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# Reactions of Nitrilium Salts.[1,2] I. With Sodium and Dimethylammonium Azide

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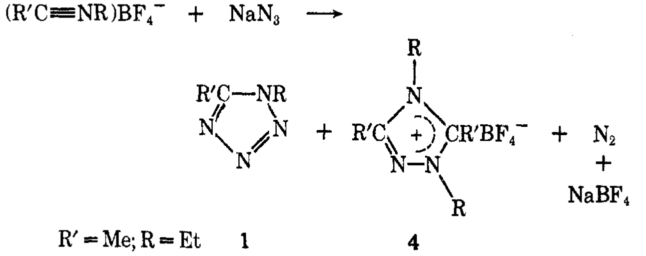
1-Methyl-5-vinyltetrazole (**11**), 1-ethyl-5-methyl- (**1**), 1,5-diethyl- (**2**), and 1-ethyl-5-phenyltetrazole (**3**) were synthesized by nucleophilic attack of azide ions on the corresponding nitrilium salts. The reaction of nitrilium salts with azide ions in toluene gives 1,3,4,5-tetrasubstituted 1,2,4-triazolium salts as well as 1,5-disubstituted tetrazoles. When acetonitrile was employed as the reaction solvent, good yields of tetrazoles and triazolium salts depended on the mode of addition of reactants.

In 1955 Klages[4] and Meerwein[5] described the first relatively stable nitrilium salts[6] and later developed general methods for their preparation. Nitrilium salts of the general formula $(R'C{\equiv}N^+R)BF_4^-$ may be prepared by the reaction of trialkyloxonium fluoroborate salts with nitriles. These salts react[7] with nucleophiles such as $OH^-$, $H_2O$, ROH, $NH_3$, and $RNH_2$ giving amides, imino ethers, and amidines.

As anticipated, nitrilium salts react with azide ion, an excellent nucleophile, to give 1,5-disubstituted tetrazoles.[8] Earlier it was reported[9] that *N*-ethylaceto- and *N*-ethylpropionitrilium fluoroborate react with sodium azide in toluene to give 1-ethyl-5-methyl- (**1**) and 1,5-diethyltetrazole (**2**), respectively. The major products which were not characterized at that time have been identified as 1,3,4,5-tetrasubstituted 1,2,4-triazolium fluoroborates.[10]



R' = Me; R = Et **1** **4**
R' = R = Et **2** **5**
R' = Ph; R = Et **3** **6**

In a typical experiment, an excess of sodium azide is added to a stirred suspension of nitrilium salt in toluene at ambient temperature. An exotherm occurs after a short induction period with evolution of nitrogen. The initial reaction and exotherm apparently occur until the unreacted sodium azide is completely coated with the toluene-insoluble triazolium salt. If, however, the reaction is stirred and heated to reflux, causing the triazolium salt to become an oil, the reaction continues. Analyses of the reaction mixtures immediately after the exotherm indicated 20% conversion to tetrazole and 90% conversion after 6 hr. The amount of nitrogen evolved during the exotherm is about 15% of the theoretical.

The summarized data in Table I show that the mode of addition of reactants in the reaction of *N*-ethylaceto-

TABLE I
REACTIONS OF NITRILIUM SALTS WITH SODIUM AZIDE IN TOLUENE

| R | Mode of addition[a,b] | Reaction temp, °C | % yield[c] Tetrazole | Triazolium salt |
|---|---|---|---|---|
| Me | A | 0–110 | 34 | 65[d,e] |
| Me | B | 25–110 | 30 | 62[e] |
| Et | B | 25–110 | 32 | 53[e] |
| Ph | B | 25–30[f] | 14 | 34 |
| Ph | B | 25–110 | 10 | 45 |

[a] A, $(RC{\equiv}N^+Et)BF_4^-$ to $NaN_3$; B, $NaN_3$ to $(RC{\equiv}N^+Et)BF_4^-$. [b] All additions of reagents, except the reaction at 0–110° (3 min), were effected in 35 min under an atmosphere of nitrogen. [c] Yields are based on nitrilium salts. [d] 87% of theory of nitrogen, based on crude triazolium salt, was evolved. [e] Crude yield. [f] 7 days at ambient temperature.

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[1] Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] Taken from the dissertation of L. A. Lee in partial fulfillment of the requirements for the Ph.D. degree, Howard University, 1970.

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[4] F. Klages and W. Grill, *Justus Liebigs Ann. Chem.*, **594**, 21 (1955).

[5] H. Meerwein, *Angew. Chem.*, **67**, 379 (1955).

[6] For a review on nitrilium salts involving heterocyclic syntheses, see F. Johnson and R. Madroñero, *Advan. Heterocycl. Chem.*, **6**, 95 (1966).

[7] H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, **89**, 209 (1956).

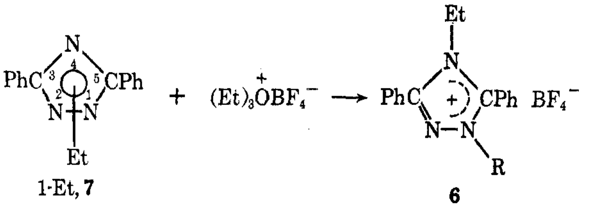
[8] For a review on tetrazoles, see (a) F. R. Benson, *Chem. Rev.*, **41**, 1 (1947); (b) F. R. Benson, *Heterocycl. Compounds*, **8**, 1 (1967).

[9] L. A. Lee, E. V. Crabtree, J. U. Lowe, Jr., M. J. Cziesla, and R. Evans, *Tetrahedron Lett.*, **No. 33**, 2885 (1965).

[10] L. A. Lee, J. W. Wheeler, Jr., M. J. Cziesla, and R. Evans, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, No. S11.

nitrilium fluoroborate with sodium azide in toluene does not significantly affect the ratio of products, as expected for a heterogeneous reaction which is not instantaneous.

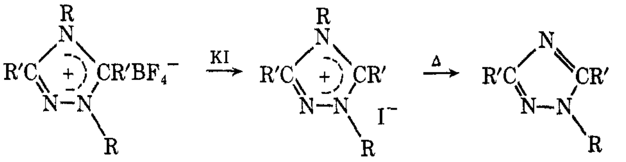
The 1,5-disubstituted tetrazoles were identified by their typically intense absorption in the 9–10-$\mu$ region of the infrared,[11a] proton magnetic resonance spectra,[11b] elemental analysis, or comparison with an authentic compound. The structure of 1,4-diethyl-3,5-diphenyl-1,2,4-triazolium fluoroborate (**6**) was confirmed by quaternization of either 1-ethyl-3,5-diphenyl-1,2,4-triazole (**7**) or 4-ethyl-3,5-diphenyl-1,2,4-triazole (**8**) with triethyloxonium fluoroborate.



1-Et, **7**
4-Et, **8**

**6**
+ Et$_2$O

1,4-Diethyl-3,5-dimethyl- (**4**) and 1,3,4,5-tetraethyl-1,2,4-triazolium fluoroborate (**5**) were identified by conversion of their crude and hygroscopic fluoroborates to the iodides with sodium iodide in acetone. Pyrolysis of the iodides at 250° *in vacuo* gave 1-ethyl-3,5-dimethyl- (**9**) and 1,3,5-triethyl-1,2,4-triazole (**10**), respectively. Symmetrical 3,4,5-trialkyl-1,2,4-triazoles were not isolated in either case.



**4**
**5**

**9**, R = Et; R′ = Me
**10**, R = R′ = Et

The infrared and proton magnetic resonance[11b] data of the isolated compounds were identical with those of authentic samples prepared by the procedure of Einhorn–Brunner.[12]

In an effort to increase the yield of tetrazole, acetonitrile was chosen as the reaction solvent. This polar aprotic media is capable of dissociating the nitrilium salts into solvent-separated ion pairs. When nitrilium salts dissolved in acetonitrile were added dropwise to suspensions of sodium azide or solutions of dimethylammonium azide *in situ* in acetonitrile, exotherms occurred with virtually no evolution of nitrogen. Good yields of tetrazoles and trace amounts of triazolium salts were isolated generally within 1 hr after the additions were complete. In reverse addition reactions, the azide was added to a solution of nitrilium salt in acetonitrile. During the addition, exotherms occur with evolution of nitrogen. Addition of *N*-ethylbenzonitrilium fluoroborate to sodium azide gave virtually no evolved nitrogen, a 73% yield of tetrazole, and only trace amounts of triazolium salt. Reverse addition of the same reagents at −20 to −25° produced practically no nitrogen gas. However, when the solution was warmed to −5°, evolution of nitrogen was observed. In general, the ratio of tetrazole to triazolium salt formed depends on the mode of addition of nitrilium salts and sodium azide in acetonitrile. During the normal addition, there is never an excess of unreacted nitrilium salt in the reaction mixture. However, in reverse addition, there is always an excess of nitrilium salt present and the major product afforded is tetrazole plus a significant amount of triazolium salt. Regardless of the mode of addition, excess nitrilium salt is also present in the heterogeneous reactions carried out in toluene. Because of the insoluble nature of the reactants, it is conceivable that sodium azide molecules could be surrounded by excess nitrilium salt. The reactions investigated are summarized in Table II.

TABLE II

REACTIONS OF NITRILIUM SALTS WITH SODIUM AND DIMETHYLAMMONIUM AZIDE IN ACETONITRILE

| R | Mode of addition[a,b] | Reaction temp, °C | % yield[c] Tetrazole | Triazolium salt |
|---|---|---|---|---|
| Me | A | 25–35 | 85 | *d* |
| Et | A | 25–35 | 80 | *d* |
| Et | C | 25–35 | 84 | *e* |
| Et | B | 25–35 | 52 | 36 |
| Et | D | 25–35 | 72 | *e* |
| Et | B | 60–70 | 29 | 64 |
| Et | D | 60–70 | 53 | *e* |
| Ph | A | 25–35 | 80 | *d* |
| Ph | A | 0–5 | 73 | *d* |
| Ph | B | −20 to −25 | 40 | 8 |
| Ph | B | 25–35 | 55 | 13 |
| Vinyl | A | 25–35 | 13 | *f* |
| Vinyl | C | 25–35 | 80 | *e* |

[a] A, $(RC{\equiv}N^+R')BF_4^-$ to $NaN_3$; B, $NaN_3$ to $(RC{\equiv}N^+R')BF_4^-$; C, $(RC{\equiv}N^+R')BF_4^-$ to dimethylammonium azide; D, dimethylammonium azide to $(RC{\equiv}N^+R')BF_4^-$. R′ = Et except where R = vinyl. [b] All additions of reagents were carried out within 35 min under an atmosphere of nitrogen. [c] Yields are based on nitrilium salts. [d] Yields are less than 1%. [e] Triazolium salts were not separated from unreacted azide and dimethylammonium fluoroborate. [f] Triazolium salt was not isolated from the mixture of polymeric nitrilium salt.

During the normal and reverse additions of dimethylammonium azide to *N*-ethylpropionitrilium fluoroborate in acetonitrile, the yield of 1,5-diethyltetrazole (**2**) is less dependent on the mode of addition of dimethylammonium azide than sodium azide. These results suggest that surface reactions play some role in the formation of tetrazoles and triazolium salts. When the addition of nitrilium salt to dimethylammonium azide in acetonitrile was carried out at 60–70° rather than at 25–35°, the yield of 1,5-diethyltetrazole (**2**) was decreased by 23% and that of 1,3,4,5-tetraethyl-1,2,4-triazolium fluoroborate (**5**) was increased by 28%. These results are consistent with enhanced decomposition of an azide intermediate at higher temperatures.

The low yield of 1-methyl-5-vinyltetrazole (**11**) afforded in the reaction of *N*-methylacrylonitrilium fluoroborate with sodium azide, inhibited with hydroquinone, may be a result of ionic polymerization of the nitrilium salt. Yields were improved when dimethylammonium azide was utilized as the azide source. *N*-Methylacrylonitrilium fluoroborate reacts with water to give *N*-methylacrylamide.

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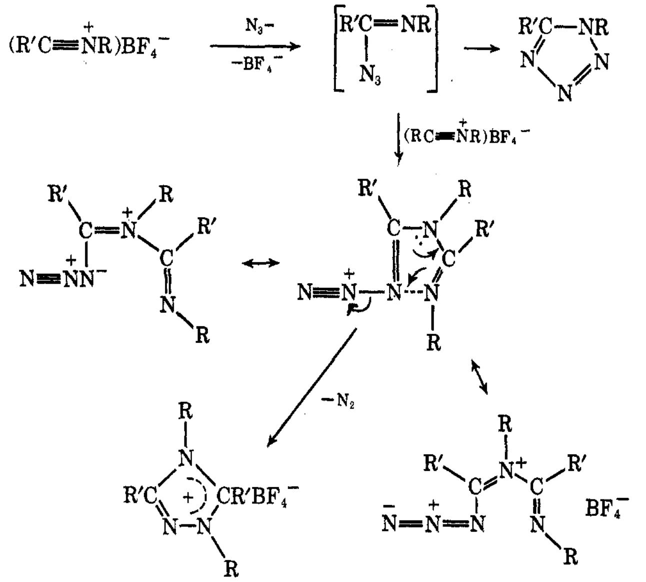
[11] (a) E. Lieber, D. R. Levering, and L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951); (b) L. A. Lee and J. W. Wheeler, *J. Org. Chem.*, **37**, 348 (1972).

[12] M. R. Atkinson and J. B. Polya, *J. Chem. Soc.*, 141 (1954).

To ensure that tetrazoles formed in the presence of nitrilium salts did not decompose with liberation of nitrogen, tetrazoles and their corresponding nitrilium salts were refluxed in acetonitrile and toluene for 21 hr. In both cases no evolution of nitrogen was detected and virtually all of the starting tetrazoles were recovered.

A possible mechanism[13] for formation of triazolium salts and tetrazoles involves a cyclic transition state. A high degree of participation by nitrilium salts in the nitrogen elimination step may account for the mild conditions needed for decomposition of the imidoyl azide intermediates. A nitrilium salt–imidoyl azide complex appears to be formed at low temperatures which then undergoes elimination of nitrogen to form triazolium salts.



Concentrated solutions of nitrilium salts should enhance the formation of such complexes between imidoyl azides and nitrilium salts and should lead to higher yields of triazolium salts. This assumption is supported by several pieces of experimental evidence. A significant amount of triazolium salt is formed when sodium azide is added to a solution of the nitrilium salt in acetonitrile. Only trace amounts of triazolium salts are formed from addition of nitrilium salts in acetonitrile to sodium azide at ambient temperature.

The existence of a stable imidoyl azide–nitrilium salt complex is suggested by the following observations. Addition of sodium azide to a stirred solution of *N*-ethylbenzonitrilium fluoroborate in acetonitrile at −20 to −25° produced virtually no nitrogen gas. However, evolution of nitrogen was observed when the solution, after filtration to remove unreacted sodium azide and sodium fluoroborate, was allowed to warm to −5°.

Vapor phase chromatographic analysis of the solution of postulated azide complex before and after decomposition indicated no increase in tetrazole concentration. Attempts to isolate the imidoyl azide intermediate at −20 to −25° were unsuccessful. These results suggest that tetrazoles are not formed during the decomposition of the postulated complex and that tetrazoles are formed only by direct rearrangement of thir imidoyl azide intermediate.

It has been suggested[14] that nucleophilic additions to imidoyl chlorides proceed through a nitrilium ion intermediate. Taking into consideration the possibility of nitrilium ion formation, imidoyl chlorides were investigated to determine if the reaction with sodium azide was dependent on the mode of addition of reagents. The mode of addition in the reaction of *N*-ethylbenzimidoyl chloride with sodium azide in either toluene or acetonitrile was found to be unimportant since yields of tetrazole were essentially the same. During the normal and reverse addition, 1-ethyl-5-phenyltetrazole (**3**) was produced in 85–94% yield in acetonitrile and toluene. There was no evidence of gas evolution during these rapid and exothermic reactions. The purity of 1-ethyl-5-phenyltetrazole (**3**) prepared from *N*-ethylbenzimidoyl chloride was superior to that of **3** afforded from nitrilium salts during the normal addition reactions.

## Experimental Section

All nitriles were rigorously dried by distillation from phosphorus pentoxide. Toluene was dried over sodium ribbons. Reagent grade cyclohexene was used without further purification. Finely divided sodium azide was prepared by a reported procedure.[15]

Infrared spectra (ir) were obtained with a Beckman IR-5 or IR-8 spectrophotometer with sodium chloride optics. Proton magnetic resonance (pmr) spectra were taken on a Varian Associates A-60 or HR-60 spectrometer. Positions are reported in parts per million from tetramethylsilane ($\delta$). Mass spectra were taken on a Bendix Model 12-101 time-of-flight instrument at 70 eV.

Melting points of nitrilium salts were determined in sealed capillaries on a Büchi (capillary) melting point apparatus and, like the boiling points, are reported uncorrected. All other melting points reported were taken on a calibrated Kofler micro hot-stage apparatus.

For vapor phase chromatography (vpc) Perkin-Elmer vapor fractometer, Model 154D, and Beckman GC-100 units were used. The following columns were used, respectively: column A, 2 ft × 0.25 in., containing 20% GE-SF-96 silicon oil stationary phase on 35–80 mesh Chromosorb W support; column B, 6 ft × 0.625 in., containing 20% Paraplex on 40-60 mesh Chromosorb W support.

Gas evolution was measured with a Precision wet test meter or a gas burette. Microanalyses were performed by Mrs. P. P. Wheeler and Miss A. C. Richardson, Naval Ordnance Station, Indian Head, Md., and Galbraith Laboratories, Knoxville,. Tenn.

**Nitrilium Salts.**[6,16]—*N*-Ethylaceto- (mp 75–77°), *N*-ethylpropio- (95–97°), and *N*-ethylbenzonitrilium fluoroborates (98–101°) were prepared from the corresponding nitriles and trialkyloxonium fluoroborates.

***N*-Methylacrylonitrilium Fluoroborate.**—Acrylonitrile (46.52 g, 0.876 mol), inhibited with hydroquinone (1.0 g), was slowly added to trimethyloxonium fluoroborate[17] (128.98 g, 0.876 mol). During the addition an exotherm (25–40°) occurred with evolution of dimethyl ether. After the addition was complete, the reaction mixture was allowed to stand at 25° for 18 hr. The reaction mixture was filtered and yellow needle-like crystals of *N*-methylacrylonitrilium fluoroborate (81.3 g, 60%) separated. The yellow crystals were washed with dry ethyl ether, dried undereduced pressure, and recrystallized several times from acrylonirtrile. The light-yellow salt obtained melted at 132–137° and was very hygroscopic.

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[13] Another possible mechanism involves decomposition of an imidoyl azide intermediate yielding a nitrene which could react with a nitrilium salt molecule and cyclize to form a triazolium salt. Attempts to trap the postulated nitrene intermediate with cyclohexene as an acceptor or isolate carbodiimides resulting from a 1,2 shift in the intermediates were unsuccessful.

[14] I. Ugi, F. Beck, and U. Fetzer, *Chem. Ber.*, **95**, 126 (1962).

[15] P. A. S. Smith, *Org. React.*, **3**, 382 (1946).

[16] R. F. Borch, *Chem. Commun.*, 442 (1968); *J. Org. Chem.*, **34**, 627 (1969).

[17] H. Meerwein, G. Hinz, P. Hoffman, E. Kronig, and E. Pfeil, *J. Prakt. Chem.*, **147**, 257 (1937).

**Boron Trifluoride–Acetonitrile Complex.**—The addition compound was prepared by the procedure of Coerver and Curran.[18]

**Addition of *N*-Ethylacetonitrilium Fluoroborate to Sodium Azide in Toluene.**—The following description of the reaction of *N*-ethylacetonitrilium fluoroborate with sodium azide in toluene is typical of the procedure employed for reactions mentioned in Table I. All reactions were carried out under nitrogen atmosphere and started at room temperature, rather than at 0°, except the following.

*N*-Ethylacetonitrilium fluoroborate (15.7 g, 0.10 mol) was was added to a stirred suspension of finely divided sodium azide (7.15 g, 0.11 mol) in toluene (250 ml) at 0°. After the addition was complete (3 min), the ice bath was removed and the reaction mixture was allowed to warm to room temperature. After a short induction period, an exotherm (40°) occurred with gas evolution, which was identified as nitrogen by mass spectrometry. After the ice bath had been removed (1 hr), the reaction temperature decreased to 25° and the evolution of nitrogen became negligible. During that time, 0.15 l. of nitrogen was liberated. The reaction mixture was finally heated and stirred at reflux temperature for 20 hr. A total of 0.63 l. of nitrogen (87% based on crude triazolium salt) was evolved in 21 hr. After the reaction mixture had cooled, suspended sodium fluoroborate and unreacted sodium azide were removed by filtration. The residue was washed with methylene chloride (400 ml) and the washings were combined with the filtrate. The solvents were removed at 60° under reduced pressure leaving a brown residue which was continuously extracted with ether for 72 hr. The ethereal extract was concentrated and distilled giving 3.81 g (34%) of hygroscopic 1-ethyl-5-methyltetrazole (**1**): bp 100–101° (1 mm); $n^{25}$D 1.4611; ir (neat) 2985 (m), 2941 (w), 1520 (s), 1404 (s), 1377 (m), 1253 (m), 1236 (m), 1178 (m), 1089 (s), 1050 (m), 1004 (m), 969 (m), 712 (m), 666 (m), 641 (m), and 1111–1000 cm$^{-1}$ (tetrazole ring[11]).

*Anal.* Calcd for $C_4H_8N_4$: C, 42.84; H, 7.19; N, 49.97. Found: C, 42.61; H, 7.40; N, 49.74.

The ether-insoluble residue from the extraction was heated at 80–85° (1 $\mu$) for 7 hr in an effort to dry the material assumed to be 1,4-diethyl-3,5-dimethyl-1,2,4-triazolium fluoroborate (**4**) (7.86 g, 65%), but this attempt was unsuccessful. Conversion of the salt to the iodide by treatment with sodium iodide in boiling acetone did not give a crystalline product either.

**Pyrolysis of 1,4-Diethyl-3,5-dimethyl-1,2,4-triazolium Iodide.**—Pyrolysis of the crude iodide (6.02 g, 0.021 mol) was carried out at 250° (5 $\mu$) using a short-path distillation apparatus. The distillate (0.85 g) was redistilled affording 0.63 g (24%) of hygroscopic 1-ethyl-3,5-dimethyl-1,2,4-triazole (**9**): bp 82–84° (12 mm) [lit.[12] bp 80.5–81.5° (12 mm)]. The analytical and pmr samples were obtained by preparative vpc on column B (injector 225°; column 191°; flow 25 psi, $R_t$ 3 min): ir (neat) 2976 (s), 2924 (s), 2874 (w), 1522 (s), 1408 (s), 1370 (s), 1333 (s), 1081 (m), 1033 (m), 1005 (m), 980 (m), and 778 cm$^{-1}$ (m). The ir, pmr, boiling point, and $R_t$ data of **9** were identical with those obtained from an authentic sample.[12]

*Anal.* Calcd for $C_6H_{11}N_3$: C, 57.57; H, 8.86; N, 33.57. Found: C, 56.45; H, 8.99; N, 32.73.

The hygroscopic nature of the substance no doubt accounts for the discrepancies in the analyses.

**Addition of Sodium Azide to *N*-Ethylpropionitrilium Fluoroborate in Toluene.**—Sodium azide (14.04 g, 0.22 mol) was added in small portions to a stirred suspension of *N*-ethylpropionitrilium fluoroborate (36.54 g, 0.21 mol) in 150 ml of toluene. The reaction temperature was maintained between 25 and 35° by controlling the rate of addition of azide (30 min). After a short induction period, gas evolution was observed. After the addition had been completed (1 hr), the reaction mixture was stirred and heated at reflux temperature for 20 hr. The isolation procedure was the same as previously described for **1**. Very hygroscopic 1,5-diethyltetrazole (**2**) (9.01 g, 32%), bp 104–105° (1 mm), mp 36–37° after recrystallization from hexane–ether, showed ir max (neat) at 3003 (s), 2950 (m), 2882 (w), 1513 (s), 1449 (s), 1374 (m), 1302 (m), 1252 (m), 1217 (m), 1174 (m), 1089 (s), 1064 (s), 971 (m), 800 (w), and 665 cm$^{-1}$ (m).

*Anal.* Calcd for $C_5H_{10}N_4$: C, 47.60; H, 7.99; N, 44.41. Found: C, 47.60; H, 8.01; N, 44.61.

A crude hygroscopic compound assumed to be 1,3,4,5-tetraethyl-1,2,4-triazolium fluoroborate (**5**) (14.92 g, 53%) was also isolated.

**Pyrolysis of 1,3,4,5-Tetraethyl-1,2,4-triazolium Iodide.**—Preparation of the iodide from **5**, pyrolysis, and isolation of the product was the same as for **4**. Pyrolysis of the iodide (6.23 g, 0.02 mol) gave 0.5 g (16%) of 1,3,5-triethyl-1,2,4-triazole (**10**), bp 79–82° (8 mm). An analytical sample was obtained from preparative vpc ($R_t$ 4.7 min column B, 225°; inlet 225°; flow 20 psi): $n^{20}$D 1.4765; ir (neat) 2985 (s), 2941 (m), 2882 (m), 1449 (m), 1372 (m), 1300 (m), 1269 (m), 1065 (s), 1044 (s), 962 (m), and 800 cm$^{-1}$ (w). The ir, pmr, boiling point, and $R_t$ data of **10** were identical with those obtained from an authentic sample prepared below.

*Anal.* Calcd for $C_8H_{15}N_3$: C, 62.71; H, 9.87; N, 27.43. Found: C, 61.99; H, 9.15; N, 27.55.

**1,3,5-Triethyl-1,2,4-triazole (10).**—A mixture of dipropioamide[19] (9.70 g, 0.075 mol) and ethylhydrazine oxalate (6.75 g, 0.045 mol) heated at 145° for 5 hr afforded 1.99 g (29%) of hygroscopic **10**, bp 84–85° (8 mm). Compound **10** was isolated and purified as previously described for **9**.

*Anal.* Calcd for $C_8H_{15}N_3$: C, 62.71; H, 9.87; N, 27.43. Found: C, 62.65; H, 9.80; N, 27.49.

**Addition of Sodium Azide to *N*-Ethylbenzonitrilium Fluoroborate in Toluene.**—Sodium azide (4.00 g, 0.06 mol) was slowly added to a stirred suspension of *N*-ethylbenzonitrilium fluoroborate (10.31 g, 0.047 mol) in 250 ml of toluene. An exotherm (25–50°) occurred with evolution of nitrogen. After the addition was complete, the reaction mixture was stirred and heated at reflux temperature for 20 hr. The toluene layer was decanted and the insoluble material was washed with toluene. The toluene washings and decanted solvent were combined and then removed on a rotary evaporator leaving 0.82 g (10%) of 1-ethyl-5-phenyltetrazole (**3**), mp 70–71° (lit.[20] mp 70–71°) after recrystallization from ethanol. The toluene-insoluble material was washed with chloroform and then filtered leaving chloroform-insoluble sodium fluoroborate and unreacted sodium azide. The solvent was removed from the filtrate affording 4.00 g (45%) of 1,4-diethyl-3,5-diphenyl-1,2,4-triazolium fluoroborate (**6**): mp 165–166° after recrystallization from ethanol; ir (solid film) 3077 (w), 3003 (w), 1608 (m), 1548 (m), 1449 (m), 1387 (w), 1000–1111 (s), 778 (m), 743 (m), and 696 cm$^{-1}$ (s). A mixture melting point with an authentic sample prepared below was not depressed and the ir and pmr spectra were identical.

*Anal.* Calcd for $C_{18}H_{20}BF_4N_3$: C, 59.19; H, 5.52; N, 11.51. Found: C, 59.70; H, 5.59; N, 11.57.

**4-Ethyl-3,5-diphenyl-1,2,4-triazole (8).**—*N*-Ethylbenzamide (59.68 g, 0.4 mol) was treated with phosphorus pentachloride (83.30 g, 0.4 mol) and benzhydrazide (54.46 g, 0.4 mol) in 200 ml of chloroform by the method of Scheuing and Walach[21] to give 37.74 g (38%) of **8**: mp 163.5–164.5° after recrystallization from ethanol; ir (KBr) 3040 (w), 2941 (m), 2849 (w), 1471 (s), 1433 (m), 1342 (m), 1247 (m), 1075 (m), 1022 (m), 795 (m), 775 (s), 725 (s), 722 (s), and 699 cm$^{-1}$ (s).

*Anal.* Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.86. Found: C, 77.48; H, 6.24; N, 16.84.

**1-Ethyl-3,5-diphenyl-1,2,4-triazole (7).**—3,5-Diphenyl-1,2,4-triazole[22] (**20**) (14.00 g, 0.064 mol) was dissolved in a solution of sodium ethoxide (0.07 mol) in 15 ml of ethanol, then mixed with ethyl iodide (10.8 g, 0.07 mol), and heated in a Fischer-Porter tube (20 × 2.5 cm) at 120° for 15 hr. The product was slurried with 5% aqueous sodium carbonate and extracted with benzene. The extract was evaporated to dryness and the residue was recrystallized from petroleum ether–benzene (1:9) to give 6.45 g (39%) of **7**: mp 75–76°; ir (KBr) 3077 (w), 2976 (w), 1458 (m), 1433 (s), 1350 (s), 1126 (m), 1087 (w), 1064 (w), 1026 (w), 1015 (s), 786 (m), 769 (s), 741 (s), 724 (s), 698 (s), 687 (s), and 655 cm$^{-1}$ (w).

*Anal.* Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.86. Found: C, 77.11; H, 6.32; N, 16.81.

**1,4-Diethyl-3,5-diphenyl-1,2,4-triazolium Fluoroborate (6).**—A solution of 4-ethyl-3,5-diphenyl-1,2,4-triazole (**8**) (1.00 g, 3.8 mmol) and triethyloxonium fluoroborate (0.77 g, 4.0 mmol) in 25 ml of ethylene chloride was heated with stirring at 65° for 3 hr. The reaction mixture was concentrated *in vacuo* and the residue obtained was washed with ether and recrystallized from absolute ethanol affording 1.41 g (95%) of **6**, mp 165–166°.

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A solution of 1-ethyl-3,5-diphenyl-1,2,4-triazole (**7**) (1.00 g, 3.8 mmol) in 25 ml of ethylene chloride gave 1.10 g (80%) of **6**, mp 165–166°. A mixture melting point with a sample from the synthesis above was not depressed and the ir and pmr spectra were identical.

**Addition of Sodium Azide to *N*-Ethylbenzonitrilium Fluoroborate in Acetonitrile at −20 to −25°.**—To a stirred solution of *N*-ethylbenzonitrilium fluoroborate (4.38 g, 0.02 mol) in acetonitrile (25 ml) was added in small portions sodium azide (1.96 g, 0.03 mol) at −20 to −25°. After the addition was complete (30 min), the reaction mixture was allowed to stir for 1 hr. During this time no nitrogen evolution was detected. After an aliquot was taken from the reaction mixture for vpc analysis, the reaction mixture was filtered quickly at −20 to −25° removing unreacted sodium azide and sodium fluoroborate. The filtrate was stirred vigorously with a magnetic stirring bar and was allowed to warm up to −5 ± 0.5° in a constant temperature flask (50 ml) fitted with an alcohol thermometer and gas outlet. The method used for determining the rate of decomposition was the measurement of the volume of nitrogen evolved *vs.* time. Because it is impossible to bring the flask containing the postulated 1:1 nitrilium salt–imidoyl azide complex to the required temperature instantaneously, nitrogen evolution was recorded 20 min after the desired temperature was obtained, allowing thermal equilibration and saturation of the solution with nitrogen. After 2 hr the reaction mixture was allowed to warm to room temperature and then another aliquot was taken from the reaction mixture for vpc analysis (column A at 170°). Vpc analyses of the solution before and after decomposition indicated no apparent increase in tetrazole concentration. The reaction mixture was filtered to remove unreacted sodium azide and sodium fluoroborate. The filtrate was concentrated under reduced pressure and the remaining residue was washed with methylene chloride and then filtered leaving sodium fluoroborate. The filtrate was concentrated and the residue was washed with benzene leaving a mixture of salts. The benzene washings were combined and concentrated giving 1.39 g (40%) of **3**. The benzene-insoluble material was treated with 25 ml of 10% aqueous sodium hydroxide and extracted with ether and methylene chloride. The respective extracts were combined and dried over anhydrous sodium sulfate. The ethereal solution was concentrated affording 0.20 g (7%) of *N*-ethylbenzamide. Removal of solvent from the methylene chloride solution gave 0.30 g (8%) of **6**.

**Addition of *N*-Methylacrylonitrilium Fluoroborate to Sodium Azide in Acetonitrile.**—*N*-Methylacrylonitrilium fluoroborate (15.4 g, 0.10 mol) dissolved in acetonitrile (25 ml) and inhibited with hydroquinone (0.1 g) was added dropwise to a stirred suspension of sodium azide (9.75 g, 0.15 mol) in 225 ml of acetonitrile under nitrogen. The reaction temperature was maintained at 25–35° by controlling the rate of addition. After the addition was complete, an immediate analysis of the reaction mixture by vpc indicated 5% yield of 1-methyl-5-vinyltetrazole (**11**). The reaction mixture was stirred an additional 2 hr and further analysis showed no increase in tetrazole concentration. Finally the reaction mixture was stirred and heated to reflux for 3 hr. The reaction mixture was cooled and filtered to remove suspended sodium fluoroborate and unreacted sodium azide (9.36 g). The filtrate was concentrated under reduced pressure at 40–50° and the remaining residue was extracted with ether. The ether-insoluble material was the major product (15.1 g) which appeared to be a polymer. The ethereal extract was concentrated under reduced pressure at 40° giving 0.52 g (5%) of crude 1-methyl-5-vinyltetrazole (**11**). The ir and pmr spectra and $R_t$ and $R_f$ values were identical with those of authentic[23] **11**.

**Reaction of *N*-Methylacrylonitrilium Fluoroborate with Water.**—*N*-Methylacrylonitrilium fluoroborate (3.10 g, 0.02 mol) was added slowly to distilled water (25 ml). The solution was then stirred at ambient temperature for 1 hr. The reaction mixture was made basic (pH 10) with 10% aqueous sodium hydroxide and extracted with ether. The ethereal extract was dried ($Na_2SO_4$), concentrated, and distilled giving 0.70 g (41%) of the monomer of *N*-methylacrylamide: bp 93–95° (7 mm) [lit.[24] bp 84° (3 mm)]; ir (neat) 3279 (NH), 2941 ($CH_3$–), 1890 ($H_2C{=}CH$), 981, 952, and 1645 $cm^{-1}$ (amide II); pmr ($CD_3CN$) 7.54 (br, 1, NH), 5.53 (m, 1, $H_2C{=}CH$), 6.22 (m, 2, $H_2C{=}CH$).

**Addition of Sodium Azide to *N*-Ethylbenzimidoyl Chloride in Toluene.**—Sodium azide (0.98 g, 0.015 mol) was added to a stirred solution of *N*-ethylbenzimidoyl chloride[14] (1.68 g, 0.01 mol) in toluene (25 ml). The reaction temperature was maintained between 25 and 35° with an ice bath during the addition of imidoyl chloride. After the addition was complete, the reaction mixture was allowed to stir at ambient temperature (25°) for 2 hr. The reaction mixture was filtered, removing sodium chloride and unreacted sodium azide, and the solvent was removed from the filtrate under reduced pressure leaving 1.57 g (90%) of 1-ethyl-5-phenyltetrazole (**3**), mp 70–71° after recrystallization from ethanol.

**Addition of *N*-Ethylbenzimidoyl Chloride to Sodium Azide in Toluene.**—Dropwise addition of *N*-ethylbenzimidoyl chloride (1.68 g, 0.01 mol) to a stirred suspension of sodium azide (0.98 g, 0.015 mol) in 25 ml of toluene gave 1.64 g (94%) of **3**, mp 70–71° after recrystallization from ethanol.

**Registry No.**—**1**, 32675-38-0; **2**, 32675-39-1; **3**, 32675-43-7; **6**, 32675-53-9; **7**, 32675-48-2; **8**, 32675-51-7; **9**, 32675-46-0; **10**, 32675-47-1; sodium, 7440-23-5; dimethylammonium azide, 32649-51-7; *N*-methylacrylonitrilium fluoroborate, 32830-06-1; *N*-methylacrylamide, 1187-59-3.

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