low 0° over a period of 30 min. After the reaction mixture was stirred at room temperature for 30 min, it was poured into 50 ml of ice–water containing acetic acid (1 ml). The mixture was extracted with chloroform, and the extract was dried ($MgSO_4$). The extract was evaporated *in vacuo* to leave 3.3 g (88%) of crystals. Recrystallization from petroleum ether (bp 45–70°) afforded **11b**, mp 103° as colorless prisms: ir (KBr) 2180 (N_3), 1680 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 375 (M^+), 305 ($M^+ - CON_3$, base peak).

Anal. Calcd for $C_{20}H_{14}N_5OCl$: C, 63.92; H, 3.76; N, 18.64. Found: C, 64.03; H, 3.48; N, 18.90.

Similarly, the reaction of carbamoyl chloride **10c** with tetramethylguanidium azide in dry chloroform afforded the corresponding acyl azide **11c**, mp 93.5°, as colorless prisms: yield 83%; ir (KBr) 2160 (N_3), 1690 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 355 (M^+), 285 ($M^+ - CON_3$, base peak).

Anal. Calcd for $C_{21}H_{17}N_5O$: C, 70.96; H, 4.82; N, 19.71. Found: C, 70.87; H, 4.71; N, 19.68.

Thermolysis of Acyl Azide 11b.—A solution of **11b** (0.5 g) in dry xylene (5 ml) was heated at 135° for 2 hr. The reaction mixture was evaporated *in vacuo* to leave an oily substance, which on trituration with a mixture of methanol, acetone, and diethyl ether afforded crystals. Recrystallization from ethanol gave 0.18 g (39%) of triazolinone **8b**, mp 201–202°, as colorless prisms.

Similarly, thermolysis of acyl azide **11c** afforded triazolinone **5c**, mp 222–223°, in 41% yield.

Reaction of Benzoyl Isothiocyanate (12) with 3a.—A solution of **3a** (1.1 g) in dry benzene (20 ml) was added dropwise to a solution of **12** (1.0 g) in dry benzene (10 ml) at room temperature. Filtration afforded 1.85 g (88%) of yellow crystals, which were washed with benzene to give 1,2-diphenyl-4-benzoylthiosemicarbazide (**13**), mp 139.5–140° dec. This compound was submitted to microanalysis without further purification.

Anal. Calcd for $C_{20}H_{17}N_3OS$: C, 69.15; H, 4.93; N, 12.10. Found: C, 69.29; H, 4.81; N, 11.73.

1,2-Diphenyl-1-benzoylthiosemicarbazide (14).—A solution of **13** (0.2 g) in ethanol (10 ml) was refluxed for 5 min. The solution was concentrated to give 0.17 g (85%) of colorless crystals. Recrystallization from ethanol afforded **14**, mp 210–211° dec, as colorless prisms: nmr ($CDCl_3$) δ 6.23 (broad, 2, NH_2); mass spectrum (70 eV) *m/e* 347 (M^+).

Anal. Calcd for $C_{20}H_{17}N_3OS$: C, 69.15; H, 4.93; N, 12.10. Found: C, 69.38; H, 4.83; N, 12.14.

1,2,3-Triphenyl-Δ^3-1,2,4-triazoline-5-thione (15).—Heating of **13** (0.5 g) at 160° for 10 min or treatment of **13** (0.5 g) with 15% hydrochloric acid (20 ml) at 90–95° for 30 min afforded 0.47 g (99%) or 0.45 g (95%) of **15**, mp 251°, as colorless needles: mass spectrum (70 eV) *m/e* 329 (M^+), 297 ($M^+ - S$), 296 ($M^+ -$ SH), 180 ($PhC{\equiv}\overset{+}{N}Ph$).

Anal. Calcd for $C_{20}H_{15}N_3S$: C, 72.93; H, 4.59; N, 12.76. Found: C, 72.71; H, 4.37; N, 12.51.

Reaction of 2 with Phenylhydrazine (16).—A mixture of a standard solution of **2** and **16** (0.56 g) was stirred at −5° for 5 min. Dry diethyl ether was added to the reaction mixture, giving 1.3 g (92%) of 1-phenyl-4-thiobenzoylsemicarbazide (**17**) as yellow crystals. Compound **17** decomposed gradually under the evolution of hydrogen sulfide at room temperature: ir (KBr) 3220, 3150, 3080 (NH), 1680 cm^{-1} (C=O).

Heating of **17** at 140–160° for 5 min or treatment with concentrated hydrochloric acid at room temperature for 30 min afforded 3-hydroxy-1,5-diphenyl-1,2,4-triazole (**20**)[5] in 91 or 86% yield, respectively.

Reaction of 17 with 16.—A solution of **17** (0.2 g) and **16** (0.18 g) in benzene (10 ml) was refluxed for 5 min. After cooling, filtration gave 0.16 g (91%) of 1,3-diphenyl-Δ^3-1,2,4-triazolin-5-one (**19**),[2] mp 230–231° (lit.[15] mp 235°; lit.[16] mp 233°).

Registry No.—**1**, 4461-33-0; **2**, 3553-61-5; **3a**, 122-66-7; **3b**, 949-88-2; **3c**, 621-94-3; **3d**, 953-12-8; **4a**, 40587-77-7; **4b**, 40587-78-8; **4c**, 40587-79-9; **4d**, 40587-80-2; **5a**, 5378-13-2; **5b**, 40587-82-4; **5c**, 40587-83-5; **5d**, 40587-84-6; **6a**, 40587-85-7; **8b**, 40594-85-2; **8c**, 40594-86-3; **9b**, 40594-87-4; **9c**, 40594-88-5; **10b**, 40594-89-6; **10c**, 40594-90-9; **11b**, 40594-91-0; **11c**, 40594-92-1; **12**, 532-55-8; **13**, 40594-93-2; **14**, 40594-94-3; **15**, 40594-95-4; **16**, 100-63-0; **17**, 40594-96-5.

[15] J. Goerdeler and H. Schenk, *Chem. Ber.*, **99**, 782 (1966).

[16] G. Baccar and F. Mathis, *C. R. Acad. Sci.*, **261** (1), 174 (1965).

The Reaction of Aluminum Azide with Cyano Esters. Preparation of Tetrazolo[1,5-*c*]pyrimidin-5(6*H*)-one and Tetrazolo[1,5-*c*]quinazolin-5(6*H*)-one

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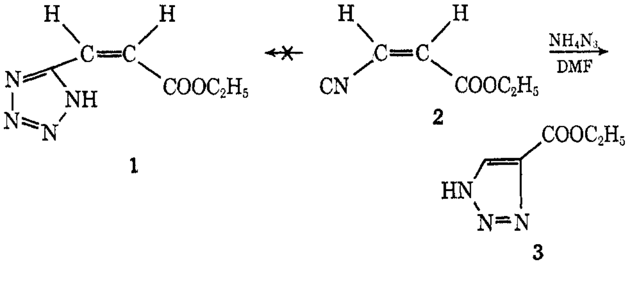
The reaction of aluminum azide and a variety of unsaturated β-cyano esters was studied. Both *cis*- and *trans*-3-cyanoacrylates gave *trans*-3-tetrazole-5-acrylate. *trans*-3-Cyanocrotonate produced *trans*-3-methyltetrazole-5-acrylate, while *cis*-3-cyanocrotonate gave a mixture consisting mainly of 1-(2-cyanopropenyl)tetrazolin-5(4*H*)-one and tetrazolo[1,5-*c*]pyrimidin-5(6*H*)-one. The reaction of aluminum azide and ethyl *o*-cyanobenzoate gave a mixture of four products: tetrazolo[1,5-*c*]quinazolin-5(6*H*)-one, 1-[*o*-(tetrazol-5-yl)phenyl]tetrazolin-5(4*H*)-one, ethyl *o*-(5-tetrazolyl)benzoate, and *o*-(5-oxo-2-tetrazolin-1-yl)benzonitrile. An explanation for the formation of the quinazolinone *via* a Curtius rearrangement is proposed. Alkaline hydrolysis of tetrazolo[1,5-*c*]quinazolin-5(6*H*)-one produced 5-(*o*-aminophenyl)tetrazole, which could be reconverted to the tetrazolo[1,5-*c*]quinazolinone by reaction with phosgene.

Because the previously unreported ethyl *cis*-tetrazole-5-acrylate (**1**) was required as a synthetic intermediate, an attempt was made to prepare it from the readily available ethyl *cis*-3-cyanoacrylate (**2**).[2] Several excellent methods are known for converting nitriles to tetrazoles, the most convenient being that of Finnegan, Henry, and Lofquist,[3] which employs ammonium azide in dimethylformamide. This reagent, however, caused elimination of cyanide from the cyanoacrylate



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[1] Chemical Biology Research, The Dow Chemical Company, Midland, Mich. 48640.

[2] C. K. Sauers and R. J. Cotter, *J. Org. Chem.*, **26**, 6 (1961).

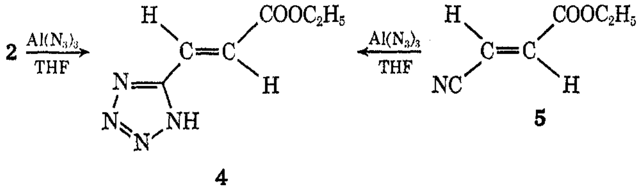
[3] W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Amer. Chem. Soc.*, **80**, 3908 (1958).

and produced only triazolecarboxylate **3**.[4] The same product was obtained by the reaction of sodium azide with **2** in acetonitrile.

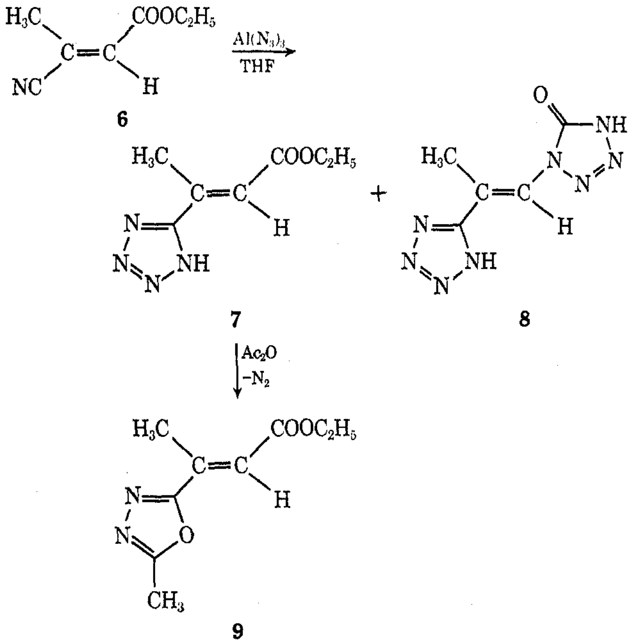
More recently, Arnold and Thatcher[5] have used aluminum azide, prepared *in situ* in anhydrous THF, to obtain 5-vinyltetrazole from acrylonitrile. Unfortunately, this reagent also failed to produce **1** from **2**, but the subsequent study of the reaction of aluminum azide on cyano esters uncovered some novel chemistry that is the subject of this discussion.

Results and Discussion

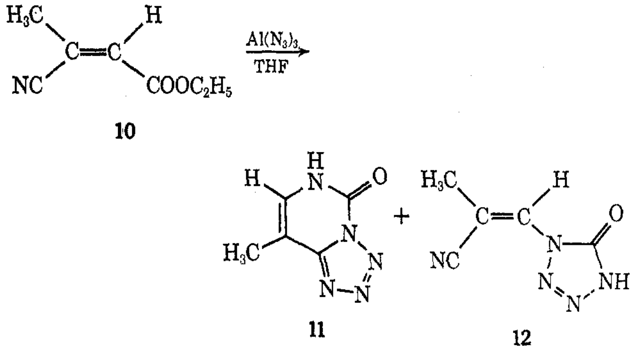
Cyanoacrylates.—When ethyl *cis*-3-cyanoacrylate was refluxed in THF with an equimolar amount of aluminum azide, a crystalline tetrazoleacrylate **4** was formed in 30% yield. However, in the nmr the coupling constant for the AB quartet of the vinyl protons was now 16.5 cps rather than the original 11.5 cps in **2**, indicating that **4** contained a trans double bond.[6] Treatment of ethyl *trans*-3-cyanoacrylate (**5**) with aluminum azide produced a crystalline compound identical with that obtained from the *cis*-acrylate. Aliquots removed at various times from the reaction of the *cis*-cyanoacrylate clearly showed by nmr initial formation of the *trans*-cyanoacrylate from the *cis*-cyanoacrylate followed by conversion to the *trans*-tetrazoleacrylate. No peaks that could be ascribed to the *cis*-tetrazoleacrylate could be detected then or in the product after work-up, indicating that under these conditions the isomerization was preceding the formation of the tetrazole.



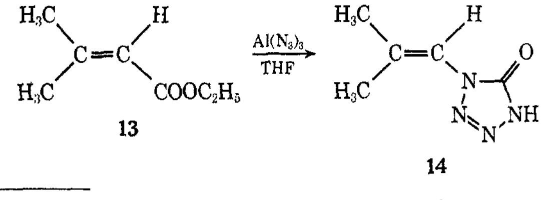
Cyanocrotonates.—In an effort to reduce the rate of isomerization in this system, ethyl *cis*- and *trans*-3-cyanocrotonates[7] were studied. Ethyl *trans*-3-cyanocrotonate (**6**) behaved normally when treated with aluminum azide to produce a 66% yield of ethyl *trans*-3-methyltetrazole-5-acrylate (**7**) and a small amount of **8**, discussed below. The *trans*-tetrazolecrotonate **7** displayed typical tetrazole behavior by forming oxadiazole **9** when treated with refluxing acetic anhydride.[5]



The reaction of aluminum azide with ethyl *cis*-3-cyanocrotonate (**10**), however, produced a completely unexpected result. In this case a mixture of two crystalline products was obtained, but this only amounted to about 14% by weight of the starting material. The remainder was unreacted **10** and polymeric oils which were not characterized. Of the crystalline product, 82% was an insoluble $C_5H_5N_5O$ compound **11**, melting at 210–211°. The remaining 18% was an isomeric $C_5H_5N_5O$ material **12** melting at 187–189°. No **7** was detectable, though it could possibly have been present in the large, noncrystalline fraction.



The structure of **12** was the more readily apparent, since the nmr spectrum showed that the ethyl protons of the ester had been lost while the ir clearly indicated that the cyano group was still present. Apparently the azide ion had attacked the ester instead of the nitrile, forming a new carbonyl function absorbing at 1740 cm^{-1}. Such a reaction has not been previously reported in the literature, but it is given good precedent in the work of Horwitz, *et al.*,[8] who showed that isocyanates, acid chlorides, and α-ketonitriles are transformed by aluminum azide *via* a Curtius rearrangement into 1-substituted tetrazolin-5(4*H*)-ones. Therefore, the low-melting isomer was assigned structure **12**, 1(2-cyanopropenyl)tetrazolin-5(4*H*)-one. To confirm that such a reaction would occur in this system, ethyl β,β-dimethylacrylate (**13**) was treated under the same



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[4] Y. Shunichi, M. Tomishige, and A. Akira, *Yakugaku Zasshi*, **77**, 452 (1957); *Chem. Abstr.*, **51**, 14697e (1957).

[5] C. Arnold, Jr., and D. N. Thatcher, *J. Org. Chem.*, **34**, 1141 (1969).

[6] R. H. Bible, "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, p 38.

[7] D. T. Mowry and A. G. Rossow, *J. Amer. Chem. Soc.*, **67**, 926 (1945). Although correct nomenclature would label **6** as the *cis*-crotonate and **10** as the *trans*-crotonate, the opposite terminology is used in this paper as in Mowry's paper so that cis and trans refer to the functional groups of interest, the nitrile and the ester.

[8] J. P. Horwitz, B. E. Fisher, and A. J. Tomasewski, *J. Amer. Chem. Soc.*, **81**, 3076 (1959).

conditions with aluminum azide and formed a 24% yield of 1-(2-methylpropenyl)tetrazolin-5(4*H*)-one (**14**).

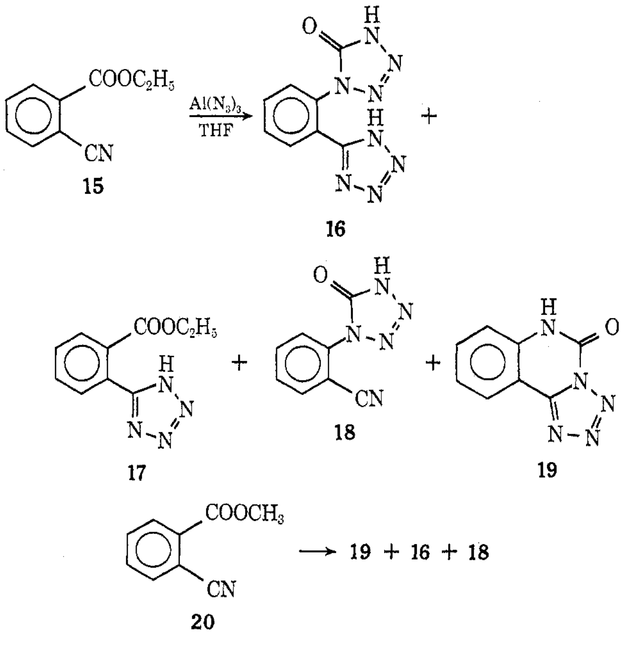
The structure of **8** was assigned by analogy on the basis of its empirical formula and spectral properties to be that of the *trans*-tetrazolypropenyltetrazolinone.

Although the presence of the unchanged nitrile in **12** suggested a possible isomerization to the trans isomer, a nuclear Overhauser effect determination showed a 19% increase in the vinyl proton integral and confirmed the cis form as shown. That **12** was not a precursor of **11** was indicated by the failure of further treatment of **12** with aluminum azide to produce any **11**. The only crystalline product isolated was unchanged **12**.

Compound **11**, though it was not the product of further reaction of the nitrile with the tetrazolinone, nor was it a *cis*-tetrazolylpropenyl tetrazolinone such as **8**, had lost both the original ester and nitrile functions. Its ir spectrum revealed a complex carbonyl region with peaks at 1770, 1730, 1640, and 1550 cm^{-1}. The high-frequency absorption in the 1770-cm^{-1} region was suggestive of 1-acylated tetrazoles.[9] A Curtius rearrangement to an isocyanate resulting from azide attack on the carboethoxy group, followed by cyclization with the adjacent tetrazole, would form 8-methyltetrazole[1,5-*c*]pyrimidin-5(6*H*)-one (**11**). Though not supported by direct degradative evidence, this assignment was corroborated and a better understanding of the rearrangement was obtained by a study of the reaction of aluminum azide on the analogous *o*-cyanobenzoates.

Cyanobenzoates.—Ethyl *o*-cyanobenzoate (**15**) (Scheme I) was treated with aluminum azide in refluxing THF for 42 hr. On work-up, about 50% of the starting ester was recovered unchanged. The remainder had been transformed into a mixture of four crystalline materials, **16, 17, 18,** and **19,** which separated fairly well on tlc, and three of these, **16, 17,** and **19,** could be obtained in a pure state by fractional crystallization.

SCHEME I



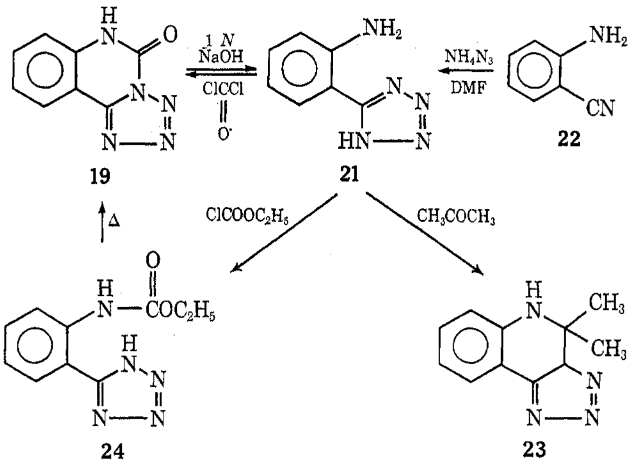
About 25% of the product consisted of the $C_8H_6N_8O$ compound **16**, mp 262–263°, which had a 1690-cm^{-1} carbonyl band in the ir. This data plus a titration with sodium hydroxide, which revealed two acidic protons, indicated that **16** was 1-[*o*-(tetrazol-5-yl)phenyl]-tetrazolin-5(4*H*)-one in which the ester had been converted to the tetrazolinone and the nitrile to the tetrazole.

A second crystalline component comprising 10% of the product was a $C_{10}H_{10}N_4O_2$ material, **17**, mp 142–143°. The nmr spectrum indicated that it had retained the carboethoxy function and the ir showed that it had lost the nitrile. This could therefore be assigned the structure of ethyl (5-tetrazolyl)benzoate (**17**).

Although it could not be isolated pure from this reaction mixture, the alternate compound **18** was also obtained. This $C_8H_5N_5O$ material could be isolated in a pure form from the reaction product of aluminum azide on methyl *o*-cyanobenzoate (**20**). Spectral data showed that the nitrile had been retained and the ester converted to the tetrazolinone, forming 1-(*o*-cyanophenyl)tetrazolin-5(4*H*)-one (**18**).

The largest portion (about 50%) of the crystalline reaction product from ethyl cyanobenzoate consisted of **19** (Scheme II), $C_8H_5N_5O$, mp 273–275°. In the carbonyl region of its ir spectrum, **19** corresponded closely to the compound **11** obtained from the cis crotonate, having in particular a high-frequency carbonyl absorption at 1770 cm^{-1}. The assignment of the tetrazolo[1,5-*c*]quinazolin-5(6*H*)-one structure **19** was, however, made on the basis of the results of alkaline hydrolysis. Being acidic, the compound dissolved readily in 1 *N* aqueous sodium hydroxide, and, after warming on the steam bath for 1 hr and acidification, a new crystalline material precipitated simultaneously with copious evolution of carbon dioxide. Analysis showed this new material to be a $C_7H_7N_5$ compound, having simply lost the carbonyl. Since it was a nitrogeneous material containing no oxygen, yet still retaining its acidic properties, it undoubtedly contained a tetrazole ring. The presence of primary NH_2 absorption at 3450–3400 cm^{-1} in the ir indicated the compound to be 5-(*o*-aminophenyl)tetrazole (**21**). The entire spectrum corresponded closely to that reported

SCHEME II



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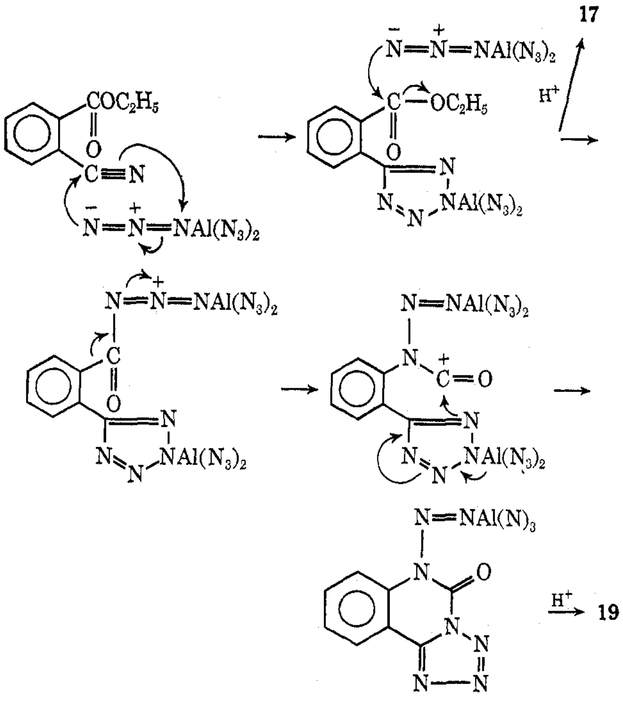
[9] H. W. Thompson and R. J. L. Popplewell, *Z. Electrochem.*, **64**, 746 (1960).

by Postovskii,[10] who prepared it by acid treatment of 5,6-dihydro-5-methyl-5-hydroxytetrazolo[1,5-*c*]quinazoline. Authentic **21** was prepared from anthranilonitrile **22** with ammonium azide in dimethylformamide. It was difficult to obtain this material in pure form and the ir spectrum and melting point seemed to be highly variable depending on the crystallization solvent (solution spectra were identical). Therefore, the acetone condensation products **23** from each source were prepared and were found to have identical ir spectra and showed no depression of the mixture melting point.

On treatment of **21** with phosgene in benzene, a 64% yield of crystalline material identical with **19** was obtained, proving that this compound is tetrazolo[1,5-*c*]quinazolin-5(6*H*)-one. It could also be prepared in about 40% overall yield by treatment of **21** with ethyl chloroformate in ethanol to give **24**, which on pyrolysis at 195–200° produced **19**.

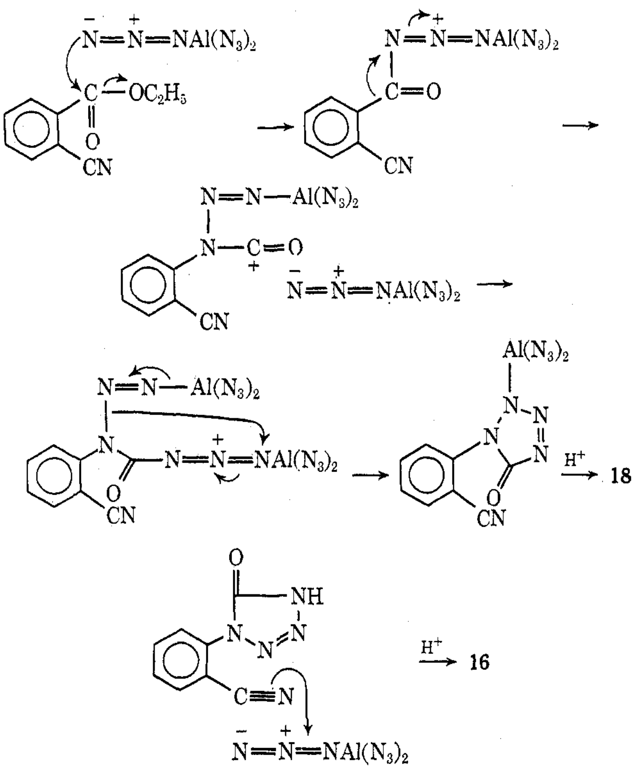
The mechanism of this rearrangement and cyclization probably involves initial 1,3-dipolar addition of azide to the nitrile[11] to form the tetrazole ester **17** in the normal fashion. A second molecule of azide then attacks the ester carbonyl, eliminating ethoxide. A Curtius rearrangement[8] to give the isocyanate intermediate is followed by rapid attack from the adjacent tetrazole nitrogen to give **19**, or **11** in the crotonate case (Scheme III).

SCHEME III



However, in the cases where the ester is the site of the initial azide attack (Scheme IV), the nitrile is not capable of reacting with the intermediate isocyanate which is susceptible to 1,3-dipolar addition of more azide. There is no evidence yet to establish that a free isocyanate is formed in this reaction nor, in fact, has the possibility of the aluminum chloride removing the ethoxide group to form a preliminary carbonium ion intermediate[12] been eliminated.

SCHEME IV



It is presumably further azide attack on the cyanophenyltetrazolinone **18** that produces the fourth product of the reaction, the tetrazolylphenyltetrazolinone **16**. The high reactivity of the tetrazole in condensation reactions of carbonyl compounds with the ortho amino group in 5-(*o*-aminophenyl)tetrazole would indicate that very little of **16** is formed from **17**.

The relative proportions of the various products are dependent upon the relative rate of primary attack on the ester or the nitrile. Surprisingly, there appears to be little difference, although the nitrile seems to be preferred. A quantitative separation of the components has not been attempted, since their relatively low solubility in common solvents has discouraged quantitative chromatographic separation.

Experimental Section[13]

Ethyl *v*-Triazole-4-carboxylate (3) from Sodium Azide.—To a stirred suspension of 3.35 g of NaN_3 in 100 ml of dry CH_3CN was added, over a 10-min period, a solution of 6.26 g of ethyl *cis*-3-cyanoacrylate[2] (**2**) in 50 ml of CH_3CN. The reaction solution turned pink and after stirring at room temperature for 4 hr was refluxed for 2 days. After cooling, the reaction was filtered and the resulting white solid was washed with CH_3CN. The solid was dissolved in 100 ml of 6 *N* HCl and extracted four times with 50-ml portions of $CHCl_3$. The $CHCl_3$ solution was dried (Na_2SO_4) and evaporated to leave 0.8 g of white solid. Recrystallization from CCl_4–$CHCl_3$ mixture gave 0.1 g of colorless crystals of **3**, mp 112–113°.

From Ammonium Azide.—A mixture of 42.3 g of NaN_3, 34.4 g of NH_4Cl, 0.65 g of LiCl, and 56.6 g of **2** in 250 ml of DMF was stirred and heated at 125° for 6 hr. The reaction was filtered hot and the DMF in the filtrate was removed under reduced pressure. The residue was poured into 500 g of ice water and filtered from a

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[10] I. Ya. Postovskii and N. N. Vereshchagina, *Khim. Geterotsikl. Soedin.*, **3**, 944 (1967).

[11] E. Wilberg and H. Michaud, *Z. Naturforsch. B*, **9**, 496 (1954).

[12] P. A. S. Smith, *J. Amer. Chem. Soc.*, **70**, 320 (1948).

[13] Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. Nmr spectra were obtained using a Varian A-60 spectrometer; ir spectra were obtained using a Perkin-Elmer 337 grating infrared spectrophotometer; all melting points were determined using a Thomas-Hoover Uni-melt apparatus and are uncorrected; mass spectral determinations were obtained using a CEC 110B high-resolution mass spectrometer, D. P.

trace of amorphous solid. The resulting dark solution was extracted four times with $CHCl_3$, and the combined extracts were washed twice with H_2O, dried (Na_2SO_4), and evaporated under reduced pressure to leave a dark oil that crystallized on cooling. The crystals were filtered, washed carefully with $CHCl_3$, and dried in air to yield 9.65 g. Recrystallization from $CHCl_3$ after decolorizing with charcoal gave 7.22 g of **3**: mp 112–113° (lit.[4] mp 117–118°); nmr (acetone-d_6) δ 8.0 (s, 1 H, vinyl H) and typical ethyl ester pattern; ir (Nujol) 3170 (NH), 1710 cm^{-1} (C=O). Material was identical with that obtained from sodium azide above.

Anal. Calcd for $C_5H_7N_3O_2$: C, 42.55; H, 5.00; N, 29.77. Found: C, 42.33; H, 4.89; N, 30.03.

Ethyl *trans*-5-Tetrazoleacrylate (4) from Ethyl *cis*-3-Cyanoacrylate (2).—Anhydrous $AlCl_3$ (200 g, 1.5 mol) was added in portions to 3 l. of anhydrous THF stirred and cooled under N_2. To this solution was added 400 g (6.16 mol) of NaN_3 and 187.5 g (1.5 mol) of ethyl *cis*-3-cyanoacrylate and the mixture was warmed to reflux. After refluxing for 19 hr under N_2, the reaction was cooled and 2 l. of 6 *N* HCl was added carefully. The resulting mixture was filtered and the precipitated inorganic solid was washed with THF. The THF was removed under reduced pressure until about 2 l. of a brown solution remained. This was extracted four times with 400-ml portions of $CHCl_3$, and the combined extracts were washed twice with 200-ml portions of saturated NaCl solution, dried (Na_2SO_4), and evaporated to leave a tan solid. This residue was triturated with 900 ml of hot $CHCl_3$, filtered to remove the insoluble amorphous solid, concentrated to 300 ml, and allowed to cool. The total yield of crystalline **4** obtained in three crops was 76 g (30% yield): mp 135–136°; nmr (acetone-d_6) AB quartet centered at δ 7.41 (J = 16.5 cps, 2 H, vinyl H) and typical ethyl ester pattern; ir (Nujol) 3170, 3070 (NH), 1710 (C=O), 1660 (C=C), 1550 cm^{-1}.

Anal. Calcd for $C_6H_8N_4O_2$: C, 42.85; H, 4.80; N, 33.32. Found: C, 42.73; H, 4.86; N, 33.72.

Ethyl *trans*-5-Tetrazoleacrylate (4) from Ethyl *trans*-3-Cyanoacrylate (5).—Ethyl *trans*-3-cyanoacrylate was prepared from ethyl α-chloroacrylate according to the modified method of Sauers and Cotter,[2] but it could not be completely separated from the acetone cyanohydrin also formed. The material used in this reaction was shown by glc to contain 67% of the desired ethyl *trans*-3-cyanoacrylate. A mixture of 19.9 g (0.15 mol) of $AlCl_3$ and 43.2 g (0.665 mol) of NaN_3 in 300 ml of cold, anhydrous THF was treated with 18.7 g of the crude *trans*-cyanoacrylate. After stirring under N_2 at reflux for about 20 hr, the cooled reaction solution was treated with 200 ml of 6 *N* HCl and filtered, and the THF was removed under reduced pressure. The aqueous residue was extracted four times with $CHCl_3$. These extracts were washed twice with saturated NaCl and dried (Na_2SO_4). Evaporation of the solvent left 10.52 g of a viscous orange oil that produced 1.48 g of crystalline **4** when cooled and scratched. This material was identical with that obtained from the *cis*-cyanoacrylate above.

Ethyl *trans*-3-Methyltetrazole-5-acrylate (7).—Ethyl *trans*-3-cyanocrotonate (**6**) was prepared by the method of Mowry and Rossow.[7] The reaction was carried out exactly as with the cyanoacrylates above using 0.4 mol of crotonate, 0.4 mol of $AlCl_3$, and 1.8 mol of NaN_3 in 1 l. of anhydrous THF. After acidification with 600 ml of 6 *N* HCl, the THF was evaporated and the residue was poured into H_2O and extracted with $CHCl_3$. This $CHCl_3$ solution was dried (Na_2SO_4) and filtered. On standing a fine, crystalline solid separated weighing 0.92 g and identical with another 1.67 g of material that slowly separated from the aqueous fraction. It had a melting point of 187–188° after recrystallization from acetone–$CHCl_3$. It is ascribed structure **8** based on its analysis, ir (broad H-bonded NH, carbonyl at 1710, C=C at 1660 cm^{-1}), and nmr, which showed only a vinyl methyl at δ 1.90 (d, 3 H) and a single adjacent vinyl proton at δ 7.05 (m, 1 H).

Anal. Calcd for $C_5H_6N_8O$: C, 30.93; C, 3.11; N, 57.72. Found: C, 30.63; H, 3.11; N, 56.59.

The $CHCl_3$-soluble product from the reaction was isolated by evaporation. The resulting yellow oil crystallized on cooling. It was recrystallized from CCl_4–$CHCl_3$ to produce 48.3 g of **7**, light yellow crystals, mp 83–87°, 66% yield. Recrystallized for analysis from $CHCl_3$, the pure material melted at 88–89°: nmr ($CDCl_3$) δ 1.35 (t, 3 H, ethyl CH_3), 2.80 (d, 3 H, vinyl CH_3), 4.34 (q, 2 H, ethyl CH_2), 7.10 (m, 1 H, vinyl H); ir (Nujol) broad NH, 1740 and 1720 (C=O), 1650 (C=C), 1050 cm^{-1} (tetrazole).

Anal. Calcd for $C_7H_{10}N_4O_2$: C, 46.15; H, 5.53; N, 30.75. Found: C, 45.85; H, 5.18; N, 30.76.

Ethyl *cis*-5-Dimethyl-1,3,4-oxadiazole-2-acrylate (9).—A mixture of 5 g of **7** and 0.29 g of hydroquinone in 100 ml of acetic anhydride was refluxed for 1 hr. The cooled reaction solution was poured into 500 ml of ice water and stirred until a clear solution resulted. The solvents were removed on the rotary evaporator and the residue was extracted into $CHCl_3$. After the extract was dried (Na_2SO_4) and the solvent was removed, a yellow oil remained that crystallized on standing. Recrystallization from EtOH–H_2O produced 3 g of **9**, mp 47–53°. Recrystallized several times for analysis, the pure compound melted at 58–59°: nmr ($CDCl_3$) normal ethyl ester pattern, δ 2.57 (s, 3 H, oxadiazole CH_3), 2.60 (d, 3 H, vinyl CH_3), 6.70 (m, 1 H, vinyl H); ir (Nujol) no NH, 1730 (C=O), 1650 (C=C), 1580 and 1540 cm^{-1} (C=N).

Anal. Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.16; N, 14.28. Found: C, 55.34; H, 6.06; N, 14.05.

Reaction of Aluminum Azide with Ethyl *cis*-3-Cyanocrotonate.—Ethyl *cis*-3-cyanocrotonate prepared with the trans compound above was treated on a 0.8-mol scale just as was the trans isomer except that it was refluxed for 42 hr. The brown oil that remained after removal of the THF was taken up in 300 ml of H_2O and 300 ml of $CHCl_3$. A crystalline solid separated; so the mixture was filtered and the solid was washed with H_2O and $CHCl_3$. Dried in air, it weighed 13.1 g, mp 202–204°. Recrystallization for analysis from acetone or from EtOH gave 8-methyltetrazolo[1,5-*c*]pyrimidin-5(6*H*)-one (**11**): mp 210–211°; nmr (DMSO-d_6) δ 2.28 (d, 3 H, vinyl CH_3), 7.55 (m, 1 H, vinyl H); ir (Nujol) 3260–3180 (NH), 1790 (shoulder), 1770, 1730, 1640, 1550 cm^{-1} (C=O, C=C, C=N, N=N); mass spectrum m/e 151 (M^+), 122 [$(M - N_2 - H)^+$], 68 [$(C_3H_4N_2)^+$]; uv (H_2O) max 252 mμ (ϵ 9050), shoulder at 275.

Anal. Calcd for $C_5H_5N_5O$: C, 39.73; H, 3.33; N, 46.34. Found: C, 39.40; H, 3.36; N, 46.26.

The two-phase filtrate layers were separated and the aqueous layer was washed twice with $CHCl_3$. The combined $CHCl_3$ layers were dried (Na_2SO_4) and filtered, and the solvent was removed under reduced pressure. The residue was a brown oil containing fine crystals which after standing several days were collected, washed with $CHCl_3$ and CCl_4, and dried to yield 2.88 g of 1-(2-cyanopropenyl)tetrazolin-5(4*H*)-one (**12**), mp 168–170° dec. A sample recrystallized for analysis from acetone–$CHCl_3$ melted at 186–187°: nmr (acetone-d_6) δ 1.43 (d, 3 H, vinyl CH_3), 6.48 (m, 1 H, vinyl H); ir (Nujol) 3100 (NH), 2220 (C=N), 1740, 1660 cm^{-1} (C=O, C=C).

Anal. Calcd for $C_5H_5N_5O$: C, 39.73; H, 3.33; N, 46.34. Found: C, 39.31; H, 3.36; N, 45.79.

1-(2-Methylpropenyl)tetrazolin-5(4*H*)-one (14).—To a suspension of 66.7 g of $AlCl_3$ and 146 g of NaN_3 in 1 l. of cold anhydrous THF was added 64.1 g of ethyl β,β-dimethylacrylate (**13**) and the resulting mixture was heated to reflux under nitrogen for 43 hr. To the cooled reaction was added 700 ml of 6 *N* HCl and the reaction solution was filtered from the inorganic salt. The THF was removed from the filtrate under reduced pressure and the remaining solution was extracted three times with $CHCl_3$. The combined $CHCl_3$ layers were washed twice with saturated NaCl solution, dried (Na_2SO_4), and evaporated to yield a light yellow oil weighing 51.6 g. Crystals formed on standing and were filtered, washed with hexane, and dried, yield 7.78 g. A second crop weighed 9.1 g. These were combined (24% yield) and recrystallized from 50 ml of $CHCl_3$–hexane to give 15.3 g of 1-(2-methylpropenyl)tetrazolin-5(4*H*)-one (**14**), mp 69–71°. A sample recrystallized for analysis from the same solvents melted at 72–73°: nmr (acetone-d_6) δ 1.82 and 1.88 (each d, 3 H, vinyl CH_3), 6.29 (m, 1 H, vinyl H); ir (Nujol) 3200–3000 (NH), 1740 (C=O), 1700 cm^{-1} (C=C).

Anal. Calcd for $C_5H_8N_4O$: C, 42.85; H, 5.75; N, 39.98. Found: C, 42.79; H, 5.73; N, 40.58.

Reaction of Aluminum Azide with Ethyl *o*-Cyanobenzoate (15).—A mixture of 0.4 mol of ethyl *o*-cyanobenzoate,[2] 0.4 mol of $AlCl_3$, and 1.78 mol of NaN_3 in 1 l. of anhydrous THF was refluxed for 45 hr under N_2 as before. The precipitate formed by addition of 600 ml of 6 *N* HCl was washed with THF and then partially dissolved in 500 ml of H_2O. The residual H_2O-insoluble crystalline solid, 3.7 g, was pure **19**. The THF acid filtrate was evaporated and the solid suspended in the remaining aqueous phase was collected, washed with H_2O and $CHCl_3$, and dried in air to yield 20.0 g of a mixture of **19** and **16** as shown by tlc.[14]

The H_2O layer was extracted twice more with 200-ml portions of

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[14] Solvent system used was the top phase of an equilibrated mixture of 4 parts ethyl acetate, 1 part *n*-PrOH, and 2 parts H_2O.

$CHCl_3$ and the combined $CHCl_3$ layers were washed two times with 100 ml of H_2O, dried (Na_2SO_4), and evaporated to leave a solid residue weighing 52.4 g. Acetone (70 ml) was added and on refrigeration, 12.6 g of crystals formed which was a mixture of starting material **15**, **19**, and **17**. The various components were obtained in a pure form, but were not quantitatively isolated by fractional crystallization. The unreacted starting material had the highest solubility in benzene and could be removed by trituration with that solvent. Compound **19** could be recrystallized from large volumes of acetone or EtOH, while compound **16** could be purified by recrystallization from acetone or EtOH after most of the **19** was removed. Compound **17** was obtained by careful fractionation of the mother liquors and could be recrystallized from benzene. Compound **18** could not be obtained in a pure form from this mixture, but was isolated from the product resulting when methyl *o*-cyanobenzoate was used as a substrate.

The following amounts of pure materials were isolated: **19**, 15.8 g; **16**, 7.56 g; and **17**, 0.66 g. Tlc showed larger amounts of starting material and **16**, **17**, **18**, and some **19** present as complex mixtures in the residues which totaled 48 g. Of this 48 g about 35 g was unreacted starting cyanobenzoate.

Tetrazolo[1,5-*c*]quinazolin-5(6*H*)-one (19) had mp 274.5–275.5° dec; nmr (DMSO-d_6) δ 8.3–7.2 (m, 4 H, aromatic H); ir (Nujol) 3300 and 3250 (NH), 1770, 1730 (C=O), 1640, 1600, 1560, 1510 cm^{-1}; mass spectrum *m/e* 187 (M^+), 159 ($M^+ - N_2$), 131 ($M^+ - N_2 - CO$), 104 ($M^+ - C_2HN_3O$); uv (methanol) max 306 mμ (ϵ 4900), max 250 (14,100), max 219 (40,300); uv (alkaline methanol) max 326 mμ (ϵ 4900), max 271 (7500), max 207 (371,100).

Anal. Calcd for $C_8H_5N_5O$: C, 51.34; H, 2.69; N, 37.42. Found: C, 51.28; H, 2.84; N, 37.03.

1-[*o*-(Tetrazol-5-yl)phenyl]tetrazolin-5(4*H*)-one (16) had mp 262–263° dec; nmr (DMSO-d_6) δ 8.2–7.6 (m, 4 H, aromatic H); ir (Nujol) 3100–2700 (NH), 1690 (C=O), 1610, and 1555 cm^{-1}. Titration with NaOH showed two acidic protons and gave mol wt 230.6 compared to the theoretical value of 230.2.

Anal. Calcd for $C_8H_6N_8O$: C, 41.74; H, 2.63; N, 48.68. Found: C, 42.05; H, 2.82; N, 50.01.

Ethyl *o*-(5-tetrazolyl)benzoate (17) had mp 141–142°; nmr (acetone-d_6) δ 1.20 (t, 3 H, ester CH_3), 4.25 (q, 2 H, ester CH_2), 8.1–7.5 (m, 4 H, aromatic); ir (Fluorolub/Nujol) 3000–2600 (NH), 1725 (C=O), 1275 (C=C), 1090, and 1070 cm^{-1} (tetrazole).

Anal. Calcd for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68. Found: C, 55.09; H, 4.63; N, 26.07.

***o*-(5-Oxo-2-tetrazolin-1-yl)benzonitrile (18).**—This material was obtained pure from work-up of an exactly identical reaction of methyl *o*-cyanobenzoate with $Al(N_3)_3$. Compounds **19** and **16** were isolated as before with identical work-up, but no material corresponding to the methyl analog of the tetrazole ester **17** could be detected. Pure **18** melted at 146–148°: ir (Nujol) 3200–3000 (NH), 2225 (CN), 1740, 1720, 1700 (C=O), 1610, 1580, 1570, 1540 cm^{-1}.

Anal. Calcd for $C_8H_5N_5O$: C, 51.34; H, 2.69; N, 37.42. Found: C, 51.39; H, 2.70; N, 37.94.

Alkaline Hydrolysis of 19.—A solution of 2 g of **19** dissolved in 40 ml of 1 *N* NaOH was warmed on the steam bath for 1 hr. The resulting yellow solution was cooled and diluted to 60 ml. It was carefully acidified to pH 6 with 6 *N* HCl. A vigorous evolution of CO_2 was observed and near pH 6 the solution turned cloudy and needle-like crystals of **21** began to form. The mixture was filtered and the crystals, washed with water and dried, weighed 0.6 g. Further acidification to pH 3 caused more crystallization and another 0.59 g of **21** was isolated. The combined crystals were recrystallized from $CHCl_3$. The melting point after 2 hr drying under reduced pressure was 143–144° (lit.[10] mp 140–144°); ir (Nujol) 3500–3300 (NH), 1620, 1560 cm^{-1}; mass spectrum *m/e* 161 (M^+). This material proved to be identical with that produced from anthranilonitrile below.

5,6-Dihydro-5,5-dimethyltetrazolo[1,5-*c*]quinazoline (23).—To a mixture of 2 g of **21** in 30 ml of $CHCl_3$ was added 5 ml of acetone and the solution was boiled until crystals formed in the hot solution. Filtered and dried in air, the crystals of **23** weighed 1.48 g, mp 202–204°. Mixture melting point with **23** prepared from **21** obtained from anthranilonitrile was undepressed; nmr (acetone-d_6) δ 1.80 (s, 6 H, CH_3) 8.0–7.0 (m, 4 H, aromatic); ir (Fluorolub/Nujol) 3340 (NH), 1630 (C=N), 1590, 1540, 1500 cm^{-1}; mass spectrum *m/e* 201 (M^+).

Anal. Calcd for $C_{10}H_{11}N_5$: C, 59.69; H, 5.51; N, 34.80. Found: C, 59.85; H, 5.66; N, 34.92.

5-(*o*-Aminophenyl)tetrazole (21) from Anthranilonitrile.—A mixture of 59.1 g (0.5 mol) of anthranilonitrile, 42.3 g (0.65 mol) of NaN_3, 0.65 g (0.65 mol) of NH_4Cl, and 0.65 g of LiCl in 250 ml of DMF was heated and stirred at 125° for 16 hr. The reaction was filtered hot, the solid was washed with a little solvent, and the DMF was removed under reduced pressure. The residue was poured into 750 ml of water, and a yellow oil separated which was extracted into three portions of $CHCl_3$. The aqueous layer was acidified to pH 3–4 and a yellow crystalline solid separated. It was filtered, washed with water, and dried in air and weighed 15 g (**21**). The $CHCl_3$ extracts crystallized on standing, yielding another 18.7 g of **21**. The product could be recrystallized from $CHCl_3$ and proved identical with the **21** isolated from **19**.

Ethyl *o*-Tetrazol-5-ylcarbanilate (24).—To a solution of 10 g of 5-(*o*-aminophenyl)tetrazole (**21**) in 20 ml of absolute EtOH was added about 5 g of K_2CO_3 and then, with stirring, 10 g of ethyl chloroformate. The reaction solution warmed and foamed. When the effervescence ended and no further warming was apparent (5–10 min) the reaction was filtered from the insoluble salt. The filtrate was diluted to 250 ml with H_2O and a white, crystalline precipitate formed. Filtered, washed with H_2O and partially dried, it was redissolved in 75 ml of EtOH. H_2O was added carefully to the point of incipient precipitation and crystals of **24** separated. Filtered, washed with H_2O–EtOH, and dried in air, the crystals weighed 12.5 g, mp 140–141°. Recrystallized for analysis from EtOH–H_2O, the compound lost solvent at 120°, melted at 147–150°, bubbled at 180°, recrystallized at 220°, and remelted at 265°: nmr (DMSO-d_6) δ 1.40 (t, 3 H, ethyl CH_3), 4.28 (q, 2 H, ethyl CH_2), 8.4–7.0 (m, 4 H, aromatic); ir (Nujol) 3200 (NH), 1710 (shoulder), 1700 (C=O), 1620, 1600, 1550 cm^{-1}.

Anal. Calcd for $C_{10}H_{11}N_5O_2$: C, 51.50; H, 4.75; N, 30.03. Found: C, 51.44; H, 4.93; N, 30.02.

Pyrolysis of Carbanilate 24.—Carbanilate **24** (5 g) was heated to 200°, by which time the resulting melt was bubbling and had turned brick red. The heating bath was maintained at 195° for about 15–20 min until the melt suddenly solidified. The reaction was cooled and triturated with 30 ml of EtOH. The insoluble solid was collected on a filter, washed with EtOH, and dried to leave 1.67 g (42%) of a fine yellow solid, mp 271–272°. Recrystallized from 900 ml of hot acetone, filtered, and concentrated to 100 ml, the crystals that formed weighed 0.96 g and were identical with the previously isolated **19** from the aluminum azide reaction in every respect.

Synthesis of 19 *via* the Reaction of Phosgene with 21.—Phosgene was bubbled through a clear solution of 3.2 g of **21** and 4.0 g of Et_3N in 150 ml of CH_2Cl_2 for 5 min. A precipitate formed after 2 min but the reaction was stirred for a total of 20 min, then treated with excess dilute HCl and filtered, and the solid was washed with H_2O. The damp solid was dissolved in 900 ml of hot acetone, concentrated to 300 ml, diluted to 400 ml with H_2O, and allowed to crystallize. The product **19** weighed 2.4 g (64%) after filtration and drying, mp 273–274°, identical with material obtained by other methods above.

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