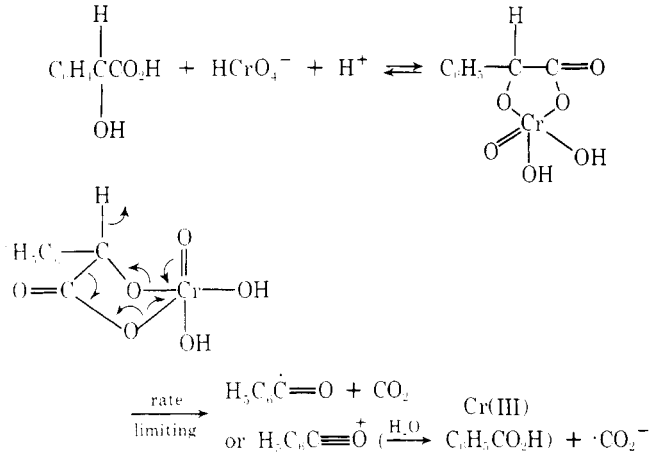
large enough to explain the very low yield of phenylglyoxylic acid and the high yield of benzoic acid, unless one of the chromium intermediates, Cr(IV) or Cr(V), had a much higher selective preference for the keto acid. We oxidized *m*-methylmandelic acid in the presence of phenylglyoxylic acid, assuming that a *m*-methyl substituent will have only a minimal effect on the reactivity of either the hydroxy or the keto acid and will therefore serve as a noninterfering label. The results in Table II show that the yields of *m*-toluic acid are only slightly reduced and those of *m*-tolylglyoxylic acid only slightly increased if an equivalent amount of phenylglyoxylic acid ((0.5 mol/Cr(VI)) is added. The yields of benzoic acid are in good agreement with calculated values based on the relative reactivities of phenylglyoxylic and *m*-methylmandelic acids toward chromium(VI).

Our results provide convincing evidence that neither benzaldehyde nor phenylglyoxylic acid is an intermediate in the formation of benzoic acid. In order to explain the formation of benzoic acid one has to postulate that it is formed through a reactive intermediate of a higher oxidation level and the formation of which involves the breaking of the carbon–hydrogen bond. Both requirements are met by $C_6H_5\dot{C}{=}O$ or $C_6H_5C{\equiv}O^+$, either of which can be formed in a three-electron oxidation of mandelic acid.



The only known example of a three-electron oxidation of a single molecule is the recently reported oxidation of 2,7-dihydroxyheptanoic acid,[2] in which the two reacting centers are separated by a long chain of methylene groups. *The chromic acid oxidation of mandelic acid represents the first example of a three-electron oxidation of a molecule in which a C–C and a C–H bond on the same carbon atom are broken simultaneously in the rate-limiting step.*

The free-radical intermediates formed in the rate-limiting step would be expected to reduce chromium(VI) to chromium(V). In order to account for the observed reaction products one must assume that chromium(V) [directly or after disproportionation to chromium(VI) and chromium(IV)] will oxidize mandelic acid to benzaldehyde and carbon dioxide

$$Cr(VI) + C_6H_5\dot{C}{=}O \text{ (or } \cdot CO_2H) \rightarrow Cr(V) + C_6H_5CO_2H \text{ (or } CO_2)$$

$$C_6H_5CH(OH)CO_2H + Cr(V) \rightarrow C_6H_5CHO + CO_2 + Cr(III)$$

This reaction sequence leads to the observed 1:1 benzoic acid/benzaldehyde ratio.

References and Notes

(1) Support for this investigation by a grant of the National Science Foundation is gratefully acknowledged.
(2) Part 14: S. Ramesh, J. Roček, and D. A. Schoeller, *J. Phys. Chem.*, in press.
(3) K. H. Heckner, K. H. Grupe, and R. Lansberg, *Z. Phys. Chem. (Leipzig)*, **242**, 225 (1969); *ibid.*, **247**, 91 (1971); *J. Prakt Chem.*, **313**, 161 (1971).
(4) The mechanism proposed by Lansberg[3] postulates a two-electron oxidation of mandelic acid to benzaldehyde. No explicit explanation for the observed deuterium isotope effect is given, although the proposed reaction scheme indicates a breaking of the carbon–hydrogen bond during the formation of benzaldehyde.

Dominic Ip, Jan Roček*
Department of Chemistry
University of Illinois at Chicago Circle
Chicago, Illinois 60680
Received September 28, 1978

Trifluoroacetyl Triflate: An Easily Accessible, Highly Electrophilic Trifluoroacetylating Agent

Summary: Trifluoroacetyl triflate (TFAT, **3**) is easily prepared and isolated. It is a powerful electrophile capable of uncatalyzed trifluoroacetylation of reactive aromatic rings as well as attack at chlorine of covalent chlorides and reaction with other nucleophiles.

Sir: Studies of mixed anhydrides of carboxylic acids and trifluoromethanesulfonic (triflic) acid (**2**) have shown them to be extremely powerful acylating agents.[1] However, no reports of perfluoroacyl analogues have appeared. Mixed anhydrides of perfluorocarboxylic acids and fluorosulfonic acid have been reported.[2,3] The possible application of these in synthesis has not been explored. Although salts involving the trifluoroacetylium ion have been reported,[4] further work[5] showed these not in fact to be acylium salts but covalent acyl fluoride complexes.

Trifluoroacetyl triflate (TFAT, **3**) is conveniently prepared by the action of a threefold excess of phosphorus pentoxide on an equimolar mixture of trifluoroacetic acid (**1**) and triflic acid (**2**). The mixture is boiled for 2 h and distilled. A fractional redistillation from phosphorus pentoxide gives trifluoroacetic anhydride (**4**, 23%, bp 37.5–40.5 °C) and TFAT (**3**,[6] 52%, bp 62.5 °C). Surprisingly, no triflic anhydride was observed.

$$\underset{\mathbf{1}}{CF_3CO_2H} + \underset{\mathbf{2}}{CF_3SO_3H} \xrightarrow[\text{excess}]{P_2O_5} \underset{\mathbf{3}\ (TFAT)}{CF_3C(=O)OSO_2CF_3} + \underset{\mathbf{4}}{(CF_3CO)_2O}$$

Pure TFAT (**3**) is a colorless liquid which is stable indefinitely at room temperature in the absence of moisture. It can be repeatedly distilled from P_2O_5 without any detectible reequilibration to form the symmetrical anhydrides. It reacts almost explosively with water, but does not react at room temperature with the sterically hindered base 2,6-di-*tert*-butyl-4-methylpyridine (**5**).[7,8]

The utility of **3** as a trifluoroacetylating agent is demonstrated in the reaction with anthracene (**6**) to give 81%[9] of 9-(trifluoroacetyl)anthracene (**7**) when a mixture of 1.1 equiv of **3** and 1.1 equiv of **5** were heated in benzene at 80 °C with **6** for 44 h. The mild conditions used for this reaction are to be

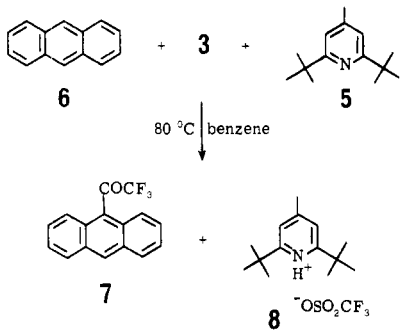
$$\underset{\mathbf{12}}{Ph_3CCl} + \mathbf{3} \longrightarrow \underset{\mathbf{13}}{Ph_3C^+\ {}^-OSO_2CF_3} + \underset{\mathbf{14}}{CF_3COCl}$$

contrasted with those used previously by Pirkle[10] for making **7**, which involved heating anthracene with trifluoroacetic anhydride in benzene at 200 °C for 15 h in a sealed tube to yield 73% of the product.

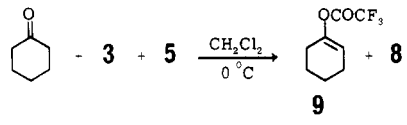
Cyclohexanone is converted to enol ester **9** (72%) upon slow addition to a mixture of 2 equiv of **3** and 1 equiv of **5** in dry CH_2Cl_2 at 0 °C.[12] The trifluoroacetylation by **3** at atoms other

0022-3263/79/1944-0313$01.00/0

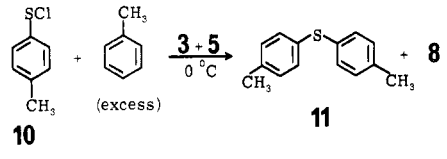
than carbon also promises to be of synthetic utility, as in the reaction with some covalent chlorides at chlorine. When 1.05



equiv of **3** is added to 1 equiv of *p*-toluenesulfenyl chloride (**10**) in 8 equiv of toluene with 1 equiv of **5** at 0 °C, 36%[12] of sulfide **11** is formed. When trityl chloride (**12**) is mixed with an excess of **3** at 25 °C, it is quantitatively converted to trityl triflate (**13**).[13]



One driving force for these reactions at chlorine stems from the high volatility of the trifluoroacetyl chloride (**14**) (bp −18 °C), which is evolved from the reaction medium.



The reactions cited above are simply illustrations of some of the types of reactions which have been observed. Details of other reactions will be reported in a later publication.

Acknowledgment. This research was supported in part by a grant from the National Cancer Institute (CA-13963).

References and Notes

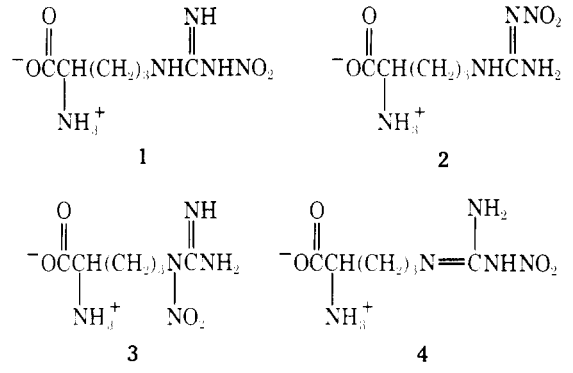
(1) R. D. Howells and J. D. McCown, *Chem. Rev.*, **77**, 69 (1977), and references cited therein.
(2) These were prepared by the reaction of perfluoroacyl fluorides with sulfur trioxide[3a] or by the reaction of perfluoro acid anhydrides[3b] and bromides[3c] with peroxydisulfuryl difluorides.
(3) (a) C. G. Krespan and D. C. England, *J. Org. Chem.*, **40**, 2937 (1975); (b) D. D. Desmarteau and G. H. Cady, *Inorg. Chem.*, **5**, 169 (1966); (c) J. J. Deefino and J. M. Shreeve, *Ibid.*, **5**, 308 (1966).
(4) E. Lindner and H. Kranz, *Z. Naturforsch. B*, **20**, 1305 (1965); *Chem. Ber.*, **99**, 3800 (1966).
(5) G. A. Olah, A. Germain, and H. C. Lin, *J. Am. Chem. Soc.*, **97**, 5481 (1975).
(6) ^{19}F NMR spectrum of TFAT ($CHCl_3$) δ 72.90 (3 F, s), 74.45 (3 F, s); IR ($CHCl_3$): 1845 cm^{-1} (s). Anal. $C_3F_6O_4S$: C.
(7) A. G. Anderson and P. J. Stang, *J. Org. Chem.*, **41**, 3034 (1976).
(8) The base can be recovered from these reactions as the triflate salt (**8**) and regenerated.
(9) The yield of **7** was determined by NMR. The identity of **7** was confirmed by comparisons of its spectra with ^1H and ^{19}F spectra of an authentic sample.[10]
(10) W. H. Pirkle, D. L. Sikkenga and M. S. Pavlin, *J. Org. Chem.*, **42**, 384 (1977).
(11) ^1H NMR of **9** ($CDCl_3$) δ 5.53 (1 H, m), 2.40–2.03 (4 H, m), 1.96–1.56 (4 H, m); ^{19}F NMR ($CDCl_3$) δ 75.74 (3 F, s).
(12) Determined by GLC of the isolated product. The identity of **11** was confirmed by comparison (^1H NMR and GLPC retention time) with an authentic sample (R. J. Maner, Ph.D. Dissertation, University of Iowa, 1967).
(13) ^1H NMR of **13** (CF_3CO_2H) δ 8.26 (3 H, tt, J = 7.5 and ~1 Hz), 7.90 (6 H, tt, J = 7.5 and ~1 Hz), 7.78 (6 H, tt, J = 7.5 and ~1 Hz).

T. R. Forbus, Jr., J. C. Martin*
Roger Adams Laboratory, University of Illinois
Urbana, Illinois 61801
Received September 6, 1978

Structure of Nitroarginine. A Nitrogen-15 Nuclear Magnetic Resonance Study

Summary: The methyl ester hydrochloride of N^G-nitroarginine exists in the nitrimine form in aqueous solution, as determined by ^{15}N and ^1H nuclear magnetic resonance studies.

Sir: The N^G-nitro protecting group for arginine was first employed in 1934[1] and has since found broad application in syntheses of arginine-containing peptides.[2] However, the structure of nitroarginine has eluded unambiguous assignment. Four isomeric structures are conceivable for the guanidino portion of nitroarginine (**1**–**4**). Structure **1**, a nitramine,



was proposed when the first synthesis of nitroarginine was described by Kossel and Kennaway.[3] But the nitrimine structure **2** and nitramines **3** and **4** were not excluded. Other early reports[1,4] also favored nitroarginine structure **1**. Later studies[5] of nitroguanidine and its derivatives based on dipole moment, ultraviolet absorption, and pK_a measurements indicated a nitrimine-type structure (cf. **2**). Subsequently, both structures **1**[6] and **2**[7] for nitroarginine began to appear in the literature, and the confusion persists today.[8]

Nitrogen-15 NMR at the natural abundance level has become a practical structure elucidation technique, and was applied to the nitroarginine structural problem. This technique is unambiguous, and unlike earlier studies[5] does not rely heavily on arguments concerning the relative contributions of various zwitterionic and resonance forms.

Figure 1a shows the proton broad band decoupled natural abundance ^{15}N FT NMR spectrum at 9.12 MHz of a 58 wt % solution of N^G-nitroarginine methyl ester monohydrochloride[2b] in water. The spectrum was obtained in a 10-mm sample tube using a repetition time of 10 s. Chemical shifts are reported in ppm upfield from external 1.0 M $Na^{15}NO_3$ in D_2O. Five resonances were observed. Since the chemical shifts of nitro groups generally fall in the range −30 to +60 ppm,[9] the peak at 8.4 ppm arises from this group. The resonance at 138.5 ppm is due to the imino nitrogen atom. This rather unusual chemical shift value will be discussed below. The three upfield resonances are characteristic of amine-type nitrogen nuclei.[9] The resonance at 335.6 ppm is readily assigned to the α-amino group and is in good agreement with the value of 332.5 ppm reported[10] for the hydrochloride of arginine methyl ester itself. The resonances at 281.0 and 293.1 ppm must then arise from the two amine-type nitrogen atoms of the nitroguanidino group.

Additional information concerning the structure of nitroarginine was obtained from the proton-coupled ^{15}N NMR spectrum. Figure 1c was obtained under conditions similar to those employed for Figure 1a, with the exception that a gated decoupling scheme was employed. The decoupler was turned off only during the pulse and acquisition period in order to obtain a coupled spectrum which retains the (negative) nuclear Overhauser effect. The resonance at 281.0 ppm was split

0022-3263/79/1944-0314$01.00/0