Superelectrophilic Nitration of the Triphenylcarbenium Ion[1]

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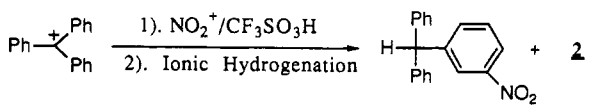
Received April 5, 1993

The reactivity of electrophiles capable of further coordination with strong protic or Lewis acids can be greatly enhanced.[2] These electrophiles generally contain nonbonded electron pairs, such as acyl cations and various onium ions. The resulting superelectrophiles are of doubly electron deficient (dipositive) nature, the reactivity of which greatly exceeds that of their parents in aprotic or conventional acidic media.[2] It was recently shown that linear NO_2^+ is activated in superacids via NO_2H^{2+}, which was subsequently directly observed in mass spectrometric studies.[3] Superelectrophilic nitration can readily be effected even with highly deactivated aromatics such as polyfluorinated arenes, polyfluoronitrobenzene, or dinitrobenzene, which generally do not react with conventional nitrating agents or nitronium salts in aprotic media.[2,4] The possibility of electrophilic nitration of carbocationic substrates is of substantial interest. Vorlander[5] originally studied the nitration of triphenylcarbenium salts, but could not isolate defined compounds. Wolf and Shriner reported the nitration of triphenylmethyl alcohol in concentrated sulfuric acid with fuming nitric acid.[6] They obtained 15% of 3-diphenylmethylnitrobenzene (1) but concluded that it was not possible to find experimental conditions which would give acceptable yields of nitro products. We now report the effective nitration of the triphenylcarbenium ion under superelectrophilic conditions.

The nitrations were carried out by reacting equivalent amounts of nitronium tetrafluoroborate and triphenylcarbenium tetrafluoroborate in an excess of trifluoromethanesulfonic acid. The reaction was started at 0 °C and the temperature was then gradually allowed to rise to room temperature. After the reaction mixture was quenched with ice, nitrated triphenylmethanols were observed. Due to the difficulty of separating the products from triphenylmethanol, the mixture of alcohols was reduced to the corresponding hydrocarbons under ionic hydrogenation conditions with boron trifluoride monohydrate and triethylsilane.[7] 3-(Diphenylmethyl)nitrobenzene (1) (64%) and bis(*m*-nitrophenyl)methylbenzene (2) (3%) were isolated by column chromatography. A solution of triphenylcarbenium ion in trifluoromethanesulfonic acid can be prepared by dissolving triphenylmethanol in the



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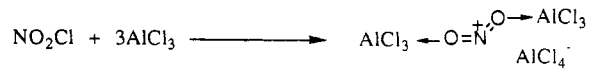
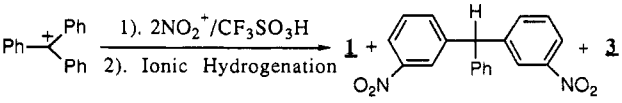
acid at room temperature. Nitration of the *in situ*-prepared triphenylcarbenium ion in excess trifluoromethanesulfonic acid gave the same results as nitrating preprepared trityl salt.

When the reaction of trityl salt with nitronium salt was attempted in aprotic methylene chloride solution, no nitration was observed. The nitration, however, also readily occurred in methylene chloride when $NO_2Cl/3AlCl_3$ was used as nitrating agent instead of nitronium tetrafluoroborate. 3-(Diphenylmethyl)nitrobenzene (1) (70%) was isolated when 1:1 equiv of triphenylcarbenium ion and $NO_2Cl/3AlCl_3$ were reacted. With a 1:2 ratio a 100% yield of the mononitro compound 1 was obtained. No dinitration was observed in these cases. Apparently, either protic superacid CF_3SO_3H or Lewis acid $AlCl_3$ can activated the nitronium ion. The results obtained with CF_3SO_3H are in accord with our previous studies on the superelectrophilic protonitronium dication in superacidic media.[3a] As for the case with Lewis acid $AlCl_3$, we suggest that the nitronium ion is activated by coordination of $AlCl_3$ to the oxygen lone pair electrons, which is an aprotic analog to the protonation (protosolvation) of the nitronium ion.[3a]



The exclusive meta nitration indicates that the nitration takes place on a strongly deactivated phenyl group of the carbocation. In the propeller-shaped triphenylmethyl cation, two of the phenyl groups are conjugatively interacting at the same time with the carbocationic center, with the third phenyl group out of the plane.[8] The Ph_2C^+ group thus acts as a deactivating substituent to the phenyl group undergoing substitution. No isomerization of the nitro group is feasible, because nitro compounds do not isomerize in trifluoromethanesulfonic acid. Furthermore, isomerization will not lead exclusively to formation of the meta-substituted product.

Reacting 2:1 equiv of nitronium ion and triphenylcarbenium ion, the reaction gave 54% 3-(diphenylmethyl)-nitrobenzene (1), 35% bis(*m*-nitrophenyl)methylbenzene (2), and 5% trinitrotriphenylmethane (3). The formation



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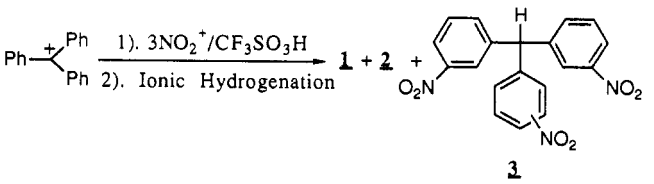
of bis(*m*-nitrophenyl)methylbenzene (2) shows that in trifluoromethanesulfonic acid the *m*-nitrotriphenylcarbenium ion can be further nitrated.

Increasing the ratio of nitronium and triphenylcarbenium ions to 3:1 led to formation of 14% 3-(diphenylmethyl)-nitrobenzene (1), 37% bis(*m*-nitrophenyl)methylbenzene

(1) Chemistry in Superacids. 14. Part 13, see: Olah, G. A.; Hartz, N.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.*, in press.
(2) For a review, see: Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.
(3) (a) Olah, G. A.; Rasul, G.; Aniszfeld, R.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 5608. (b) Weiske, T.; Koch, W.; Schwarz, H. *J. Am. Chem. Soc.*, submitted.
(4) For example, see: (a) Olah, G. A.; Lin, H. C. *Synthesis* **1974**, 444. (b) Yato, M.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 691. (c) Olah, G. A.; Laali, K. K.; Sandford, G. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 6670.
(5) Vorlander, D. *Ber.* **1925**, *58*, 1893.
(6) Wolf, C. N.; Shriner, R. L. *J. Org. Chem.* **1950**, *15*, 367.
(7) (a) Olah, G. A.; Wang, Q.; Trivedi, N. J.; Prakash, G. K. S. *Synthesis* **1992**, 465. (b) Larsen, J. W.; Chang, L. W. *J. Org. Chem.* **1979**, *44*, 1168.
(8) (a) Newman, M. S.; Deno, N. C. *J. Am. Chem. Soc.* **1951**, *73*, 3644. (b) Deno, N. C.; Jaruselski, J. J.; Schriesheim, A. *J. Org. Chem.* **1954**, *19*, 155. (c) Schuster, I. I.; Colter, A. K.; Kurland, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 4679.

0022-3263/93/1958-5017$04.00/0



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(2), and 23% trinitrophenylmethane (3). The trinitrotriphenylmethane 3 is a mixture of [bis(*m*-nitrophenyl)methyl]nitrobenzenes. ^{13}C NMR of the mixture suggests that [bis(*m*-nitrophenyl)methyl]-*p*-nitrobenzene (3a) is the major isomer (60%). The attachment of the second nitro group to triphenylcarbenium ion may have led to partial collapse of the cation to the trityl triflate under these reaction conditions (due to strong electron-withdrawing effect) and its nitration, resulting in the observed isomers after reduction.

In conclusion we have demonstrated that an activated electrophile (superelectrophile) can react efficiently with a carbocationic substrate. The reported reaction opens up the possibility of carrying out other Friedel–Crafts-type electrophilic substitutions on carbocationic substrates.

Experimental Section

Trifluoromethanesulfonic acid was obtained from 3M. Boron trifluoride was from Matheson Gas Products. Boron trifluoride monohydrate was prepared in our previous work.[7a] Nitroxyl chloride was prepared according to a reported procedure[9] and used as 0.5 M solution in CH_2Cl_2. All other compounds were purchased from Aldrich.

NMR spectra were obtained on a Varian Associate Model VXR-200. MS analyses were performed on a Hewlett-Packard 5971 mass spectrometer (EI) or a Finnigan INCOS 50 Mass Spectrometer (CI). Melting points were measured on a Fisher-Johns melting point apparatus. High resolution MS analyses were conducted at the University of California–Riverside facility.

(9) (a) Kaplan, R.; Shechter, H. In *Inorganic Synthesis*; Bailar, J. C., Jr., Ed.; McGraw-Hill Book Co., Inc.: New York, 1953; Vol. IV, p 52. (b) Price, C. C.; Sears, S. A. *J. Am. Chem. Soc.* **1953**, *75*, 3276.

Typical Experimental Procedure with $NO_2^+BF_4^-$/CF_3SO_3H as Nitrating Agent. To a mixture of triphenylcarbenium tetrafluoroborate (1 g, 3 mmol) and trifluoromethanesulfonic acid (10 mL) was added the corresponding amount of nitronium tetrafluoroborate (see text) at 0 °C. After stirring at 0 °C for 0.5 h and room temperature for another 2 h, the reaction mixture was quenched with ice and extracted with CH_2Cl_2 (3 × 20 mL), washed with water, aqueous $NaHCO_3$, and brine, and dried on $CaCl_2$. After filtering off $CaCl_2$ and concentrating to 30 mL, the methylene chloride solution was treated with triethylsilane and BF_3/H_2O under similar conditions used in ref 6. The reduction products were finally separated by column chromatography on silica gel with a mixture of hexanes and methylene chloride (85:15 by volume) as eluent.

Experimental Procedure with $NO_2Cl/4AlCl_3$ as Nitrating Agent. To 0.49 g of $AlCl_3$ (3.7 mmol) in 4 mL of dry CH_2Cl_2 was added 1.8 mL of a 0.5 M solution of NO_2Cl (0.9 mmol) at −78 °C with stirring. The temperature of the mixture was then allowed to warm up to 0 °C. A solution of triphenylcarbenium tetrafluoroborate (0.15 g, 0.45 mmol) in 2 mL of dry CH_2Cl_2 was subsequently introduced to the mixture. After being stirred at 0 °C for 2 h, the reaction was stopped with ice–water and subjected to a similar treatment as described previously in the Experimental Section. A quantitative yield of compound 1 was obtained.

3-(Diphenylmethyl)nitrobenzene (1): mp 90–91 °C, reported[4] 91–92 °C; MS (EI) 289 (M^+, 100); ^1H NMR (TMS), 8.07 (m, 1H), 8.03 (1H), 7.44 (m, 2H), 7.30 (m, 6H), 7.10 (m, 4H), 5.64 (s, 1H); ^{13}C NMR ($CDCl_3$) 148.38, 146.13, 142.32, 135.50, 129.24, 129.18, 128.66, 126.91, 124.17, 121.55, 56.42; HRMS calcd 289.1103, found 289.1117.

[Bis(*m*-nitrophenyl)methyl]benzene (2): mp 108–109 °C; MS (CI) 335 ($M^+ + 1$, 30); ^1H NMR (TMS), 8.14 (m, 2H), 8.00 (2H), 7.49 (m, 4H), 7.33 (m, 3H), 7.11 (m, 2H), 5.76 (s, H); ^{13}C NMR ($CDCl_3$) 148.46, 144.54, 140.80, 135.28, 129.64, 129.08, 129.03, 127.52, 124.00, 122.11, 55.89. HRMS calcd 334.0954, found 334.0957.

[Bis(*m*-nitrophenyl)methyl]-*p*-nitrobenzene (3a): MS (CI) 380 ($M^+ + 1$, 60); ^{13}C NMR ($CDCl_3$), 148.69, 148.06, 143.02, 142.96, 135.05, 130.18, 130.08, 124.30, 123.96, 122.82, 55.61; HRMS calcd 379.0804, found 379.0810.

Acknowledgment. We thank Dr. Robert Aniszfeld for performing MS (CI) analyses and the Office of Naval Research and the National Institutes of Health for financial support.