derived from authentic compounds. Product isomers were identified by comparison of their infrared spectra to that of the authentic compounds.

The light emitting from the fluorine plasma glow discharge has been analyzed during a reaction using a Welch No. 3690A spectrometer with a 600-mm grating and the following wavelengths were observed: 6242, 6353, 6412, 6908, and 6862 Å. These values are consistent with those reported for atomic fluorine by Stringanov and Sventitskii.[10] This laboratory found the shorter wavelength lines to be the most intense while Stringanov and Sventitskii reported the longer wavelength lines to be the most intense. This should be expected since our lines were measured on light coming from a high-energy plasma discharge and their lines were measured on light coming from a low-energy arc discharge. Realizing that it would have been very helpful to know the exact percentage of atomic fluorine passing from our plasma generator, a careful survey of the literature has been undertaken. Rosner and Allendorf[11] endeavored to determine atomic fluorine concentrations in several different ways. They included in their methods chemiluminescent titration reactions and calorimetric probes. In the chemiluminescent titration reactions using NOCl the simultaneous presence of molecular fluorine seriously complicates the determination, since molecular fluorine is able to react with NO to form NOF as well as atomic fluorine. Although Rosner and Allendorf studied calorimetrically the reactions of atomic fluorine with many different metals, their data regarding atomic fluorine concentration resulted only in qualitative estimates. In an effort to gain quantitative data regarding the output of the atomic fluorine generator used, our group undertook a study involving the reaction between silver mirrors and atomic fluorine which resulted again only in qualitative information. The best information regarding atomic fluorine concentration has come from the relative intensity of the atomic fluorine emission lines known to originate from atomic fluorine.[10]

In Table I reactions A–E were carried out in a manner as indicated below. The fluorine and benzotrifluoride flow rates were established in a manner necessary to give increasing fluorine to benzotrifluoride ratios.

In a typical reaction undiluted elemental fluorine was passed through metering valve V(1) and flow transducer FT(1) into the previously evacuated reactor which was cooled by condensers maintained at 0 °C. The fluorine was then allowed to pass into the discharge region where the red glow characteristic of atomic fluorine[12] was initiated by the radio-frequency field. A beam of fluorine atoms then passed into the reaction chamber by way of a 0.75-mm hole in a glass septum, as shown in Figure 2. The temperature of the beam of fluorine atoms was measured after passing through the 0.75-mm hole and was found to be 14 °C. Following the stabilization of the fluorine flow, benzotrifluoride vapor was introduced by placing the substrate in a small flask, maintained at 25 °C, and allowing the autogenous vapor pressure ($\simeq$23 Torr) to cause a flow through metering valve V(2), flow transducer FT(2), and then into the reaction chamber through the 0.75-mm i.d. capillary tube. The flow carried the products from the reaction chamber and they were condensed in trap T(1) which was cooled by liquid nitrogen.

At completion of the reaction the contents of trap T(1) were removed and analyzed according to Seiler.[9]

Registry No.—Atomic fluorine, 14762-94-8; benzotrifluoride, 98-08-8.

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The Apparent Oxidation of Triphenylmethane by Triflic Acid[1]

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The apparent oxidation of triphenylmethane to triphenylcarbonium ion by triflic acid is shown to be the result of dealkylation of one of the benzene rings followed by hydride transfer from unreacted triphenylmethane to the diphenylcarbonium ion, a disproportionation rather than an oxidation. Some other apparent oxidations in strong acid solvents may be similar. Triflic acid is a convenient solvent in which to study the chemistry of stabilized carbonium ions.

The apparent abstraction of hydride ion from hydrocarbons by Lewis and/or Brønsted acids is a well-known process.[2–5] Three mechanisms have been demonstrated.[4] The purpose of this paper is to demonstrate a fourth mechanism and to show that trifluoromethanesulfonic acid (triflic acid) is a convenient solvent for such reactions.

Results

Treatment of triphenylmethane with about ten times its own weight of triflic acid gave about a 50% yield of the triphenylcarbonium ion, a 76% yield of benzene, and a 22% yield of diphenylmethane, as judged by the visible (Figure 1) and NMR spectrum of the reaction mixture and the products obtained after quenching with aqueous base. A 0.1% yield of antracene was also formed. No gas is produced or consumed in this reaction.

On the other hand, a dilute solution of triphenylmethane in triflic acid (7×10^{-3} M) gave an essentially quantitative yield of diphenylcarbonium ion, as judged by its visible spectrum (Figure 2). At intermediate concentrations intermediate results were obtained, as shown in Table I.

Diphenylmethane was not completely soluble in ten times its own weight of triflic acid. After stirring for 1 h at room temperature and quenching, the steam distillate was mostly starting material but also contained 0.8% yield of anthracene, which dominated its visible and UV spectrum because of its spectral intensity (Figure 3).

For comparison purposes the visible and UV spectroscopic behavior of a number of aromatic hydrocarbons and ions was examined in triflic acid. Benzene gave essentially the same spectrum as in cyclohexane. Toluene gave an additional broad band centering around 320 nm. The apparent extinction

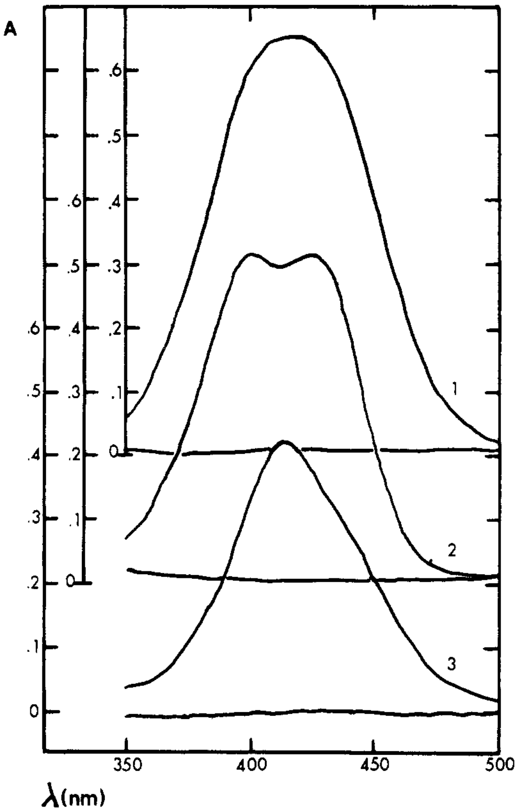


Figure 1. (1) Spectrum of a solution originally made up to contain 7.9×10^{-2} M triphenylmethane in triflic acid and then diluted to a nominal concentration of 3.2×10^{-4} M. (2) Spectrum of 1.3×10^{-4} M triphenylcarbonium ion in triflic acid, generated from triphenylcarbinol. (3) Spectrum of a solution nominally containing 3.9×10^{-4} M diphenylmethane in triflic acid. The spectrum is thought to be mainly that of its conjugate acid. All the spectra were obtained in cells of 1.0 nm path and all show the experimental baselines. Spectrum 1 is thought to be a combination of 2 and 3.

Table I. Product Dependence on the Initial Concentration of Triphenylmethane, $[(C_6H_5)_3CH]_i$

$[(C_6H_5)_3CH]_i$	$[C_6H_5)_3C^+]$	$[(C_6H_5)_2CH^+]$ all × 10^2, M	$\{2[(C_6H_5)_3C^+] + [(C_6H_5)_2CH^+]\}$
1.58	0.44	0.67	1.55
2.84	1.04	0.93	3.01
3.30	1.25	0.96	3.46
3.99	1.88	0.36	4.12
4.48	2.14	0.29	4.57

coefficient, ϵ_{max}, is low (around 200) but this may be due to incomplete reaction. A similar band, formed in $AlCl_3$–HCl, has been attributed to ring-protonated toluene.[6,7] The spectrum generated by diphenylmethane in triflic acid is shown in Figure 1. It is similar in ϵ_{max} to protonated aromatics, but its long wavelength λ_{max} is larger than might have been expected.[7] Benzyl alcohol could not be dissolved in triflic acid without depositing an insoluble material; the visible and UV spectrum of the supernatant was not reproducible, and seemed to be generated by several species formed in varying proportions. One of these, with λ_{max} around 250 nm, appears to be the benzyl cation.[8] Small quantities of diphenylcarbinol could be dissolved in triflic acid, either at room temperature or at −15 °C, and gave spectra (Figure 2) previously identified with the diphenylcarbonium ion.[9] This spectrum is unchanged after several hours of standing at room temperature. Triphenylcarbinol gave the spectrum previously identified with the triphenylcarbonium ion.[9]

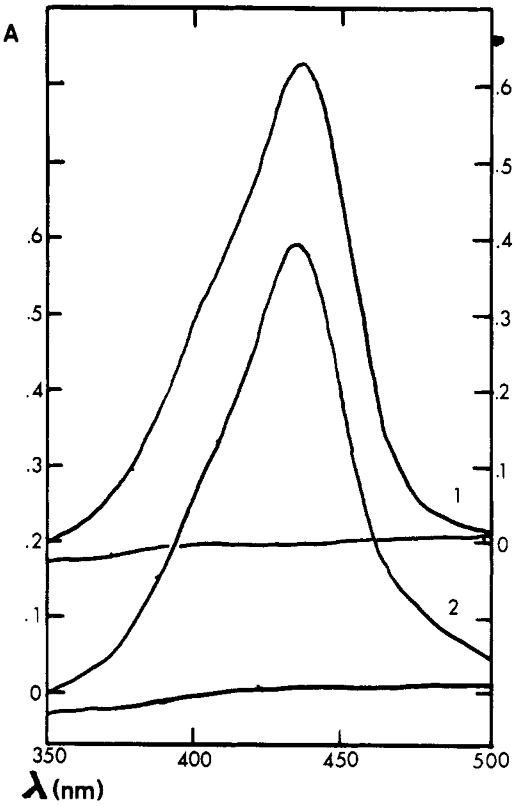
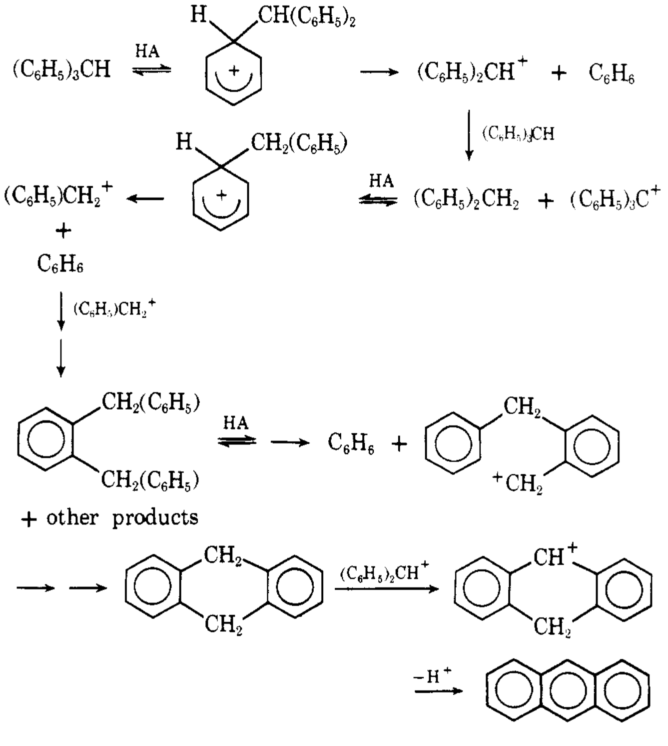


Figure 2. (1) Spectrum of a solution originally made up to contain 7.0×10^{-3} M triphenylmethane in triflic acid, diluted to a nominal concentration of 1.4×10^{-4} M, and thought to contain that concentration of diphenylcarbonium ion. (2) Spectrum of 1.36×10^{-4} M diphenylcarbonium ion in triflic acid, derived from a similar concentration of diphenylcarbinol. Both spectra were obtained in cells of 1 mm path.

Discussion

All the foregoing observations can be rationalized as shown by Scheme I. When high initial concentrations of triphenylmethane are used, the first-formed diphenylcarbonium ion

Scheme I



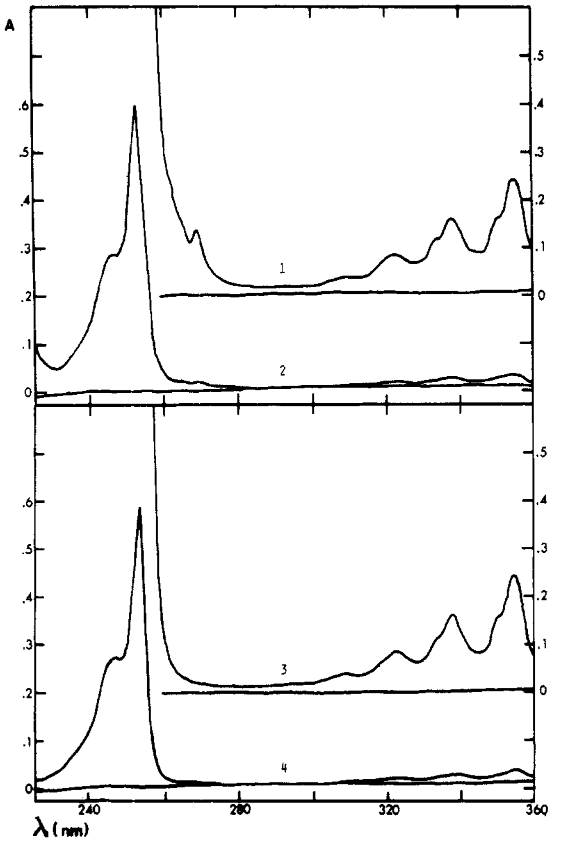


Figure 3. (1) The UV spectrum of the cyclohexane extract of the steam distillate obtained after diphenylmethane was treated with ten times its own weight of triflic acid and then quenched. (2) The same material, diluted ten times with cyclohexane. (3) Anthracene, 2.9 × 10^{-4} M, in cyclohexane. (4) Anthracene, 2.9 × 10^{-5} M, in cyclohexane. All spectra were obtained in 0.1-cm cells.

abstracts a hydride ion from the starting material to give triphenylcarbonium ion, diphenylmethane, and the further products shown. There are, undoubtedly, other minor products formed from the phenylcarbonium ion, but its unique volatility and the intensity of its spectrum make anthracene observable. At very low initial triphenylmethane concentrations the diphenylcarbonium ion is persistent, since, as shown by the experiments with diphenylcarbinol, it is stable in triflic acid, and the concentration of unreacted triphenylmethane is too low for the hydride transfer to be significant. Scheme I is really a disproportionation rather than a simple oxidation. Oxidation and reduction products are produced in equivalent amounts, and nothing other than the substrate itself is reduced.

Dealkylation and hydride transfer, the basic reactions of Scheme I, are well known and widespread reactions.[2,3,10,11] The cleavage of triphenylmethane in superacid medium, to give benzene and the diphenylcarbonium ion, has been previously reported.[12] The combination should, therefore, be added as a fourth general mechanism for apparent oxidations in strong acid medium, in addition to the three listed by Larsen et al.[4] For example, the "oxidation" of xanthene, 4,4′-dimethoxydiphenylmethane, and 4,4′,4″-trimethoxytriphenylmethane by sulfuric and phosphoric acids may be an example of its working[13] (although others have obtained different results under similar conditions[5]). Dealkylation, at least, definitely seems to occur on treatment of 4,4′,4″-trimethoxytriphenylmethane with very strong acids.[14]

Experimental Section

Materials. Triflic acid was twice distilled, the last time within one day of use, since it darkened on standing, bp 164 °C, reported[15] 162 °C. Triphenylmethane (Eastman Kodak Co.) was recrystallized from methanol, mp 93–94.5 °C, reported[16] 92.5 °C. Triphenylcarbinol (Matheson Coleman and Bell) was recrystallized from methanol, mp 159–161.5 °C, reported[17] 159 °C. All other materials were of the best quality commercially available and were used without further purification. Their suitability for the present work was verified spectroscopically.

Spectrophotometric Measurements. Visible and UV spectra were obtained with a Beckman DK-2 spectrophotometer using quartz cells of 1 cm or 1 mm path length, as required by the absorptivity of the solutions.

In determining the product compositions shown in Table I the method of Baughman and Kreevoy[18] was used. The two wavelengths chosen were 404 (λ_1) and 432 nm (λ_2). It was assumed that triphenylcarbonium ion and the conjugate acid of diphenylmethane would always occur in the same proportions in these experiments, so that they could be treated as a single substance. By making concentrated solutions of triphenylmethane in triflic acid and then diluting them as required, this "substance" was found to have ϵ_1 1.76 × 10^4 and ϵ_2 1.79 × 10^4. Extinction coefficients for diphenylcarbonium ion were obtained from very dilute solutions of triphenylmethane in triflic acid, ϵ_1 being 2.14 × 10^4 and ϵ_2 4.32 × 10^4. These measurements were all made with a Beckman DU spectrophotometer, modernized with a Gilford Update, at 25.0 ± 0.2 °C.

Each mole of triphenylmethane that reacts as shown in Scheme I can produce 1 mol of diphenylcarbonium ion, but 2 mol of triphenylmethane is required to produce 1 mol of triphenylcarbonium ion. Therefore, the methodology outlined above can be tested by comparing the sum, $2[(C_6H_5)_3C^+] + [(C_6H_5)_2CH^+]$, with the initial triphenylmethane concentration. This is done by comparing columns 1 and 4 of Table I. It is entirely satisfactory.

Infrared spectra were made in the usual way with a Perkin-Elmer 537 infrared spectrophotometer.

NMR spectra were made with a Varian T-60 NMR spectrophotometer. For isolated products, carbon tetrachloride or deuteriochloroforam were used as solvent with tetramethylsilane as reference. For solutions in triflic acid, tetramethylammonium chloride was used as a reference. Its signal was assumed to come 3.10 ppm below tetramethylsilane.[19] The NMR spectrum of triphenylcarbonium ion in triflic acid consists of peaks at 7.7, 7.8, 8.0, 8.1, and 8.25 ppm, essentially as previously reported.[20] Other required NMR spectra were compared with those of knowns, and were unexceptional.

Gasometric Measurements. The absence of gas evolution or uptake was determined using 0.1 g of triphenylmethane and 25 ml of triflic acid in a Warburg constant volume respirometer.[21]

Product Isolation. Triphenylmethane (3.3 g, 13.5 mmol) was dissolved in 25 ml of triflic acid and the solution allowed to stand at room temperature for 1 h. It was then quenched by pouring it slowly into 30 ml of chilled 20% aqueous sodium hydroxide. The aqueous solution was steam distilled and the steam distillate was extracted with cyclohexane. From its UV spectrum 10.2 mmol of benzene and 1.9 × 10^{-2} mmol of anthracene were identified in the cyclohexane solution. The residue from the steam distillation was a waxy, orange solid. It was shown by IR and NMR spectroscopy to contain 6.8 mmol of triphenylcarbinol and 3.0 mmol of diphenylmethane. From this material a poor yield of pure triphenylcarbinol, mp 151–158 °C, was obtained by twice recrystallizing from carbon tetrachloride.

Product isolation from the reaction of diphenylmethane was carried out similarly.

Registry No.—Triphenylmethane, 519-73-3; triflic acid, 1493-13-6; triphenylcarbinol, 76-84-6; triphenylcarbonium ion, 13948-08-8; diphenylcarbonium ion, 709-82-0; diphenylmethane, 101-81-5; diphenylcarbinol, 91-01-0.

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Semipinacol Rearrangements Involving Trifluoromethylphenyl Groups[1]

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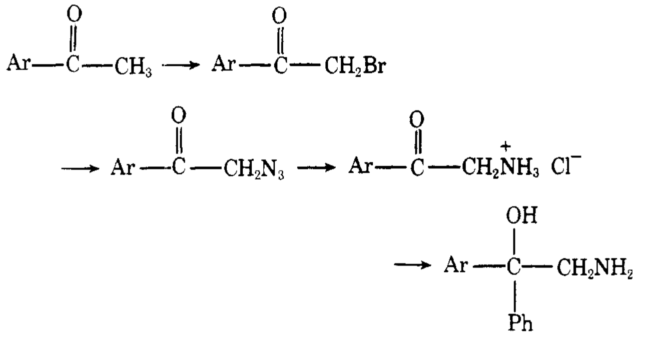
Semipinacolic deamination of 2-amino-1-(3-trifluoromethylphenyl)-1-phenylethanol (1) with sodium nitrite in aqueous acetic acid yields 3′-trifluoromethyldeoxybenzoin (3) and 3-trifluoromethyldeoxybenzoin (4). The migratory aptitude of the *m*-trifluoromethylphenyl group (phenyl = 1.0) is 0.47 at 0 °C and 0.39 at 25 °C. Similarly, deamination of 2-amino-1-(4-trifluoromethylphenyl)-1-phenylethanol (2) yields 4′-trifluoromethyldeoxybenzoin (5) and 4-trifluoromethyldeoxybenzoin (6). The migratory aptitude of the *p*-trifluoromethylphenyl group is 0.30 at 0 °C.

Little information is available regarding the behavior of trifluoromethylphenyl groups in pinacol-type reactions.[2] Our interest in deaminative rearrangements has led us to investigate semipinacol rearrangements of 2-amino-1-(3-trifluoromethylphenyl)-1-phenylethanol (1) and 2-amino-1-(4-trifluoromethylphenyl)-1-phenylethanol (2).

Results

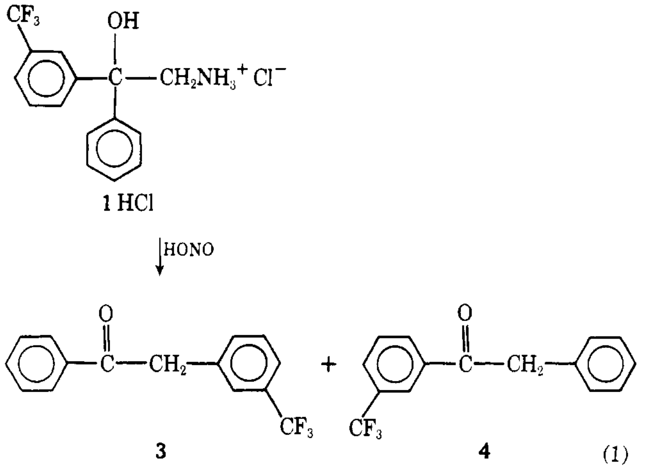
The amino alcohols were synthesized according to the general outline of Scheme I (see Experimental Section).

Scheme I



$Ar = m$- or p-$CF_3C_6H_4$; $Ph = C_6H_5$

Deamination of the meta-substituted amino alcohol hydrochloride, 1 HCl, was carried out with sodium nitrite in aqueous acetic acid at 0 °C[3] and at 25 °C (eq 1). The ketones 3 and 4 (combined yield 77% of theoretical at 0 °C) were separated from nonketonic products by column chromatography on alumina, and the ratios of 3 to 4 were determined by ^1H NMR and also by ^{19}F NMR spectroscopy using comparisons with authentic samples of 3 and 4 independently prepared (see Experimental Section). Results are summarized in Table I. The ketones were shown to be stable to the deamination conditions.



Deamination of the para-substituted amino alcohol 2 was carried out with sodium nitrite at 0 °C in aqueous acetic acid (eq 2). The ketonic fraction (67% of theoretical) was isolated