Polynitroalkyltetrazoles (1)

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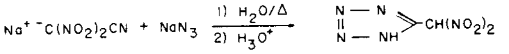
5-(Fluorodinitromethyl)-and 5-(trinitromethyl)tetrazoles were synthesized in the reactions of fluorodinitroacetonitrile with sodium azide, and trinitroacetonitrile with trimethylsilyl azide, respectively, and characterized as their ammonium salts.

J. Heterocyclic Chem., 18, 1477 (1981).

Nitriles react with hydrazoic acid or metallic azides to give 5-substituted tetrazoles (2). These reactions generally require strenuous conditions (3), but electronegatively substituted nitriles, such as trifluroacetonitrile, react readily (4). 5-(2,2 Dinitromethyl)tetrazole, the sole reported polynitroalkyltetrazole, was obtained in 9% yield only after prolonged heating of aqueous sodium salt of dinitroacetonitrile with sodium azide (5).



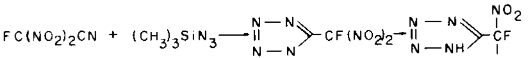
The need for polynitroalkyltetrazoles in this laboratory led to an investigation of tetrazole-forming reactions of fluorodinitroacetonitrile and trinitroacetonitrile with azides.

Fluorodinitroacetonitrile (6) is a very reactive nitrile and readily adds alcohols and amines (7). We found that this nitrile also reacts readily with azides. Thus, sodium salt of 5-(fluorodinitromethyl)tetrazole was obtained in 80-90% yields in the reaction with aqueous sodium azide at ambient temperatures.

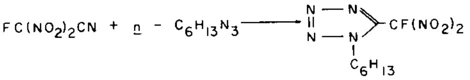
This mildly exothermic reaction also proceeded well in 1,2-dimethoxymethane, methanol, tetrahydrofuran and in acetonitrile.

The sodium salt of 5-(fluorodinitromethyl)tetrazole was hygroscopic and therefore difficult to purify. Acidification of the salt yielded 5-(fluorodinitromethyl)tetrazole which also was hygroscopic. Its structure was assigned on the basis of ir and nmr spectra. The ammonium salts of 5-(fluorodinitromethyl)tetrazole was obtained by neutralizing the tetrazole with ammonium hydroxide. This nonhygroscopic salt, purified by crystallization and sublimation, was identified by its elemental analysis and its ir and nmr spectra.

1,5-Disubstituted tetrazoles can by obtained by reacting alkyl (or aryl) azides with electronegatively substituted nitriles (8). Fluorodinitroacetonitrile did not react with phenyl azide on prolonged heating at 90-100°. It reacted readily with trimethylsilyl azide in refluxing 1,1,2-trichloro-1,2,2-trifluoroethane and gave 5-(fluorodinitromethyl)tetrazole, apparently *via* 1-trimethylsilyl intermediate which decomposed during the process of isolation.



The reaction between fluorodinitroacetonitrile and hexyl azide was much more sluggish than that with trimethylsilyl azide. A solution of reagents was heated in a sealed tube for 3 days to give a 50% yield of 1-*n*-hexyl-5-(fluorodinitromethyl)tetrazole:



The compound was identified by its elemental analysis, ir and nmr spectra.

Alkylation of 5-substituted tetrazoles generally leads to mixture of 1- and 2-substituted products (9) in approximately equal amounts. Electronegative substituents in the 5-position tend to direct substitution predominanty to the 2-position (10). When an equal molar mixture of 5-(fluorodinitromethyl)tetrazole and *n*-hexyl bromide was refluxed for a few hours in acetonitrile, the tetrazole was converted to its 1-*n*-hexyl derivative. The compound was identical with the material obtained in the reaction of fluorodinitroacetonitrile with *n*-hexyl axide above. It is not obvious why this tetrazole was alkylated exclusively at the 1-position.

Trinitroacetonitrile, readily available in the nitration of cyanoacetic acid (11) was tested in reactions analogous to those described for fluorodinitroacetonitrile. Unlike fluorodinitroacetonitrile, the nitrile did not yield tetrazole when treated with sodium azide. In either aqueous or anhydrous medium at temperature ranging from 25 to -65° these reactions yielded sodium nitroform. Trinitroacetonitrile also did not react with *n*-hexyl azide in refluxing carbon tetrachloride. On the other hand, the nitrile reacted with trimethylsilyl azide to give

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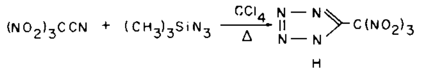
5-(trinitromethyl)tetrazole quantitatively.



The free tetrazole, an orange-yellow oil, evolved nitrogen oxides on prolonged standing at ambent temperatures. This very acidic tetrazole was neutralized with ammonium hydrixide and the resulting ammonium salt was purified by cryatallization and sublimation. The ammonium salt of 5-(trinitromethyl)tetrazole was characterized by its ir spectrum and elemental analysis.

Many aliphatic polynitro derivatives are sensitive to impact and friction, and these properties of 5-(polynitromethyl)tetrazoles, prepared in this work were tested. The ammonium salt of 5-(fluorodinitromethyl)tetrazole could not be detonated by hitting the material with a hammer against a steel plate. The 5-(trinitromethyl)-tetrazole salt, on the other hand, was found to be quite sensitive to impact under these testing conditions and extreme care must be exercised in handling this material.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer model 700 spectrophotometer and the nmr spectra obtained on a Verian model T-60 nmr spectrometer. Analytical data was obtained from Chemalytics Inc., Tempe, Arizona.

Caution: Many compounds described in this paper are either known or suspected explosives and safety shielding must be employed in their synthesis. Polynitroalkyltetrazole salts should be handled with utmost care: remotedly and in small quanities.

5-(Fluorodinitromethyl)tetrazole.

To a stirred solution of 1.2 g (8.8 mmoles) of fluorodinitroacetonitrile (6) in a mixture of 10 ml each of tetrahydrofuran and 1,1,2-trichloro-1,2,2-trifluoromethane was added all at once at 32°, 585 mg (9 mmoles) of sodium azide. The temperature of the suspension rose slowly to 36.5° and then decreased to 32°. After 20 hours the mixture was concentrated leaving a hygroscopic semi-solid sodium salt of 5-(fluorodinitromethyl)tetrazole.

The sodium salt was dissolved in 10 ml of water. The resulting yellow solution was filtered and the filtrate was extracted with an equal volume of ether. The aqueous layer was acidified with 3.5 ml of 6 *N* hydrochloric acid and extracted with three 10 ml portions of ether. The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed leaving 1.34 g (79%) of 5-(fluorodinitromethyl)tetrazole, an orange viscous liquid; ir (Nujol): 3350 (N-H), 1580, 1300 (NO_2), 1100, 1080, 1005 (tetrazoles) (12) cm^{-1}; ^{19}F nmr (methanol, external fluorotrichloromethane): Φ 96.5 ppm (m). The material displayed one spot on tlc using silica gel, dichloromethane-methanol (2:1) or acetone-ethyl acetate (1:1), uv 254 or iodine. A low melting hygroscopic solid was obtained when an etheral solution of the product was dried over anhydrous magnesium sulfate or passed through silica gel.

5-(Fluorodinitromethyl)tetrazole was also obtained in 85% yield by refluxing equimolar amounts of fluorodinitroacetonitrile and trimethylsilyl azide in 1,1,2-trichloro-1,2,2-trifluoroethane for 12 hours. The mixture was cooled to ambient temperature and extracted with water. The aqueous solution was concentrated and 5-(fluorodinitromethyl)tetrazolo was isolated as its ammonium salt.

Ammonium salts of 5-(fluorodinitromethyl)tetrazolo.

5-(Fluorodinitromethyl)tetrazole (1.34 g), from the above preparation, was dissolved at 0-5° in 4 ml of concentrated ammonium hydroxide. The resulting yellow solution was evaporated to dryness yielding 1.41 g, 77% yield (based on fluorodinitroacetonitrile used above), of light tan ammonium salt, 164-165° dec. The crude salt was recrystallized from ethyl acetate-toluene mixture to give 1.07 g (73.5% yield) of a white solid, mp 164-165° dec. An analytical sample, mp 164-165° dec, was obtained by subliming the recrystallized material at 95° (°0.04 mm); ir (potassium bromide): 3060 (NH_4), 1600, 1310 (NO_2), 1100, 1050, 990 (tetrazole) cm^{-1}; ^{19}F nmr (methanol, external fluorotrichloromethane):Φ 95.6 ppm (m).

Anal Calcd. for $C_2H_4FN_7O_4$: C, 11.49; H, 1.93; N, 46.89. Found: C, 11.17; H, 1.77; N, 47.02.

1-Hexyl 5-(fluorodinitromethyl)tetrazole.

From Fluorodinitroacetonitrile and Hexy Azide.

To 0.5 ml of 1,1,2-trichloro-1,2,2-trifluoroethane solution containing 0.43 mmole fluorodinitroacetonitrile was added 56 mg (0.44 mmole) of hexyl azide and the resulting solution was heated in a sealed glass tube at 80° for 20 hours, and then at 95-100° for 44 hours. All volatile matetials were removed under high vacuum at room temperature leaving 60 mg of product which was distilled in a molecular still at 100° (0.05 mm) to give a light yellow liqiud; ir (sodium chloride): 2970 (s, CH stretch), 2900 (m, CH_3 stretch), 1610 z)s, NO_2 stretch), 1300 (m, NO_2 stretch), 1200 (m, 980 (m), 840 (m), 800 (m), cm^{1}; ^{19}F nmr (1,1,2-trichloro-1,2,2-trifluoroethane, external fluorotrichloromethane): Φ 96.2 ppm (m).

Anal. Calcd. for $C_8H_{13}FN_6O_4$: C, 34.78; H, 4.74. Found: C, 34.80; H, 4.69.

From 5-(Fluorodinitromethyl)tetrazole and Hexyl Bromide.

A stirred solution of 120 mg (0.6 mmole) of 5-(fluorodinitromethyl)-tetrazole and 0.1 ml (0.71 mmole of hexyl bromide in 1 ml of acetonitrile was refluxed for 2 hours. The mixture was cooled and filtered to remove sodium bromide. Fluorine nmr spectrum of the filtrate exhibited a strong signal at Φ 96.3 (product) and a weaker signal at Φ 93, of unreacted starting material.

Ammomium Salt of 5-(Trinitromethyl)tetrazole.

Attempted preparation from Trinitroacetonitrile and Sodium Azide.

To a stirred carbon tetrachloride solution (0.5 ml) cantaining 0.18 g (1 mmole) of trinitroacetonitrile was added 1.0 ml of 1,2-dimethyoxyethane and 0.08 g (1.2 mmoles) of sodium azide. The mildly exothermic reaction was controlled at 25 ± 2° by external cooling. After the exothermic reaction subsided the resulting orange suspension was stirred at room temperature for 1.5 hours. The mixture was diluted with 4 ml of ether and filtered to give 83 mg of an orange solid, which was identified as the sodium salt of nitroform by comparing its ir spectrum with that of an authentic sample. Several further attempts were made to produce the desired tetrazole using the above reaction conditions, but at lower reaction temperature (5, -40, -50 and -65°). In all cases the same salt was obtained.

From Trinitroacetonitrile and Trimethylsilyl Azide.

A mixture of 0.18 g (1 mmole) of trinitroacetonitrile and 0.2 ml (1.5 mmoles)of trimethylsilyl azide in 0.5 ml of carbon tetrachloride was heated at 60-70° for 70 hours. Reaction mixture was concentrated using a water aspirator leaving a dark orange liquid. The liquid was triturated with 1 ml of water for 10 minutes in order to completely hydrolyze all the trimethylsilyl intermidiate, and excess of water was removed under high vacuum. This produced 180 mg of crude 5-(trinitromethyl)tetrazole, an orange liquid which on standing slowly evolved nitrogen oxides.

The crude product was neutralized with 0.5 ml of concentrated ammonium hydroxide and the resulting solution was concentrated under high vacuum leaving 170 mg (72% yield) of orange solid, mp 135° dec. The crude product was crystallized from ethyl acetate-toluene mixture to give a light yellow solid **very sensitive to impact.** An analytical sample, a white crystalline solid, mp 135 dec, was prepared by sublimiting the recrystallized material at 93° (0.1 mm); ir (potassium bromide): 3200 (s), 3090 (s). 2900 (s, NH_4), 1600, 1590 (s), 1295 (m, NO_2), 800 (m), cm^{-1}.

Anal. Calcd. for $C_2H_4N_8O_6$: C, 10.17; H, 1.71; N, 47.26. Found: C, 10.41; H, 1.58; N, 47.68.

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(1) This work was supported by the University of California, Lawrence Livermore Laboratory.

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