

A NEW SYNTHESIS OF 1,5-DIALKYL TETRAZOLES
FROM NITRILIUM SALTS AND SODIUM AZIDE

Lester A. Lee, Eleanor V. Crabtree*, James U. Lowe, Jr.,
M. J. Cziesla and Robert Evans

U. S. Naval Propellant Plant, Indian Head, Md.

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Numerous investigators have reported the synthesis of various types of 1,5-disubstituted tetrazoles (1). The versatile reaction between arylimide chlorides and hydrazoic acid in chloroform or benzene, first reported by von Braun and Rudolph (2), was extended to the synthesis of 1,5-dialkyl tetrazoles by Harvill et al. (3). Use of sodium azide in this reaction, in order to avoid handling hazardous hydrazoic acid, is restricted by the instability of the dialkyl substituted imide chlorides at the required reaction temperature, especially with small alkyl substituents.

A new synthesis of 1,5-dialkyl tetrazoles was discovered in this laboratory when nitrilium salts and sodium azide were allowed to react in toluene.

Nitrilium salts (4) of the general formula $\left[R' - \overset{+}{C} = N - R \leftrightarrow R' - C \equiv \overset{+}{N} - R \right] X$ (I) can be prepared by the reaction of trialkyloxonium salts with nitriles. These nitrilium salts (I) react with sodium azide to form 1,5-disubstituted tetrazoles (III) according to the following equations:

*Army Chemical Center, Edgewood Arsenal, Edgewood, Maryland

analytical sample was obtained by chromatographing the distillate on a column (2 x 33 cm.) of silica gel (43.90 g.) with 500 ml. of 1:9 methanol-ether as developing solvent. $n_D^{25^\circ}$, 1.4593; infrared max. (liquid film) 2990, 2945, 1531, 1412, 1095, 1055, and 1009 cm^{-1} , tetrazole ring (6) 1111-1000 cm^{-1} ; R_f^* 0.47; Anal. calcd. for $\text{C}_4\text{H}_8\text{N}_4$: C, 42.84; H, 7.19; N, 49.97. Found: C, 42.82; H, 7.12; N, 49.94.

1,5-Diethyl tetrazole was prepared and isolated in the same manner as 1-ethyl-5-methyl tetrazole. N-ethylpropionitrilium fluoborate (4.29 g., 0.027 mole) gave 1,5-diethyl tetrazole, 1.36 g.; (36% yield, based on nitrilium salt); b.p. 83-85 $^\circ$, 0.12 mm. Analytical sample, $n_D^{25^\circ}$, 1.4605; infrared max. (liquid film) 3003, 2950, 1513, 1447, 1418, 1089, and 1064 cm^{-1} ; R_f^* 0.67; Anal. calcd. for $\text{C}_5\text{H}_{10}\text{N}_4$: C, 47.60; H, 7.99; N, 44.41. Found: C, 47.70; H, 7.94; N, 43.80.

References:

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*Data refer to silica gel G activated at 100 $^\circ$ with 1:9 methanol-ether as the developing solvent.