

Triflones (CF₃SO₂C). A Survey of Reactivity and Synthetic Utility

Sir:

The trifluoromethanesulfonyl group (CF₃SO₂-) is probably the strongest neutral electron-withdrawing group known, as attested by its acidifying influence in triflic acid (CF₃SO₂OH)¹ and its amides (CF₃SO₂NHR)² as well as its deactivating potential in aromatic substitution.³ When attached to carbon, in the "triflones" (CF₃SO₂C), this property and the innate stability of the group itself imply it may have considerable value in synthesis. We envision it as an activating synthetic tool, attached to a small carbon skeleton nucleus to direct several successive constructions, then finally removed. Hence we undertook an initial systematic survey of this reactivity in three parts.

A. Triflate Anion (CF₃SO₂:⁻) as Nucleophile and Leaving Group. Alkyl triflones may be formed by nucleophilic substitution of primary halides (with iodide ion catalysis) by potassium triflate^{2,4-6} in boiling acetonitrile, in a slow but clean displacement reaction (1). The secondary bromodeoxybenzoin formed the



R	% yield ⁷	Time	Mp	Nmr (CH ₂) ^(δ)
C ₆ H ₅	95	6 hr	103°	4.49
C ₆ H ₅ CO	80	48 hr	28-29°	5.01
<i>p</i> -BrC ₆ H ₄ CO	80	3 days	129-130°	5.46
<i>n</i> -C ₃ H ₇	70	7 days	(liquid)	3.24
C ₆ H ₅ CH ₂	70	7 days	76°	m 3.0-3.7
C ₂ H ₅ OCO	89	40 hr	bp 38-40° (0.5 mm)	4.35

corresponding keto triflone (mp 97-99°, δ 6.48) in 85% in 17 days and cinnamyl bromide yielded directly (85%) the isomerized and conjugated unsaturated triflone (C₆H₅CH₂CH=CHSO₂CF₃, mp 34-35°). Under these conditions neither cyclohexene oxide nor acrylonitrile reacted with potassium triflate. Also there was no reaction with benzaldehyde or formaldehyde in accord with expectation of an unfavorable aldehyde-sulfinate equilibrium for such a stable sulfinate. When mixed with acid chlorides (in CH₃CN) a new but unstable species is formed by O-acylation, *i.e.*, RCOOSOCF₃, which in turn reacts with aniline to yield PhNH₂SOCF₃ and PhNHCOR (9:1 for R = Ph). O-Alkylation also occurs with silver triflate and alkyl halides, phenethyl bromide yielding PhCH₂CH₂OSOCF₃, isomeric with the known triflone.⁸

Removal of the triflone group may be effected in

(1) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 4228 (1954); T. Gramstad, *Tidsskr. Kjemi, Bergv. Met.*, **19**, 62 (1959); *Chem. Abstr.*, **54**, 12739 (1959).

(2) J. B. Hendrickson, R. Bergeron, A. Giga, and D. Sternbach, *J. Amer. Chem. Soc.*, **95**, 3412 (1973).

(3) A. Senning, *Chem. Rev.*, **65**, 385 (1965); W. A. Sheppard, *J. Amer. Chem. Soc.*, **85**, 1314 (1963).

(4) Potassium triflate (KSO₂CF₃, mp 180° dec)⁶ is conveniently prepared by adding CF₃SO₂Cl⁶ over a 10 min period to KI (1:2) slurried in cold acetone, evaporating, washing the solids with CH₂Cl₂ to remove I₂ then with ethyl acetate to remove KSO₂CF₃ from KCl. The triflate is also soluble in acetonitrile.

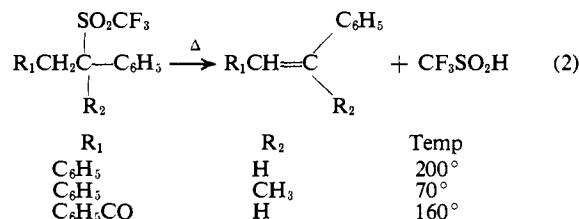
(5) The sodium and zinc salts have been reported: R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 2901 (1955); F. J. Pavlik, U. S. Patent 3,420,877 (Jan 7, 1969).

(6) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 4069 (1957).

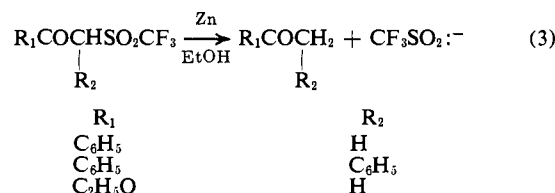
(7) Yields were not optimized but nmr and tlc on crude products were generally identical with those of the pure products. All product spectra (ir, nmr) were consistent with the formulations shown or with those of authentic compounds, where known.

(8) P. Skipper, private communication.

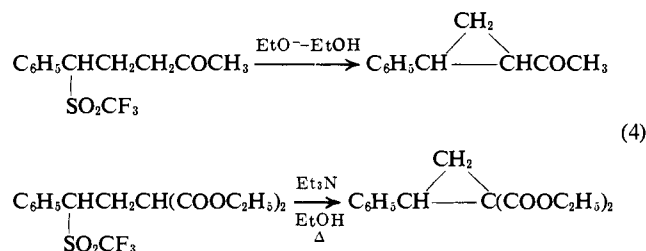
several ways. Ordinary 1,2-eliminations of triflinic acid (CF₃SO₂H) were readily and quantitatively effected by thermolysis of triflones with activated β-protons (2); the benzoyl derivative also yields chalcone with K₂CO₃-CH₃CN overnight at room temperature.^{7,9} The primary triflone (PhCH₂CH₂SO₂CF₃) was stable to 300° but its tertiary analog, (PhCH₂)₂C(CH₃)SO₂CF₃, afforded a 2:1 mixture of geometric isomers of PhCH=C(CH₃)CH₂Ph at 170-180°.



Thus while basic β-elimination removes the triflyl group from γ-keto triflones, zinc reductive elimination (in ethanol with catalytic acetic acid at 20°, 1 min) serves quantitatively to remove it from β-keto triflones or the analogous esters (3).⁹



A more important loss of the group with concomitant construction was sought by direct carbanion displacement of triflate, the initial cases chosen being favorable cyclopropane cyclizations (4). The first example afforded the known cyclopropyl ketone (semicarbazone, mp 138-140°, lit. mp 140°)¹⁰ in 65% yield with ethoxide-ethanol (20 hr, room temperature), while the second (see below) occurred cleanly with triethylamine in boiling ethanol.



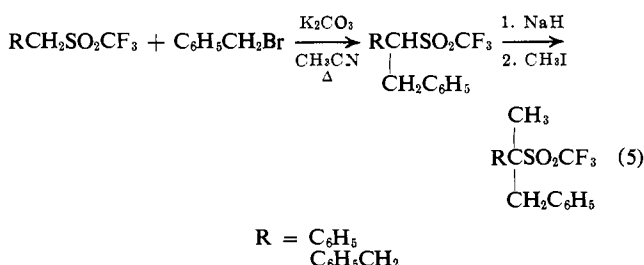
Thus, the triflone is readily removed from positions α (3), β (2), and γ (4) to carbonyl groups. Finally, simple reductive removal of triflyl² was examined. Benzyl triflone was unaffected by aluminum amalgam or sodium borohydride but reduced to benzyl mercaptan⁹ by lithium aluminum hydride in ether. Reduction of 2-phenylethyl and 1,2-diphenylethyl triflones with Raney nickel afforded phenylethane and 1,2-diphenylethane, respectively,⁹ and quantitative nickel triflate. Platinum-catalyzed hydrogenation of 1,2-diphenylethylene triflone yielded both hydrogenation and benzylic hydrogenolysis (to 1,2-diphenylethyl triflone and 1,2-diphenylethane) but hydrogenation of the non-

(9) Products were identified in each case by comparison with known compounds.

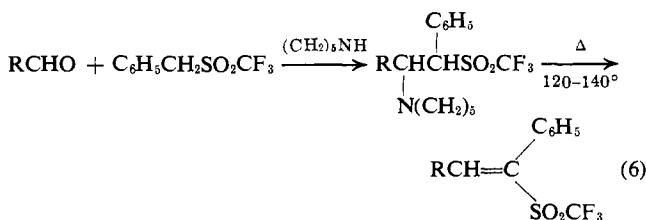
(10) J.-M. Conia and J. C. Limaet, *Tetrahedron Lett.*, 3151 (1965).

benzylic 2-benzylethylene triflone proceeded without hydrogenolysis.

B. Triflone α -Carbanions. Simple monoalkylation of α -methylene triflones (5) occurs readily with refluxing K_2CO_3 - CH_3CN with no evidence of dialkylation, the mild base required implying the considerable acidifying influence of the triflyl group. A second alkylation of the α -methine, however, was easily achieved *via* prior carbanion formation using sodium hydride (in tetrahydrofuran); carbanion formation is rapid and alkylation proceeds at room temperature in excellent yields.⁷



Extended to conjugate addition, benzyl triflone yielded simple adducts with methyl vinyl ketone (Et_3N - $EtOH$, reflux, 30 hr; 70%; bp 120–140° (0.07 mm)) or acrylonitrile (EtO^- - $EtOH$, 25°, 2 hr; mp 49–51°), the former proceeding with ethoxide *via* internal displacement of triflate to a cyclopropyl ketone (4). At the next oxidation state, benzyl triflone undergoes the Mannich reaction with aldehydes in the presence of piperidine in refluxing benzene (6). Heating the adduct (with R = C_6H_5 , or its salt with R = H) smoothly eliminated piperidine⁷ to form the vinyl triflones (6).



R = C_6H_5 : mp 108–112° (75%) mp 100–101° (80%)
R = H: mp 64–65° (65%) bp 130° (20 mm)(100%)

C. Additions to Vinyl Triflones. Piperidine adds smoothly to $PhCH_2CH=CHSO_2CF_3$, but reactive anions (cyanide, malonate) create more complex products, presumably through formation of the stabilized triflone carbanion. 1,2-Diphenylethylene triflone, however, adds butyllithium instantly to form 1,2-diphenylhexyl triflone and reacts with cyanide (12 hr, 40° in ethanol-water-ether with ammonium chloride) *via* addition and triflate elimination to cyanodiphenylethylene⁹ in 75% yield. α -Styryl triflone (see (6), R = H) reacted quickly in ethanol with diethyl malonate and triethylamine to form a 1:2 molar mixture of mono- and dialkylated malonates in 88% overall yield; the dialkylated product was $(C_6H_5CH(SO_2CF_3)CH_2)_2C(COOC_2H_5)_2$, isolated crystalline, mp 134–135°. The mixture proceeded to cyclize as in (4) on long refluxing in the same medium to the known cyclopropane diester.¹¹

Finally, the vinyl triflone (6, R = H) acted as a facile dienophile with butadiene; after several days at room temperature the elimination product of the adduct, 1-

(11) J. Gosselck, H. Ahlbrecht, F. Dost, H. Schenk, and G. Schmidt, *Tetrahedron Lett.*, 995 (1968).

phenyl-1,3-cyclohexadiene, mp 83–85°, λ_{max} 248 nm (ϵ 8200) (lit.¹² 85°, 248 nm (ϵ 9000)) was isolated in 75% yield. An adduct retaining the triflyl group was similarly obtained with cyclopentadiene.

Further exploration of these triflones as versatile synthetic tools is under active study, but it is already clear that their 1,2- and 1,3-eliminations are significantly more facile than those of other sulfones^{13–15} and their ease of alkylation with mild bases offers considerable synthetic advantage.

(12) G. F. Woods, N. C. Bolgiano, and D. E. Duggan, *J. Amer. Chem. Soc.*, 77, 1800 (1955).

(13) Thermal elimination of other sulfones is uncommon while 1,3-elimination of toluene sulfinate requires much more active base (*tert*-butoxide in dimethylformamide).^{14,16}

(14) W. L. Parker and R. B. Woodward, *J. Org. Chem.*, 34, 3085 (1969).

(15) R. V. M. Campbell, L. Crombie, and G. Pattenden, *Chem. Commun.*, 218 (1971).

James B. Hendrickson,* Aziz Giga, James Wareing

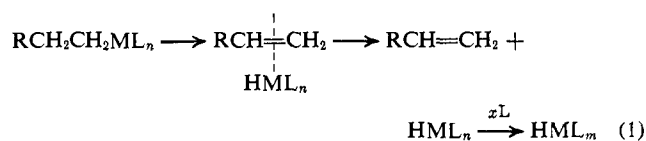
Edison Chemical Laboratory, Brandeis University
Waltham, Massachusetts 02154

Received September 24, 1973

Thermal Decomposition of Bis(triphenylphosphine)-(carbonyl)octyliridium(I). A New Decomposition Mechanism for Transition Metal Long Chain Alkyls

Sir:

Transition metal alkyls are of widespread use both as reagents and as unisolable intermediates in organic synthesis. The mechanism of thermal decomposition of transition metal alkyls has been extensively studied because of the insights afforded by such investigations into the electronic structure of these complexes and into reactivity patterns available to them.^{1–10} Significant among the observations thus far reported is that β -elimination of metal hydride constitutes the lowest energy decomposition pathway for coordinatively unsaturated long chain alkyl metal complexes (reaction 1).^{1–3} Degradation through intramolecular oxidative



addition of a C–H bond of a coordinated ligand followed by reductive elimination of alkane is common when β -hydride elimination is either impossible (no β -

(1) G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, 91, 6542 (1969); 92, 1426 (1970), and references cited therein.

(2) (a) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 94, 5258 (1972); (b) J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, 95, 4452 (1973).

(3) G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

(4) J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, 94, 6226 (1972).

(5) G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, 92, 5625 (1970); W. Keim, *J. Organometal. Chem.*, 14, 179 (1968).

(6) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, 91, 4990 (1969).

(7) G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

(8) G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 94, 232 (1972).

(9) G. Wilkinson, *et al.*, *J. Chem. Soc., Dalton Trans.*, 533 (1972); P. S. Braterman and R. J. Cross, *ibid.*, 657 (1972).

(10) B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, 94, 2512 (1972).