Journal of Fluorine Chemistry, 27 (1985) 275–284

Received July 6, 1984, accepted August 3, 1984

PERFLUOROCYCLOALKYL(ARYL) DIAZENES FROM HEPTAFLUORONITROSOCYCLOBUTANE AND NONAFLUORONITROSOCYCLOPENTANE

HELEN M. MARSDEN [1] and JEAN'NE M. SHREEVE*

Department of Chemistry, University of Idaho, Moscow, Idaho 83843 (U.S.A.)

SUMMARY

The perfluoronitrosocycloalkanes, heptafluoronitrosocyclobutane and nonafluoronitrosocyclopentane, are convenient precursors to a family of new perfluorocycloalkyl(aryl) diazenes. With aniline and *o*-aminobenzamide, $\overline{CF_2(CF_2)_xC}FN{=}N\overline{C(CH)_4C}H$ and $\overline{CF_2(CF_2)_xC}FN{=}N\overline{C(CH)_4C}C(O)NH_2$ (x = 2,3) are formed. Additionally, heptafluoronitrosocyclobutane gives $\overline{CF_2(CF_2)_2C}FN{=}N\overline{CCFCFCHCFC}F$ and $\overline{CF_2(CF_2)_2C}FN{=}N\overline{C(CH)_4C}NH_2$ with 2,3,5,6-tetrafluoroaniline and *o*-phenylenediamine

INTRODUCTION

The chemical behavior of fluorinated acyclic alkyl nitroso compounds has been studied extensively since CF_3NO was synthesized by Emeléus et al [2]. Reactions of nitroso compounds with primary amines were demonstrated to result in the formation of diazenes via the elimination of water [3-5]. Renewed interest has developed in studying the interactions of CF_3NO with aromatic amines as a method for introducing the trifluoromethyl group as a substituent on the aromatic ring via decomposition of the diazene intermediates [6-9].

We have reported recently the improved preparation and some reactions of two fluorinated cyclic nitroso compounds, heptafluoronitrosocyclobutane and nonafluoronitrosocyclopentane [10]. Thus, we were prompted to examine the behavior of these fluorinated cyclic alkyl nitroso compounds with aromatic amines, particularly since we had demonstrated that c-C_4F_7NO and c-C_5F_9NO undergo rather surprising rearrangement, but not condensation, reactions with methyl amine [11]. Here we describe the synthesis and characterization of some new perfluorocycloalkyl(aryl) diazenes from the reactions of heptafluoronitrosocyclobutane and nonafluoronitrosocyclopentane with several aromatic primary amines.

0022-1139/85/$3.30

$$\overline{CF_2(CF_2)_xC}FNO + H_2NAr \xrightarrow[-H_2O]{CH_3OH} \overline{CF_2(CF_2)_xC}FN{=}NAr$$

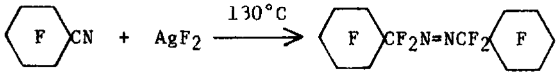
x = 2; Ar = C_6H_5(*I*), C_6F_4H (*II*), o-$C_6H_4NH_2$(*III*)

o-$C_6H_4C(O)NH_2$(*IV*)

x = 3; Ar = C_6H_5(*V*), o-$C_6H_4NH_2$(*VI*);

RESULTS AND DISCUSSION

A large number of diaromatic diazenes of the type ArN=NAr', where Ar' is totally or partially fluorinated, are in the literature [12-15]. Benzenediazonium chloride with perfluoroalkyl carbanions provides a route to ArN=NR$_f$ where R$_f$ is acyclic or an acyclic fluoroalkyl [16]. In a recent report [17], the first symmetric fluorocycloalkyl diazene was prepared



In this work, we have found that heptafluoronitrosocyclobutane and nonafluoronitrosocyclopentane can be reacted with a variety of aromatic primary amines to give diazenes in relatively low yields. The reactions are vigorous and normally carried out in methanol solutions. In the case of aniline, the reaction proceeds in the absence of solvent but the yield of the product is further reduced.

Purification of the crude diazenes was difficult in some cases despite the use of Chromatatron as well as column chromatographic techniques and molecular distillation methods. The diazenes are bright yellow materials. The stretching vibration $\nu_{N=N}$ is observed in the 1520 cm^{-1} vicinity. In the ^{19}F NMR spectra, the fluorine atoms geminal to the diazenediyl functionality are characteristically shifted upfield to ϕ -160 to -175.

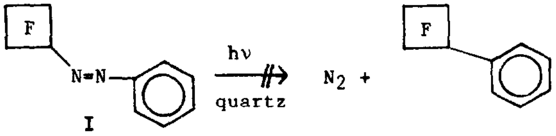
After several days at room temperature, no reaction was obtained when $\overline{CF_2(CF_2)_2C}FNO$ was mixed with acetamide or trifluoroacetamide, presumably due to the very low basicity of the amino nitrogen. More forcing conditions are

$$RC(O)NH_2 + \overline{CF_2(CF_2)_2C}FNO \xrightarrow{CH_3OH}\!\!\!\!\!\!/\!\!/\;\; \overline{CF_2(CF_2)_2C}FN{=}NC(O)R$$

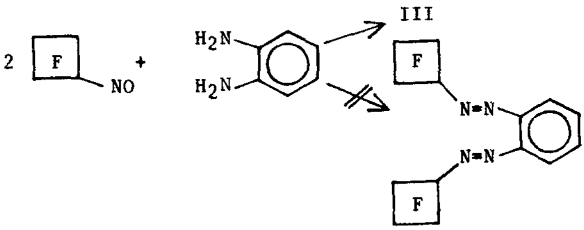
R = CH_3, CF_3

not possible due to the thermal instability of the nitroso compound.

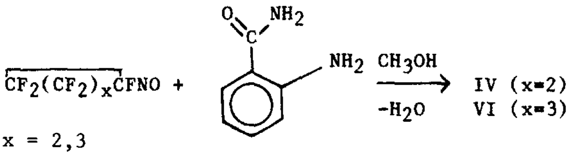
Although elimination of dinitrogen from trifluoromethyl diazenes has proved to be an excellent route for introducing a trifluoromethyl group into an aromatic ring [6-9], we were unsuccessful in our attempts to produce similar compounds. No nitrogen was produced. For example, the yellow compound I was decomposed to a unidentified brown oil.



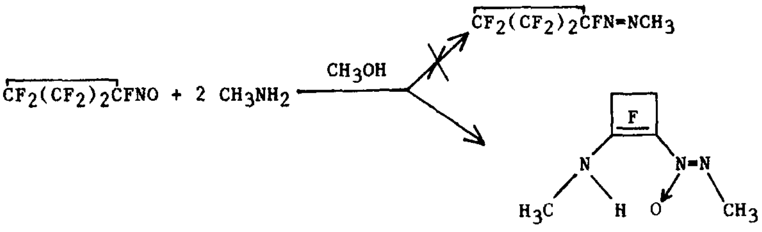
In the reactions with *o*-phenylenediamine only the monosubstituted product was formed. The failure to obtain the disubstituted product may arise from the decrease in the basic character of the remaining amino nitrogen arising from the presence of a strongly electron withdrawing group.



Similarly, the reaction between *o*-aminobenzamide also gave only the monosubstituted product



Although when CF_3NO was reacted with methyl amine, $CF_3N{=}NCH_3$ [4] was produced, the reactions between $\overline{CF_2(CF_2)_xCFNO}$ (x=2,3) and methylamine, gave a diazene 1-oxide rather than the anticipated diazene [11].



However, this mode of behavior was not observed in reactions with aromatic primary amines.

EXPERIMENTAL

Materials

Heptafluoronitrosocyclobutane and nonafluoronitrosocyclopentane were prepared by the literature method [10]. Aniline was obtained from Baker and distilled over potassium hydroxide prior to use. All other reagents were used as received from commercial suppliers without further purification. Sources were as follows: 2,3,5,6-tetrafluoroaniline, PCR; *o*-phenylenediamine and *o*-aminobenzamide, Aldrich.

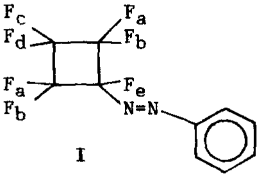
General Procedures Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise-Bourdon tube gauge and a Televac thermocouple gauge. The nitroso compounds were measured quantitatively using PVT techniques. Various methods were used to purify the diazenes including chromatography columns containing silica gel #12, molecular distillation, recrystallization and the use of a Chromatatron. Infrared spectra were recorded with a Perkin-Elmer 599 spectrometer as liquid films between KBr windows. ^{19}F NMR spectra were obtained on a JEOL FX-90Q Fourier transform spectrometer operating at 84.26 MHz. $CDCl_3$ was used as a solvent with $CFCl_3$ as an external reference. Chemical shifts upfield of Freon-11 are assigned negative values. ^{1}H NMR spectra were obtained at an operating frequency of 89.46 MHz. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E or a VG 7070 HS mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

General Method To a 125 or 250 mL Pyrex round-bottomed flask, equipped with a 19/22 ground glass joint, a Kontes stopcock, and a Teflon-coated stirring bar was added ~10 mL of methanol and one to nine mmoles of aromatic amine. After the vessel was evacuated at -196°C, a slight excess of the nitroso compound was condensed into the flask which was allowed to warm to room temperature over a period of one hour. The resulting solution was stirred for several days to ensure complete reaction. The mixture was worked up as given below.

Reaction of heptafluoronitrosocyclobutane with aniline to give I

Distillation of the solution into a trap at -78°C gave a yellow methanol solution. After the solvent was removed on a rotary evaporator, the diazene was purified using a molecular distillation apparatus. I was collected as a yellow oil, in ~50% yield, at -78°C under static vacuum.

The infrared spectrum of I contains bands at: 3070 (w), 2970 (m), 1595 (w), 1515 (s), 1485 (w), 1462 (ms), 1412 (s), 1280 (vs), 1270 (vs, br), 1220 (vs, br), 1166 (ms), 1110 (s, vbr), 1080 (s, vbr), 1025 (s, vbr), 950 (vs), 910 (ms), 825 (w), 815 (ms), 775 (s), 695 (s), 637 (w), 625 (w), 585 (s), 565 (s), cm^{-1}. The mass spectrum shows a molecular ion at m/e 286 ($C_{10}F_7N_2H_5^+$). Other principal peaks are observed at m/e 248 ($C_{10}F_5N_2H_5^+$), 105 ($C_6N_2H_4^+$), 91 ($C_6NH_4^+$) and 77 ($C_6H_5^+$). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts and area ratios:



I

Area		ϕ/ppm
2	F_a	-128.1
2	F_b	-128.6
1	F_c	-131.8
1	F_d	-132.1
1	F_e	-166.9

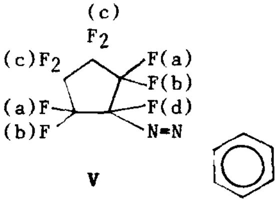
The ^1H NMR spectrum shows the expected monosubstituted pattern with an *o* : m + p ratio of 2H:3H centered at δ7.9 and δ7.5 respectively.

Anal. Calcd. for $C_{10}F_7N_2H_5$: C, 41.97; F, 46.5. Found: C, 39.93; F, 47.1.

Reaction of nonafluoronitrosocyclopentane with aniline to give V

Distillation gave a yellow methanol solution in a trap at -78°C with the excess nitroso compound passing into a trap at -196°C. After the methanol was removed, the remaining yellow oil was prepurified on a 1' liquid chromatography column by using silica gel #12, and chloroform as the elutant. The pure compound was isolated in ~10% yield by preparative plate chromatography (using silica gel) as the first band off the plate. Chloroform was used as the elutant.

The infrared spectrum of **V** contains bands at 3070 (w), 2970 (s), 2915 (w), 1520 (ms, br), 1459 (m), 1343 (ms), 1320 (s), 1266 (vs), 1212 (vs, br), 1162 (ms, 1080 (vs, vbr), 1020 (vs, vbr), 980 (vs), 946 (ms), 911 (m), 872 (m), 812 (vs, br), 775 (ms), 693 (ms), 620 (m), 565 (m), 559 (mw), 550 (m), 517 (mw), cm^{-1}. The mass spectrum shows a molecular ion at m/e 336 ($C_{11}F_9N_2H_5^+$). Other principal peaks are observed at m/e 317 ($C_{11}F_8N_2H_5^+$), 298 ($C_{11}F_7N_2H_5^+$), 231 ($C_5F_9^+$), 105 ($C_6N_2H_5^+$), 91 ($C_6NH_5^+$), 77 ($C_6H_5^+$), 69 (CF_3^+) and 50 (CF_2^+). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts and area ratios:



V

Area		ϕ/ppm
2F	F_a	-128.6
2F	F_b	-128.9
4F	F_c	-129.4
1F	F_d	-173.2

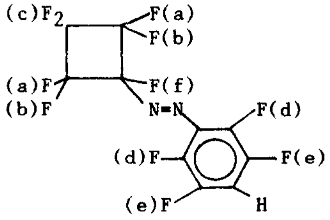
The ^1H NMR spectrum has the expected monosubstituted pattern with an *o* : m + p pattern ratio of 2H:3H centered at $\delta 7.9$ and $\delta 7.55$ respectively.

Anal. Calcd. for $C_{11}F_9N_2H_5$: C, 39.29; F, 50.89. Found: C, 38.54; F, 50.5.

Reaction of heptafluoronitrosocyclobutane with 2,3,5,6-tetrafluoroaniline to give II

Distillation gave a yellow methanol solution in the trap at -78°C and the excess nitroso compound passed into a trap at -196°C. After the methanol was removed on a rotary evaporator, the yellow diazene remained behind. The pure compound, which is a yellow oil, was obtained in ~25% yield. The infrared spectrum of II contains bands at 3095 (w), 1665 (w), 1615 (w), 1532 (s), 1512 (s), 1388 (m), 1287 (s), 1265 (sh), 1220 (s), 1190 (ms), 980 (s), 948 (s), 868 (m), 840 (m), 725 (m), 590 (ms), 580 (ms), cm^{-1}.

The mass spectrum shows a molecular ion at m/e 358 ($C_{10}F_{11}N_2H^+$). Other principal peaks are observed at m/e 339 ($C_{10}F_{10}N_2H^+$), 258 ($C_8F_7N_2H^+$), 208 ($C_7F_5N_2H^+$), 181 ($C_4F_7^+$), 177 ($C_6F_4N_2H^+$), 163 ($C_6F_4NH^+$) and 149 ($C_6F_4H^+$). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts and area ratios:



II

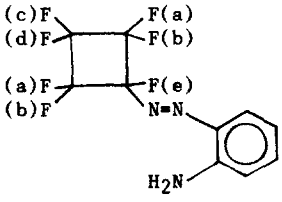
Area		ϕ/ppm
2F	F_a	-127.9
2F	F_b	-128.8
2F	F_c	-132.1
2F	F_d	-137.2
1F	F_e	-147.8
1F	F_f	-169.1

The ^{1}H NMR spectrum shows a multiplet centered at δ7.3 , due to coupling with F_d and F_e.

Anal. Calcd. for $C_{10}F_{11}N_2H$: C, 33.54; F, 58.3. Found: C, 33.58; F, 56.9.

Reaction of heptafluoronitrosocyclobutane with *o*-phenylenediamine to give III

Distillation into a trap held at -50°C gave a yellow methanol solution. Evaporation of the solvent, and preparative plate chromatography led to the pure compound as a yellow oil in ~10% yield. The infrared spectrum of III is 3490 (m), 3410 (w), 3360 (w), 1623 (s), 1586 (ms), 1515 (m), 1498 (ms), 1397 (s), 1305 (s, br), 1255 (s, br), 1210 (vs, vbr), 1173 (ms), 1120 (ms, vbr), 1055 (m), 945 (vs), 965 (m), 770 (vs), 585 (vs), cm^{-1}. The EI$^+$ mass spectrum at 15 eV showed a molecular ion at m/e 301 ($C_{10}F_7N_3H_6^+$) 21%. Other prominent peaks are at m/e 201 ($C_8F_3N_3H_6^+$) 6%, 151 ($C_7FN_3H_6^+$) 10%, 120 ($C_6N_3H_6^+$) 35%, 92 ($C_6NH_6^+$) 100%. The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts and area ratios:



III

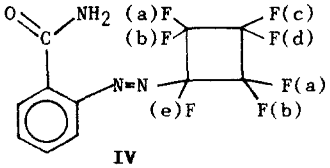
Area		ϕ/ppm
2F	F_a	-128.8
2F	F_b	-129.2
1F	F_c	-132.2
1F	F_d	-132.3
1F	F_e	-162.2

The ^{1}H NMR spectrum shows the aromatic protons between δ6.7 and δ7.8 and a broad resonance at δ5.4 for the NH_2 group. The area ratio is 4H:2H.

Reaction of heptafluoronitrosocyclobutane with *o*-aminobenzamide to give **IV**

All volatile materials, methanol and unreacted heptafluoronitrosocyclobutane, were removed under vacuum to leave a brown oily solid. The pure bright yellow crystals were obtained in ~13% yield by successive recrystallizations from methylene chloride, then a methylene chloride and hexane mixture, and finally neat hexane (mp 140-141°C). The infrared spectrum of **IV** is 3420 (vs), 3170 (ms, br), 1684 (s), 1580 (m, br), 1520 (m), 1395 (s), 1295 (s), 1220 (s, br), 1100 (w, br), 1007 (w), 945 (vs), 903 (m), 804 (m), 776 (s), 736 (w), 1616 (s), 593 (s), 532 (s), 463 (w), 410 (w), 335 (w), cm^{-1}.

The EI^+ spectrum does not show a molecular ion. But a peak at m/e 313 ($C_{11}F_7NH_4O^+$)(0.3%) arises from the loss of NH_2. Other principal peaks are observed at m/e 291 ($C_{11}F_5N_3H_6O^+$) 4%, 148 ($C_7N_3H_6O^+$) 78%, 92 ($C_6NH_6{}^+$) 50%, 62 (CF_2C^+) 46%, and 45 (CNH_3O^+) 95%. The CI^+ mass spectrum shows a $M^+ + 1$ peak at m/e 330 ($C_{11}F_7N_3H_7O^+$) (5%). The other major peaks are seen at m/e 313 ($C_{11}NH_4F_7O^+$) 100%, 275 ($C_{11}F_5N_2H_4O$) 7%, 148 ($C_7N_3H_6O^+$) 15% and 120 ($C_7NH_6O^+$) 12%. The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts and area ratios:



IV

Area		ϕ/ppm
2F	F_a	-127.4
2F	F_b	-128.2
1F	F_c	-131.5
1F	F_d	-132.1
1F	F_e	-167.4

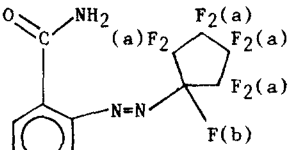
The ^1H NMR spectrum shows multiplets centered at δ8.45 (1H), δ8.38 (1H), δ7.6 (2H) and a broad NH_2 peak at δ6.1.

Anal. Calcd. for $C_{11}N_3H_6F_7O$: C, 40.12; F, 40.4; H, 1.82; N, 12.76. Found: C, 39.84; F, 39.3; H, 1.83; N, 11.46.

Reaction of nonafluoronitrosocyclopentane with *o*-aminobenzamide to give **VII**

The excess nitroso compound was removed under vacuum. The green crystals were obtained in ~13% yield by successive recrystallizations from methylene chloride (m.p. 112-115°C, decomp.). The infrared spectrum of **VII** contains bands at 3430 (s), 3175 (s, br), 1683 (vs), 1602 (m), 1530 (m), 1450 (w), 1393 (s), 1313 (s), 1280 (s), 1205 (vs), 1083 (m), 1042 (m), 973 (vs), 825 (m), 780 (s), 732 (m), 600 (s), 560 (m), 525 (m), cm^{-1}.

The EI^+ mass spectrum at 70 eV does not show a molecular ion. However an M^+ + 1 peak at m/e 380 ($C_{12}F_9N_3H_7O^+$) (0.1%) is seen due to self chemical ionization of the acidic protons. The other major peaks are seen at 363 ($C_{12}F_9N_2H_4O^+$) 0.8%, 148 ($C_7N_3H_6O^+$) 60%, 120 ($C_7NH_6O^+$) 100%, 92 (C_6NH_6) 62% and 77 ($C_6H_5^+$) 18%. The CI^+ mass spectrum shows a M^+ + 1 peak at m/e 380 ($C_{12}F_9N_3H_7O^+$) 9%. Other major peaks appear at 363 ($C_{12}F_9N_2H_4O^+$) 100%, 325 ($C_{12}F_7N_2H_4O^+$) 11%, 148 ($C_7N_3H_6O^+$) 32%, 120 ($C_7NH_6O^+$) 32%, and 92 (C_6NH_6) 9%. The ^{19}F NMR spectrum consists of complex multiplets with the following chemical shifts and area ratios:



VII

Area		ϕ/ppm
8F	F_a	-127.1
1F	F_b	-170.2

The ^1H NMR spectrum shows multiplets centered at δ8.4 (1H), 8.3 (1H), 7.6 (2H) and a broad NH_2 resonance at δ5.6.

Anal. Calcd. for $C_{12}F_9N_3H_6O$: C, 37.99; H, 1.58; N, 11.08; F, 45.1. Found C, 38.03; H, 1.59; N, 11.17; F, 45.0.

ACKNOWLEDGEMENTS

Acknowledgement is expressed to the National Science Foundation (Grant CHE-8100156), and the Air Force Office of Scientific Research (82-047) for support of this research. H.M.M. thanks the American Association of University Women for an International Fellowship Award. We thank Dr. Gary Knerr for mass spectral data.

REFERENCES

1 American Association of University Women International Fellow, 1982-83.

2 M. C. Henry, C. G. Griffis and E. C. Stump, Fluorine Chem. Rev. 1 (1967) 1.

3 J. P. Makarov, A. Ya. Yakubovich, V. A. Ginsburg, A. S. Filatov, M. A. Englin and T. Ya Nikoforova, Dokl. Akad. Nauk. SSSR 141 (1961) 357.

4 A. H. Dinwoodie and R. N. Hazeldine, J. Chem. Soc. (1965) 2266.

5 V. A. Ginsburg and M. N. Vasil'eva, Zhur. Organ. Khim. 9 (1973) 1080.

6 A. de Meijere and P. Golitz, Angew. Chem. Int. Edn. Engl. 16 (177) 854.

7 U. Hartkopf and A. de Meijere, Angew. Chem. Int. Edn. Engl., 21 (1982) 443.

8 T. Umemoto and O. Miyamo, Tetrahedron Lett., 23 (1982) 3929.

9 T. Umemoto and A. Sekiya, Chem. Lett. (1982) 1519.

10 H. M. Marsden and J. M. Shreeve, Inorg. Chem. 23 (1984) 000.

11 H. Hope, C. B. Shoemaker, D. P. Shoemaker, H. M. Marsden and J. M. Shreeve, J. Am. Chem. Soc., submitted.

12 M. J. Namkung, N. K. Naimy, C. A. Cole, N. Ishikawa and T. L. Fletcher, J. Org. Chem., 35 (1970) 728.

13 G. M. Brooke, E. J. Forbes, R. D. Richardson, M. Stacey and J. C. Tatlow, J. Chem. Soc. (1965) 2088.

14 C. Crogan, R. Fields, A. C. Pratt, L. M. N. Saleem and P. E. Dawson, J. Fluorine Chem., 22 (1983) 61.

15 H. Iwamoto, T. Sonoda and H. Kobayashi, J. Fluorine Chem. 24 (1984) 535.

16 B. L. Dyatkin, L. G. Zhuravkova, B. I. Martynov, S. R. Sterlin and I. L. Knunyants, J. Chem. Soc., Chem. Commun., (1972) 618.

17 C. S. Phull, G. Plevey and J. C. Tatlow, J. Chem. Soc. Perkin Trans. I (1984) 455.