Higher Order Dipolar Cycloaddition Reactions of Diazoazoles with Electron-Rich Dipolarophiles

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A study of the cycloaddition behavior of a series of diazoazoles with electron-rich dipolarophiles has been carried out. 3-Diazo-4-methyl-5-phenylpyrazole readily reacts with ynamines, enamines, and vinyl ethers to give 1,7-cycloadducts. The trisubstituted olefinic dipolarophiles, 1-(diethylamino)-2-methyl-1-propene and 1-ethoxy-2-methyl-1-propene, were also found to react regiospecifically with the above diazopyrazole to give the anticipated derivatives of the dihydropyrazolo[5,1-*c*][1,2,4]triazine ring system. The detection and isolation of two discrete, sequential intermediates in the reaction of 1,1-dimethoxyethylene with diazopyrazole is clearly inconsistent with initial union via 1,7-dipolar cycloaddition. The mechanism advanced to account for the formation of the pyrazolotriazine involves an initial 1,3-dipolar cycloaddition followed by a [1,5]-sigmatropic shift. Cycloaddition reactions of the closely related diazoindazole and 3-diazo-5-phenyl-1,2,4-triazole systems were also carried out. The products isolated from the reactions of each of these diazoazoles with electron-rich olefins formally correspond to those expected for a 1,7-union of the dipole and dipolarophile. Equally as plausible, however, is the possibility that the cycloadducts are formed from an initial 1,3-cycloaddition followed by a subsequent rearrangement.

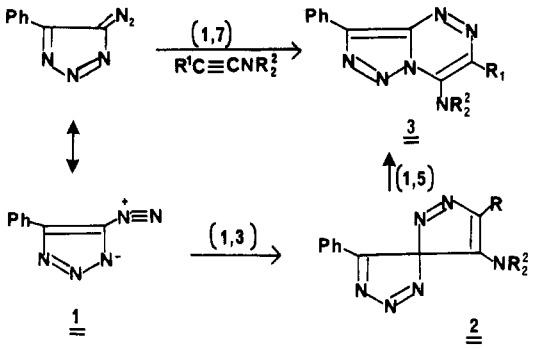
1,3-Dipolar cycloaddition is a thermally allowed $_{\pi}4_{s} + _{\pi}2_{s}$ process involving a total of six electrons.[1-3] This reaction has been extensively utilized for the synthesis of a vast number of structurally diverse heterocyclic ring systems.[4-6] Higher order dipolar cycloadditions are also known and occur when the dipolar system contains more than four π electrons.[7-18] Selection rules for higher order dipolar cycloadditions are similar to those of the corresponding isoelectronic polyenes and are allowed in the suprafacial–suprafacial mode when the total number of participating electrons is $4n + 2$.[19,20] The wide variety of available dipoles makes higher order dipolar cycloaddition a potentially attractive route for the synthesis of a variety of heterocyclic systems.[21] It is therefore perhaps surprising that relatively little systematic study has been reported in this area.

Aromatic diazoazoles are systems which are ideally suited to a study of the various possible modes of extended dipolar cycloaddition.[7-9] The reactions of derivatives of the diazocyclopentadiene and certain diazoazole ring systems can be formally classified as proceeding via an initial 1,3 or 1,7 union of the component dipole and dipolarophile.[13-17] Whereas diazocyclopentadienes react almost exclusively by 1,3-addition to acetylenes,[13-16] the behavior of azaheterocyclic analogues toward various substrates is much less obvious although such reactions appear to give rise to products resulting from 1,7-cycloaddition. For example, the reactions of the diazo-1,2,3-triazole **1** with a series of ynamines afford the triazolo-[5,1-*c*][1,2,4]triazines **3**.[7] While this ring system formally corresponds to that expected of a concerted 1,7-cycloaddition, an alternate route involving initial 1,3 union followed by a [1,5]-sigmatropic shift is equally plausible (Scheme I). In this paper we describe the results of a study of the profiles of reactivity of several relatively easily accessible diazoazole systems toward cycloaddition with a selection of electron-rich dipolarophiles and present evidence which, in one instance, lends support to the latter mechanism.[22]

Results and Discussion

As our first model we chose to investigate the cycloaddition behavior of 3-diazo-4-methyl-5-phenylpyrazole **4**. Cycloaddition reactions of diazopyrazole **4**, prepared by neutralization of the diazonium pyrazole precursor,[23] with

Scheme I



various dipolarophiles were typically performed in methylene chloride solutions and were monitored qualitatively by the disappearance of the diazo compound according to both infrared and TLC analysis. The reaction of **4** at 0 °C with an excess of 1-(diethylamino)propyne furnished (83%) the yellow crystalline pyrazolo[5,1-*c*][1,2,4]triazine **5**. The structure of the cycloadduct was assigned on the basis of its spectral data and by analogy to the fused

* Alexander von Humboldt Senior Scientist, 1983–1984.

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(23) We thank Professor Harold Shechter for providing us with a detailed procedure for the preparation of diazopyrazole **4**.

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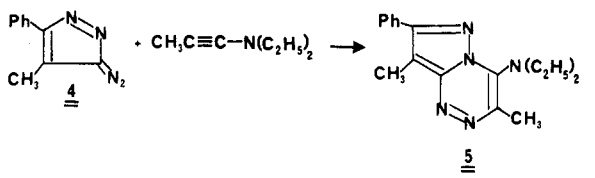
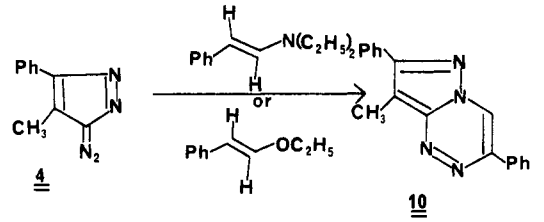


azolo[5,1-*c*][1,2,4]triazine system previously reported as the product of cycloaddition of ynamines to various monocyclic and fused diazoazoles.[7]

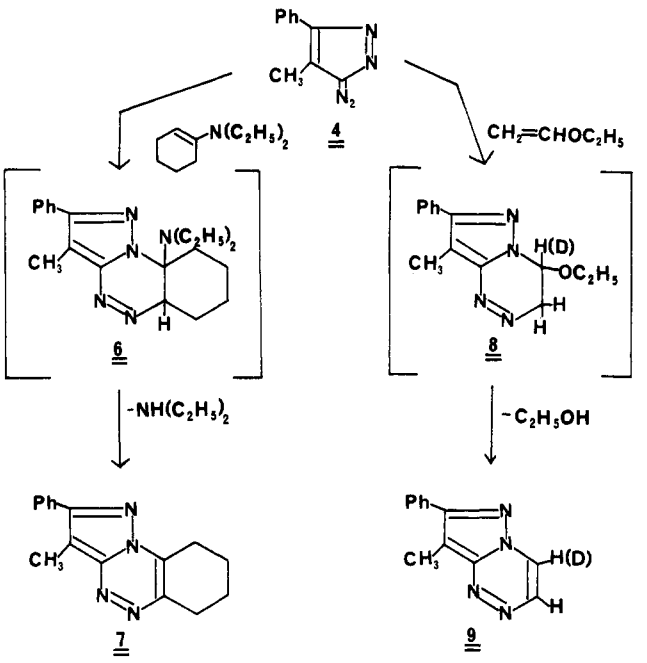
From the reaction of diazopyrazole **4** with 1-(diethylamino)cyclohexene, a yellow crystalline product was isolated in good yield by rapid chromatography over neutral alumina and characterized as the tetrahydropyrazolo[5,1-*c*][1,2,4]naphthotriazine derivative **7** (Scheme II). The absence of the diethylamino function was demonstrated prior to chromatographic purification. The low-temperature (−60 °C) addition of ethyl vinyl ether to the diazopyrazole **4** furnished a dark product mixture from which the bright yellow crystalline pyrazolo[5,1-*c*][1,2,4]triazine **9** could be isolated (54%) by chromatography over neutral alumina. Again the loss of the elements of ethanol was shown by NMR spectroscopy to have taken place prior to purification. The well-defined one-proton doublets (J = 4.8 Hz) for triazine **9** were observed at δ 8.38 and 8.63 and have been assigned to the aromatic ring protons H_3 and H_4, respectively. Precedence for such assignments stems from chemical shift data recorded for related azaheteroaromatic systems possessing a saturated bridgehead nitrogen atom.[24] The proton attached to the α-carbon (e.g., C_4–H) is consistently observed at lower fields than the proton bound to the β-carbon (e.g., C_3–H). Under identical conditions the addition of 1-deuterioethyl vinyl ether afforded a crystalline 1:1 adduct, the ^{1}H NMR spectrum of which exhibited only a single resonance at δ 8.38. These data are clearly consistent with deuterium incorporation at C_4 of the pyrazolotriazine nucleus. The formation of each of the pyrazolotriazine cycloadducts can be conveniently pictured as proceeding via an initial 1,7-dipolar cycloaddition followed by aromatization made facile by the ready β elimination of diethylamine to give **7** and ethanol to give **9**. Isolation of the 4-deuterio derivative (**9**-*d*) as the sole addition product is also in accord with expectation from a qualitative consideration of frontier MO theory.[14]

From the reaction of both β-(diethylamino)styrene and β-ethoxystyrene with diazopyrazole **4** at ambient temperature, only 3,7-diphenyl-8-methylpyrazolo[5,1-*c*]-[1,2,4]triazine (**10**) could be isolated in yields exceeding

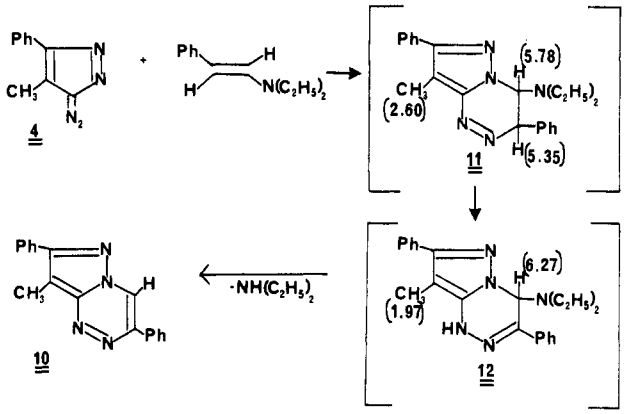


90%. Under these conditions, the cycloadditions were sufficiently slow to permit easy detection of discrete intermediates. Equimolar proportions of **4** and β-(diethylamino)styrene were mixed in benzene-d_6, and the progress of the reaction was monitored by NMR spectroscopy. After 6 min, both starting materials had been consumed, and a new species still retaining the diethylamino moiety was formed (Scheme III). In addition to the pyrazole methyl resonance at δ 2.60, two one-proton doublets (J = 4.0 Hz) centered at δ 5.35 and 5.78 were observed. At the

Scheme II



Scheme III



expense of this initial intermediate **11**, a second transient species also retaining the amine substituent was formed which, after 1 h, comprised ca. 50% of the product mixture. This latter intermediate (i.e., **12**) displayed singlet resonances at δ 1.97 and 6.27. After the mixture was stirred for an additional 5 h, the only resonances remaining were those characteristic of pyrazolotriazine **10**. To account for this stepwise sequence of rearrangements, we suggest the profile of reactivity outlined in Scheme III.

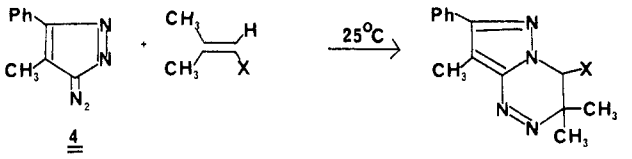
It is interesting to note that only one transient species from the stoichiometric interaction of diazopyrazole **4** with β-ethoxystyrene could be detected by NMR spectroscopy. After reaching a maximum concentration after 1 h, this intermediate displayed the pyrazolo methyl singlet at δ 2.66 and two one-proton multiplets at δ 5.52 and 6.07. Resonances attributable to the familiar pyrazolotriazine **10** were the only signals present after a total elapsed time of 2 h. An intermediate species with a structure analogous to that suggested for **11** seems reasonable.[25] In this case elimination of ethanol is faster than the 1,3 hydrogen shift.

The trisubstituted olefinic dipolarophiles 1-(diethylamino)-2-methyl-1-propene and 1-ethoxy-2-methyl-1-

(24) Daunis, J.; Lopez, H.; Maury, G. *J. Org. Chem.* **1977**, *42*, 1018.

(25) The possibility still remains that intermediate **11** might be a spiro compound formed by 1,3-dipolar cycloaddition. A similar doubt might also be raised about the analogous intermediate in the addition of β-ethoxy styrene to diazopyrazole **4**.

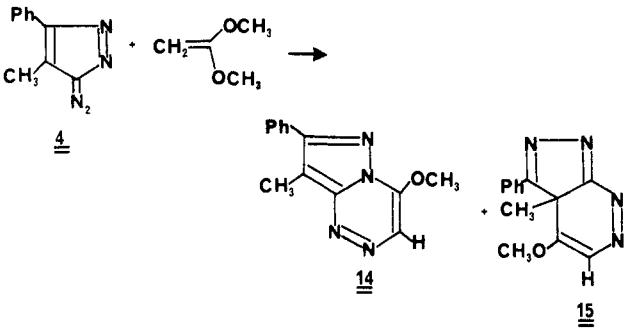
propene were also found to react regiospecifically with diazopyrazole 4 to give the anticipated derivatives of the dihydropyrazolo[5,1-c][1,2,4]triazine ring system 13. The



13a; X=N(C2H5)2
13b; X=OC2H5

presence of any transient species could not be detected when the cycloadditions were monitored by NMR spectroscopy. Interestingly, the singlet resonances due to each of the geminal methyl substituents in each of the cycloadducts were separated by 0.7–0.8 ppm; the axially disposed methyl is evidently shielded by the underside (syn) N or O lone-pair electrons. Here again the formation of the cycloadducts can be most conveniently rationalized as arising from a simple 1,7-dipolar cycloaddition or by a 1,3-dipolar addition followed by rearrangement of the initial spiro adduct.

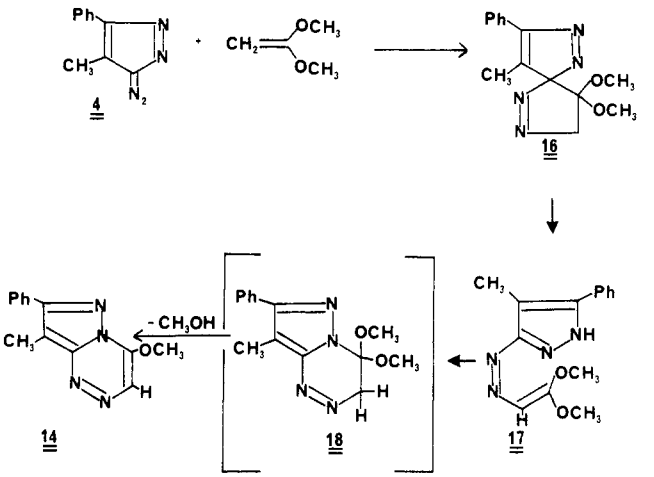
From the thermal reaction of diazopyrazole 4 with 1,1-dimethoxyethylene, two crystalline adducts were isolated by preparative thick-layer chromatography. The major species (45%), to which the 4-methoxypyrazolo[5,1-c]-[1,2,4']triazine structure (14) has been assigned, exhibits



characteristic signals at δ 2.71, 4.31, and 8.42. The minor component (3%) from the reaction was an amorphous tan solid which was assigned as 7-methoxy-7a-methyl-1-phenyl-4*H*,7a*H*-pyrazolo[3,4-c]pyridazine (15) on the basis of its spectral characteristics. Specifically, the singlets at δ 2.46, 4.28, and 7.39 have been assigned to the methyl, methoxyl, and olefinic protons, respectively. The nonaromatic pyrazolopyridazine formally corresponds to the adduct expected of the alternative mode of 1,7-cycloaddition, i.e., cyclization at C_4 rather than at N_2 of the pyrazole system of compound 4.

A study by NMR spectroscopy of this particular cycloaddition reaction as a function of time established the presence of two discrete transient intermediates leading to the formation of 14. Moreover, these species could actually be isolated and characterized. The first transient (16, Scheme IV) was clearly discernible approximately 90 s after mixing and, upon standing for 40 min, isomerized to a second transient (17) which itself slowly rearranged ($t_{1/2}$ = 10 min at 35 °C) to the stable methoxypyrazolotriazine 14. The assignments of structure to each of these intermediates have been deduced principally from an examination of the respective NMR spectra. For the initial intermediate 16, the appearance of a methylene singlet at δ 4.51 together with a six-proton singlet at δ 3.36 is consistent with the spiro 3*H*-pyrazole adduct 16 which can be regarded as being formed from an initial 1,3-dipolar cycloaddition. Support for the structure of the 1,2-diaza

Scheme IV

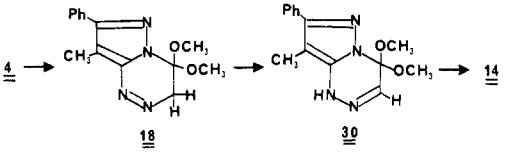


1,3-diene system (i.e., 17) stems from the appearance of a one-proton singlet at δ 6.53, an exchangeable one-proton signal at δ 9.69, and two methoxyl groups at δ 3.31 and 3.46. Conversion of 17 to the stable aromatic heterocycle 14 is believed to proceed by way of 18 which aromatizes by elimination of methanol.[26]

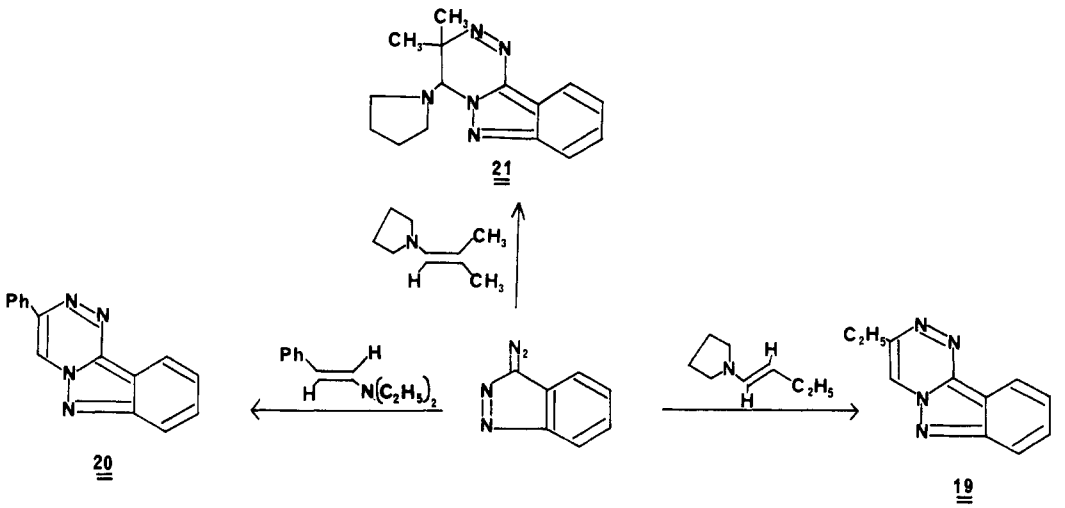
As a continuation of our work in this area we have also studied the cycloaddition behavior of diazoindazole with several enamines. By analogy with the results encountered with diazopyrazole 4, the reaction of diazoindazole with 1-pyrrolidinyl-1-butene or β-(diethylamino)styrene afforded 3-ethyl- and 3-phenyl-1,2-4-triazino[3,4-b]indazoles 19 and 20, respectively (Scheme V), in excellent yields. Under similar conditions the reaction of diazoindazole with the trisubstituted enamine, 1-pyrrolidinyl-2-methyl-1-propene, afforded a 1:1 cycloadduct whose structure was assigned as dihydrotriazino[4,3-b]indazole 21. Geminal methyl and methine resonances observed for 21 at δ 0.71, 1.71, and 4.92 are very similar with those exhibited by pyrazolotriazines 13a (δ 1.12, 1.81, and 4.83) and 13b (δ 1.05, 1.92, and 5.02).

Cycloaddition reactions of the diazopyrazole and diazoindazole systems so far described have given rise to products which result from ultimate cycloaddition upon that nitrogen atom immediately flanking the diazoalkane moiety. Reactions with diazoazole systems bearing two different flanking nitrogen atoms might therefore be expected to display reactivity characteristic of both modes of addition. As a representative of this class of diazoazoles, the reactions of 3-diazo-5-phenyl-1,2,4-triazole (22) with several electron-rich olefins were investigated. The diazotriazole 22 was prepared by low temperature neutralization of the diazonium triazole precursor and was extracted directly into cold methylene chloride. Treatment

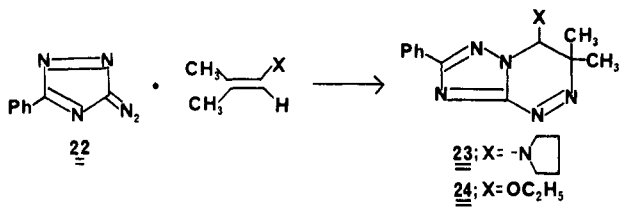
(26) One of the reviewers has suggested that structure 18 corresponds to the initially formed cycloadduct which, in turn, undergoes a subsequent tautomerization to structure 30 prior to the loss of methanol. Although this is not an unreasonable possibility, we still prefer the sequence proceeding through intermediates 16 and 17. The δ 6.53 chemical shift found for 17 is not consistent with the imine proton of structure 30. Moreover, structure 30 should have two equivalent methoxy groups. In fact, the second formed intermediate shows two nonequivalent methoxy groups at δ 3.31 and 3.46 in CCl_4 which is also inconsistent with structure 30. In addition, one would expect that structure 18 would rapidly undergo loss of methanol to give 14.



Scheme V



of **22** with 1-pyrrolidinyl-2-methyl-1-propene or 1-ethoxy-2-methylpropene gave rise to the respective dihydro-1,2,4-triazolo[5,1-*c*][1,2,4]triazine cycloadducts **23** and **24**.

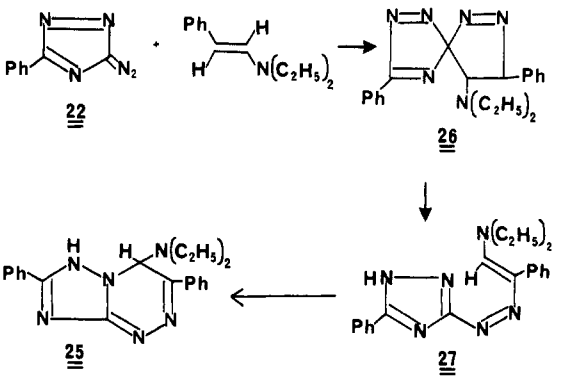


NMR resonances characteristic of those observed for cycloadducts **13a,b** and **21** were also recorded for adducts **23** (δ 1.12, 1.86, and 5.19) and **24** (δ 1.13, 1.94, and 5.19). Assignment of these structures as derivatives of the 1,2,4-triazolo[5,1-*c*][1,2,4]triazine system rather than the alternative 1,2,4-triazolo[3,4-*c*][1,2,4]triazine system is also based on analogy to observations reported by both Ege[7] and Tennant.[27,28]

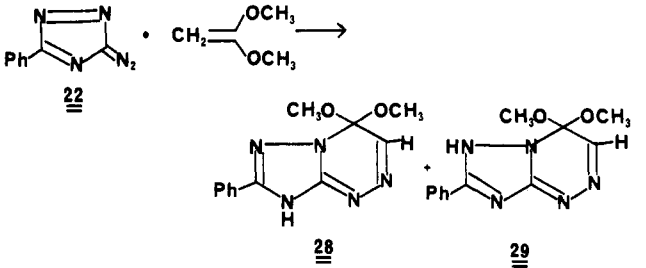
Unlike the reactions of the diazoheterocycles **4** and **18**, the addition of β-(diethylamino)styrene to diazotriazole **22** gave rise to a single compound (65%) possessing the stoichiometry of a 1:1 cycloadduct which still retains the diethylamino residue. The NMR spectrum showed two one-proton singlets at δ 6.40 and 12.55, the latter being exchanged with D_2O washing. While it is difficult to make an unequivocal structure assignment from this spectrum, it seems reasonable to assume that the cycloadduct is 4,6-dihydro-1,2,4-triazolo[5,1-*c*][1,2,4]triazine (**25**). The origin of this material is conveniently accounted for as shown in Scheme VI. Thus, one can envisage the formation of **25** as proceeding by an opening of the initially produced 1,3-dipolar cycloadduct **26** to give the 1*H*-1,2,4-triazole **27**. This material, in turn, undergoes a 6π electrocyclization to the fused heterocycle **25**.

One additional cycloaddition reaction from which characterizable products could be isolated was that of diazotriazole **22** with 1,1-dimethoxyethylene. When performed at temperatures ranging from −78 to +30 °C, a colorless crystalline substance was isolated in almost quantitative yield. The stoichiometry of this compound as a 1:1 adduct still retaining the elements of methanol was confirmed from its analytical and spectral data. The NMR

Scheme VI



data indicates that the product is a 7:3 mixture of tautomers, subsequently shown to be inseparable by chromatography. The appearance of two pairs of singlets at δ 3.16 and 6.68 and at δ 3.41 and 6.80, each in the ratio of 6:1, is suggestive of a mixture of two structurally similar compounds. Only a single broad resonance was, however, observed at δ 13.0. Given these NMR data, the most plausible structures which can be assigned are those of the two dihydro-1,2,4-triazolo[5,1-*c*][1,2,4]triazines **28** and **29**.



Upon thermolysis in benzene at temperatures between 100–120 °C, one of the adducts was shown to rearrange smoothly to that species formerly present as the minor (30%) component of the reaction mixture. While it is impossible to make an unequivocal structural assignment of this more stable isomer, it is tempting to suggest that the compound is in fact the more extensively conjugated 4,6-dihydro derivative **29** rather than the 4,8-dihydro tautomer **28**.[29]

(27) Tennant, G., Vevers, R. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 421.

(28) Gray, E. J.; Stevens, M. F. G.; Tennant, G.; Vevers, R. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1496.

(29) It is somewhat surprising that interconversion between tautomers **28** and **29** is so slow. Another possibility is that the less stable isomer is actually the adduct derived from reversible addition to the nitrogen atom in the 5-position of the triazole ring (i.e., 1,2,4-triazolo[3,4-*c*] system).

All of the products isolated from the reactions of each of the diazoazole systems formally correspond to those expected of an $8_{\pi s} + 2_{\pi s}$ [1,7] union of the dipole with the dipolarophile. Equally as plausible, however, is the possibility that the 1:1 adducts are formed from an initial 1,3-cycloaddition, the products of which undergo subsequent rearrangement–elimination processes to give the observed fused heterocycles. The regiospecificity with which each of the reactions takes place is in accord with expectation for either a 1,3 or an extended 1,7 interaction.[14] The detection and isolation of two discrete, sequential intermediates (16 and 17) in the reaction of 1,1-dimethoxyethylene with diazopyrazole 4 is clearly inconsistent with initial union via 1,7-dipolar cycloaddition. The mechanism advanced to account for the stepwise formation of pyrazolotriazine 14 is that presently considered to be the most plausible.

Experimental Section[30]

Preparation of 3-Diazo-4-methyl-5-phenylpyrazole (4). To a stirred suspension containing 3.46 g of 3(5)-amino-4-methyl-5(3)-phenylpyrazole[31] in 25 mL of concentrated hydrochloric acid was added a solution containing 1.50 g of sodium nitrite in 5 mL of water over a 10-min period, keeping the temperature under 5 °C. The mixture was allowed to stir for 20 min at 0 °C, and then 50 mL of ice–water was added. The mixture was filtered and washed with 30 mL of cold water to give 2.72 g (62%) of 4-methyl-5(3)-phenyl-3(5)-pyrazolediazonium chloride as a light yellow solid: mp 157 °C dec; IR (KBr) 3150, 2670, 2250, 1579, 1483, 1460, 1437, 1380, 1306, 1280, 1220, 1174, 1102, 928, 758, 680 cm^{-1}.

To a stirred suspension containing 2.55 g of the above diazonium chloride in 50 mL of methylene chloride was added 20 mL of a 10% sodium carbonate solution at 0 °C. The mixture was stirred for 10 min, the yellow organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic layer was dried over sodium sulfate, and the solvent was removed under reduced pressure at 0 °C in the dark to give 1.87 g (88%) of 3-diazo-4-methyl-5-phenylpyrazole (4) as an explosive yellow solid: mp 99 °C dec; IR (KBr) 2160, 1372, 1102, 928, 755, 680 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.38 (s, 3 H), 7.2–7.5 (m, 3 H), 7.6–7.8 (m, 2 H). Anal. Calcd for $C_{10}H_8N_4$: C, 65.20; H, 4.38; N, 30.42. Found: C, 65.06; H, 4.41; N, 30.37.

Reaction of 3-Diazo-4-methyl-5-phenylpyrazole (4) with 1-(Diethylamino)cyclohexene. A mixture containing 569 mg of 1-(diethylamino)cyclohexene and 712 mg of diazopyrazole 4 in 20 mL of chloroform was stirred at 25 °C for 4 h. The solvent was removed under reduced pressure, and the resulting residue was purified by chromatography through a neutral alumina column with methylene chloride as the eluent to give 412 mg (42%) of 10-methyl-9-phenyl-3,4,5,6-tetrahydropyrazolo[5,1-*c*][1,2,4]benzotriazine (7) as yellow needles: mp 146–147 °C; IR (KBr) 2975, 2950, 1538, 1528, 1466, 1381, 1262, 1008, 764, 685 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.9–2.2 (m, 4 H), 2.73 (s, 3 H), 3.2–3.4 (m, 4 H), 7.4–7.7 (m, 3 H), 7.8–8.0 (m, 2 H); UV (ethanol) 268 nm (ϵ 39 600), 306 (3400), 341 (3200), 376 (2900); mass spectrum, *m/e* 264 (M^+,base), 156, 115, 104, 91, 77. Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.64; H, 6.13; N, 21.17.

Reaction of 3-Diazo-4-methyl-5-phenylpyrazole (4) with 1-(Diethylamino)propyne. A mixture containing 353 mg of 1-(diethylamino)propyne and 486 mg of 3-diazo-4-methyl-5-phenylpyrazole (4) in 20 mL of methylene chloride was stirred at 0 °C for 30 min. Removal of the solvent left a dark residue which was chromatographed on a neutral alumina column with methylene chloride as the eluent to give 620 mg (83%) of 4-(diethylamino)-3,8-dimethyl-7-phenylpyrazolo[5,1-*c*][1,2,4]triazine (5) as yellow needles: mp 145–146 °C; IR (KBr) 2975, 2955, 1538, 1528, 1466, 1381, 1262, 1128, 685 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 0.85 (t, 6 H, J = 8.0 Hz), 2.73 (s, 3 H), 2.79 (s, 3 H), 3.66 (q, 4 H, J = 8.0 Hz), 7.4–7.6 (m, 3 H), 7.8–8.0 (m, 2 H); UV (ethanol) 268 nm (ϵ 29 500), 400 (6100); mass spectrum, *m/e* 295 (M^+), 266, 252, 239, 224, 156, 130, 115, 104. Anal. Calcd for $C_{17}H_{21}N_5$: C, 69.12; H, 7.17; N, 23.71. Found: C, 69.14; H, 7.20; N, 23.63.

Reaction of 3-Diazo-4-methyl-5-phenylpyrazole (4) with Ethyl Vinyl Ether. A mixture containing 433 mg of ethyl vinyl ether and 1.11 g of diazopyrazole 4 in 20 mL of methylene chloride was stirred at 0 °C for 1 h. Removal of the solvent under reduced pressure left a dark residue which was purified by chromatography on a neutral alumina column with methylene chloride as the eluent to give 682 mg (54%) of 7-phenyl-8-methylpyrazolo[5,1-*c*][1,2,4]triazine (9) as yellow needles: mp 180–181 °C; IR (KBr) 3050, 1460, 1384, 1379, 1247, 1083, 832, 765, 681 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.77 (s, 3 H), 7.3–7.6 (m, 3 H), 7.7–7.9 (m, 2 H), 8.38 (d, 1 H, J = 4.8 Hz), 8.63 (d, 1 H, J = 4.8 Hz); UV (ethanol) 267 nm (ϵ 32 800), 329 (2600), 390 (1300); mass spectrum, *m/e* 210 (M^+), 156, 103, 77 (base). Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.55; H, 4.79; N, 26.65. Found: C, 68.44, H, 4.87; N, 26.58.

When the reaction was carried out with 1-deuterioethyl vinyl ether, the exclusive product obtained from the reaction was 4-deuterio-7-phenyl-8-methylpyrazolo[5,1-*c*][1,2,4]triazine (9-*4*-*d*) in 37% isolated yield.

Reaction of 3-Diazo-4-methyl-5-phenylpyrazole (4) with β-(Diethylamino)styrene. A mixture containing 148 mg of β-(diethylamino)styrene and 173 mg of diazopyrazole 4 in 2.0 mL of chloroform was allowed to stand at 25 °C for 24 h. Removal of the solvent under reduced pressure left a dark residue which was subjected to column chromatography on a neutral alumina column with benzene as the eluent. The major component isolated from the column contained 218 mg (90%) of 3,7-diphenyl-8-methylpyrazolo[5,1-*c*][1,2,4]triazine (10) as yellow needles: mp 176–177 °C; IR (KBr) 3070, 1588, 1552, 1522, 1465, 1443, 1382, 1244, 1140, 764, 682 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.79 (s, 3 H), 7.4–8.3 (m, 10 H), 8.73 (s, 1 H); UV (ethanol 286 nm (ϵ 56 000), 324 (ϵ 5500), 410 (1400); mass spectrum, *m/e* 285 (M^+), 240, 210, 156, 102, 77 (base). Anal. Calcd for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.47; H, 4.95; N, 19.54.

The reaction of diazopyrazole 4 with β-(diethylamino)styrene was followed by NMR spectroscopy. A mixture containing 106 mg of β-(diethylamino)styrene and 111 mg of diazopyrazole 4 in 2.0 mL of benzene-d_6 was allowed to stand at 25 °C, and the reaction was monitored by NMR spectroscopy. After 6 min both starting materials had disappeared, and a new component was present in the reaction mixture: ^1H NMR (60 MHz) δ 0.83 (t, 6 H, J = 8.0 Hz), 2.53 (q, 4 H, J = 8.0 Hz), 2.60 (s, 3 H), 5.35 (d, 1 H, J = 4.0 Hz), 5.78 (d, 1 H, J = 4.0 Hz), 7.0–7.5 (m, 8 H), 7.9–8.1 (m, 2 H). This material slowly disappeared and another transient was formed. After 63 min it was present in 48% yield and showed signals at δ 0.90 (t, 6 H, J = 8.0 Hz), 1.97 (s, 3 H), 2.73 (q, 4 H, J = 8.0 Hz), 6.27 (s, 1 H), 7.0–8.1 (m, 10 H). After standing for an additional 30 min the peaks associated with this compound disappeared and were eventually replaced by the signals associated with 3,7-diphenyl-8-methylpyrazolo[5,1-*c*][1,2,4]triazine (10).

Reaction of 3-Diazo-4-methyl-5-phenylpyrazole (4) with β-Ethoxystyrene. A mixture containing 103 mg of β-ethoxystyrene and 129 mg of 4 in 1 mL of deuteriochloroform was allowed to stand at room temperature for 7 h. The reaction was monitored by NMR spectroscopy over a period of time. After 90 min the starting diazopyrazole had completely disappeared. A transient intermediate was formed and reached a maximum value after 65 min. This material showed signals at δ 0.89 (t, 3 H, J = 8.0 Hz), 2.66 (s, 3 H), 2.71 (q, 2 H, J = 8.0 Hz), 5.52 (m, 1 H), 6.07 (m, 1 H), and 7.0–8.0 (m, 10 H). After the mixture was allowed to stand for 120 min, this material disappeared and was eventually replaced by the signals associated with 3,7-diphenyl-8-methylpyrazolo[5,1-*c*][1,2,4]triazine (10).

Reaction of 3-Diazo-4-methyl-5-phenylpyrazole (4) with 1,1-Dimethoxyethene. A mixture containing 97 mg of 1,1-dimethoxyethene and 195 mg of diazopyrazole 4 in 1.0 mL of

(30) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer 467 infrared spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer by using 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz by using a Varian EM-390 spectrometer and at 60 MHz by using a Varian EM-360 spectrometer. Mass spectra were determined with a Finnigan 4000 mass spectrometer at an ionizing voltage of 70 eV.

(31) Ridi, M. *Gazz. Chim. Ital.* **1955**, *85*, 1160.

deuteriochloroform was allowed to stand at 25 °C for 72 h. At the end of this time the solvent was removed under reduced pressure, and the crude residue was chromatographed on a thick-layer plate with a 1:1 acetone–ether mixture as the eluent. The major fraction contained 108 mg (45%) of a light yellow solid (mp 136–137 °C) whose structure was assigned as 4-methoxy-7-phenyl-8-methylpyrazolo[5,1-*c*][1,2,4]triazine (**14**): IR (KBr) 2960, 2875, 1538, 1378, 1317, 1310, 1049, 940, 678 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.71 (s, 3 H), 4.31 (s, 3 H), 7.4–7.6 (m, 3 H), 7.8–8.0 (m, 2 H), 8.42 (s, 1 H); UV (ethanol) 264 nm (ϵ 33 800), 298 (3500), 360 (3000); mass spectrum, *m/e* 240 (M^+), 156, 149, 137, 103, 94, 77 (base). Anal. Calcd for $C_{13}H_{12}N_4O$: C, 64.98; H, 5.03; N, 23.32. Found: C, 64.88; H, 5.06; N, 23.28.

The second component isolated from the thick-layer plate contained 8 mg of a tan solid, mp 222–223 °C dec. The structure of this material is assigned as 7-methoxy-7a-methyl-1-phenyl-4*H*-pyrazolo[3,4-*c*]pyridazine (**15**) on the basis of its spectral properties: IR (KBr) 1660, 1582, 1556, 1462, 1398, 1150, 825, 770, 685 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.46 (s, 3 H), 4.28 (s, 3 H), 7.39 (s, 1 H), 7.4–7.6 (m, 3 H), 7.9–8.1 (m, 2 H); UV (ethanol) 253 nm (ϵ 20 400), 291 (14 800), 296 (14 300), 390 (6100); mass spectrum, *m/e* 240 (M^+), 156, 149, 137, 103, 77. Anal. Calcd for $C_{13}H_{12}N_4O$: C, 64.98; H, 5.03; N, 23.32. Found: C, 65.02; H, 5.06; N, 23.28.

The reaction of 1,1-dimethoxyethene and diazopyrazole **4** in deuteriochloroform was monitored as a function of time. After the mixture was allowed to stand for 20 min at room temperature, all of the starting materials had disappeared, but the final product had not yet formed. Removal of the solvent under reduced pressure left a pale brown solid (mp 139–142 °C dec) whose spectral data suggest it to be 1-(4-methyl-5-phenylpyrazolo)-4,4-dimethoxy-1,2-diazabuta-1,3-diene (**17**): IR (KBr) 3150, 2950, 2920, 1618, 1581, 1568, 1434, 1392, 1332, 1282, 1270, 1228, 1214, 1094, 1046, 1002, 766, 698, 688 cm^{-1}; NMR (CCl_4, 60 MHz) δ 2.11 (s, 3 H), 3.31 (s, 3 H), 3.46 (s, 3 H), 6.53 (s, 1 H), 7.1–7.7 (m, 5 H), 9.69 (1 H, m). Purification of this material was not possible since it rapidly rearranged to a mixture of **14** and **15** on chromatography, on recrystallization, or on standing in solution.

The reaction of 1,1-dimethoxyethene and diazopyrazole **4** was monitored by NMR spectroscopy for short periods of time. After 90 s at ambient temperature all of the starting material had been consumed, and a single new species which exhibited a sharp two-proton singlet at δ 4.51 was formed. When allowed to stand, this compound was found to rearrange to the diazadiene **17**, and, after 40 min, it had completely disappeared, affording diazadiene **17** as the major component in the reaction mixture. The structure of this transient species has been assigned as spiro[4-methyl-5-phenyl-3*H*-pyrazole-3,3′-4′,4′-dimethoxy-1-pyrazoline] (**16**) on the basis of its NMR spectrum ($CDCl_3$, 60 MHz) which showed signals at δ 2.61 (s, 3 H), 3.36 (s, 6 H), 4.51 (s, 2 H), and 7.4–8.0 (m, 5 H). This material isomerized to azadiene **17** with a half-life of 10 min at 35 °C.

Reaction of 3-Diazo-4-methyl-5-phenylpyrazole (4) with 1-(Diethylamino)-2-methyl-1-propene. A mixture containing 106 mg of 1-(diethylamino)-2-methyl-1-propene[32] and 154 mg of diazopyrazole **4** in 0.8 mL of deuteriochloroform was allowed to stand at 25 °C for 12 h. Removal of the solvent under reduced pressure left a residue which was chromatographed on a neutral alumina column with methylene chloride as the eluent to give 118 mg (45%) of 4-(diethylamino)-3,4-dihydro-7-phenyl-3,3,8-trimethylpyrazolo[5,1-*c*][1,2,4]triazine (**13a**): mp 87–88 °C; IR (KBr) 2990, 2950, 1604, 1458, 1420, 1382, 1287, 1212, 1119, 1069, 1008, 858, 818, 772, 699, 690 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 0.93 (t, 6 H, J = 7.3 Hz), 1.12 (s, 3 H), 1.81 (s, 3 H), 2.34 (q, 4 H, J = 7.3 Hz), 2.63 (s, 3 H), 4.83 (s, 1 H), 7.3–7.6 (m, 3 H), 7.7–7.9 (m, 2 H); mass spectrum, *m/e* 311 (M^+), 241, 239, 225, 200, 186, 170, 158, 157, 127, 111, 77. Anal. Calcd for $C_{18}H_{25}N_5$: C, 69.42; H, 8.09; N, 22.47. Found: C, 69.30; H, 7.80; N, 22.11.

Reaction of 3-Diazo-4-methyl-5-phenylpyrazole (4) with 1-Ethoxy-2-methyl-1-propene. A mixture containing 71 mg of 1-ethoxy-2-methyl-1-propene and 130 mg of diazopyrazole **4** in 2 mL of chloroform were allowed to stand at room temperature for 6 h. At the end of this time the solvent was removed under reduced pressure, and the residue was chromatographed on a neutral alumina column with methylene chloride as the eluent. The major component isolated from the column was a pale oil (25%) whose structure was assigned as 2-ethoxy-3,3,7-trimethyl-8-phenyl-1,4,5,9-tetraazabicyclo[4.3.0]nona-4,6,8-triene (**13b**): IR (neat) 2990, 2940, 1600, 1555, 1411, 1379, 1310, 1294, 1091, 1009, 909, 855, 829, 776, 690 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.05 (s, 3 H), 1.08 (t, 3 H, J = 7.2 Hz), 1.92 (s, 3 H), 3.59 (q, 2 H, J = 7.2 Hz), 5.02 (s, 1 H), 7.2–7.6 (m, 3 H), 7.6–7.9 (m, 2 H); mass spectrum, *m/e* 284 (M^+), 249, 232, 211, 185, 171, 155, 130, 115, 103, 77 (base). Anal. Calcd for $C_{16}H_{20}N_4O$: C, 67.58; H, 7.09; N, 19.71. Found: C, 67.49; H, 7.10; N, 19.56.

Reaction of 3-Diazoindazole with 1-Pyrrolidinyl-1-butene. A solution containing 960 mg of 1-pyrrolidinyl-1-butene in 10 mL of anhydrous benzene was added dropwise at room temperature to a solution containing 1.06 g of 3-diazoindazole.[33] After 10 min the reaction mixture was concentrated under reduced pressure and chromatographed on silica gel with 1:1 hexane–chloroform as the eluent. The first 1.5 L of solvent contained 1.19 g (82%) of a yellow solid identified as 3-ethyl[1,2,4]triazino[4,3-*b*]indazole (**19**). Recrystallization from hexane afforded shimmering yellow crystals: mp 127–128 °C; NMR (benzene-d_6, 90 MHz) δ 1.04 (t, 3 H, J = 8 Hz), 2.61 (q, 2 H, J = 8 Hz), 6.73–7.53 (m, 2 H), 7.58 (s, 1 H), 7.83–8.00 (m, 2 H), 8.46–8.64 (m, 2 H); IR (KBr) 3055, 2980, 1620, 1560, 1550, 1495, 1450, 1430, 1375, 1320, 1265, 1225, 1160, 1140, 1110, 1075, 1000, 980, 930, 865, 745, 715 cm^{-1}; UV (95% ethanol) 357 nm (ϵ 3900), 338 (3400), 284 (16 000), 271 (27 000); mass spectrum, *m/e* 198 (M^+,base), 197, 116, 102, 89, 62. Anal. Calcd for $C_{11}H_{10}N_4$: C, 66.65; H, 5.09, N, 28.27. Found: C, 66.50; H, 5.11, N, 28.18.

Reaction of 3-Diazoindazole with β-(Diethylamino)-styrene. A solution containing 1.31 g of β-(diethylamino)styrene[34] in 20 mL of anhydrous benzene was added dropwise at room temperature to a solution containing 1.02 g of 3-diazoindazole in 35 mL of benzene. The reaction mixture immediately turned red upon addition and warmed slightly. After 15 min a solid separated from the reaction mixture. This was suction filtered, washed with benzene, and air-dried to yield 1.36 g of 3-phenyl[1,2,4]triazino-[4,3-*b*]indazole (**20**) as a yellow powder. Recrystallization from hexane–benzene afforded an analytically pure sample as bright yellow crystals: mp 229–230 °C; NMR (pyridine-d_5, 90 MHz) δ 7.3–8.8 (m, 9 H), 9.97 (s, 1 H); IR (KBr) 1632, 1675–1655, 1490, 1447, 1387, 1354, 1343, 1285, 1227, 1155, 1105, 1030, 1000, 935, 922, 855, 782, 770, 758, 750, 735, 728, 690, 679, 650 cm^{-1}; UV (95% ethanol) 362 nm (ϵ 35 000), 293 (34 000), 248 (9400); mass spectrum, *m/e* 246 (M^+,base), 245, 189, 137, 116. Anal. Calcd for $C_{15}H_{10}N_4$: C, 73.15; H, 4.09; N, 22.75. Found: C, 73.09; H, 4.09; N, 22.72.

Reaction of 3-Diazoindazole with 1-Pyrrolidinyl-2-methyl-1-propene. A solution containing 1.25 g of 1-pyrrolidinyl-2-methyl-1-propene[35] in 15 mL of anhydrous benzene was added dropwise at room temperature to a solution containing 1.33 g of 3-diazoindazole in 35 mL of benzene. After 40 min the reaction mixture was concentrated under reduced pressure. The resulting brown semisolid material was chromatographed on silica gel with hexane as the eluent to yield 650 mg of a yellow powder, mp 124–127 °C. Recrystallization from hexane afforded 3,4-dihydro-3,3-dimethyl-4-(1-pyrrolidinyl)[1,2,4]triazino[4,3-*b*]indazole (**21**) as deep yellow crystals: mp 127–128 °C; NMR (benzene-d_6, 90 MHz) δ 0.70 (s, 3 H), 1.0–1.3 (m, 4 H), 1.71 (s, 3 H), 1.7–2.1 (m, 2 H), 2.4–2.8 (m, 2 H), 4.92 (s, 1 H), 7.0–7.3 (m, 3 H), 7.8–8.0 (m, 1 H), 8.2–8.4 (m, 1 H); IR (KBr) 2980, 2945, 2875, 2840, 1620, 1500, 1455, 1405, 1380, 1365, 1320, 1295, 1260, 1245, 1200, 1160, 1130, 1105, 980, 950, 885, 855, 730 cm^{-1}; UV (95% ethanol) 362 nm (ϵ 9400), 251 (8200); mass spectrum, *m/e* 269 (M^+), 125, 110, 70 (base), 55.

Preparation of 3-Diazo-5-phenyl-1,2,4-triazole (22). In a typical experiment, 0.50 g of 3-amino-5-phenyl-4*H*-1,2,4-triazole[36] was suspended in 10 mL of concentrated nitric acid, and the suspension was cooled to 0 °C. To this mixture was added dropwise, with vigorous stirring, a concentrated aqueous solution

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containing 0.24 g of sodium nitrite. The resulting clear solution was diluted with 5 mL of water and 30 mL of methylene chloride. The solution was basified with a saturated aqueous sodium carbonate solution, maintaining the temperature at less than 10 °C. The organic phase was separated and washed once with water before being dried and concentrated under reduced pressure to 10 mL. To this bright yellow solution was added a solution of the appropriate dipolarophile in methylene chloride. The diazotriazole could, alternatively, be isolated as a bright yellow crystalline solid. However, owing to the fact that manipulations of this substance frequently resulted in violent decomposition, isolation as a solid was generally avoided.

Reaction of 3-Diazo-5-phenyl-1,2,4-triazole (22) with 1-Pyrrolidinyl-2-methyl-1-propene. To a cold stirred solution containing 0.20 g of diazotriazole **22** in 10 mL of dry methylene chloride was slowly added 0.20 g of 1-pyrrolidinyl-2-methyl-1-propene in 3 mL of the same solvent. After the addition, the mixture was stirred at 0 °C for 30 min, and then the solution was allowed to warm to ambient temperature. Concentration of the solution gave a dark orange gum which was chromatographed with methylene chloride over a short column of silica. The mobile yellow forerun was concentrated to a homogeneous yellow oil (0.12 g) which slowly solidified. A single recrystallization from hexane afforded 3,3-dimethyl-3,4-dihydro-7-phenyl-4-(1-pyrrolidinyl)-1,2,4-triazolo[5,1-*c*][1,2,4]triazine (**23**) as dark yellow needles: mp 153 °C dec; IR (KBr) 1460, 1450, 1400, 1350, 1310, 1220, 1110, 1080, 990, 930, 870, 830, 780, 710, 690 cm^{-1}; UV (95% ethanol) 246 nm (ϵ 22 780), 319 (2210); NMR ($CDCl_3$, 90 MHz) δ 1.12 (s, 3 H), 1.49–1.80 (m, 4 H), 1.86 (s, 3 H), 1.96–2.26 (m, 2 H), 2.45–2.72 (m, 2 H), 5.19 (s, 1 H), 7.43–7.60 (m, 3 H), 8.18–8.29 (m, 2 H); mass spectrum, *m/e* 296 (M^+), 226, 200, 178, 137, 125, 110, 70. Anal. Calcd for $C_{16}H_{20}N_6$: C, 64.84; H, 6.80; N, 28.36. Found: C, 64.84; H, 6.83; N, 28.30.

Reaction of 3-Diazo-5-phenyl-1,2,4-triazole (22) with 1-Ethoxy-2-methyl-1-propene. To a stirred solution containing 0.50 g of diazotriazole **22** in methylene chloride at 0 °C was added dropwise a solution containing 0.34 g of 1-ethoxy-2-methyl-1-propene in the same solvent. After being stirred for 30 min at 0 °C, the dark brown solution was allowed to warm to ambient temperature before being concentrated to a brown oil. After filtration through a short column of silica, eluting with methylene chloride, the yellow forerun was concentrated and subjected to preparative thin-layer chromatography (50% ether/hexane). That prominent species with R_f 0.5 was extracted and concentrated to an oil which slowly solidified. A single recrystallization from hexane gave 0.37 g (40%) of 3,3-dimethyl-3,4-dihydro-4-ethoxy-7-phenyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazine (**24**) as shiny yellow prisms: mp 80–81 °C; IR (neat) 1530, 1510, 1450, 1380, 1340, 1270, 1100, 1030, 930, 860, 830, 790, 730, 695 cm^{-1}; UV (95% ethanol) 244 nm (ϵ 22 890), 320 (1733); NMR ($CDCl_3$, 90 MHz) δ 1.10 (t, 3 H, J = 7.2 Hz), 1.13 (s, 3 H), 1.94 (s, 3 H), 3.70 (q, 2 H, J = 7.2 Hz), 3.73 (q, 1 H, J = 7.2 Hz), 5.19 (s, 1 H), 7.43–7.69 (m, 3 H), 8.16–8.32 (m, 2 H). Anal. Calcd for $C_{14}H_{17}N_5O$: C, 61.97; H, 6.32; N, 25.81. Found: C, 61.74; H, 6.39; N, 25.72.

Reaction of 3-Diazo-5-phenyl-1,2,4-triazole (22) with β-(Diethylamino)styrene. To a stirred solution of diazotriazole **22** in 10 mL of methylene chloride at 0 °C was added dropwise a solution containing 0.50 g of β-(diethylamino)styrene in 2 mL of dry methylene chloride. After an immediate dissipation of color, the solution was stirred for an additional 30 min while warming to ambient temperature. Concentration of the solution and trituration of the resulting solid with a small volume of cold acetone gave an off-white solid which was recrystallized from ethanol to give 0.60 g (62%) or 4-(diethylamino)-4,6-dihydro-β-phenyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazine (**25**) as colorless needles: mp 169–170 °C; IR (KBr) 1630, 1580, 1555, 1440, 1365, 1255, 1215, 1120, 1070, 785, 755, 730, 690, 655 cm^{-1}; UV (95% ethanol) 235 nm (ϵ 20 660), 302 (20 260); NMR ($CDCl_3$, 90 MHz) δ 1.03 (t, 6 H, J = 8.4 Hz), 2.75 (q, 4 H, J = 8.4 Hz), 6.40 (s, 1 H), 7.33–7.66 (m, 3 H), 8.00–8.40 (m, 2 H), 12.55 (s, 1 H); mass spectrum, *m/e* 273, 187, 142, 115, 104, 102, 77. Anal. Calcd for $C_{20}H_{22}N_6$: C, 69.34; H, 6.40; N, 24.26. Found: C, 69.36; H, 6.42; N, 24.21.

Reaction of 3-Diazo-5-phenyl-1,2,4-triazole (22) with 1,1-Dimethoxyethylene. To a stirred solution of diazotriazole **22** maintained at 0 °C was added, in a single portion, 0.28 g of freshly distilled 1,1-dimethoxyethylene. After an immediate dissipation of color the solution was stirred for 30 min while warming to ambient temperature. Concentration of the solution afforded a pale yellow solid (0.68 g, 84%) which was triturated with a small volume of cold acetone. Recrystallization once from ethanol gave a mixture of 4,6-dihydro- and 4,8-dihydro-4,4-dimethoxy-7-phenyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazines (**29** and **28**) as shiny colorless prisms: mp 168–180 °C; IR 1630, 1580, 1440, 1410, 1390, 1330, 1260, 1230, 1130, 1030, 780, 720 cm^{-1}; UV (95% ethanol) 234 nm (ϵ 16 360), 258 (14 350); NMR ($CDCl_3$, 90 MHz) δ 3.16, 3.41 (2 s, 6 H), 6.68, 6.80 (2 s, 1 H), 7.43–7.60 (m, 3 H), 8.08–8.31 (m, 2 H), 13.10 (br s, 1 H); mass spectrum, *m/e* 259 (M^+), 236, 228 (base), 200, 174, 158, 144, 118, 117, 104, 103, 91, 77. Anal. Calcd for $C_{12}H_{13}N_5O_2$: C, 55.59; H, 5.05; N, 27.02. Found: C, 55.60; H, 5.12; N, 26.84.

A sealed tube thermolysis of a benzene solution of this material at 120 °C gave an off-white solid which was recrystallized once from benzene to give 4,6-dihydro-4,4-dimethoxy-7-phenyl-1,2,4-triazolo[5,1-*c*][1,2,4]triazine (**29**) as a colorless solid: mp 186–187 °C; IR (KBr) 1630, 1580, 1440, 1420, 1380, 1340, 1260, 1230, 1130, 1035, 980, 780, 720 cm^{-1}; UV (95% ethanol) 233 nm (ϵ 19 490), 260 (14 590); NMR (Me_2SO-d_6, 90 MHz) δ 3.32 (s, 6 H), 6.96 (s, 1 H), 7.43–7.62 (m, 3 H), 8.01–8.17 (m, 2 H), 12.52 (s, 1 H); mass spectrum, *m/e* 259 (M^+), 236, 228 (base), 200, 174, 104, 103, 91, 77. Anal. Calcd for $C_{12}H_{13}N_5O_2$: C, 55.59; H, 5.05; N, 27.02. Found: C, 55.74; H, 5.10; N, 26.90.

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Registry No. **4**, 62072-08-6; **4** amine derivative, 66367-67-7; **4** diazonium chloride derivative, 85939-82-8; **5**, 78680-98-5; **7**, 78680-99-6; **9**, 85939-74-8; **10**, 85939-75-9; **13a**, 78681-00-2; **13b**, 78681-01-3; **14**, 78681-03-5; **15**, 85939-76-0; **16**, 78681-04-6; **17**, 78681-05-7; **19**, 85939-77-1; **20**, 85939-78-2; **21**, 85939-79-3; **22**, 80670-36-6; **22** amine derivative, 4922-98-9; **23**, 85939-80-6; **24**, 85956-50-9; **25**, 85956-35-0; **28**, 85956-51-0; **29**, 85939-81-7; 1-(diethylamino)cyclohexene, 10468-24-3; 1-(diethylamino)propyne, 4231-35-0; ethyl vinyl ether, 109-92-2; β-(diethylamino)styrene, 56672-27-6; β-ethoxystyrene, 17655-74-2; 1,1-dimethoxyethene, 922-69-0; 1-(diethylamino)-2-methyl-1-propene, 16826-16-7; 1-ethoxy-2-methyl-1-propene, 927-61-7; 3-diazoindazole, 2596-89-6; 1-pyrrolidinyl-1-butene, 13937-89-8; 1-pyrrolidinyl-2-methyl-1-propene, 2403-57-8.