surements[6] that the Mo(V)–cysteine complex ($Na_2Mo_2O_4(Cys)_2$) was reversibly reduced at −0.33 V (Mo(VI) ⇄ Mo(V)), −1.03 V (Mo(V) ⇆ Mo(IV)), and −1.9 V (Mo(IV) ⇄ Mo(III)), *vs.* "she" in a borate or carbonate (Na_2CO_3–$NaHCO_3$) buffer solution (pH 9.6, 27°) on a mercury electrode. When 0.5 atm of acetylene was admitted onto the solution of $Na_2Mo_2O_4(Cys)_2$ (pH 9.6 borate buffer, 27°) and the cathodic voltage from 0 to −2.0 V *vs.* a saturated calomel electrode ("sce") was applied to an inactive graphite electrode,[7] the selective ethylene formation occurred with cathodic voltage higher than −0.9 V *vs.* "she" (−1.14 V *vs.* "sce"). A considerable amount of hydrogen gas was also evolved at the graphite electrode at the cathodic voltage around −0.9 V *vs.* "she" in the absence of acetylene. The reduction of water proceeds in an alkaline solution as follows[8]

$$2H_2O + 2e^- = H_2 + 2OH^- \qquad (E_0 = -0.828 \text{ V } vs. \text{ "she"})$$

It was accordingly concluded that the charge carriers which have redox potentials around −0.9 V *vs.* "she" enhanced not only the charge transfer from the strong donors such as $NaBH_4$ and $Na_2S_2O_4$ to the Mo(V)–cysteine complex (it may facilitate the reduction of Mo(V) to Mo(IV) as an active state for acetylene reduction) but also the activation of hydride in $NaBH_4$ solution to produce reactive hydrogen, which could be responsible for the specific enhancement of catalytic efficiency of the Mo(V)–cysteine complex in the presence of charge carriers.

(6) $Na_2Mo_2O_4(Cys)_2 \cdot 5H_2O$ was dissolved in a borate buffer solution (0.05 g/50 cm³) and the *i*–*E* curves were observed under N_2 atmosphere at 27° with reference to the calomel electrode connected with a KCl salt bridge.

(7) In the absence of the Mo(V)–cysteine complex, acetylene was reduced to a mixture of ethylene and ethane (molar ratio *ca.* 4:1) at much lower rates (less than one-tenth of those with Mo(V)–cysteine present) at the cathodic voltages higher than −1.2 V *vs.* "sce."

(8) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, N. Y., 1938.

Masaru Ichikawa,* Shunsuke Meshitsuka
Sagami Chemical Research Center, Nishi-Onuma
Sagamihara, Kanagawa, Japan
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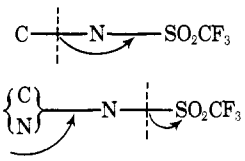
Triflamides ($CF_3SO_2N<$). A Survey

Sir:

The sulfonyl group offers unusually versatile reactivity in its capability of acting both as electrophile– and nucleophile–leaving group as well as its electron-withdrawing power to stabilize adjacent anions. These modes of reaction are all enhanced if the electron withdrawal is enhanced. Hence, we have surveyed the reactivity of trifluoromethanesulfonyl[1] (CF_3SO_2–; "trifyl") on nitrogen and carbon. The former, the triflamides, are generally stable, crystalline soluble sulfonamides quantitatively prepared[2] from amines with the anhydride $(CF_3SO_2)_2O$.[1] The acidity of primary triflamides is indicated by their solubility in bicarbonate ($CF_3SO_2NH_2$, pK_a = 5.8).

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

(2) The structures assigned are supported by ir, nmr, and mass spectral evidence as well as elemental analyses. In general these were all clean, high-yield reactions in which, however, no effort was made to optimize yields.



(1)

(2)

Two kinds of cleavages of triflamides may be envisioned, as summarized in eq 1 and 2. The first of these has been examined for SN2 displacements of triflamide as stabilized leaving group[3] and displacement is facile only if two trifyl residues are present on the nitrogen. In corroboration we found benzyltriflimide, $C_6H_5CH_2N(SO_2CF_3)_2$, readily converted to benzyl bromide and methyl ether with bromide and methoxide ions. We observed the analogous elimination when isobutylene bubbled quantitatively from a bis triflation of *tert*-butylamine at −78°, *i.e.*, eq 3.

$$2(CF_3SO_2)_2O + (CH_3)_3CNH_2 \xrightarrow{NaH} [(CH_3)_3CN(SO_2CF_3)_2] \longrightarrow CH_2{=}C(CH_3)_2 + HN(SO_2CF_3)_2 \quad (3)$$

Cleavage 1 of acyl monotriflamides is very rapid, as evidenced by fast basic hydrolysis, ethanolysis, and aminolysis of the acyl group at room temperature. The acyl derivatives $RCON(C_6H_5)SO_2CF_3$ are cleanly prepared in high yield by treating $C_6H_5NHSO_2CF_3$ (mp 66–67°) with acid chlorides and triethylamine in methylene chloride (R = CH_3, mp 93–94°, 97%; R = C_6H_5, mp 97–98°, 85%; R = $C_6H_5CH{=}CH$, mp 109°, 85%)[2]; the acyltriflamides are somewhat less reactive than acyl chlorides and offer some advantages (*cf.* the otherwise difficult N-acetylation of pyrrole proceeds smoothly with $CH_3CON(C_6H_5)SO_2CF_3$).[4] Conversely, amides are readily N-triflated; caprolactam was converted to the salt with *tert*-butyllithium in benzene at 0° to form the cyclic acyltriflamide (mp 134–135°, 93%),[2] which was rapidly opened to the ester $CF_3SO_2NH(CH_2)_4COOCH_3$ with methoxide–methanol at room temperature.

$$RCH_2N(C_6H_5)SO_2CF_3 \xrightarrow{B:} RCH{=}NC_6H_5 + CF_3SO_2{:}^- \quad (4)$$

a, R = *p*-BrC_6H_4CO (mp 144–145°)
b, R = C_6H_5 (mp 79–80°)
c, R = *n*-C_4H_9 (oil)

Elimination of trifluoromethanesulfinate ("triflinate" anion from nitrogen (eq 2)) was examined in three representative cases with varying activation of the α proton. The models were all made by smooth room-temperature alkylation of phenyltriflamide in potassium carbonate–acetone.[2] The first case (**a**) was transformed into *p*-bromphenacylidene anil (mp 59–61°; lit.[5] 60–61°; 90%) on long stirring (or brief reflux) with K_2CO_3 in acetone.[6] The second case (**b**) was unreactive to prolonged boiling with K_2CO_3 in acetone but eliminated smoothly in 3 hr at 100° with NaH in dimethylformamide; aniline and benzaldehyde were isolated in over 80% yield following mild acid hydrolysis.

(3) (a) R. S. Glass, *Chem. Commun.*, 1546 (1971); (b) P. J. DeChristopher, G. D. Lyon, J. P. Adamek, R. J. Swedo, S. A. Klein, and R. J. Baumgarten, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1971, No. 14 (see also *J. Amer. Chem. Soc.*, **91**, 2384 (1969)).

(4) P. Keehn and J. Haley, private communication.

(5) W. A. Malik, D. R. Gupta, and C. L. Taploo, *J. Indian Chem. Soc.*, **46**, 253 (1969).

(6) By contrast the toluenesulfonamide was stable to several days boiling (K_2CO_3–acetone).

The third case (c) was unreactive to refluxing 3 days with NaH in dimethylformamide. This elimination of triflinate from triflamides provides a basis for a useful new "Gabriel synthesis" of primary amines, outlined in eq 5 and carried out for R = $C_6H_5CH_2$ and n-C_7H_{15}

$$\mathrm{RBr} + \mathrm{C_6H_5CH_2NHSO_2CF_3} \xrightarrow{\mathrm{K_2CO_3}} \underset{\displaystyle \mathrm{CH_2C_6H_5}}{\mathrm{RNSO_2CF_3}} \xrightarrow[\text{2. } \mathrm{H_2O\text{-}H^+}]{\text{1. NaH}} \mathrm{RNH_3^+} + \mathrm{C_6H_5CHO} + \mathrm{CF_3SO_2{:}^-} \quad (5)$$

in 70–80% overall yields.

Comparable elimination of triflinate from carbon was also observed in the preparation of chalcone in high yield by stirring $C_6H_5COCH_2CH(C_6H_5)SO_2CF_3$ (mp 134°)[2] in acetonitrile with potassium carbonate (36 hr) or simply on pyrolysis (neat) at 160°. The potassium triflinate formed in all these eliminations was isolated in near quantitative yield as a stable acetone- or water-soluble salt (KSO_2CF_3, mp 180° dec; ir 8.7, 9.3, 9.9 μ).

Elimination of sulfinates from hydrazine derivatives is characteristic of several reactions like the McFadyen–Stevens aromatic aldehyde synthesis or the Cava diazo ketone preparation from α-diketone monohydrazones. Under much milder conditions the corresponding triflic derivatives undergo these reactions. The N'-trifylbenzhydrazide ($C_6H_5CONHNHSO_2CF_3$, mp 159–160°)[2] decomposes smoothly in boiling triethylamine (89°) to afford benzaldehyde and an 80% yield of nitrogen (determined manometrically), while brief boiling of the lithium salt in dimethylformamide at 100° yielded 75% of the 2,4-dinitrophenylhydrazone of benzaldehyde. Furthermore, the triflated hydrazide also afforded benzaldehyde (40%) simply by distillation at 170°.

The conversion of benzil monohydrazone to azibenzil was carried out by triflation with $(CF_3SO_2)_2O$ and triethylamine (1 mol) in methylene chloride at −78°; on warming to about 0° and addition of excess triethylamine, the diazo ketone is quickly formed in over 80% yield.

Finally, as the triflamides appear in most ways to be desirable, stable amine derivatives or protecting groups for synthesis, their direct removal was examined. First, removal from a primary amine is easily effected by phenacylation and elimination as described above. Thus, aniline is recovered from its triflamide ($C_6H_5NHSO_2CF_3$) by stirring overnight with p-bromphenacyl bromide and potassium carbonate in acetone and working up with mild acid hydrolysis (80% recovery). In addition we have found triflamides of secondary amines to be quantitatively and rapidly reduced to the parent amine with lithium aluminum hydride in boiling ether. The primary triflamides are quite stable under these conditions, however, since the stable salt is formed first, but they may be reduced in minutes with sodium bismethoxyethoxyaluminum hydride ("Red-Al") in boiling benzene,[7] also nearly quantitatively.

These initial studies imply a broad range of synthetically useful, clean, and practical reactions of triflamides as well as attractive potential for normally stable, easily removed amine protecting groups. Many of these applications are under further study in our laboratory, as is a comparable survey of the reactions of the trifyl group attached to carbon (the "triflones," CF_3SO_2C).

(7) E. H. Gold and E. Babad, *J. Org. Chem.*, 37, 2208 (1972), found reduction of primary toluenesulfonamides moderately successful at higher temperatures and much longer time.

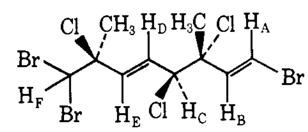
James B. Hendrickson,* Ray Bergeron
Aziz Giga, Daniel Sternbach
Edison Memorial Laboratory, Brandeis University
Waltham, Massachusetts 02154
Received October 30, 1972

(3R,4S,7S)-*trans,trans*-3,7-Dimethyl-1,8,8-tribromo-3,4,7-trichloro-1,5-octadiene, a Novel Monoterpene from the Sea Hare, *Aplysia californica*

Sir:

The sea hare, *Aplysia californica*, is a large shell-less opistobranch which is commonly found intertidally, feeding on red algae. Analysis of the digestive (midgut) gland of *Aplysia* showed a high concentration of bromine,[1] which has subsequently been attributed to the presence of a large number of halogenated terpenes derived from compounds found in the algae ingested by the sea hare.[2] Most of the halogenated terpenes were obviously related to known algal metabolites but the algal source of the title compound is unknown.

The ether-soluble portion (31 g) of an ethanolic extract of the digestive glands from adult sea hares[3] was subjected to chromatography on Florisil. Elution with 20% benzene in petroleum ether gave the highly halogenated monoterpene **1** (2 g): $C_{10}H_{12}Br_3Cl_3$;[4] mp 54°, $[\alpha]^{23}D$ −50.2° (c 1.0). The mass spectrum[5] showed no molecular ion but had peaks corresponding to the loss of chlorine ($M^+ - 35, 37$) and bromine ($M^+ - 79, 81$). The nmr spectrum[5] indicated the presence of two tertiary methyl groups, two trans-disubstituted olefinic functions, one of which was adjacent to a methine proton, and a second methine proton. In order to definitively elucidate the structure, a single-crystal X-ray diffraction analysis was undertaken.



Transparent needles, obtained from methanol recrystallization, belong to the monoclinic crystal class with a = 5.934 (6), b = 12.061 (3), and c = 11.141 (3) Å, and β = 82.1 (2)°.[6] An observed density of 2.00 g/cm³ requires two molecules per unit cell which on the basis of the known optical activity and systematic absences (0k0 missing if $k = 2n + 1$) indicated the space group $P2_1$. All data in the hkl and $\bar{h}kl$ octants (1450 reflections) were collected on a fully automated Hilger-Watts diffractometer using Zr-filtered Mo Kα

(1) L. Winkler, *Veliger*, 11 (3), 268 (1969).
(2) D. J. Faulkner and M. O. Stallard, manuscript in preparation.
(3) Six individuals (5.7 kg) were collected intertidally at La Jolla.
(4) A satisfactory elemental analysis was obtained.
(5) Mass spectrum: m/e 439, 441, 443, 445, 447 (M^+ − Cl), 395, 397, 399, 401 (M^+ − Br); base peaks 167, 169, 171 $(C_4H_5BrCl)^+$. 220-MHz nmr spectrum: ($CDCl_3$) δ 1.75 (s, 3 H), 1.95 (s, 3 H), 4.51 (d of d, H_C), 5.76 (s, H_F), 6.08 (m, H_D), 6.11 (AB d, H_E), 6.43 (AB d, H_B), 6.55 (AB d, H_A).
(6) A right-handed coordinate system was maintained throughout the structural analysis.