added $(CF_3SO_2)_2O$ (144 g, 0.51 mol) in 200 ml of dry $CH_2Cl_2$ (addition time was 2 hr). The mixture was allowed to warm to RT overnight. The $CH_2Cl_2$ solution was washed with $H_2O$ (5x500 ml), 10% NaOH (3x250 ml), $H_2O$ (2x500 ml), saturated NaCl (3x500 ml), and dried ($MgSO_4$). The dry solution was boiled with Norit, filtered through Celite and concentrated to give 84 g (94%) of crude material. Recrystallization (hexane) gave 79 g (89%) of pure product, mp 95-96°.

Preparation 5. Anhydrous Potassium Triflinate [23]

A. N-Phenyl Triflamide. - Aniline (60.7 g, 0.653 mol) and $NEt_3$ (65.9 g, 0.653 mol) in 1000 ml of dry $CH_2Cl_2$ were cooled to -78°. To this was added $(CF_3SO_2)_2O$ (188 g, 0.653 mol) in 200 ml of dry $CH_2Cl_2$ (addition time was 2 hr). The mixture was allowed to warm to RT overnight. The reaction was then washed with 10% HCl (3x200 ml), $H_2O$ (3x200 ml), dried ($MgSO_4$), and concentrated to give 149 g (100%) of crude

crystals. Recrystallization ($CH_2Cl_2$/hexane) gave 130 g (89%) of white needles, mp 64-66°.

B. N-Phenacyl Phenyl Triflamide. - Phenacyl bromide (95 g, 0.477 mol), N-phenyl triflamide (108 g, 0.480 mol) and anhydrous $K_2CO_3$ (69 g, 0.5 mol) were added to 2000 ml of dry acetone. The two-phase system was stirred for 24 hr. at RT. The solution was filtered to remove inorganic salts and concentrated to give 159 g (97%) of crude yellow crystals. The material was recrystallized ($CH_2Cl_2$/hexane) to give 151 g (92%) of white crystals, mp 110-111°.



C. Anhydrous Potassium Triflinate. - N-Phenacyl phenyl triflamide (103.2 g, 0.3 mol) and anhydrous $K_2CO_3$ (138 g, 1 mol) were added to 2000 ml of dry acetone. The two-phase system was stirred for 48 hr. at RT. The mixture was filtered under $N_2$ to remove inorganic salts and concentrated to give a yellow oil with small white crystals in it. To this material dry $CH_2Cl_2$ (750 ml) was added dropwise over 1 hr. The slurry was then filtered in a Schlenk tube under $N_2$. The crystals remaining in the tube were washed with dry $CH_2Cl_2$ (10x50 ml) and then dried under vacuum (30 μ) for 3 hr. Final yield of anhydrous $KSO_2CF_3$ is 44.3 g (86%). This material is very hygroscopic and is best used immediately after preparation.

Preparation 6. Anhydrous Sodium Triflinate.

A. N'-trifyl-N-t-butyloxycarbonyl Hydrazine. - To a solution of t-butyl carbazate (t-$BuOCONHNH_2$ / Aldrich Chemical Co.) (0.984 g, 7.4mmol) in 15 ml of $CH_2Cl_2$, containing roasted $K_2CO_3$ (2.065 g, 14.9 mmol) and chilled to -78°, was added (dropwise) a solution of $(CF_3SO_2)_2O$ (2.09 g, 7.4 mmol) in 2 ml of $CH_2Cl_2$, with stirring. After 15 min at -78° the contents were immediately extracted with chilled water (3x20 ml) and the aqueous layer washed with chilled $CH_2Cl_2$ (3x20 ml). The aqueous layer was acidified to pH ~ 2 with chilled 10% HCl (~ 25 ml) and the suspension extracted with $CH_2Cl_2$ (3x20 ml). The $CH_2Cl_2$ extract was dried ($MgSO_4$) and evaporated to a white crystalline solid, 1.476 g (76%), mp (dec) 88°. Warmer reaction and extraction or longer time led to decreased yield owing to bicarbonate-catalyzed decomposition of the product. Recrystallization of the crude product (to mp 91°) was unnecessary.

B. Sodium Salt of A. - A solution of N'-trifyl t-butyl carbazate (above) (0.476 g, 1.8 mmol) in 2 ml ether (freshly dried and distilled from $LiAlH_4$) was syringed dropwise under nitrogen into a stirred suspension of sodium hydride (0.132 g, 1.8 mmol 50% NaH washed oil-free with hexane) in 5 ml ether. After gas evolution had ceased the salt was filtered to yield 470 g (91%), as a white solid which can be stored

without concern.

C. Sodium Triflinate. - The salt may be pyrolyzed neat in a flame-dried flask at 140°-150° to afford sodium triflinate as a white powder.

Preparation 7. Preparation of Triflones from Alkyl Halides. - Benzyl bromide (4.28 g, 25 mmol), anhydrous $KSO_2CF_3$ (5.17 g, 30 mmol), and KI (10 mg) were refluxed under $N_2$ in dry $CH_3CN$ (80 ml) for 14 hr. The solvent was removed and dry $CH_2Cl_2$ (100 ml) was added. The material was filtered through Celite and the $CH_2Cl_2$ removed to give 6.31 g (100%). The solid was dissolved in $CCl_4$ (200 ml) and decolorized with Norit. The material was again filtered through Celite and the solvent removed to give 5.59 g (100%) of the triflone. Recrystallization ($CCl_4$) gave 5.16 g (92%) of pure product, mp 104°.

Procedure 8. Synthesis of Triflones from Alcohols (2-Phenethyl Triflone)

A. 2-Phenethyl Triflinate. - Mesitylenesulfonyl chloride (1.09 g, 5 mmol) and anhydrous $KSO_2CF_3$ (0.904 g, 5.25 mmol) were dissolved in 10 ml of dry $CH_3CN$. The mixture was stirred at RT for 0.5 hr. and cooled to 0°. A solution of 2-phenethyl alcohol (0.610 g, 5 mmol) and pyridine (0.40 g, 5 mmol) in 5 ml of $CH_3CN$ was then added dropwise to the mixture. The reaction mixture was allowed to warm to RT and was

stirred an additional 3 hr. The mixture was diluted with 75 ml of $Et_2O$ and then washed with $H_2O$ (6x25 ml), satd. NaCl (25 ml), dried ($MgSO_4$) and concentrated in vacuo to give 1.02 g (80%) of product which was used without further purification.

B. 2-Phenethyl Triflone. - 2-Phenethyl triflinate (1.02 g, 4 mmol) was dissolved in dry DMF (10 ml). The solution was refluxed under $N_2$ for 4 hr. The solution was then cooled diluted with $Et_2O$ (300 ml), washed with 6 N HCl (5x50 ml), satd. $NaHCO_3$ (50 ml), dried ($MgSO_4$) and concentrated in vacuo to give 571 mg of brown crystals, mp 78-78.5° (56%). Sublimation (70% 0.1 mm) gave the pure triflone, mp 80°.

Preparation 9. Synthesis of Triflones from N-Phenyl Triflimide (n-Butyl Triflone). - CuI [(purified by the procedure of Kauffman) 1.90 g, 10 mmol] was suspended in dry $Et_2O$ (100 ml) and cooled to -50°. n-BuLi (9 ml, 21.6 mmol) was added dropwise over 10 min. The solution turns dark brown and then black during this time. The $Et_2O$ solution was warmed to -30° until all the CuI dissolves. The resulting homogeneous black solution was cooled to -78°. To this was added a solution of N-phenyl triflimide (1.79 g, 5 mmol) in $Et_2O$ (50 ml) over 15 min. The mixture was stirred for 3 hr. at -78°, warmed to RT, stirred for 1 hr and poured into saturated $NH_4Cl$ (100 ml). The crude reaction mixture was

extracted with $Et_2O$ (3x100 ml); the $Et_2O$ layer was washed with 10% NaOH (3x50 ml), $H_2O$ (3x50 ml), saturated NaCl (2x50 ml), dried ($MgSO_4$), and concentrated on a steam bath. Kugelrohr distillation (185°) at atmospheric pressure gave 0.87 g (92%) of an oil spectrally identical with a sample from triflinate displacement on butyl bromide.

Preparation 10. Synthesis of Aryl Triflones (Phenyl Triflone).

Dry benzene (20 ml) and anhydrous $AlCl_3$ (1.47 g, 11 mmol) were cooled in an ice bath. To this was added $(CF_3SO_2)_2O$ (2.82 g, 10 mmol) in dry benzene (10 ml) over 15 min. The reaction mixture was allowed to warm to RT and stirred overnight. It was then poured into $H_2O$ (100 ml), extracted with $Et_2O$ (2x100 ml). The $Et_2O$ layer was washed with $H_2O$ (2x100 ml), saturated NaCl (2x100 ml), and dried ($MgSO_4$); the $Et_2O$ and excess benzene were removed on a steam bath to give 1.38 g (65%) of crude product. Distillation gave 1.29 g (61%) of pure product, bp 110°/30 mm.

Preparation 11. Synthesis of Methyl Triflone. - Potassium triflinate (24.08 g, 0.180 mol) and t-butyl bromoacetate (25.5 g, 0.131 mol) were dissolved in $CH_3CN$ (250 ml). The resultant solution was heated at reflux for 48 hr. under $N_2$. After cooling it was filtered and the filtrate concentrated in vacuo. The residue was dissolved in $CH_2Cl_2$ and filtered. Removal of the solvent under reduced pressure afforded 26.8 g

of brown oil which was pyrolysed at reflux for 4 hr. in a bath kept at 145-155°. Subsequent distillation afforded 12.0 g (62%) of $CH_3SO_2CF_3$ as a colorless liquid, bp 126-127°.

Preparation 12. Alkylation of Triflones (1-Phenylpropyl-3-Triflone). - Sodium hydride (472 mg of a 57% oil dispersion, 11mmol) was placed in a round bottom flask under $N_2$ and washed with hexane (3x25 ml). A solution of $CH_3SO_2CF_3$ (1.48 g, 10 mmol) in DMF (20 ml) was then added to the flask dropwise over 5 min. and the mixture stirred until $H_2$ evolution had ceased (a clear solution was obtained). To the flask was added a solution of $PhCH_2CH_2Br$ (1.85 g, 10 mmol) in DMF (20 ml) over 10 min. The reaction mixture was stirred at RT for 18 hr. The reaction mixture was then diluted with $Et_2O$ (300 ml). The solution was washed with 6 N HCl (4x50 ml), $H_2O$ (2x50 ml), saturated NaCl (2x50 ml), dried ($MgSO_4$), and concentrated in vacuo to give 2.56 g (> 100%) of crude product. Distillation (80°/0.1 mm) gave 1.85 g, (73%) of the pure triflone, mp 24-25°.

Preparation 13. Cyclopropyl Triflone. - Sodium hydride (1.34 g of a 57% oil dispersion, 32 mmol) was placed in a flame-dried flask under $N_2$, washed with dry petroleum ether (3x20 ml) and covered with glyme (25 ml). To this was added, fairly rapidly, a solution of propyl 1,3-ditriflone (8.94 g, 29 mmol) in glyme (40 ml). After bubbling had ceased, the

mixture was heated at reflux for 4 hr., cooled, and filtered. The solvent was removed by fractional distillation to afford 4.03 g (80%) of a brown oil. Simple distillation of this material gave 3.46 g (69%) of pure cyclopropyl triflone, bp 164°.

Preparation 14. Synthesis of Ketones from Triflones (Deoxybenzoin). - To a round bottom flask was added 57% NaH-oil dispersion (926 mg, 22 mmol). The oil was removed by washing the dispersion with dry hexane (2x10 ml). Dry glyme (50 ml) was then added to the flask. To the flask was added dropwise a solution of 1,2-diphenyl ethyl triflone (3.12 g, 10 mmol). After 1 hr. the flask was cooled to 0° and a solution of $TosN_3$[14] (1.97 g, 10 mmol) in 10 ml of glyme was added dropwise over 20 min. The mixture was allowed to warm to RT and stirred for 2 hr.

The reaction mixture was diluted with an equal volume of $Et_2O$ and washed with $H_2O$ (3x100 ml) and saturated NaCl (100 ml). The aqueous washings were combined and extracted with $Et_2O$ (100 ml). The $Et_2O$ washings were combined, dried ($MgSO_4$), and concentrated in vacuo to give 2.60 g (> 100%) of the crude vinyl azide.

The vinyl azide was resuspended in cyclohexane (25 ml). To this was added dropwise a solution of $P(OEt)_3$ (1.58 g, 9.5 mmol) in 10 ml of cyclohexane (the flask warmed and $N_2$

evolved). The reaction mixture was stirred for 21 hr., poured into an equal volume of 10% HCl solution and shaken intermittently for 5 min. The two phases were extracted with pentane (3x50 ml). The extracts were combined and washed with $H_2O$ (50 ml), saturated NaCl (50 ml), dried ($MgSO_4$, and concentrated to give crude deoxybenzoin as an oil. The crude product was then dissolved in $CHCl_3$ (50 ml). The solution was boiled with Norit, filtered through Celite and concentrated in vacuo to give 1.62 g (84%) of crude deoxybenzoin. Recrystallization ($CCl_4$) gave 1.49 g (76%) of pure product, mp 54-55°.



Preparation 15. Synthesis of Triflamides (9-Fluorenyltriflamide). - 9-Fluoreneamine hydrochloride (2.17 g, 10 mmol) was dissolved in a solution of $NEt_3$ (2.02 g, 20 mmol) in 100 ml of $CH_2Cl_2$. To this was added dropwise at -78°, with stirring, a solution of $(CF_3SO_2)_2O$ (2.82 g, 10 mmol) in 20 ml of $CH_2Cl_2$. A precipitate formed after about 2/3 of the anhydride had been added. After the addition was complete (about 30 min.) the reaction mixture was allowed to warm to RT and stirred overnight. The reaction mixture was filtered and the filtrate washed with 10% HCl (2x20 ml), saturated NaCl (2x20 ml), dried ($Na_2SO_4$) and evaporated to yield 2.20 g (70%) of product. (The precipitate was unreacted 9-fluoreneamine hydrochloride. The yield based on recovered starting material was 97%). The 9-fluorenyltriflamide was recrystallized

from benzene, mp 183-184°.

Preparation 16. N-Benzoyl-N-Phenyl Triflamide.

A. From Benzoyl Chloride. - A solution of N-phenyl triflmide (22.5 g, 0.10 mol) and $NEt_3$ (10.1 g, 0.10 mol) in 100 ml of $CH_2Cl_2$ was cooled to -78°. A solution of benzoyl chloride (14.0 g, 0.10 mol) in 50 ml of $CH_2Cl_2$ was then added dropwise to the flask over 1 hr. The solution was allowed to warm to RT and then washed with $H_2O$ (4x30 ml), dried ($MgSO_4$) and concentrated to give 33 g (> 100%) of solid. This was crystallized (hexane/$CH_2Cl_2$) to give 30.0 g (91%) of pure $PhCON(Ph)SO_2CF_3$, mp 97-98°.

B. From Benzanilide.- Sodium hydride (2.40 g of 57% oil dispersion, 0.10 mol) was washed with hexane (3x25 ml) and suspended in benzene (100 ml) and cooled to 5°. Benzanilide (19.7 g, 0.10 mol) was added and the reaction mixture stirred until $H_2$ evolution ceased. $(CF_3SO_2)_2O$ (28.2 g, 0.10 mol) was added dropwise and the resulting mixture then stirred for 0.5 hr. at RT. $H_2O$ (1 ml) was then added and the benzene layer washed further with $H_2O$ (4x50 ml), dried ($MgSO_4$) and evaporated to give a solid which was then crystallized (hexane) to give 30.6 g (93%) of pure product, mp 97-98°.

Preparation 17. Acylation of Amines (N-Benzoyl benzylamine). - A solution of N-Benzoyl-N-phenyltriflamide (3.30 g, 10 mmol) in 50 ml of $CH_2Cl_2$ was cooled to 0°. A solution of $NEt_3$

(2.02 g, 20 mmol) and benzylamine (1.07 g, 10 mmol) in 20 ml of $CH_2Cl_2$ was then added dropwise over 10 min. to the flask. The resulting solution was stirred for 14 hr. and then washed with 10% HCl (3x10 ml), 0.1 M NaOH (6x25 ml), $H_2O$ (3x20 ml), dried ($MgSO_4$) and concentrated to give 2.10 g (98%) of pure N-benzoyl benzylamine, mp 105°.

Preparation 18. Alkylation of Primary Triflamides (N-Ethyl-N-Benzyltriflamide). - A solution of ethyl iodide (0.18 g, 5 mmol) in 5 ml of dry acetone was added quickly (2 min.) to a stirred mixture of N-benzyltriflamide (1.18 g, 5 mmol) and anhydrous $K_2CO_3$ (0.69 g, 5 mmol). The reaction mixture was stirred at RT for 14 hr. The acetone was then removed *in vacuo* and the residue extracted with $CHCl_3$ (3x25 ml). The $CHCl_3$ extracts were combined, washed with $H_2O$ (3x20 ml), dried ($Na_2SO_4$), and concentrated *in vacuo* giving 1.21 g (91%) of a pure clear oil with the correct spectra.

Preparation 19. Reduction of Secondary Triflamides to Amines (N-Ethyl-N-Benzylamine). - A solution of N-ethyl-N-benzyltriflamide(2.67g,10 mmol) in dry $Et_2O$ (ml) was added dropwise to a suspension of LAH (1.14 g, 30 mmol) in dry $Et_2O$ (75 ml). The mixture was refluxed for 3 hr. and then cooled to 0°. The excess LAH was decomposed by dropwise addition of cold $H_2O$ (3.5 ml), then 15% NaOH (3.5 ml), followed by $H_2O$ (10.5 ml). The mixture was then filtered,

dried ($Na_2SO_4$), and evaporated in vacuo leaving 1.21 g (90%) of a yellow liquid. This was dissolved in dry $Et_2O$ (20 ml) and saturated with HCl gas. The white precipitate which formed was filtered and dried in vacuo giving 1.50 g (88%) of N-ethyl-N-benzylamine.HCl, mp 183°.

Preparation 20. Reduction of Primary Triflamides to Amines (Benzylamine). - A solution of N-benzyltriflamide (2.40 g, 10 mmol) and Red-Al (40 mmol) in 50 ml of benzene was refluxed under $N_2$ for 8 hr. The reaction mixture was cooled and the excess reducing agent decomposed by addition of 10% NaOH solution (20 ml). The mixture was then extracted with $Et_2O$ (5x50 ml). The organic layer was washed with 10% NaOH (2x20 ml), $H_2O$ (3x20 ml), and then extracted with 5% HCl (5x100 ml). The aqueous layer was then basified with 40% NaOH and extracted with $Et_2O$ (3x100 ml). The organic layer was dried ($Na_2SO_4$), concentrated to a volume of ~ 20 ml and then saturated with HCl gas. After filtration and drying 1.31 g (92%) of benzylamine·HCl, mp 256°, was obtained.

Preparation 21. Gabriel Synthesis of Primary Amines (1-Amino-3-Phenylpropane). - 9-Fluorenyl triflamide (313 mg, 1.0 mmol) and 1-bromo-3-phenylpropane (199 mg, 1 mmol) were dissolved in dry $CH_3CN$ (10 ml). The resultant solution was stirred with anhydrous $K_2CO_3$ (276 mg, 2 mmol) at reflux for 16 hr. The reaction mixture was filtered, evaporated

in vacuo, dissolved in a mixture of THF (20 ml) and 10% HCl (5 ml) and stirred at RT for 1 hr. The THF was evaporated in vacuo and the residue was extracted with $Et_2O$ (2x50 ml). The $Et_2O$ was washed with 10% HCl (2x5 ml). The aqueous fractions were combined, evaporated in vacuo and the residue recrystallized from EtOH, yielding 110 mg (65%) of 1-amino-3-phenylpropane hydrochloride, mp 217-218°.

Preparation 22. Synthesis of Acylhydrazones (Hydrocinnamaldehyde hydrazine). - A solution of N'-trifyl-t-butoxycarbonyl hydrazine (792 mg, 3 mmol) and 1-bromo-3-phenylpropane (398 mg, 2 mmol) in dry $CH_3CN$ (15 ml) was stirred with anhydrous $K_2CO_3$ at 60° for 42 hr. The reaction mixture was filtered through Celite, evaporated, taken up in $CH_2Cl_2$ and filtered again. After evaporation of the solvent, 405 mg (82%) of a crystalline solid remained. Recrystallization from benzene/hexane yielded 378 mg (77%), mp 135-137°, compared with an authentic sample, made from t-butyl carbazate and hydrocinnamaldehyde (mp 139-140°).

Preparation 23. Dehydration of Amides with $Ph_3P(OTf)_2$ (Benzonitrile). - A solution of triphenylphosphine oxide (2.78 g, 10 mmol) in 20 ml of $CH_2Cl_2$ was cooled to 0°. To this was added dropwise over 10 min. a solution of $(CF_3SO_2)_2O$ (2.82 g, 10 mmol) in 20 ml of $CH_2Cl_2$. After 5 min. a solution of benzamide (1.21 g, 10 mmol) in 10 ml of $CH_2Cl_2$ was added

dropwise to the flask. The reaction mixture was allowed to warm to RT and was stirred for 24 hr. The product was then distilled and the fraction boiling at 185-195° collected giving 720 mg (70%) of pure benzonitrile.

Preparation 24. Dimethyl Disulfide Ditriflate Oxidation of Alcohols (Benzil). - A solution of $(CF_3SO_2)_2O$ (1.55 g, 5.5 mmol) in 5 ml of $CH_2Cl_2$ was added dropwise to a solution of dry dimethyl sulfoxide (390 mg, 5.0 mmol) in 10 ml of $CH_2Cl_2$ at -78° under $N_2$ atmosphere. After 5 min. a solution of benzoin (530 mg, 2.5 mmol, in 10 ml of $CH_2Cl_2$ was added dropwise to the reaction mixture. After 15 min. a solution of $NEt_3$ (2.02 g, 20 mmol) in 25 ml of $CH_2Cl_2$ was added. The solution was allowed to warm to RT and stirred for 15 min. The solution was then diluted with $Et_2O$ (200 ml), washed with 10% HCl (3x50 ml), satd. NaCl (2x50 ml), dried ($Na_2SO_4$), and the solvent removed in vacuo to give 1.02 g (97%) of pure product, mp 93-94°.



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23. More recent unpublished work in our laboratories has shown that the potassium salt of the N-trifyl t-butylcarbazate may also be made with potassium t-butoxide/t-butanol and similarly stored and pyrolyzed to anhydrous potassium triflinate on demand. We have also noted that N-trifyl t-butylcarbazate itself decomposes on storage at room temperature but its salts are quite stable.

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