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PERFLUOROGLUTARYL CHLORIDE -- A USEFUL PRECURSOR TO HETEROCYCLES

M. MOHAMMADI and JEAN'NE M. SHREEVE

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

SUMMARY

Perfluoroglutaryl chloride formed heterocyclic compounds with 2,3-dihydroxynaphthalene and with o-phenylenediamine. However, only a disubstituted acyclic compound resulted with bis(trimethylsilyl)piperazine.

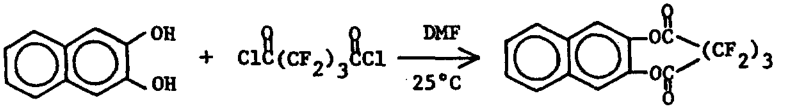
INTRODUCTION

Perfluoroglutaryl chloride is an excellent precursor to heterocyclic compounds. Bradshaw et al. [1] have utilized perfluoroglutaryl chloride in reaction with ethylene glycol to give a macrocyclic ether-ester but surprisingly it has been used rarely to form cyclic compounds.

In contrast, perfluoroglutaryl chloride has been employed in many other kinds of studies. As an example in a negative chemical ionization study [2], perfluoroglutaryl chloride has been found to fragment differently than the nonfluorinated materials with the loss of the elements of phosgene an important process. In reaction with sodium perfluorotertiary alkoxides (e.g., $C_6F_5C(CF_2)_2ONa$), $RO_2C(CF_2)_3CO_2R$ is obtained [3]. With an excess of $Na[Co(CO)_4]$, Haszeldine [4] found $(CO)_9Co_3C(CF_2CF_2CO_2H)$ as a major product. It has been used in syntheses of aryl perfluoroalkyl ether ketones by Friedel Crafts acylation [5]. Relative reactivity studies of $XC(O)(CF_2)_3C(O)X$ (X = Br, Cl, F) with dimethylacetamide showed that a decrease occurred in going from Br to Cl to F [6]. Also, there are a great many polymeric compounds which are formed using perfluoroglutaryl chloride or fluoride as the monomer.

RESULTS AND DISCUSSION

When perfluoroglutaryl chloride was reacted with 2,3-dihydroxynaphthalene, a nine-membered heterocyclic compound (I) was obtained in very good yield (86%).



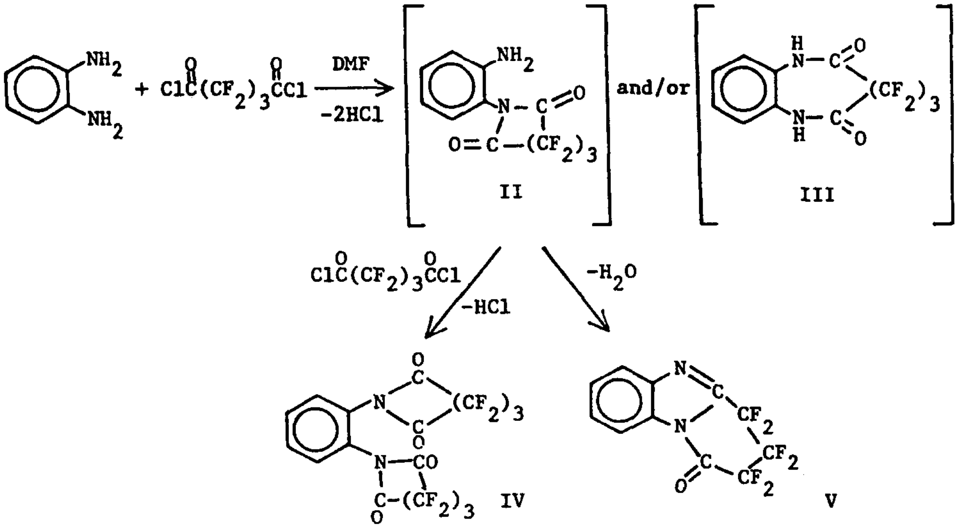
I

When dry tetrahydrofuran (rather than dimethylformamide) was used as solvent, little or no reaction took place. Compound (I) decomposes readily to a purple solid at ambient temperature. The infrared spectrum of the latter solid material contained a broad band in the ν_{OH} region and the ν_{C-F} bands were retained, but no bands which could be attributed to a carbonyl function were observed. Dissolving I in water gave a reddish-purple solution.

It has been reported [7,8] that heterocyclic compounds of the general structure $CF_3\overline{NN(CF_3)C(O)R_fC}O$ and perfluoro-N-methylpyrrolidone undergo contraction through decarbonylation when irradiated with ultra violet radiation. In one instance when compound (I) was pyrolyzed at 145-150°C/0.15 torr, an oily liquid was obtained (5%). The infrared spectrum of the pyrolysate did not contain a band in the carbonyl region but bands which likely arise from C-F, C-H (unsaturated) and -C-O-C were present. Compound I apparently suffers decarbonylation under the conditions used. This is also indicated by the fact that the mass spectral fragmentation pattern of I showed the loss of two carbonyl groups at 17 eV.

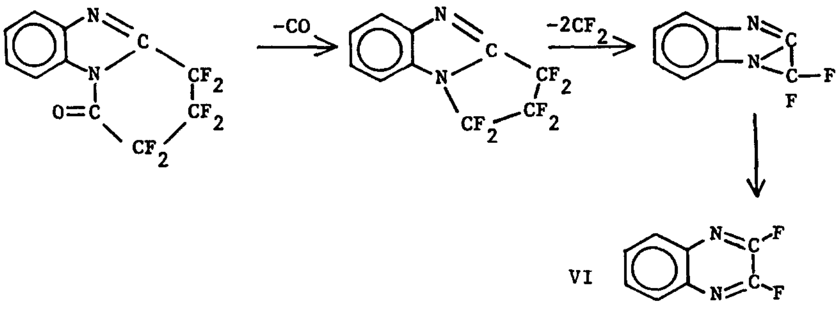
The reaction of perfluoroglutaryl chloride with o-phenylenediamine in dimethylformamide gave two products in low yields,

While evidence for compounds (II) and/or (III) was observed in infrared and mass spectra (molecular ion at m/e 312) of a crude white solid mixture which melted over a 85-92°C range, it is not clear due to the complex nature of the ^{19}F and ^{1}H nmr spectra whether both II and III existed. However, based on compounds (IV) and (V) which are well characterized, it is more likely that compound (II) is the actual precursor.

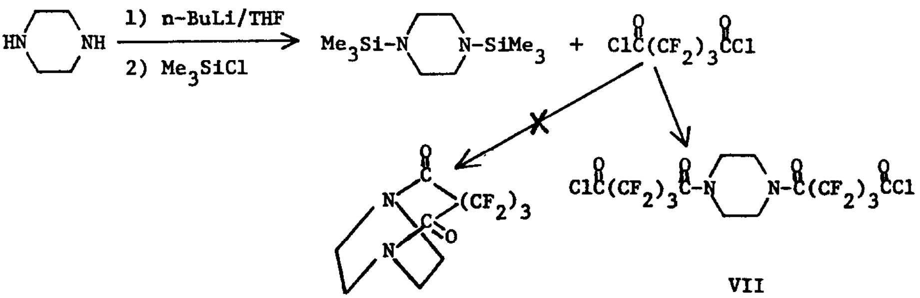


The spectral data for compound IV do not necessarily preclude a structure in which the two carbonyl carbons of each glutaryl group are bonded to different nitrogen atoms to give two nine-membered heterocycles. However, if II is the precursor to IV and, most particularly, to V, III and the compound with two nine-membered rings are not likely to exist.

Mass spectral fragmentation patterns of II and IV invariably are composed of peaks which may be assigned to loss of $(CF_2)_2$ and $(CF_2)_3$. However, in the case of V, no evidence is observed for loss of $(CF_2)_3$. This can be rationalized based on the formation of the stable 2,3-difluoroquinoxaline (VI) in the fragmentation of V. This fragmentation supports the structure as postulated.



Under the reaction conditions used, a heterocyclic compound was not found when perfluoroglutaryl chloride was reacted with bis(trimethylsilyl)-piperazine. Rather a disubstituted acyclic material was formed. This material



VII

is a white nonsublimable solid with molecular ions in the mass spectrum which indicate the presence of two chlorine atoms.

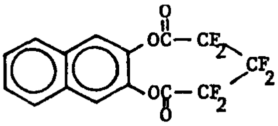
EXPERIMENTAL

Starting Materials. Perfluoroglutaryl chloride was purchased from PCR Research Chemicals, Inc. 2,3-dihydroxynaphthalene (98%) and o-phenylene diamine (98%) were obtained from Aldrich Chemical Company, Inc. and were purified prior to use. The other reagents were standard shelf items and were used after drying over molecular sieves in the case of liquids. Tetrahydrofuran was dried over $LiAlH_4$ and freshly distilled before use.

Apparatus. The reactions were carried out in a 50 mL Pyrex flask fitted with a Kontes Teflon stopcock. Volatile liquids and sublimable solids were handled in a standard glass vacuum line equipped with a Heise-Bourdon gauge. The products were purified by fractional distillation and sublimation in a Kügel Rohr sublimator.

Analysis. Infrared spectra were taken by using a Perkin-Elmer 599 spectrometer. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E spectrometer at 17 eV. The ^{19}F and ^{1}H nmr spectra were obtained by using a Jeol FX-90Q Fourier transform nmr spectrometer with CCl_3F and $(CH_3)_4Si$ as internal references. Deuterated chloroform or dimethylformamide were used as solvents. Elemental analyses were performed at the University of Idaho.

Preparation of

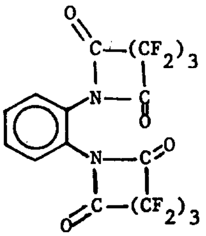


(I) (nc)

To 1.5 mmol (0.25 g) of 2,3-dihydroxynaphthalene in dry dimethylformamide (10-15 mL) was added 1.6 mmol perfluoroglutaryl chloride at -196°C by using standard vacuum line techniques. This mixture was warmed to ambient temperature and was stirred overnight. After evaporation of solvent by vacuum, 0.6 g of crude yellow involatile oil was obtained. Distillation at 110°C/0.2 torr gave 0.47 g (1.3 mmol) colorless oil that upon standing at 25°C under N_2 changed to a white solid. The best yield obtained was approximately 86%. The infrared spectrum (KBr disc) has bands at 3580 (w), 3035 (w), 3025 (sh), 1800 (vs), 1600 (m), 1515 (m), 1470 (m), 1390 (w), 1375 (m), 1300 (m), 1250 (s), 1180 (s), 1135 (s), 1080 (w), 1040 (w), 945 (m), 895 (m), 810 (m), 750 (m), 650 (w), and 490 (m) cm^{-1}. The ^{19}F nmr spectrum consists of two peaks: α-CF_2 (complex at ϕ - 116.6, -116.7, -117.0, - 117.1) and β-CF_2 (singlet at -123.9) with the ratio of 4:2 respectively. The ^1H nmr spectrum has two multiplets centered at δ 7.5 and 7.8 (ratio of 2:4 respectively). A molecular ion at m/e 364 was observed in the mass spectrum and other appropriate fragment peaks, such as m/e 336 $(M-CO)^+$; 308 $(M-2CO)^+$, 262, 220, 180, 179 (all small peaks), and also m/e at 150 and 100 for $(CF_2)_3$ and $(CF_2)_2$, respectively, were found.

Anal. Calcd: C, 49.45; H, 1.64. Found: C, 46.58%; H, 2.18%. This compound decomposed readily at 25°C to a purple solid which, in its infrared spectrum, has a band in the OH region without $\nu_{C=O}$ activity. However, C-F bands are still present

Preparation of

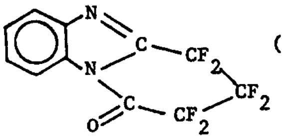


(IV) (nc)

To 2.6 mmol (0.29 g) of o-phenylenediamine in dimethylformamide (DMF) (15 mL) was added 2.7 mmol of perfluoroglutaryl chloride at -196°C by using standard vacuum line techniques. This mixture was stirred overnight at 25°C. Removal of solvent under dynamic vacuum at ∿ 20°C gave 1.26 g of a crude brown liquid (still contains some DMF). Sublimation at 100°C.0.35 torr gave 0.8 g of a white solid (V) plus a colorless solid contaminated with yellow liquid. Resublimation of the latter solid at 100°C/0.3 torr gave colorless crystals (IV) (0.21 g; 0.4 mmol; 15% yield; m.p. 132-133°C). The infrared spectrum (KBr disc) has bands at 1750 (vs), 1500 (m), 1341 (s), 1225 (s), 1196 (m), 1172 (m), 1145 (s), 1092 (w), 1040 (s), 995 (s), 950 (w), 865 (m), 810 (m), 760 (s), 750 (sh), 745 (sh), 660 (w), 595 (m), 568 (w), and 480 (m) cm^{-1}. The ^{19}F nmr spectrum consists of two peaks: α-CF_2 (complex at ϕ -121.3 and 121.9) and β-CF_2 (complex at -136.7, -136.8, -137.5, -137.6) with an area ratio of 4:2 respectively. The ^1H nmr spectrum has two multiplets centered at δ 7.4 and 7.7 (1:1). A molecular ion at m/e 516 was observed in the mass spectrum and other major fragment peaks, such as m/e 488 $(M-CO)^+$; 338 $[M-CO(CF_2)_3]^+$; and $[M-N(CO)_2(CF_2)_3]^+$.

Anal. Calcd for $C_{16}H_4N_2O_4F_{12}$: C, 37.21; H, 0.775; N, 5.43. Found: C, 37.79; H, 0.58; N, 5.57.

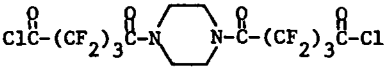
Preparation of



(V) (nc)

Resublimation of the white solid obtained above (V) at 75°C/0.3 torr gave 0.16 g (0.54 mmol, 21% yield) white solid which melts at 90-92°C. The infrared spectrum (KBr pellet) has bands at 3360, 3540 (w, broad), 3100 (w), 1765 (vs), 1610 (m) 1595 (sh), 1560 (m), 1480 (m), 1449 (m), 1430 (sh), 1382 (s), 1370 (sh), 1319 (s), 1289 (s), 1240 (m), 1223 (m), 1180 (sh), 1135 (vs), 1100 (sh), 1040 (s), 1010 (w), 994 (s), 950 (w), 910 (m), 855 (m), 773 and 760 (s (doublet), 660 (w), 640 (m), 620 (w), 597 and 582 (m, doublet), 521 (m), and 450 (m) cm^{-1}. The ^{19}F nmr spectrum consists of three peaks: complexes centered at -112.8, -121.7 due to α-CF_2 and at -135 due to β-CF_2 with the appropriate area ratio. The ^1H nmr spectrum has three multiplets centered at δ 7.6, 7.7, and 8.3 with the ratio of 2:1:1, respectively. A molecular ion at m/e 294 was observed in the mass spectrum and other appropriate fragment peaks, such as m/e 266 $(M-CO)^+$; 166 $(M-COCF_2CF_2)^+$; and 147 $(M-COCF_2CF_3)^+$ were found.

Anal. Calcd. for $C_{11}H_4N_2OF_6$: C, 44.89; H, 1.36; N, 9.52. Found: C, 40.90; H, 1.37, N, 8.92

Preparation of  (VII)(nc)

To 1.4 mmol (0.32 g) of bis(trimethyl)silylpiperazine was added 1.5 mmol perfluoroglutaryl chloride at -196°C by using standard vacuum line techniques. This mixture was stirred for only 0.5 hr at 25°C. At this time, a pale brown solid was formed. Part of this solid was soluble in CH_2Cl_2. After evaporation of solvent by vacuum a slush of pale brown color was obtained. Distillation at 145-155°C/0.2-0.3 torr gave 0.21 g (0.37 mmol, yield 26.5%) of a colorless oil that upon standing at 25°C under argon changed to a white solid. The infrared spectrum has bands at 2940 (m), 2885 (sh), 1795 (vs), 1672 (vs), 1500 (w), 1483 (sh), 1448 (s), 1372 (m), 1275 (w), 1250 (m), 1170 (vs), 1120 (m, sh), 1005 (m), 970 (ms), 940 (w), 858 (w), 790 (m), 755 (w), 705 (ms), and 540 (m) cm^{-1}. The ^{19}F nmr spectrum consists of two singlets at ϕ -111.3 and -122.9 for $\overset{O}{\mathrm{C}}\text{-}CF_2$ and $C\text{-}CF_2\text{-}C$ respectively. The ^{1}H nmr spectrum has one sharp singlet at δ 3.78. A molecular ion at m/e 566, 568 and 570 was observed in the mass spectrum and other major fragments peaks, such as m/e 531 $(M\text{-}Cl)^+$, 503 $(M\text{-}ClCO)^+$ and 353 $(M\text{-}ClCO(CF_2)_3)^+$ (base peak) were found.

Anal. Calcd: C, 29.63; H, 1.41; N, 4.93. Found: C, 28.82%; H, 3.74%, N, 4.49%.

Preparation of bis(trimethylsilyl)piperazine

Piperazine, slurried in dry tetrahydrofuran at -78°C, was treated with two molar equivalents of n-butyllithium/hexane. After stirring at 0°C and recooling to -78°C, the milky slurry was treated with two molar equivalents of trimethylchlorosilane. Warming, filtration, and evaporation gave a colorless liquid which was purified by fractional distillation at 53°C/0.2 torr. The ^{1}H nmr spectrum has two sharp singlets at 0.01 δ and 2.9 δ with the ratio of 17.8:8 respectively. A molecular ion at m/e 230 was observed in the mass spectrum.

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