Tetrahedron. Vol 32, pp. 1627 to 1635 Pergamon Press 1976. Printed in Great Britain

SYNTHETIC MANIPULATION OF THE TRIFLONE GROUP

FORMATION FROM ALCOHOLS, CONSTRUCTIONS, AND CONVERSION TO KETONES AND AMINES

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(*Received in USA 29 September 1975; Received in UK for publication 9 February 1976*)

Abstract—The rearrangement of trifluoromethanesulfinates to trifluoromethanesulfones ("triflones") was developed as a synthetic method for obtaining these compounds Their utility as reagents for the construction of carbon skeletons is explored with regard to reactions such as alkylation, conjugate addition, and cycloaddition. In addition, the conversion of triflones to more common functionality is described.

As part of a study of the synthetic utility of trifluoromethanesulfones (triflones)[1] we sought simpler ways of routine synthesis of these reagents as well as the removal of the trifyl (CF_3SO_2–) group from a carbon skeleton, after its synthetic use in activating constructions, by its conversion to other functionality. Several transformations that serve these ends are described here and mainly summarized in Chart 1.

(a) *Formation of triflones.* The best general preparation of triflones to date has been S_N2 S-alkylation of potassium triflinate (KSO_2CF_3) by alkyl halides in boiling acetonitrile.[1] The reaction proceeds cleanly but slowly on primary halides, unactivated halides requiring 5–20 days owing to the low nucleophilicity of the rather stable triflinate anion. Secondary halides were unreactive.

O-Alkylation[2] to triflinate esters, R–SO–O–R′, occurs at a more rapid rate either with silver triflinate and alkyl halides or with potassium triflinate on alkyl nosylates (*p*-nitrobenzenesulfonates). Thus, γ-phenylpropyl bromide with silver triflinate yielded γ-phenylpropyl triflinate in boiling acetonitrile for 18 hr in 65% yield, most of the remainder being unreacted bromide. Similarly, β-phenethyl nosylate and potassium triflinate in the same medium produced the ester in 98% yield in 24 hr. Other sulfonate esters did not function as cleanly, the mesylate affording no reaction in 10 days. Simple secondary substrates were unsatisfactory,† cyclohexyl bromide and silver triflinate affording no recognizable products and cyclohexyl mesylate yielding only cyclohexene (61%) with potassium triflinate. Isopropyl nosylate and potassium triflinate yielded 74% of potassium nosylate but only 23% of isopropyl triflinate, the difference again implying elimination to propylene.

We sought an alternative synthesis of triflones from alcohols, as more accessible than halides, and examined the rearrangement of triflinate esters to triflones. Such rearrangements have previously been carried out with other sulfinate esters, ionization and ion-pair recombination being implicated in simple cases[4–6] and [2,3]-sigmatropic rearrangement implied in allylic[7] and propargylic[8] cases.

Direct preparation of triflinate esters from alcohols required a triflinating agent, and, while the unstable gas, CF_3SOF, has been successfully used for this purpose,[9] we required a simpler procedure. We had previously observed[1] that acid chlorides react with potassium triflinate to create an unstable substance (presumably the mixed anhydride $CF_3SOOCOR$) which on reaction with aniline afforded both φ $NHSOCF_3$ and φ NHCOR (9:1). Thus we sought a hindered mixed anhydride to suppress nucleophilic attack from the wrong side. When mesitylenesulfonyl chloride was mixed with potassium triflinate in acetonitrile at room temperature, potassium mesitylenesulfonate precipitated and the filtrate esterified 3-phenyl-1-propanol (eqn 1). The reagent is presumably CF_3SOCl, previously made[10] from the fluoride and HCl and exhibiting a similar IR spectrum.

†Similar results attended alkyl halide reaction with other silver sulfinates, primary halides affording sulfinates and secondary none.[3]

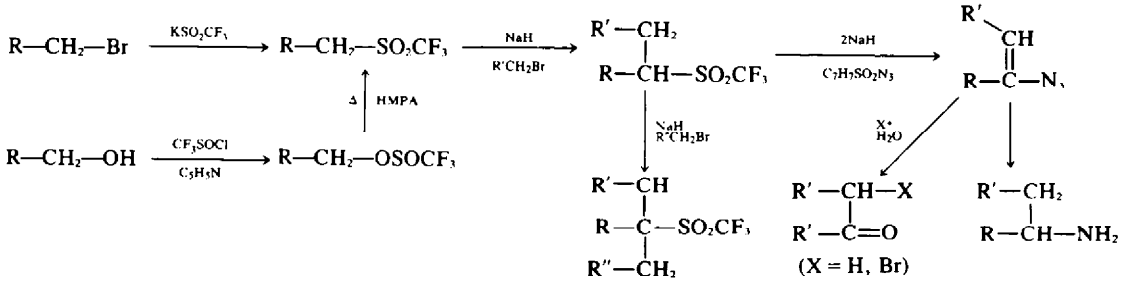
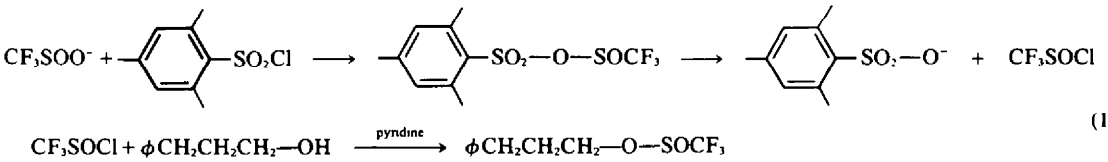


Chart 1. Interconversions of triflones.



(1)

A general procedure for triflination of alcohols thus evolved: equimolar amounts of potassium triflinate and mesitylenesulfonyl chloride in acetonitrile are stirred and cooled, and an equimolar solution of the desired alcohol and pyridine in acetonitrile is added slowly at 0° and stirred. Normal extractive work-up produces the triflinates, tabulated in Table 1. Alkaline hydrolysis readily affords the parent alcohol and the triflinate esters are also easily distinguished from the isomeric triflones by their spectra: (a) the IR spectra exhibit only a single S=O stretch (8.9μ)[10] instead of the two (*ca.* 7.4 and 8.9μ) common to all triflones; and (b) the methylene absorption in $-CH_2-OSOCF_3$ (4.0–4.7δ) is shifted about 0.8 ppm downfield from that of the corresponding triflone ($-CH_2SO_2CF_3$) and is in contrast as well by being invariably a complex multiplet signal owing to the proximal asymmetric S atom.[9]

Simple primary triflinates rearranged cleanly (Table 2) to triflones on heating at 145° in hexamethylphosphoramide for 4 hr, or in dimethylformamide at 155°, but were unchanged at these temperatures in less polar solvents like diglyme or sulfolane, or on neat pyrolysis, and decomposed at higher temperatures. This rearrangement of primary triflinates is in sharp contrast to the unreactivity of the corresponding arenesulfinates; in keeping with an ionization mechanism, arenesulfinates rearrange only when located at a substituted or stabilized carbonium ion site. The greater stability of the triflinate anion, however offers a lower barrier and allows ionization-recombination to the more stable triflone even in simple primary examples.† This stability is implicit in $\Delta pK_a = 3$ for the sulfinic acids: triflinic acid (CF_3SO_2H),[11] $pK_a = -0.5$; arenesulfinic acids,[12] $pK_a = 2.68$–3.08. The same triflinate anion stability accounts for the observation that secondary esters give predominantly elimination; the triflinate of 1-phenyl-3-butanol (**1**) yielded quantitatively a 12:1 mixture of *trans*-1-phenyl-2-butene (**2**) and another product, presumably 1-phenyl-3-butyl triflone (**3**), at 125° in hexamethylphosphoramide. α-Phenethyl triflinate yielded only styrene at 60° in chloroform (in contrast to rearrangement of the corresponding toluenesulfinate to sulfone at 120°).[5] Secondary and tertiary triflones also undergo easy pyrolytic elimination.[1] Thus our results with simple substrates are consistent with the ionization–recombination mechanism,[4-6] but with a more stable leaving group and consequently more frequent elimination.

Allylic alcohol triflinates rearrange under much milder conditions (Table 2). Allyl triflinate itself (**4a**) at 120° in acetonitrile changed first to allyl triflone (**4b**) evidenced by the NMR spectrum, the methylene multiplet at 4.70δ being replaced by a new doublet at 4.08δ with little change

†Benzyl iodide and silver triflinate were earlier reported[13] to afford about a 1:1 mixture of benzyl triflone and benzyl triflinate, but his now seems likely to have resulted from easy partial rearrangement of an initially formed triflinate rather than from mixed O- and S-alkylation of the ambident nucleophile.

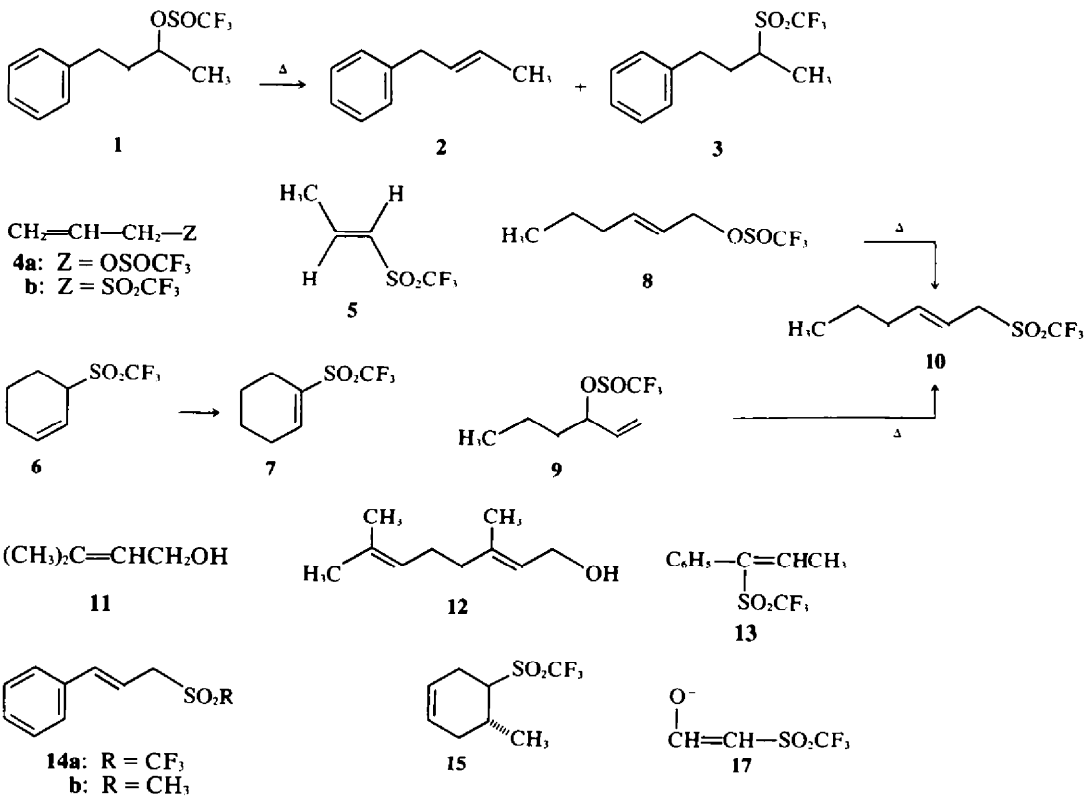


Table 1. Preparation of triflinate esters, R–O–S(=O)CF$_3$

R[a]	Method of preparation[b]	Yield (%)	NMR (H-C-OSOCF$_3$) δ (CDCl$_3$)
φCH$_2$CH$_2$-	A	98	4.02-4.78
φCH$_2$CH$_2$CH$_2$-	A	93	3.90-4.57
CH$_2$=CHCH$_2$CH$_2$CH$_2$-	A	65	3.93-4.60
n-C$_7$H$_{15}$-	A	80	3.91-4.62
φCH$_2$CH$_2$CH(CH$_3$)-	B	82	4.32-4.79
φCH(CH$_3$)-	B	78	4.92-5.84
CH$_2$=CHCH$_2$-	B	68	4.59-4.87
CH$_3$CH$_2$CH$_2$CH=^{t}CHCH$_2$-	B	74	4.60-4.92 (CD$_3$CN)
CH$_2$=CHCH(n-C$_3$H$_7$)-	B	76	4.70-5.10 (CD$_3$CN)

a) All compounds were liquids and were characterised by IR and NMR spectroscopy.

b) A: from p-nitrobenzenesulfonate and potassium triflinate

B: from CF$_3$SOCl esterification

Table 2. Triflones prepared by triflinate ester rearrangement

R-OSOCF$_3$ $\xrightarrow{\Delta}$. R-SO$_2$CF$_3$		Reaction conditions	Yield (m.p.)	NMR (H-C-SO$_2$CF$_3$) δ (CDCl$_3$)
n-C$_7$H$_{15}$-	n-C$_7$H$_{15}$-	HMPA, 145°, 4 hrs	87% (liq)	3.28, t, J=7.5
φCH$_2$CH$_2$-	φCH$_2$CH$_2$-	DMF, 155°, 4 hrs	56% (78-78.5°)	3.04-3.65, m
φCH$_2$CH$_2$CH$_2$-	φCH$_2$CH$_2$CH$_2$-	HMPA, 145°, 4 hrs	71% (25-27°)	3.19, t, J=7.5
CH$_2$=CHCH$_2$CH$_2$CH$_2$-	CH$_2$=CHCH$_2$CH$_2$CH$_2$-	HMPA, 145°, 4 hrs	78% (liq)	3.22, t, J=7.5
CH$_2$=CHCH$_2$-	CH$_3$CH=CH-	CH$_3$CN, 130°, 13 hrs	83% (liq)	see experimental
CH$_3$CH$_2$CH$_2$CH=^{t}CHCH$_2$-	CH$_3$CH$_2$CH$_2$CH=^{t}CHCH$_2$-	CH$_3$CN, 75°, 4 hrs	89% (liq)	3.95, d, J=7
CH$_2$=CHCH(n-C$_3$H$_7$)-	CH$_3$CH$_2$CH$_2$CH=^{t}CHCH$_2$-	CH$_3$CN, 60°, 20 hrs	95% (liq)	3.95, d, J=7
 [a]		CH$_3$CN, <25°, 1 hr	25% (liq)	3.82-4.25, m
φCH=CHCH$_2$- [a]	φCH=CHCH$_2$- [b]	CH$_3$CN, <25°, 7 hrs	42% (liq)	4.05, d, J=7.5

[a] The ester was not isolable; the reaction conditions given for triflone formation are those used for esterfication (see text).

[b] Contaminated by the isomeric triflone φC(Tf)=CHCH$_3$

in the vinyl portion of the spectrum. Further change occurred concurrently and the only product after 15 hr at 130° was *trans*-1-propenyl triflone (**5**) formed by a facile double bond migration into conjugation, and identified by spectra (Experimental). In the case of 2-cyclohexenol, esterification with CF$_3$SOCl afforded the unconjugated triflone (**6**) directly, apparently by rearrangement at <25° of the initial triflinate. Here the double bond also migrated into conjugation, on standing for three days with triethylamine, to yield 1-cyclohexenyl triflone (**7**).

The difference in conditions to rearrange these two allylic triflinates suggested that the mechanism was not a pericyclic one since the rearrangement of allylic benzenesulfinates, claimed to be concerted, is relatively insensitive to substituent effects.[7] A test of pericyclic mechanism was sought with the isomeric hexenyl triflinates, **8** and **9**. In acetonitrile or HMPA at 55–60° both were converted cleanly to the single unconjugated *trans*-2-hexenyl triflone (**10**). The isolation of only one allylic triflone, the less substituted one, and the temperature order reflecting increased substitution (allyl < hexenyl < cyclohexenyl) all combine to support an ionization-recombination mechanism in these allylic examples rather than the [2,3]-sigmatropic shift observed with allylic benzenesulfinates. In contrast to other propargyl sulfinates, which undergo smooth pericyclic rearrangement, propargyl triflinate yielded only tars. Esterification of two other allylic alcohols, 3-methyl-2-butenol (**11**) and geraniol (**12**), led (at <15°) to triflone products by spectral evidence, but the products proved too unstable for distillation or chromatographic purification.

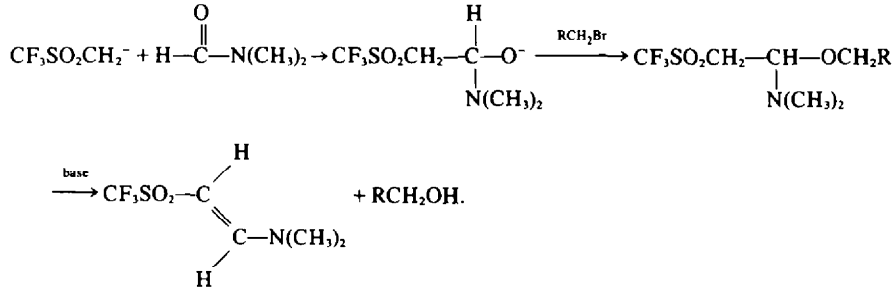
Cinnamyl alcohol, on esterification with CF$_3$SOCl, led directly to two triflone products in 42% total yield. On chromatographic separation, the minor product gave spectral evidence of being the isomer expected from pericyclic rearrangement followed by double bond migra-

tion, i.e. **13**, exhibiting a 3-proton doublet at 1.84δ and a 6-proton multiplet at 7.17–7.56δ. The major product was the normal unconjugated cinnamyl triflone, **14a**, as indicated by its UV spectrum, essentially identical with that[14] of **14b**. Treatment of **14a** with triethylamine and D_2O resulted in exchange of all three α- and γ-protons, but no change in the UV, and little in the IR, spectrum, indicating that in this case the double bond is more stable out of conjugation with triflone. Similar NMR behavior was also observed on triethylamine-catalyzed deuteration of the hexenyl triflone, **10**, but in this case only the two α-protons were exchanged.

Spectrally, the conjugated triflones (**5**, **7**, **13**) exhibited a medium-strong 6.14μ band in the IR spectrum and the UV spectrum of the substituted vinyl triflone **7** showed a maximum at 214 nm (ϵ = 5900) whereas the parent vinyl triflone was reported[15] to be "transparent" above 200 nm. The *trans*-geometry of the double bonds in **5**, **10** and **14** is based on vicinal coupling constants, J = 15 Hz in the NMR, and a medium strong band at 10.3–10.5 in the IR.

(b) *Construction reactions.* The synthetic interest in vinyl triflones lies in construction reactions by conjugate addition or cycloaddition.[1] While steric and electronic influences by the triflone group apparently impede equilibration into conjugation in some cases (cf., **10**, **14**), we were able to confirm these reactions with propenyl triflone (**5**). On treatment with butadiene at 100° it formed an adduct (**15**) in 71% yield, which could be hydrogenated with Pd catalysis, without loss of the triflone group, to 2-methylcyclohexyl triflone. On the other hand, addition of lithium dimethylcuprate in ether at −50° afforded isobutyl triflone in 78% yield, identical with a sample prepared by alkylation of methyl triflone with isopropyl iodide.

The main synthetic utility of triflones probably lies in the facile α-alkylation which they undergo.[1] The α-carbanions are easily formed and quite stable in solution, the pK_a values being similar to those of the corresponding α-nitro carbanions.[16] As the acidity of the secondary α-carbanions is significantly less than primary ones,[17] monoalkylation of primary triflones proceeded cleanly without contamination by dialkylated side products, either using potassium carbonate in refluxing acetonitrile, or equimolar sodium hydride to preform the anion at room temperature in hexamethylphosphoramide (or 1:4 mixed solvent wth glyme or tetrahydrofuran); anion formation with sodium hydride is rapid and appears the mode of choice. Hydroxide[18] and ethoxide ion are less effective as bases due to competing haloform reaction with the trifyl group. (Methyl triflone gave sodium methanesulfonate in 73% yield upon reaction with sodium ethoxide in refluxing ethanol). Dimethylformamide also proved a poor solvent, for alkylations on methyl triflone with either β-phenethyl or γ-phenylpropyl bromides using potassium carbonate at 100° produced β-dimethylaminovinyl triflone (**16**) and the alcohol corresponding to the bromide, presumably by eqn (2).[19] Used with sodium hydride, however, dimethylformamide was generally successful.



16 (2)

Table 3. Alkylation of triflones[a]

Triflone	Alkylating Agent	Base[b]	Conditions	Product	Yield
CH_3Tf	φCH_2CH_2Br	NaH	DMF/25°/18 hr	$\varphi CH_2CH_2CH_2Tf$	73%
CH_3Tf	φCH_2Br	NaH	DMF/25°/10 hr	φCH_2CH_2Tf $(\varphi CH_2)_2CHTf$	18% 48%
CH_3Tf	$(CH_3)_2CHI$	NaH	G-H/reflux/8 hr	$(CH_3)_2CHCH_2Tf$	60%
CH_3CH_2Tf	CH_3I	NaH	G/25°/2.5 hr	$(CH_3)_2CHTf$	60%
$n\text{-}C_6H_{13}CH_2Tf$	φCH_2Br	NaH	HMPA/25°/3 hr	$n\text{-}C_6H_{13}CH(Tf)CH_2\varphi$	73%
φCH_2Tf	φCH_2Br	K_2CO_3	CH_3CN/84°/16 hr	$\varphi CH_2CH(Tf)\varphi$[c]	95%
φCH_2CH_2Tf	φCH_2Br	K_2CO_3	CH_3CN/84°/36 hr	$(\varphi CH_2)_2CHTf$[c]	70%
$\varphi CH_2CH(Tf)\varphi$	CH_3I	NaH	THF/25°/12 hr	$\varphi CH_2C(CH_3)(Tf)\varphi$[c]	95%
$(\varphi CH_2)_2CHTf$	CH_3I	NaH	THF/25°/12 hr	$(\varphi CH_2)_2C(Tf)CH_3$[c]	80%

[a] Abbreviations: Tf=SO_2CF_3; DMF=dimethylformamide; HMPA=hexamethylphosphoramide; G=glyme; G-H=glyme-HMPA (4:1); THF=tetrahydrofuran

[b] Bases used in ~ 1.1 molar equivalents

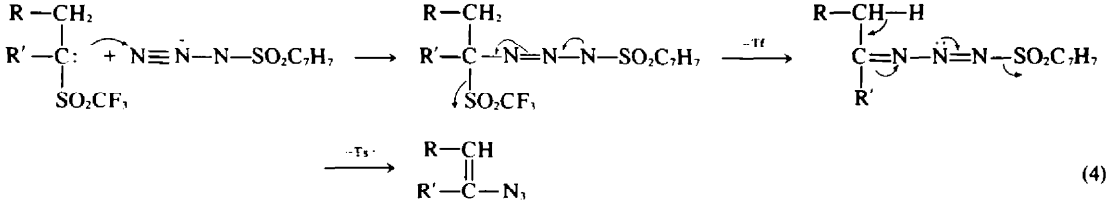
[c] Reported in ref. 1 and A. Giga Ph.D. Thesis, Brandeis University, 1974.

Examples of α-alkylation are collected in Table 3. The simplest synthon is methyl triflone, which by successive alkylations can yield $R^1R^2R^3C-SO_2CF_3$. It has been prepared[20] from trifyl fluoride, CF_3SO_2F, with methyl Grignard but in our hands this was unsuccessful on the more available triflic anhydride $(CF_3SO_2)_2O$, and simple methylations of potassium triflinate were poor. However alkylation with t-butyl bromoacetate followed directly by pyrolysis (150°) and distillation afforded 62% of methyl triflone (b.p. 127°) by eqn (3).

$$CF_3SO_2^- + BrCH_2COOC(CH_3)_3 \rightarrow CF_3SO_2CH_2COOC(CH_3)_3 \xrightarrow{\Delta} CF_3SO_2CH_3 + CO_2 + CH_2 = C(CH_3)_2. \quad (3)$$

In direct contrast to enolate carbanions, the anion of methyl triflone smoothly monoalkylated and showed no tendency to dialkylation with unactivated primary halides, although benzyl bromide yielded a mixture. Acylation of methyl triflone anion by simple esters (cf., ethyl benzoate or heptanoate) failed to yield any ketotriflones but condensation with ethyl formate via t-butoxide in t-butanol created the salt of hydroxyvinyl triflone (**17**, 87%), characterized as a 2,4-dinitrophenylhydrazone.

(c) *Oxidative removal of triflone.* Although the triflone group has been removed from a carbon skeleton by hydrogenation or elimination,[1] these are reductive or isohypsic changes and to date there has been no report of an oxidative removal, as by oxidation of the α-carbanion. However, the carbanion of 1,2-diphenylethyl triflone from sodium hydride in ether solvents was unreactive to molecular oxygen at −78° or room temperature. By contrast the anion reacted immediately at 0° with p-toluenesulfonyl azide† in glyme causing precipitation of sodium triflinate. This precipitation was only quantitative when two moles of sodium hydride were used and the worked-up organic product showed no sulfonyl bands in the IR spectrum. This product was formed quantitatively and was identified as 1,2-diphenylethylene azide by its IR bands (e.g. 4.67 μ) and its conversion by LAH to 1,2-diphenylethyl amine. Furthermore, acid hydrolysis (conc. HCl in glyme at 25°) afforded deoxybenzoin quantitatively.



(4)

The formation of a vinyl azide in this reaction is rationalized in eqn (4). The hydrolysis of vinyl azides has been shown by Hassner[24] to proceed by initial C-protonation followed by hydrolysis or Schmidt rearrangement, the former yielding ketones as in the example above, the latter creating amides. The rearrangement to amide intervened in two other cases tried, appearing as a 6 μ band in the crude product IR spectrum. Thus 1-phenyl-2-octyl triflone and 2-methylcyclohexyl triflone on similar conversion to vinyl azides and hydrolysis each afforded only 36% yield of the corresponding ketones, 1-phenyl-2-octanone and 2-methylcyclohexanone, respectively, identified by their known derivatives. Vinyl azides have also been converted to α-bromoketones by bromination in ether followed by hydrolysis,[25] a route uncomplicated by rearrangement. In any case the facile conversion of triflones to vinyl azides provides a mild and specific oxidative removal of the triflone group, leading to ketone or amine groups in its place.

In conclusion, then, our initial results give considerable promise to the use of the triflone group as a synthetic tool, created from primary halides or alcohols, or allylic alcohols, used to activate successive α-alkylations or additions, and removed by reduction, elimination or conversion to vinyl azides, ketones or amines, as largely summarized in Chart 1.

EXPERIMENTAL

M.ps were determined on a Fisher-Johns apparatus and are uncorrected. B.ps are uncorrected for changes in the barometric pressure. IR spectra were recorded with a Perkin-Elmer 137, D-69, or 567 spectrophotometer. The absorption maxima are reported in microns. NMR spectra were recorded with a Varian Associates A-60 or a Perkin–Elmer R-24 spectrometer. Chemical shifts are reported in delta (vs TMS as an internal standard) with a description of the resonance, coupling constant in Hz (if any), and integration following. In addition to the common abbreviations, the following are used: dd, double doublet; dt, double triplet; dq, double quartet; and dm, double multiplet. UV spectra were recorded in methanol with a Perkin–Elmer 124 spectrophotometer. Absorption maxima are reported in nanometers with the extinction coefficient following. Mass spectra were determined with an AEI MS-12 spectrometer purchased with aid from the National Science Foundation Grant GP-3644. Gas chromatography was performed with a Varian Associates model 1720 instrument using a 3/8" × 20' column packed with 30% SE-30 on 30–60 Chrom. W. Elemental analyses were performed by Galbraith Laboratories or Chemalytics.

Potassium triflinate (KSO_2CF_3)

Potassium triflinate was obtained by elimination of CF_3SO_2 from N-phenacylphenyltriflamide (m.p. 109–110°, prepared by the procedure reported for N-(*p*-bromophenacyl)-phenyltriflamide[26]).

A general procedure is as follows: N-phenacylphenyltriflamide is dissolved in dry acetone (~1 M soln), to which 1.1–1.2 equivs of anhyd K_2CO_3 are added. The mixture is stirred at 25° for 2 days in a closed flask. After filtering, the filtrate is concentrated *in vacuo*, the residue is extracted (2 – 3x) with CH_2Cl_2, and the insoluble KSO_2CF_3 is separated by filtration. It is important to note that KSO_2CF_3 is a very hygroscopic material and normal precautions should be observed when an anhyd preparation is required. The amount of moisture absorbed is undetermined but we have obtained satisfactory results assuming the empirical formula $KSO_2CF_3 \cdot H_2O$.

Silver triflinate ($AgSO_2CF_3$)

KSO_2CF_3 (450 mg) and $AgNO_3$ (414 mg, 243 mmol) were dissolved in MeCN (3 ml). The mixture was stirred for 2 hr at 25° and then filtered. Removal of the solvent from the filtrate *in vacuo* afforded 616 mg of white solid (105% of theory). The KNO_3 removed by filtration weighed 248 mg (2.46 mmol, 101%).

†For the reactions of enolate anions with sulfonyl azides, see Refs. 21–3.

Alkylation of $AgSO_2CF_3$ *with 1-bromo-3-phenylpropane*

$AgSO_2CF_3$ (241 mg, 1 mmol) and 1-bromo-3-phenylpropane were dissolved in MeCN (3 ml). The soln was heated at reflux for 18 hr, cooled, and filtered to collect the ppt (125 mg, 67%). Solvent was removed from the filtrate *in vacuo* and the residue was dissolved in CH_2Cl_2 which was filtered and concentrated by evaporation of the solvent to afford a light brown mobile liquid (254 mg) which was identified as a mixture of 1-bromo-3-phenylpropane and 1-phenylpropyl 3-triflinate by comparison of the spectral data with that of the known compounds and by TLC. Integration of the NMR spectrum determined the ratio to be 35:65, respectively. The yield of triflinate is thus 165 mg (0.65 mmol, 65%).

Preparation of p-nitrobenzenesulfonate esters

With the exception of isopropyl nosylate, all were prepared from *p*-nitrobenzenesulfonyl chloride essentially as described by Fieser for the preparation of tosylates.[27]

β-Phenethyl nosylate—colorless crystals from EtOH, m.p. 94° (lit.[28] 101.5–102°).

3-*Phenylpropyl* 1-*nosylate*—colorless crystals from MeOH, m.p. 64–65°. IR (CH_2Cl_2): 6.22, 6.52, 7.06, 7.34, 7.44, 7.9, 8.45; NMR ($CDCl_3$): 8.35 (d, J = 9, 2), 8.03 (d, J = 9, 2), 6.86–7.33 (m, 5), 4.14 (t, J = 6, 2), 2.69 (t, J = 7, 2).

4-*Pentenyl* 1-*nosylate*—colorless crystals from MeOH, m.p. 39–40° (lit.[29] 46–47°).

n-*Heptyl nosylate*—colorless crystals from MeOH, m.p. 64.5–65.5°. IR (CH_2Cl_2): 3.48, 3.57 6.20, 6.51, 7.30, 7.40, 8.40; NMR ($CDCl_3$): 8.43 (d J = 9, 2), 8.12 (d, J = 9 2) 4.17 (t, J = 6, 2), 0.67–2.07 (m, 13).

Isopropyl nosylate.† A soln of nosyl chloride (4.44 g, 20 mmol) in CH_2Cl_2 (10 ml) was added during 10 min to a stirred soln of isopropanol (1.20 g, 20 mmol) and pyridine (1.58 g, 20 mmol) in CH_2Cl_2 (20 ml) cooled in an ice bath. After addition was complete the reaction was held at 5° for 2 days. The CH_2Cl_2 soln was then washed 5 times with H_2O (50 ml) and dried ($MgSO_4$). Removal of the solvent *in vacuo* afforded 4.09 g (16.6 mmol, 83%) of isopropyl nosylate as light yellow crystals, m.p. 44–45.5° (lit.[30] 53–54°).

Hydrolysis of β-phenethyl triflinate

β-Phenethyl triflinate (248 mg, 1.04 mmol) was mixed with a solution of KOH (0.5 g) in H_2O (10 ml) and sufficient EtOH was added to obtain a homogeneous mixture. After stirring overnight the reaction was acidified with 10% HCl and extracted twice with CH_2Cl_2. Drying ($MgSO_4$) and evaporation of the solvent yielded 80 mg of β-phenethyl alcohol as a colorless oil (0.66 mmol, 63%) identified by comparison of the IR spectrum with that of an authentic sample and by formation of a 3,5-dinitrobenzoate (m.p. 99°, lit.[31] 105–106°).

Cyclohexene from cyclohexyl mesylate

Cyclohexyl mesylate (534 mg, 3 mmol) and KSO_2CF_3 (516 mg) were dissolved in DMF (20 ml) and the resultant soln was heated with reflux at 155° for 2 hr. The volatile materials were then collected by simple distillation to yield 150 mg cyclohexene (1.83 mmol, 61%). After cooling, the reaction was diluted with ether and filtered to collect 400 mg of ppt (100% of theory). After washing with 6 N HCl, sat $NaHCO_3$, and H_2O, the ether was dried and concentrated *in vacuo*. No material remained.

Isopropyl triflinate from isopropyl nosylate

Isopropyl nosylate (735 mg, 3 mmol) and KSO_2CF_3 (570 mg) were dissolved in MeCN (10 ml) and heated at 50–55° for 65 hr. After cooling, the mixture was filtered to collect 537 mg of ppt (74% of theory). The filtrate was diluted with ether (75 ml) and washed 5 times with H_2O and once with sat NaCl. After drying ($MgSO_4$), the ether was removed *in vacuo* to yield a light green residue which was distilled (25°, 0.1 mm), the distillate being collected at −78°. The pot residue was identified as isopropyl nosylate by examination of its IR spectrum (104 mg, 0.425 mmol, 14%). The distillate consisted of isopropyl triflinate (121 mg, 0.69 mmol, 23%). IR (CH_2Cl_2): 3.29, 8.35, 8.90, 11.0, 11.8; NMR ($CDCl_3$): 4.87 (sept, J = 6.5, 1) 1.48 (d, J = 6.5, 3), 1.44 (d, J = 6.5, 3).

General procedure for the synthesis of triflinates from nosylates

Equimolar quantities of the nosylate and KSO_2CF_3 were dissolved in MeCN and heated at reflux for 18–24 hr. After cooling, the mixture was filtered and the solvent removed from the filtrate *in vacuo*. The residue was extracted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo* to yield the desired triflinate as a colorless liquid, homogeneous by TLC and used without further purification.

β-Phenethyl triflinate—98% yield. IR (neat): 3.25, 3.35, 6.22, 6.69, 6.91, 8.35, 8.9; NMR ($CDCl_3$): 7.28 (s, 5), 4.02–4.78 (m, 2) 3.03 (t, J = 7, 2).

1-*Phenylpropyl* 3-*triflinate*—93% yield. IR (CH_2Cl_2): 3.23 3.32, 6.23, 6.68, 6.90, 8.35, 8.89; NMR ($CDCl_3$): 7.20 (s, 5) 3.90–4.57 (m, 2), 2.75 (t, J = 7, 2), 1.83–2.34 (m, 2).

4-*Pentenyl* 1-*triflinate*—70% yield. IR (CH_2Cl_2): 3.34, 6.10, 8.3, 8.88, 11.0; NMR ($CDCl_3$): 5.45–6.17 (m, 1), 4.82–5.24 (m, 2) 3.93–4.60 (m, 2), 1.57–2.43 (m, 4).

n-*Heptyl triflinate*—79% yield. IR (CH_2Cl_2): 3.38, 3.46, 8.35, 8.89; NMR ($CDCl_3$): 3.89–4.61 (m, 2), 0.66–2.06 (m, 13).

Trifluoromethanesulfinyl chloride (CF_3SOCl)

Anhyd KSO_2CF_3 (1.47 g, 8.55 mmol) and mesitylenesulfonyl chloride (1.83 g, 8.38 mmol) were dissolved in MeCN (25 ml) at 25°. The resultant soln was stirred for 1 hr and filtered to collect 1.53 g of ppt which gave a negative test for halogen when treated with aq $AgNO_3$ and was identical (IR) with an authentic sample of potassium mesitylenesulfonate. The filtrate (IR: 8.09, 8.22, 8.90)[10] was treated with 3-phenyl-1-propanol as described below to produce 1-phenylpropyl 3-triflinate in 65% yield.

General procedure for esterifying alcohols with CF_3SOCl

Anhyd KSO_2CF_3 (one equiv) and mesitylenesulfonyl chloride (0.95 equiv) are dissolved in MeCN at 25° to form a soln which is 0.5–1.0 M in each. After stirring for 0.5 hr, the mixture is cooled to 0° and a soln of the alcohol and pyridine (0.95 equivs each) in MeCN (*ca.* 2 M in each) is added dropwise. The mixture is allowed to warm to room temp. and is stirred several hr then diluted with ether (4 vols) and washed 5–8 times with H_2O and once with sat NaCl. The ether is dried ($MgSO_4$) and removed *in vacuo* to yield the product, in each case as a colorless liquid after purification.

1-*Phenylbutyl* 3-*triflinate*—81% yield (chromatographed on silica gel with CH_2Cl_2). IR (CH_2Cl_2): 3.24, 3.36, 6.22, 6.31, 6.70, 6.90, 6.99, 8.35, 8.88; NMR ($CDCl_3$): 7.20 (s, 5), 4.32–4.79 (m, 1) 2.56–2.92 (m, 2), 1.77–2.32 (m, 2) 1.47 (d, J = 6.5) 1.42 (d, J = 6.5, 1.5). (Found: C, 50.17; H, 4.99. Calc. for $C_{11}H_{13}F_3O_2S$: C, 49.61; H, 4.92%).

α-Phenethyl triflinate—78% unpurified yield (this material proved too labile to purify). IR (CH_2Cl_2): 6.23, 8.35, 8.87; NMR ($CDCl_3$): 7.0–7.33 (m) 4.92–5.84 (m), 1.32–2.03 (m).

2-*Propenyl* 1-*triflinate*—68% (distilled at 25°/0.1 mm). IR (CH_2Cl_2: 8.35, 8.89, 10.75, 11.15; NMR ($CDCl_3$): 5.20–6.38 (m, 3), 4.58–4.87 (m, 2).

trans-2-*Hexenyl* 1-*triflinate*—74% yield (distilled at 25°/0.15 mm). IR (neat): 3.32, 3.41, 5.97, 8.35, 8.86, 10.30; NMR (CD_3CN): 5.32–6.25 (m, 2) 4.60–4.82 (m, 2), 1.08–2.31 (m, 4), 0.88 (t, J = 6.5, 3).

1-*Hexenyl* 3-*triflinate*—76% yield (distilled at 25°/0.15 mm). IR (neat): 3.29, 3.40, 6.02, 8.35, 8.85; NMR (CD_3CN): 5.16–6.27 (m, 3), 4.70–5.10 (m, 1) 0.75–1.98 (m, 7).

β-Phenethyl triflone from β-phenethyl triflinate

β-Phenethyl triflinate (234 mg) was dissolved in DMF (3 ml). The resultant soln was heated under N_2 for 4 hr at 155°. After cooling the mixture was diluted with ether and washed several times with 6 N HCl and once with sat $NaHCO_3$. Drying ($MgSO_4$) and concentrating the ether *in vacuo* afforded 132 mg brown crystals, m.p. 78–78.5° (56%). An analytical sample was obtained by sublimation (70°/0.1 mm). IR (CH_2Cl_2): 6.13, 7.34, 8.3, 8.94;

†This procedure provides a significantly improved yield over that previously published.[30]

NMR ($CDCl_3$): 7.28 (s, 5), 3.04–3.65 (m, 4). (Found: C, 45.25; H, 3.82. Calc. for $C_9H_9F_3O_2S$: C, 45.37; H, 3.81%).

The following triflones were obtained in a similar manner, the only difference being the use of HMPA at 145° rather than DMF at 155°. Workup differed only in the use of H_2O in place of 6N HCl.

1-Phenylpropyl 3-triflone—colorless crystals by sublimation at 0.1 mm, m.p. 25–27°; 71% yield. Identical spectrally (IR, NMR) and by TLC with the product obtained by alkylating $CH_3SO_2CF_3$ with ϕCH_2CH_2Br.

4-Pentenyl 1-triflone—colorless liquid, b.p. = 183–185°; 78% yield. An analytical sample was obtained by preparative gas chromatography (column temp. 200°). IR (CH_2Cl_2): 3.20, 3.35, 6.09, 7.36, 8.3, 8.94; NMR ($CDCl_3$): 5.43–6.14 (m, 1), 4.82–5.27 (m, 2), 3.22 (t, J = 7.5, 2), 1.68–2.50 (n, 4). (Found: C, 35.48; H, 4.48. Calc. for $C_6H_9F_3O_2S$: C, 35.64; H, 4.49%).

n-Heptyl triflone—colorless liquid, b.p. (0.1 mm) = 37–38°; 87% yield. IR (CH_2Cl_2): 3.33, 3.42, 7.36, 8.23, 8.35, 8.94; NMR ($CDCl_3$): 3.28 (t, J = 7.5, 2), 0.66–2.23 (m, 13).

Pyrolysis of 1-phenylbutyl 3-triflinate

1-Phenylbutyl 3-triflinate (196 mg) was dissolved in HMPA (0.5 ml) and heated at 125° for 4 hr under N_2. Workup as before afforded 113 mg light yellow oil. GC analysis (column temp. 275°) revealed two compounds (12:1 in order of elution), neither of which has the same reaction time as the starting material. The major fraction was separated by distillation (25°/0.1 mm) and identified as *trans*-1-phenyl-2-butene by comparison (IR, NMR) with authentic material.

Propenyl 1-triflone

2-Propenyl 1-triflinate (203 mg) was dissolved in MeCN (1 ml). The resultant soln was sealed in a glass tube and heated at 130° for 13 hr. Evaporation of the solvent yielded propenyl 1-triflone as a clear brown liquid (168 mg, 83%). Preparative gas chromatography afforded an analytical sample (column temp. 180°). IR (CH_2Cl_2): 6.08, 6.16, 7.36, 8.3, 8.96, 10.55, 12.28; NMR ($CDCl_3$): 7.37 (dq, J = 15 and J = 7, 1) 5.48 (dm, J = 15, 1) 2.10 (dd, J = 7 and J = 1.5, 3); UV (MeOH): 205 (1600). (Found: C, 27.59; H, 2.89. Calc. for $C_4H_5F_3O_2S$: C, 27.70; H, 2.95.

2-Cyclohexenyl 1-triflone

To a soln of CF_3SOCl (4.4 mmol in MeCN (25 ml) at −35° was added dropwise with stirring a soln of 2-cyclohexen-1-ol (431 mg, 4.4 mmol) and pyridine (348 mg, 4.4 mmol) in MeCN (5 ml). The reaction was allowed to warm slowly to room temp. and was stirred for 8 hr. Workup afforded 723 mg brown liquid which was purified by preparative layer chromatography (silica gel; CH_2Cl_2/hexane, 1:1). The second band yielded 2-cyclohexenyl 1-triflone as a colorless oil (234 mg, 1.1 mmol, 25%). IR (CH_2Cl_2): 3.33, 3.42, 6.05, 7.35, 8.35, 8.95; NMR ($CDCl_3$): 6.28 (dm, J = 10, 1) 5.72 (dm, J = 10, 1), 4.02 (m, 1), 1.24–2.41 (m, 6).

Cyclohexenyl 1-triflone

2-Cyclohexenyl 1-triflone (234 mg) was dissolved in ether (1 ml). Three drops of triethylamine were added and the resultant soln allowed to stand at 25° for 3 days. More ether was added and the ether soln was washed successively with 10% HCl, sat $NaHCO_3$, and sat NaCl. Drying ($MgSO_4$) and removing the ether *in vacuo* afforded 212 mg cyclohexenyl 1-triflone (91%) as a colorless oil. Preparative gas chromatography (column temp. 240°) provided the analytical sample. IR (CH_2Cl_2): 3.33, 3.42 6.12, 7.41, 8.35, 8.90; NMR ($CDCl_3$): 7.13–7.34 (m, 1), 2.18–2.65 (m, 4), 1.32–1.96 (m, 4); UV (MeOH): 214 (5900). (Found: C, 39.33; H, 4.22. Calc. for $C_{10}H_9F_3O_2S$: C, 39.24; H, 4.23%).

trans-2-*Hexenyl 1-triflone from* 1-*hexenyl 3-triflinate*

1-Hexenyl 3-triflinate (8.11 g) was dissolved in MeCN (50 ml) and heated at 60° under N_2 for 20 hr. Evaporation of the solvent afforded 7.70 g *trans*-2-hexenyl 1-triflone as a light yellow liquid (95%). The center cut of a fractional distillation (43°/0.5 mm) provided an analytical sample. IR (CH_2Cl_2): 3.30, 3.40, 6.00, 7.37, 8.32, 8.96, 10.32; NMR ($CDCl_3$): 6.07 (dt, J = 15 and J = 6.5, 1) 5.48 (dt, J = 15 and J = 6.5, 1), 3.92 (d, J = 6.5, 2), 1.82–2.39 (m, 2) 1.18–1.72 (m, 2), 0.93 (t, J = 6, 3). (Found: C, 39.00; H, 5.16. Calc. for $C_7H_{11}F_3O_2S$: C, 38.88; H, 5.12%).

trans-2-*Hexenyl 1-triflone from* trans-2-*hexenyl 1-triflinate*

2-Hexenyl 1-triflinate (905 mg) was dissolved in HMPA (3 ml) and heated at 55° under N_2 for 7.5 hr. Workup afforded 809 mg 2-hexenyl 1-triflone as a colorless liquid (89%) identical spectrally (IR, NMR) with the product obtained in the previous experiment.

Esterification of cinnamyl alcohol with CF_3SOCl

To a soln of CF_3SOCl (4.90 mmol) in MeCN (20 ml) at 0° was added dropwise with stirring a soln of *trans*-cinnamyl alcohol (658 mg, 4.90 mmol) and pyridine (387 mg, 4.90 mmol) in MeCN (5 ml). The reaction was warmed to room temp and stirred 7 hr. Work-up afforded 515 mg (42%) light yellow oil which was chromatographed (preparative layer chromatography; silica gel, hexane/ϕH, 1:1). The third band yielded 1-phenylpropenyl 1-triflone as colorless oil (120 mg). IR (CH_2Cl_2): 6.13 6.71, 6.95, 7.39, 8.3, 8.95, 11.26; NMR ($CDCl_3$): 7.17–7.56 (m, 6), 1.84 (d, 3). The fourth band yielded *trans*-cinnamyl triflone, m.p. 39.5–40.5°, identical (NMR, IR, TLC) with the product obtained by treating *trans*-cinnamyl bromide with KSO_2CF_3 (220 mg); IR (CH_2Cl_2): 6.21, 6.70, 6.91, 7.34, 8.3, 8.94; NMR ($CDCl_3$): 7.29 (s, 5), 5.76–6.92 (m, 2), 4.05 (d, J = 7.5, 3); UV: 292.5 (1300) 254 (13 600), 216 (11,200), 210 (13,800).

trans-2-*Methyl-4-cyclohexenyl triflone*

1-Propenyl 1-triflone (1.00 g, 5.75 mmol) was dissolved in 5–6 volumes of 1,3-butadiene and sealed in a glass tube. The solution was heated at 100–105° for 10 days. After cooling to −78°, the tube was opened and the contents removed and diluted with ether. The ether was washed once with sat $NaHCO_3$ and once with sat NaCl and dried ($MgSO_4$). Evaporation of the ether *in vacuo* afforded a colorless gummy residue which was chromatographed on silica gel. Elution with pentane yielded 305 mg of a hydrocarbon fraction (IR (CH_2Cl_2): 3.22, 3.34, 6.09, 7.00, 8.81, 10.1, 11.0). Elution with a 20% ether/pet ether mixture afforded 934 mg (4.10 mmol, 71%) of *trans*-2-methyl-4-cyclohexenyl triflone as colorless oil, homogenous by TLC. IR (CH_2Cl_2): 3.33, 6.01, 7.4, 8.35, 8.99; NMR ($CDCl_3$): 5.64–5.86 (m, 2), 3.18–3.62 (m, 1), 2.26–2.79 (m, 4), 1.58–2.20 (m, 1), 1.26 (d, J = 7, 3). Further elution with the same solvent mixture yielded 70 mg of the starting triflone (7%).

trans-2-*Methylcyclohexyl triflone*

To a soln of the adduct above (56 mg, 0.245 mmol) in EtOH (4 ml) was added 10% Pd–C (10 mg). The resultant mixture was stirred under H_2 at 1 atm and 25° for 11 hr. Filtration through Celite and removal of the ethanol *in vacuo* yielded 52 mg of *trans*-2-methylcyclohexyl triflone as a colorless oil (0.226 mmol, 93%). An analytic sample was obtained by preparative gas chromatography (column temp. 250°). IR (CH_2Cl_2): 3.32, 6.90, 7.40, 7.46, 8.35, 9.0, 11.0; NMR ($CDCl_3$): 3.12 (dt, J = 3.5 and J = 9, 1), 0.9–2.5 (m, 9), 1.26 (d, J = 6.5, 3). (Found: C, 41.58; H, 5.59. Calc. for $C_8H_{13}F_3O_2S$: C, 41.72; H, 5.68).

Isobutyl triflone from 1-propenyl 1-triflone

MeLi (16.5 ml of a 1.9 M soln in ether, 31.3 mmol) was added to a slurry of purified cuprous iodide (3.0 g, 15.8 mmol) in ether (60 ml) under N_2 and stirred until a clear soln was obtained. This was cooled to −45° to −50° and a soln of 1-propenyl triflone (870 mg, 5 mmol) in ether (35 ml) was added during 20 min. After stirring for 45 min at −50°, the mixture was poured into 400 ml of vigorously stirred 1.2 N HCl at 0°. The aqueous layer was extracted 4 times with ether. The combinded ether extracts were washed once with sat $NaHSO_3$, dried ($MgSO_4$), and concentrated *in vacuo* to yield 738 mg of isobutyl triflone as a colorless liquid (3.89 mmol, 78%) identical by IR and NMR with an authentic sample.

Compound $CH_3SO_2CF_3$

KSO_2CF_3 (24.08 g) and t-butyl bromoacetate (25.5 g, 0.131 mol) were dissolved in MeCN (250 ml). The resultant soln 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 with reflux for 4 hr in a bath kept at 145–155°. Subsequent distillation afforded 12.0 g (0.081 mol, 62%) $CH_3SO_2CF_3$ as a colorless liquid, b.p. 126–127° (lit.[32] 128.9°). IR (CH_2Cl_2): 7.35, 8.19, 8.33, 8.90, 10.50; NMR ($CDCl_3$): 3.11 (q, J = 1.3).

trans-2-(*Dimethylamino*)-*vinyl triflone*

Methyl triflone (444 mg, 3 mmol) and 1-bromo-3-phenylpropane (596 mg, 3 mmol) were dissolved in DMF (8 ml). After adding K_2CO_3 (550 mg, 4 mmol) the mixture was stirred and heated under N_2 for 12 days in an oil bath maintained at 90°. The reaction was cooled and poured into H_2O which was extracted 3 times with CH_2Cl_2. The combined extracts were washed 5 times with 6N HCl and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure afforded 800 mg of a mixture of crystals and brown oil, which was chromatographed on silica gel with CH_2Cl_2. The first fraction eluted was *trans*-2-(dimethylamino)-vinyl triflone as colorless crystals m.p. 91–93° (267 mg, 1.36 mmol, 45%). IR (CH_2Cl_2): 3.39, 6.14, 7.00, 7.50, 7.63, 8.30, 8.48, 9.02, 10.22, 11.03 11.86; NMR ($CDCl_3$): 7.37 (d, J = 12, 1), 4.67 (d, J = 1, 1), 3.17 (s 3), 2.89 (s, 3); UV (MeOH): 252 (23,300); MS (*m/e*): 203 M. (Found: C, 29.72; H, 3.94; N, 7.02. Calc. for $C_5H_6F_3NO_2S$: C, 29.55; H, 3.96; N, 6.89%).

In a similar experiment using β-phenethyl bromide rather than 1-bromo-3-phenylpropane, the product was purified by recrystallisation. Concentration of the mother liquors afforded an oil identified by IR and NMR as β-phenethyl alcohol.

Sodium methanesulfonate from $CH_3SO_2CF_3$

To a soln of Na (13 mg, 0.57 mmol) in EtOH (5 ml) was added $CH_3SO_2CF_3$ (84 mg, 0.57 mmol). The resultant soln was heated at reflux for 2 days, cooled, and filtered to collect 49 mg of sodium methanesulfonate (0.42 mmol, 73%), identical by IR and NMR with an authentic sample, m.p. <300°.

Alkylation of triflones general procedures (individual reaction conditions and yields are collected in Table 3).

(a) *With sodium hydride.* NaH (dispersion in oil, 1.1 eq) was placed in a dry flask under N_2 and washed with hexane. A soln (~0.5 M) of the triflone (1.0 eq) in the appropriate solvent was added and the mixture stirred until bubbling ceased and a clear soln was obtained. A soln (0.5 M) of the alkylating agent (1.0 eq) was added dropwise. After the specified time (at the indicated temp.) the mixture was diluted with ether which was washed with H_2O and sat NaCl, dried ($MgSO_4$), and concentrated *in vacuo* to yield the product.

1-*Phenylpropyl*-3-*triflone*—m.p. 24–25°, analytical sample by distillation (0.1 mm, 80°). IR (CH_2Cl_2): 3.38, 6.23, 6.71, 6.92, 7.37, 8.3, 8.95; NMR ($CDCl_3$); 7.22 (s, 5), 3.15 (t, J = 7.5, 2) 2.75 (t, J = 7, 2), 1.93–2.47 (m, 2). (Found: C, 48.25; H, 4.33; S, 12.67. Calc. for $C_{10}H_{11}F_3O_2S$: C, 47.61; H, 4.40; S, 12.71).

Alkylation of $CH_3SO_2CF_3$ *with* ϕCH_2Br

The above procedure yielded (after distillation at 80°/0.1 mm) a colorless mixture of oil and crystals. Two recrystallizations from pet ether yielded phenethyl triflone m.p. 75°, identical by NMR with authentic material. The mother liquors yielded 1,3-diphenylpropyl 2-triflone as a colorless oil, homogeneous by TLC and identical by NMR with authentic material.

Isobutyl triflone—colorless liquid, analytical sample by preparative GC (column temp. 170°). IR (CH_2Cl_2): 3.34, 7.34, 8.3, 8.94, 11.0, 12.2; NMR ($CDCl_3$): 3.14 (d, J = 6.5, 2), 2.12–2.75 (m, 1), 1.16 (d, J = 6.5, 6). (Found: C, 31.70; H, 4.83. Calc. for $C_5H_9F_3O_2S$: C, 31.57; H, 4.77).

Isopropyl triflone—colorless liquid, analytical sample by preparative GC (column temp. 170°). IR (CH_2Cl_2): 7.41, 8.25, 8.35, 8.98; NMR ($CDCl_3$): 3.48 (sept, J = 7, 1), 1.50 (d, J = 7, 6). (Found: C, 27.05; H, 4.00. Calc. for $C_4H_7F_3O_2S$: C, 27.27; H, 4.00).

1-*Phenyloctyl* 2-*triflone*—colorless oil. IR (CH_2Cl_2): 3.35, 3.43, 6.23, 6.70, 6.90, 7.39, 8.3, 8.99; NMR ($CDCl_3$): 7.00–7.47 (m, 5) 2.62–3.70 (m, 3), 0.59–2.16 (m, 13).

1,2-*Diphenylpropyl* 2-*triflone*—colorless oil. IR (neat): 3.35, 6.72, 6.95, 7.48, 8.38, 9.03; NMR ($CDCl_3$): 6.75–7.75 (m, 10), 3.3–4.07 (m, 2), 1.8 (s, 3).

1,3-*Diphenyl*-2-*methylpropyl* 2-*triflone*—colorless oil. IR (neat): 3.3, 6.73, 6.92, 7.45, 8.4, 9.0; NMR ($CDCl_3$): 7.03–7.43 (m, 10), 2.95–3.52 (m, 4), 1.44 (s, 3).

(b) *With* K_2CO_3. A soln (0.5 M in each reactant) of the triflone (1 eq) and the alkylating agent (1 eq) in MeCN was mixed with dry K_2CO_3 and heated at reflux for the appropriate time (Table 3) under N_2. The solvent was removed *in vacuo* and the residue extracted with CH_2Cl_2. The product was obtained by evaporation of CH_2Cl_2.

1,2-*Diphenylethyl triflone*—m.p. 57–58.5°. IR (CH_2Cl_2): 3.32, 6.72, 6.90, 7.4, 8.32, 9.0; NMR ($CDCl_3$): 7.34 (s, 5), 6.84–7.25 (m, 5), 4.45–4.69 (m, 1) 3.17–3.96 (m, 2).

1,3-*Diphenylpropyl* 2-*triflone*—colorless oil. IR (CH_2Cl_2): 3.26, 3.39 6.21, 6.68, 6.89 7.35, 8.3, 8.95; NMR ($CDCl_3$): 6.94–7.34 (m, 10), 2.76–3.90 (m, 5).

Condensation of methyl triflone with ethyl formate

Sublimed t-BuOK (226 mg, 2.02 mmol) was placed in a flame-dried flask into which was distilled t-BuOH (10 ml). A mixture of $CH_3SO_2CF_3$ (298 mg, 2.01 mmol) and HCO_2Et (300 mg, 4 mmol) was added and the resultant soln was heated in a 55° bath for 8 hr. Filtration, and removal of the solvent *in vacuo* afforded 371 mg (1.75 mmol, 87%) of the potassium enolate of α-trifyl acetaldehyde. IR (KBr): 6.25, 7.65, 8.5, 9.05, 10.9; NMR (CD_2O): 8.52 (d, J = 10.5, 1), 4.78 (d, J = 10.5, 1) 2,4-dinitrophenylhydrazone, m.p. 194°. (Found: C, 30.55; H, 2.01. Calc. for $C_9H_7F_3N_4O_6S$: C, 30.34; H, 1.98%).

1,2-*Diphenylvinyl azide*

NaH (134 mg of a 57% dispersion in oil, 3.2 mmol) was placed in a flame-dried flask under N_2, washed twice with hexane, and covered with anhyd glyme (15 ml). 1,2-Diphenylethyl triflone (472 mg, 1.5 mmol) was added and the resultant mixture was stirred until bubbling had ceased. After cooling to 0°, a soln of tosyl azide (295 mg, 1.5 mmol) in glyme (3 ml) was added dropwise with stirring. A ppt began to appear very soon and the resultant mixture was stirred 0.5 hr at 0°, diluted with ether, and washed once with H_2O. The aqueous phase was extracted once with ether and the combined ether extracts were washed twice with sat NaCl, dried ($MgSO_4$) and concentrated *in vacuo* to yield 410 mg of 1,2-diphenylvinyl azide as a light brown oil. IR (CH_2Cl_2): 3.24, 3.35, 4.67, 7.23, 6.69, 6.92.

1,2-*Diphenylethylamine*

A soln of 1,2-diphenylvinyl azide (prepared from 1.0 mmol of 1,2-diphenylethyl triflone) in THF (4 ml) was added dropwise to a stirred suspension of LAH (76 mg, 2 mmol) in THF (15 ml) under N_2. The mixture was stirred for 18 hr at 25° and worked-up with NaOH by the method described by Fieser[33] to yield 1,2-diphenylethylamine as a yellow oil. IR (CH_2Cl_2): 2.92, 3.21, 3.3, 3.41, 6.23, 6.70, 6.90, 8.60. The product was dissolved in ether and treated with dry HCl to yield 198 mg (0.85 mmol, 85%) of the hydrochloride m.p. 236–242° (lit.[34] 242°).

1-*Phenyl*-2-*octanone from* 1-*phenyloctyl*-2-*triflone*

In a procedure similar to that or the preparation of deoxybenzoin, 1-phenyloctyl 2-triflone (339 mg, 1.05 mmol) was treated with TsN_3 and the product hydrolysed in glyme with conc HCl (48 hr) to yield 280 mg of clear, colorless oil (IR(CH_2Cl_2): 5.83, 5.98). This was chromatographed by preparative layer chromatography (silica gel; hexane/CH_2Cl_2, 1:1), the third band removed yielding 77 mg of 1-phenyl-2-octanone as a colorless oil (0.38 mmol, 36%). IR (CH_2Cl_2): 3.33, 3.43, 5.83, 6.23, 6.70, 6.90; semicarbazone: m.p. 120–123° (lit.[36] 121–122°).

2-*Methylcyclohexanone from* 2-*methylcyclohexyl* 1-*triflone*

In a procedure similar to that for the preparation of 1,2-diphenylvinyl azide, 2-methylcyclohexyl 1-triflone (230 mg, 1.0 mmol) was treated with TsN_3. The product was hydrolysed with 75% H_2SO_4 (1.5 ml) in glyme (15 ml) for 1 hr. The reaction mixture was diluted with ether which was washed twice with sat $NaHCO_3$. The ether was removed *in vacuo* and to the remaining

soln (20 ml) was added 2,4-dinitrophenylhydrazine (300 mg, 1.52 mmol) and 3 drops conc. HCl. The resultant mixture was stirred for 36 hr at 35–40°. The residue which resulted from removing the solvent *in vacuo* was chromatographed on silica gel (CH_2Cl_2) to yield, (the first fraction eluted), 105 mg (0.36 mmol, 36%) of the 2,4-dinitrophenylhydrazone of 2-methylcyclohexanone, m.p. 137.5–138° (lit.[37] 137.4–138°).

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