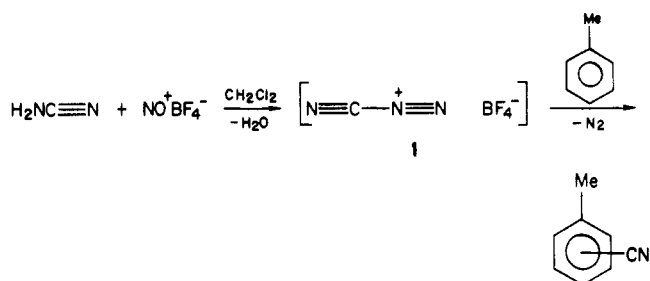


Communications

Cyanation and Nitration of Toluene with Cyanamide and Nitramide through Intermediate Cyano- and Nitrodiazonium Ions. Attempted Fluorination of Aromatics with Fluorodiazonium Ion¹

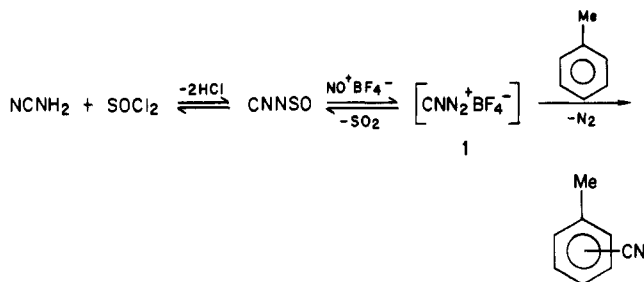
Summary: Toluene is cyanated and nitrated with cyano- and nitrodiazonium ion, generated via in situ diazotization of cyanamide and nitramide, respectively, with NO^+BF_4^- . Attempted fluorination with fluorodiazonium ion, prepared from *cis*-difluorodiazene and arsenic pentafluoride, gave only trace amounts of fluoroaromatics.

Sir: In previous studies from our laboratory aminodiazonium ions were generated by protonation of hydrazoic acid and alkyl azides in superacids and their ability for amination of aromatics was demonstrated.² In continuation of our studies we have found that cyanodiazonium tetrafluoroborate ($\text{NCN}_2^+\text{BF}_4^-$, 1) can be generated in situ by reaction of cyanamide with purified NO^+BF_4^- (1:1) at atmospheric pressure in CH_2Cl_2 at 0 °C and gives in the

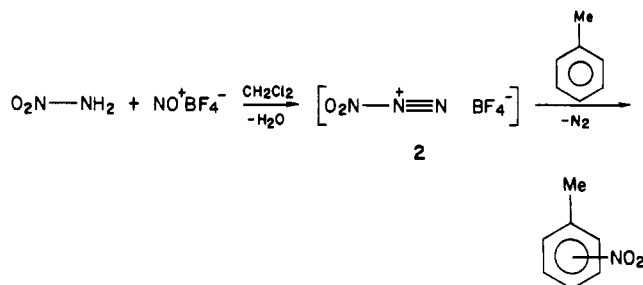


presence of excess toluene (3-fold) isomeric tolunitriles (12 mol % overall yield). The observed isomer distribution of tolunitriles is 48% ortho, 17% meta, and 35% para, close to that obtained for amination of toluene with aminodiazonium ion (46-48% ortho, 13-14% meta, and 38-39% para).² Slightly better conversion was achieved by using CH_3CN as solvent (14-15%) in which both NO^+BF_4^- and H_2NCN are more soluble.

In control experiments, when NO^+BF_4^- was allowed to react with cyanamide in acetonitrile at room temperature in the absence of toluene, the initial formation of a pale yellow solution was followed by an exothermic reaction (temperature 70-80 °C) with gas evolution (N_2 , BF_3), suggesting that the initial formation of NCN_2^+ or its precursor complex is followed by rapid dediazonation. Alternatively, NCN_2^+ can be also generated from cyanamide with thionyl chloride and NO^+BF_4^- under argon (500 psi) and reacted with toluene (50% ortho, 15% meta, 35% para).



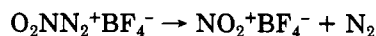
We have also found that nitrodiazonium tetrafluoroborate $\text{O}_2\text{N}^+\text{N}\equiv\text{N} \text{BF}_4^-$ (2) can be generated when a freshly prepared sample of nitramide⁴ (from ethyl carbamate and amyl nitrate) is allowed to react with a molar equivalent of purified NO^+BF_4^- in CH_2Cl_2 at 0 °C. De-



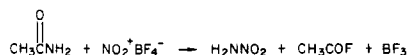
diazoniative nitration of toluene (4 equiv) gave isomeric nitrotoluenes in 36% overall yield. The observed isomer distribution of nitrotoluenes is 71% ortho, 3.5% meta, and 25.5% para and closely resembles that of electrophilic nitration of toluene with strongly electrophilic nitrating agents, such as nitronium salts.⁵

In a control experiment when nitramide was added to dry toluene in CH_2Cl_2 under the experimental condition, no nitrotoluenes were observed after workup and GC analysis, ruling out any possible nitration of toluene by nitramide itself or by nitric acid formed upon hydrolysis.

Aromatic cyanation via the cyanodiazonium ion 1 is in all probability a concerted reaction, as the cyanyl cation ^+CN is not expected to be formed, but the reaction could also involve a radical cation pathway. In contrast, dediazonation of the nitrodiazonium ion 2 to the nitronium ion is thermodynamically favorable and thus it cannot be excluded that its formation precedes nitration of aromatics.



(4) (a) Marlies, C. A.; La Mer, V. K.; Greenspan, J. *Inorg. Synth.* 1939, 1, 68. (b) Nitramide was also prepared by the reaction of acetamide (2 equiv) and $\text{NO}_2^+\text{BF}_4^-$ (1 equiv) in tetramethylene sulfone/ CH_2Cl_2 solution at 0 °C for 1 h.



(5) For a review on aromatic nitration with $\text{NO}_2^+\text{BF}_4^-$ see: Olah, G. A.; Narang, S. C.; Olah, J. A. *Proc. Natl. Acad. Sci. U.S.A.* 1978, 75, 1045.

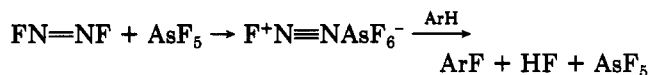
(1) Onium ions. 29. For part 28, see: Laali, K.; Olah, G. A. *J. Org. Chem.*, in press.

(2) Mertens, A.; Lammerstma, K.; Arvanaghi, M.; Olah, G. A. *J. Am. Chem. Soc.* 1983, 105, 5657.

(3) Commercially available NO^+BF_4^- (Aldrich) was purified from impurity $\text{NO}_2^+\text{BF}_4^-$ by repeated washing with dry benzene. After removal of solvent (and formed nitrobenzene), the salt was evacuated in vacuum.

As pointed out by a referee, one equimolar amount of water is also formed in the diazotization of nitramide which will hydrolyze nitronium ion, and the de facto nitrating agent may not be the free nitronium ion, although it is still possible that it is also involved in the overall nitration.

The ability of electronegative substituents in stabilizing diazonium ions was also demonstrated previously by the preparation of isolable fluorodiazonium salts, such as hexafluoroantimonate and hexafluoroarsenate, from *cis*-difluorodiazene and the strong Lewis acid fluorides SbF_5 or AsF_5 .⁶



We have in the course of our studies also attempted fluorination of aromatics such as benzene, toluene, and nitrobenzene with fluorodiazonium hexafluoroarsenate. Clearly FN_2^+ is unable to form F^+ ; thus, the reaction is expected to be that of displacement by the aromatics. The reactions were carried out at -78°C in anhydrous hydrogen fluoride solution with careful addition of the solution of the fluorodiazonium ion to excess of the aromatics. The reaction was found to be extremely exothermic even under these conditions, and only trace amounts of fluoroaromatics were formed (analyzed by gas-liquid chromatography and NMR spectroscopy). The fluorodiazonium ion thus seems to be a very strong oxidizing agent and of little practical value for aromatic fluorination.

All reported reactions can be best visualized as displacements of the diazonium ions by the aromatics, either giving the substituted products with simultaneous evolution of nitrogen or by competing reaction on nitrogen with subsequent decomposition of the intermediately formed aryldiazonium ions by the counterions (i.e., cyanide, nitrite, or fluoride).

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Registry No. 1, 95512-44-0; 2, 95512-46-2; PhCH_3 , 108-88-3; NO^+BF_4^- , 14635-75-7; H_2NCN , 420-04-2; SOCl_2 , 7719-09-7; NO_2NH_2 , 7782-94-7; $\text{NH}_2\text{C}(\text{O})\text{OEt}$, 51-79-6; $\text{CH}_3(\text{CH}_2)\text{ONO}_2$, 1002-16-0; *NC-o-C}_6\text{H}_4\text{Me}*, 529-19-1; *NC-m-C}_6\text{H}_4\text{Me}*, 620-22-4; *NC-p-C}_6\text{H}_4\text{Me}*, 104-85-8; *NO}_7\text{-o-C}_6\text{H}_5\text{Me}*, 88-72-2; *NO}_7\text{-m-C}_6\text{H}_4\text{Me}*, 99-08-1; *NO}_7\text{-p-C}_6\text{H}_4\text{Me}*, 99-99-0; $\text{FN}_2^+\text{AsF}_6^-$, 12005-87-7; $(Z)\text{-FN}=\text{NF}$, 13812-43-6; AsF_5 , 7784-36-3.

(6) Christe, K. O.; Wilson, R. D.; Sawodny, W. *J. Mol. Struct.* 1971, 8, 245 and references given therein.

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Thermodynamics of Electron Removal from Binorbornylidene and Sesquibicyclooctene

Summary: Binorbornylidene (1) is rearranged to sesquibicyclooctene (2) in $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{CO}_2\text{H}/(\text{CF}_3\text{CO})_2\text{O}$ (20:1:1) at room temperature. 1^+ is both kinetically and thermodynamically destabilized relative to 2^+ and other Bredt's rule protected radical cations. At -78°C in the above solvent mixture, it is 9.2 kcal/mol more difficult to oxidize 1 than 2 (electrochemical comparison).

Sir: Ando, Kabe, and Takata¹ found that in contrast to other Bredt's rule protected olefins,² binorbornylidene (1)³ gives a radical cation which is short-lived on the cyclic voltammetry (CV) time scale, so that no reduction wave is observed associated with the $1,1^+$ oxidation wave. Because radical cation lifetimes are often increased in the presence of acid and dehydrating agents,⁴ we investigated the CV of 1 in 20:1:1 $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{CO}_2\text{H}/(\text{CF}_3\text{CO})_2\text{O}$ containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte (used throughout this work). Although the $1,1^+$ oxidation wave remains completely irreversible at room temperature under these conditions ($E_p^{\text{ox}} = 2.06$ V vs. SCE at 200 mV/s scan rate), 1 is clearly not stable. The $1,1^+$ oxidation wave gradually decreases in size over a period of half an hour and is replaced by a completely reversible oxidation wave at lower potential, $E^{\circ'} = 1.68$ V vs. SCE. As expected from its reversible CV wave, electrochemical oxidation of this solution gives a long-lived radical, which shows ESR splittings for two sets of eight equivalent hydrogens with $a(8\text{H}) = 3.9$ G (H_a) and $a(8\text{H}) = 0.3_7$ G (H_b) and a *g* factor of 2.0024. The easily oxidized product from 1 clearly has high symmetry. Stirring 22 mg of 1 in 10 mL of CH_2Cl_2 , 0.5 mL of $\text{CF}_3\text{C}-\text{O}_2\text{H}$, and 0.5 mL of $(\text{CF}_3\text{CO})_2\text{O}$ for 5 h, followed by aqueous workup and chromatography on silica gel (hexane eluent) gave two fractions. The first fraction (R_f 0.95, ca. 10 mg) was a 1:3 mixture of 1 and the $E^{\circ'} = 1.68$ V material, which is an isomer of 1 and has a ^1H NMR spectrum consisting of a broad singlet at δ 2.48 (H_b) and two broad doublets (separation about 7 Hz) at δ 1.48 and 1.15 (H_a and H_c). From its ESR and NMR data, the rearrangement product can only be sesquibicyclooctene (2).⁵ The second fraction (R_f 0.50, 10.2 mg, 29%) shows an IR absorption at 1780 cm^{-1} and has a mass spectrum with major peaks at *m/e* 302 (M^+ , 10%), 188 ($\text{M}^+ - \text{HO}_2\text{C}_2\text{F}_3$, 51%), and 160 ($\text{M}^+ - \text{HO}_2\text{C}_2\text{F}_3 - \text{C}_2\text{H}_4$, 32%), indicating that it is a trifluoroacetate. Its ^1H NMR spectrum shows δ 2.19 (br s, 2 H), 2.13 (br s, 1 H), 1.8-1.5 (m, 8 H), 1.4-1.1 (m, 10 H). We assign this material as 3, a trifluoroacetic acid adduct of 2 (or conceivably, of 1). A plausible pathway for the conversion of 1 to 2 and 3 is shown in Scheme I. The rearrangement of 1 to 2 is exothermic. Allinger MM2 calculations⁶ give 1 as having a 12.8 kcal/mol higher steric energy than 2. We consider the conditions required for the conversion unexpectedly mild. Although the $1\text{H}^+ \rightarrow$

(1) (a) Ando, W.; Kabe, Y.; Takata, T. *J. Am. Chem. Soc.* 1982, 104, 7314. (b) This was also observed in unpublished work from our laboratory by R. Akaba.

(2) (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* 1979, 101, 2503.

(b) Gerson, F.; Lopez, J.; Akaba, R.; Nelsen, S. F. *Ibid.* 1981, 103, 6716.

(3) Bartlett, P. D.; Ho, M. *J. Am. Chem. Soc.* 1974, 96, 627.

(4) Hammerich, O.; Parker, V. D. *Electrochim. Acta* 1973, 18, 537.

(5) Systematic names: 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-diethanonaphthalene; tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-2,7-ene. We employ the common nomenclature introduced by Bartlett et al. (Bartlett, P. D.; Blackeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* 1980, 102, 1383) for the dimethano bridged compounds, which are called sesquibornenes.