Preparation and Reactions of 5-Vinyltetrazole

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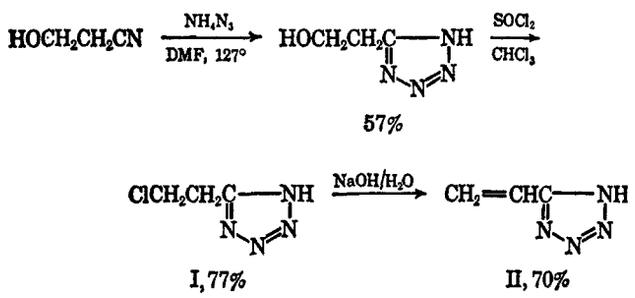
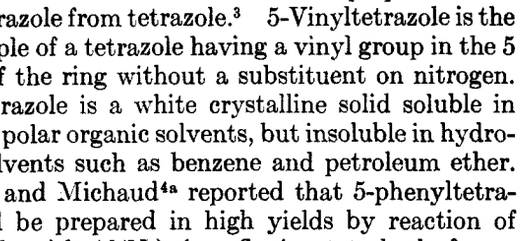
Henry reported that poly-5-vinyltetrazole could be prepared by reaction of polyacrylonitrile with NH_4N_3 in dimethylformamide at elevated temperatures but indicated that attempts to prepare monomeric 5-vinyltetrazole were unsuccessful because of the reactivity of the carbon–carbon double bond.[2] We have found that 5-vinyltetrazole can be synthesized in 31% over-all yields from hydracrylonitrile according to Scheme I.

SCHEME I

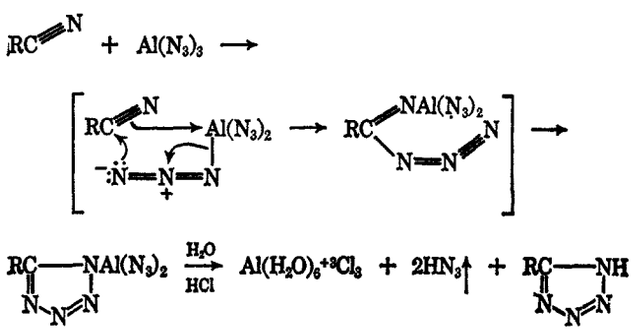


This mechanism resembled that used to prepare 1- and 2-vinyltetrazole from tetrazole.[3] 5-Vinyltetrazole is the first example of a tetrazole having a vinyl group in the 5 position of the ring without a substituent on nitrogen. 5-Vinyltetrazole is a white crystalline solid soluble in water and polar organic solvents, but insoluble in hydrocarbon solvents such as benzene and petroleum ether.

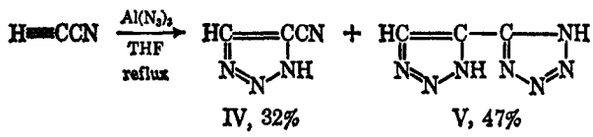
Wiberg and Michaud[4a] reported that 5-phenyltetrazole could be prepared in high yields by reaction of benzonitrile with $Al(N_3)_3$ in refluxing tetrahydrofuran. This method was extended to aliphatic nitriles by Behringer and Kohl but apparently not applied to functionally substituted or conjugated olefinic nitriles.[4b] We have found that 5(2-chloroethyl)tetrazole (I), 5-vinyltetrazole (II), and 5-isopropenyltetrazole (III) can be prepared in good yields from the corresponding olefinic or chloro nitriles. When these reactions were carried out using NH_4N_3, LiN_3, or NaN_3 in place of $Al(N_3)_3$ and dimethylformamide or methoxyethanol in place of tetrahydrofuran, tars containing azido groups were obtained. Attempts to promote tetrazole formation by use of acidic catalysts such as $BF_3O(Et)_2$ and $AlCl_3$ were unsuccessful. In these runs, it is likely that the vinyl, isopropenyl and 2-chloroethyl groups underwent addition or displacement reactions with azide ion and that the resulting azido intermediates subsequently decomposed. The fact that the azide group of $Al(N_3)_3$ did not displace the chloro group of 3-chloropropionitrile or add to the carbon–carbon double bond of acrylonitrile or methacrylonitrile tends to confirm the intramolecular scheme proposed by Wiberg and Michaud[3] (Scheme II).



SCHEME II

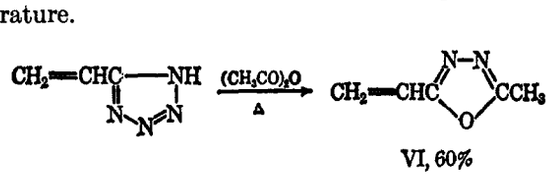


Conjugated acetylene groups, however, were found *not* to be immune to attack by $Al(N_3)_3$. Thus, when cyanoacetylene was treated with $Al(N_3)_3$ in THF, 4-cyano-1,2,3-triazole (IV) and 5[4-1,2,3-triazolyl]tetrazole (V) were obtained.



As expected, 5-vinyltetrazole was found to be a good dienophile. Thus, 2-(5-tetrazoyl)bicyclo[1.2.2]heptene-5 (presumably *endo*) was obtained in 60% conversion when 5-vinyltetrazole (in $CHCl_3$) was refluxed for 1 hr with cyclopentadiene.

5-Substituted tetrazoles are known to react with acid chlorides or anhydrides to give 2,5-disubstituted 1,3,4-oxadiazoles.[5] 5-Vinyltetrazole was found to function normally in this type of reaction, giving 2-methyl-5-vinyl-1,3,4-oxadiazole (VI) upon reaction with acetic anhydride. Oxadiazole VI has not been reported in the literature.



Experimental Section

Preparation of 5-(2-Chloroethyl)tetrazole. Method A.—5-[2-Hydroxyethyl]tetrazole (56 g, 0.49 mol), which was prepared

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(2) R. A. Henry, U. S. Patent 3,096,312 (July 2, 1963).

(3) (a) W. G. Finnegan, R. A. Henry, and S. Skolnik, U. S. Patent 3,004,959 (Oct 17, 1961); (b) W. G. Finnegan and R. A. Henry, *J. Org. Chem.*, **24**, 1565 (1959).

(4) (a) W. Wiberg and H. Michaud, German Patent 962,798 (April 25, 1957); (b) H. Behringer and K. Kohl, *Ber.*, **89**, 2648 (1956).

(5) R. Huisgen and H. G. Margraf, *Angew. Chem.*, **72**, 359 (1960).

according to the procedure of Finnegan, *et al.*,[6] was dissolved in 200 ml of chloroform and placed in a 1-l. three-necked flask equipped with a mechanical stirrer, thermometer and addition funnel. Thionyl chloride (85 g, 0.72 mol) was added dropwise to this solution at such a rate that the temperature was kept below 50°. After the addition was complete, the reaction mixture was refluxed for 2 hr. The products were worked up by the following sequence of operations: (1) the chloroform and ethyl acetate were stripped off; (2) the residue was treated with 50 g of ice; and (3) the resultant aqueous mixture was extracted with four 200-ml portions of ethyl acetate and dried ($MgSO_4$). Removal of the ethyl acetate gave crude 5-(2-chloroethyl)tetrazole, which, upon recrystallization from 1,2-dichloroethane, gave 50 g (77% conversion) of white needles melting at 103–104°. The structure of this new compound was established by its infrared spectrum: 3.6–4.7 (NH, tetrazole), 15 μ (CCl). *Anal.* Calcd for $C_3H_5ClN_4$: C, 27.2; H, 3.78; N, 42.2. Found: C, 27.14; H, 3.81; N, 42.25.

Method B.—A mixture of 8.95 g (0.1 mol) of 3-chloropropionitrile, 13.3 g (0.1 mol) of anhydrous aluminum chloride and 29 g (0.445 mol) of pulverized sodium azide suspended in 200 ml of dry tetrahydrofuran was refluxed under nitrogen for 24 hr. The reaction mixture was cooled to ambient temperature and acidified by the addition of 150 ml of 15% hydrochloric acid. The hydrazoic acid generated during acidification was removed by means of an aspirator. After separation of the THF layer from the aqueous layer and extraction of the aqueous layer with ethyl acetate, the ethyl acetate extracts were combined with the THF layer and dried. Evaporation of the solvents gave, after recrystallization from 1,2-dichloroethane, 11 g (82.5% conversion) of 5-(2-chloroethyl)tetrazole, mp 103–104°. The identity of this product was established by ir and undepressed mixture melting point with authentic 5-(2-chloroethyl)tetrazole obtained previously.

Preparation of 5-Vinyltetrazole. Method A.—A mixture of 20 g (0.15 mol) of 5-(2-chloroethyl)tetrazole and 12 g (0.3 mol) of sodium hydroxide dissolved in 100 ml of water containing a small amount of *p*-methoxyphenol was refluxed for 2 hr. This mixture was cooled, acidified with concentrated hydrochloric acid and thoroughly extracted with ethyl acetate. The yellow solid obtained upon evaporation of the ethyl acetate was purified by charcoal treatments and recrystallization from chloroform to give 10 g (70% conversion) of 5-vinyltetrazole, white crystals melting at 126–127°: infrared spectrum (Nujol mull) 3.6–4.7 (NH, tetrazole), 3.23 (CH stretch, vinyl), 6.1 (CH_2=CH– stretch), 10.1, 10.7 μ (CH bend, vinyl), other bands assigned to the tetrazole ring were observed in the 8.0–10-μ region; nmr (acetone-d_6, TMS standard), ABC pattern, quartet centered at τ 3.0 (1 H, vinyl H_a, $-CH_a$=CH_bH_c, J_{ab} = 10 Hz, J_{ac} = 18 Hz), quartet centered at 4.12 (1 H, vinyl H_b, J_{bc} = 1.3 Hz), quartet centered at 3.53 (1 H, vinyl H_c); mass, highest *m/e* 96. *Anal.* Calcd for $C_3H_4N_4$: C, 37.50; H, 4.16; N, 58.33. Found: C, 37.55; H, 4.14; N, 58.44.

Method B.—A mixture of 5.3 g (0.1 mol) of acrylonitrile, 13.3 (0.1 mol) of anhydrous aluminum chloride and 29 g (0.445 mol) of dry, powdered sodium azide suspended in 200 ml of THF was refluxed for 24 hr under nitrogen. The reaction mixture was then acidified by addition of 150 ml of 15% hydrochloric acid and the excess hydrazoic acid was removed by means of an aspirator. The THF layer (upper) was separated from the water layer and dried ($MgSO_4$). The water layer was extracted with four 50-ml portions of ethyl acetate. Evaporation of the combined THF and ethyl acetate solutions gave 5.3 g of impure 5-vinyltetrazole which was purified by solution in chloroform, treatment with charcoal two or three times, and crystallization. Thus 4.8 g (55% conversion) of 5-vinyltetrazole, mp 126–127°, was obtained. The identity of this product was established by its ir spectrum and undepressed mixture melting point with authentic 5-vinyltetrazole obtained by method A.

Preparation of 5-Isopropenyltetrazole.—Methacrylonitrile (6.7 g, 0.1 mol), anhydrous aluminum chloride (13.3 g, 0.1 mol), dry powdered sodium azide (29 g, 0.445 mol) and 200 ml of dry THF were placed in a flask and refluxed for 24 hr under nitrogen. The work-up procedure was identical with that used for the preparation of 5-vinyltetrazole (method B). Recrystallization of the crude reaction products from ethyl acetate–hexane gave 7.8 g (71% conversion) of 5-isopropenyltetrazole, a white crystalline solid melting at 169–170°: infrared spectrum (Nujol mull) 3.6–4.7 (N–H, tetrazole), 3.25 (CH stretch, vinyl), 6.1 (CH_2=C– stretch) and 10.7 μ (CH bend, vinyl); nmr (acetone-d_6), TMS standard) singlet at τ 3.92 (1 H, vinyl H_a, H_aH_{bc}), singlet at 4.42 (1 H, vinyl H_b), and singlet at 7.74 (3 H, (CH_3-). *Anal.* Calcd for $C_4H_6N_4$: C, 43.53; H, 5.45; N, 50.83. Found: C, 43.28; H, 5.59; N, 50.74.

Preparation of 2(5-Tetrazoyl)bicyclo[2.2.1]heptene-5.—To 20 ml of chloroform contained in a flask equipped with a reflux condenser was added 5 g (0.052 mol) of 5-vinyltetrazole and 10 ml (excess) of cyclopentadiene. This mixture was refluxed for 2 hr. The solvent and excess chloroform were stripped off to give 10 g of a solid residue which melted at 158–162°. Recrystallization from chloroform gave 5 g (60% conversion) of 2-(5-tetrazoyl)-bicyclo[2.2.1]heptene-5 (probably *endo*), a white crystalline solid: mp 164.5–165.5°; infrared spectrum (Nujol mull) 3.6–4.7 (NH, tetrazole), 3.25 (C–H stretch, vinyl), 10–12 μ (CH bend, vinyl); nmr ($DCCl_3$, TMS standard) singlet τ 1.84 (1 H, NH, tetrazole), quartet centered at 3.37 (1 H, vinyl H_a, H_cC=CH_b), quartet centered at 4.63 (1 H, vinyl H_b), multiplet centered at 6.29 (1 H, tertiary H_c, H_cC-tetrazole), overlapping multiplet centered at 6.64 (1 H) and 7.0 (1 H, tetriary-C–H in ring), multiplets in the range of 7.47–8.5 (other CH_2 groups in ring). *Anal.* Calcd for $C_8H_{10}N_4$: C, 59.13; H, 6.16; N, 34.60. Found: C, 59.25; H, 5.97; N, 34.48.

Reaction of Cyanoacetylene with Aluminum Triazide.—To 200 ml of tetrahydrofuran contained in a three-necked flask equipped with a mechanical stirrer was added 13.3 g (0.1 mol) of anhydrous aluminum chloride, 29.5 (0.44 mol) of dry powdered sodium azide and 5.1 g (0.1 mol) of cyanoacetylene. This mixture was refluxed under nitrogen for 24 hr. The reaction mixture was then cooled, acidified with dilute HCl and extracted thoroughly with four 50-ml portions of ethyl acetate. The dried ethyl acetate extract was stripped off to give 12.5 g of a tan solid. This material was slurried with 100 ml of hot chloroform and filtered. The filtrate was evaporated and the residue recrystallized from chloroform to give 3.0 g (32% conversion) of 4-cyano-1,2,3-triazole: mp 110–112° (lit.[7] mp 113–114°); infrared spectrum (Nujol mull) 4.5 (–CN), 3.12 (CH stretch, vinyl); nmr (acetone-d_6, TMS standard) singlet at τ 1.23 (1 H, HC=), singlet at −3.1 (1 H, NH, triazole); mass, highest *m/e* 94. *Anal.* Calcd for $C_3H_2N_4$: C, 38.4; H, 2.48; N, 59.5. Found: C, 38.43; H, 2.61; N, 59.12.

Purification of the chloroform-insoluble solids was accomplished by addition of a large amount of petroleum ether (bp 30–60°) to a methanol–ethyl acetate solution of the solids. 4-(5-Tetrazoyl)-1,2,3-triazole (6.5 g, 47% conversion), a tan, amorphous solid melting at 250° with decomposition, precipitated: infrared spectrum (Nujol mull) 3.21 (CH stretch, vinyl), 3.6–4.7 μ (NH, triazole, tetrazole); nmr (acetone-d_6, TMS standard) singlet at τ 1.37 (1 H, HC=), singlet at −0.8 (2 H, NH, triazole, tetrazole). *Anal.* Calcd for $C_3H_3N_7$: C, 26.3; H, 2.19; N, 71.5. Found: C, 26.69; H, 2.61; N, 70.96.

Preparation of 2-Methyl-5-vinyl-1,3,4-oxadiazole.—A mixture of 5 g (0.052 mol) of 5-vinyltetrazole, 0.25 g of hydroquinone and 100 ml of acetic anhydride was refluxed for 1 hr. The excess acetic anhydride was stripped off and the residue treated with ice. After the mixture thawed, it was extracted thoroughly with five 30-ml portions of ethyl acetate. The dried extract was evaporated and the residue distilled to give 3.7 g (65% conversion) of 2-methyl-5-vinyl-1,3,4-oxadiazole, a colorless liquid boiling at 78° (15 mm): infrared spectrum (Nujol mull) 3.21 (CH stretch, vinyl), 6.1 (CH_2=CH–, stretch) 10.3 (CH bend, vinyl), 9.5–9.7 10.1 μ (1,3,4-oxadiazole ring[8]); nmr (D_1CCl_3, TMS standard) ABC pattern, quartets centered at τ 3.34 (1 H), 3.87 (1 H), and 4.26 (1 H); mass, highest *m/e* 94. *Anal.* Calcd for $C_5H_6N_2O$: C, 54.5; H, 5.45; N, 25.4. Found: C, 54.09; H, 5.80; N, 24.65.

Registry No.—I, 18755-46-9; II, 18755-47-0; III, 18755-48-1; 2-(5-tetrazoyl)bicyclo[2.2.1]heptene-5, 18761-62-1; IV, 18755-49-2; V, 18755-50-5; VI, 18755-51-6.

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(7) A. Peratoner and E. Azzarello, *Gazz. Chim. Ital.*, **38I**, 84 (1908).

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