$NaHCO_3$ (420 mg, 49 mmol) was then added, and stirring was continued for 1 h. The progress of the reaction was monitored by TLC (CH_3CN, silica gel). The resulting mixture was filtered and the solvent evaporated. The residue was purified by thick-layer chromatography with silica gel (grade III) and CH_3CN as the eluent to give 255 mg (95%) of 2,6-dibromo-3-aminopyrazine 1-oxide (**27**).

General Comments. The experimental variables applicable to other compounds are listed in Tables I–III.

It is of some importance to note that bromination conditions were kept constant. Minor alterations were sometimes necessary in order to compensate for the physical properties of the reagents. For instance, acetonitrile was added to the methylene chloride in order to dissolve the amino compounds.

Registry No. **3**, 5049-61-6; **4**, 5214-29-9; **5**, 5625-94-5; **7**, 21720-40-1; **8**, 84539-02-6; **9**, 84539-03-7; **10**, 84539-04-8; **11**, 84539-05-9; **12**, 23902-69-4; **13**, 6863-77-0; **14**, 84539-06-0; **15**, 13134-49-1; **16**, 24241-18-7; **17**, 84539-07-1; **18**, 84539-08-2; **19**, 21943-12-4; **20**, 84539-09-3; **21**, 84539-10-6; **22**, 84539-11-7; **23**, 84539-12-8; **24**, 84539-13-9; **25**, 84539-14-0; **26**, 84539-15-1; **27**, 84539-16-2; **28**, 84539-17-3; **29**, 84539-18-4; **31**, 109-12-6; **32**, 931-61-3; **33**, 57356-66-8; **35**, 35034-15-2; **36**, 84539-19-5; **37**, 591-54-8; **38**, 22632-10-6; **39**, 31401-45-3; **41**, 84539-20-8; **42**, 84539-21-9; **44**, 7752-82-1; **45**, 31402-54-7; **46**, 84539-22-0; **47**, 84539-23-1; **48**, 84539-24-2; **49**, 1439-10-7; **50**, 56181-38-5; **51**, 84539-25-3; **52**, 84539-26-4; **53**, 84539-27-5; **55**, 504-29-0; **56**, 5683-33-0; **58**, 14150-95-9; **59**, 54818-70-1; **60**, 3618-79-9; **61**, 504-24-5; **62**, 1122-58-3; **63**, 1122-96-9; **64**, 3535-75-9; **65**, 1122-92-5; **66**, 1005-31-8; **67**, 14906-61-7; **68**, 1657-32-5; **69**, 54818-71-2; **70**, 36100-40-0; **71**, 1072-97-5; **72**, 35486-42-1; **73**, 84539-28-6; **74**, 26163-07-5; **75**, 696-15-1; **76**, 84539-29-7; **77**, 84539-30-0; **78**, 84539-31-1; **79**, 84539-32-2; **80**, 84539-33-3; **81**, 13534-98-0; **82**, 84539-34-4; **83**, 84539-35-5; **84**, 84539-36-6; **85**, 84539-37-7; **86**, 84539-38-8; **87**, 84539-39-9; **88**, 84539-40-2; **89**, 84539-41-3; **90**, 84539-42-4; **91**, 84539-43-5; **92**, 84539-44-6; **93**, 84539-45-7; **94**, 84539-46-8; **95**, 84539-47-9; **97**, 84539-48-0; **98**, 39856-57-0; **99**, 84539-49-1; **100**, 84539-50-4; **101**, 84539-51-5; **102**, 84539-52-6.

1,3-Dipolar Cycloaddition Reactions of Diazopyrazolinones with Electron-Deficient Dipolarophiles

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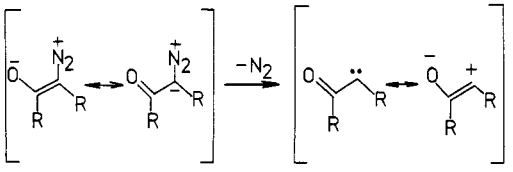
Received September 3, 1982

A study of the reactivity of a series of 4-diazopyrazolin-5-ones toward dipolar cycloaddition with electron-deficient olefinic and acetylenic dipolarophiles has been carried out. Reactions with dimethyl acetylenedicarboxylate afford pyrazolo[1,5-*d*][1,2,4]triazin-7-ones which result from dipolar cycloaddition followed by a van Alphen–Huttel rearrangement of the initially produced spiro 3*H*-pyrazole adducts. Reaction with unsymmetrical acetylenic esters afforded variable mixtures of regioisomeric pyrazolotriazinones and 1*H*-furo[2,3-*c*]pyrazoles. Product formation has been rationalized in terms of a substituent-dependent partitioning between spiro 3*H*-pyrazole adducts and ring-opened diazoalkenes. Spiro[pyrazoline-4,1′-cyclopropane]carboxylate esters were the only products isolated from reactions with acrylate ester.

Apart from the significance of diazoalkanes for the generation of carbenes,[1,2] these compounds also play a dominant role in dipolar cycloaddition chemistry.[3–5] Recent advances in the synthesis of diazoalkanes have frequently led to new application in cycloaddition chemistry.[6] α-Diazo ketones represent an interesting subclass of this family of dipoles since several discrete modes of intermolecular cycloaddition are possible.[7] Among these are those involving reaction as a 1,3-dipole, either through the diazoalkane moiety or through a reactive intermediate possessing the stoichiometry of a keto carbene species derived from an initial loss of nitrogen (see below). Much



less common modes of addition involving the extended 6-π-electron 1,5-dipolar system are also observed with certain quinonoid α-diazo ketones.[8] The use of extended diazoalkanes with six or more electrons has received little attention despite the obvious synthetic and theoretical interest in such processes.[9,10] When the diazo ketone moiety is incorporated into a heterocyclic ring, dipolar cycloaddition processes can provide ready access to more elaborate and rare heterocyclic ring systems. As part of a general program designed to study profiles of reactivity of diazoalkanes as 1,3-dipolar and/or extended dipolar systems,[11–13] we initiated a study dealing with representatives of the 4-diazopyrazolinone ring system. We now report on the mechanistic and regiochemical features as-

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[‡] Emory University.
[§] Hoffman-La Roche, Inc.

(1) Kirmse, W. "Carbene Chemistry", 2nd ed., Academic Press: New York, 1971.
(2) Moss, R. A.; Jones, M. "Carbenes"; Wiley-Interscience, New York, 1975.
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(8) Reid, W.; Dietrich, R. *Justus Liebigs Ann. Chem.* **1963**, *666*, 113.
(9) Durr, H.; Schmitz, H. *Chem. Ber.* **1978**, *111*, 2258.
(10) Magee, W. L.; Shechter, H. *J. Am. Chem. Soc.* **1977**, *99*, 633.
(11) Padwa, A.; Ku, H. *J. Org. Chem.* **1980**, *45*, 3756.
(12) Padwa, A.; Kumgai, T. *Tetrahedron Lett.* **1981**, *22*, 1199.
(13) Woolhouse, A. D.; Caruso, T. C.; Padwa, A. *Tetrahedron Lett.* **1982**, *23*, 2167.

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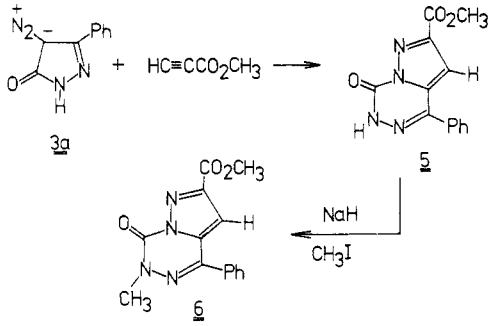
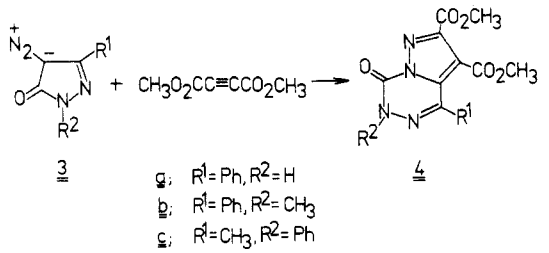
Scheme I



sociated with the cycloaddition of 4-diazopyrazolinones to electron-deficient olefinic and acetylenic dipolarophiles.

Results and Discussion

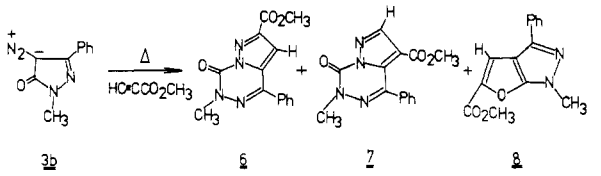
Cycloaddition reactions were performed typically by heating at 165 °C dry toluene solutions containing the diazopyrazolinone (**3**) and the dipolarophile (1.2–2.0 molar



equiv) for periods of 16–20 h. From each of the reactions of the substituted diazopyrazolinones **3a–c** with dimethyl acetylenedicarboxylate, thermally stable and crystalline 1:1 adducts were isolated in high yields (70–95%). Structural assignments as derivatives of the fused pyrazolo[1,5-*d*][1,2,4]triazin-7-one ring systems **4a–c** were deduced principally by analogy to **6**, for which a single-crystal X-ray structure determination was performed. The chemical shift values observed for each of the methyl signals are consistent with these assignments (see Experimental Section). Methylation of pyrazolotriazinone **4a** afforded the same *N*(6)-methyl adduct (**4b**), thus providing chemical support for the structure.

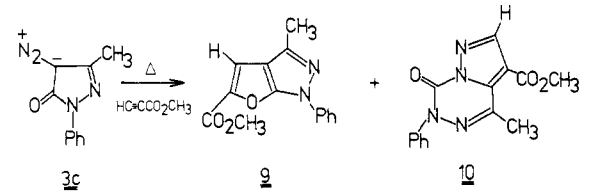
In an effort to establish the regiochemical cycloaddition behavior of these heterocyclic α-diazo ketones toward acetylenic esters, reactions with unsymmetrical acetylenes were carried out. Addition of methyl propiolate to diazopyrazolinone **3a** under the conditions described gave (73%) a single 1:1 cycloadduct, the structure of which has been assigned as the C(2)-substituted pyrazolotriazinone **5** (Scheme I). Unequivocal proof of this assignment derives from a single-crystal X-ray crystallographic analysis of the N(6)-methylated pyrazolotriazinone derivative (**6**), which in turn was synthesized (70%) by methylation of **5** (NaH/DMF, CH_3I) under standard conditions.

A somewhat unexpected profile of reactivity toward cycloaddition was encountered with the disubstituted diazopyrazolinones **3b** and **3c**. From the reaction of 4-diazo-1-methyl-3-phenylpyrazolinone (**3b**) with methyl propiolate, three crystalline products were isolated. The yields of each of the cycloadducts were invariant over the temperature range 120–170 °C, and no interconversion of the various structures could be induced under the reaction conditions. The major product (40%) was shown to be identical in all respects with that of oxopyrazolotriazine-2-carboxylate **6** obtained by methylation of cycloadduct **5**. The regioisomeric oxopyrazolotriazine-3-carboxylate **7** was the next most prevalent product (34%) and was as-

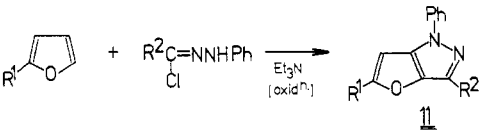


signed on the basis of both ^1H and ^{13}C NMR data recorded for the methine hydrogen and carbon atoms. Whereas the pyrazolo ring proton at C-3 in **6** was observed at δ 7.32, that proton at C-2 of regioisomer **7** was observed at a characteristically lower field (i.e., δ 8.47);[14] the ester methoxyl signal appeared at δ 3.39. This shielding of ca. 0.6 ppm when compared to those of normal carbomethoxy resonances (δ 3.9–4.0) can easily be rationalized by structure **7**, wherein the ester function located at C-3 is markedly influenced by the pendant phenyl substituent at C-4. The appearance of a low-field doublet at 146.3 ppm in the ^{13}C NMR spectrum of **7**, when compared to that for C-3 at 106.5 ppm for **6**, is also consistent with this assignment. The third and minor (28%) component from the cycloaddition of **3b** to methyl propiolate was assigned as methyl 1-methyl-3-phenyl-1*H*-furo[2,3-*c*]pyrazole-5-carboxylate (**8**). The structure of this material was assigned principally by analogy to the related derivative **9** for which a X-ray crystallographic analysis has been performed. Infrared and NMR spectra of **8** are closely related to those of **9**.

Under identical conditions the addition of propiolate ester to 4-diazo-3-methyl-1-phenylpyrazolin-5-one (**3c**) furnished two products resulting from cycloaddition. The structure of the major (45%) 1:1 adduct was assigned unambiguously as methyl 3-methyl-1-phenyl-1*H*-furo-[2,3-*c*]pyrazole-5-carboxylate (**9**) from a single-crystal X-ray



structure determination. Together with derivative **8**, these compounds are the first reported representatives of the heteroaromatic 1*H*-furo[2,3-*c*]pyrazole ring system. It is interesting to note that the 1*H*-furo[2,3-*c*]pyrazole nucleus cannot be obtained by 1,3-dipolar addition of nitrilimines to furans (with subsequent oxidation) because the isomeric 1*H*-furo[3,2-*c*]pyrazole system (i.e., **11**) is formed instead.[15]

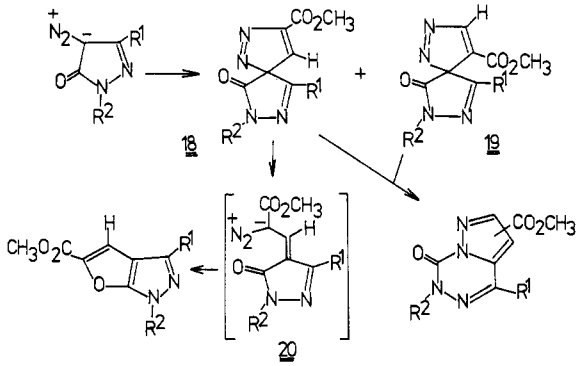


Excessive (>1 eV) energy differences between the component frontier orbital interactions required for the formation of the [2,3-*c*] isomer have been invoked to rationalize the regioselectivity of the cycloaddition.[15] The minor (31%) and only other cycloadduct detected in the reaction of **3c** with methyl propiolate has been assigned as methyl 4-methyl-6-phenylpyrazolo[1,5-*d*][1,2,4]triazin-7-one (**10**) on the basis of striking NMR spectral similarities with those recorded for regioisomer **7**.

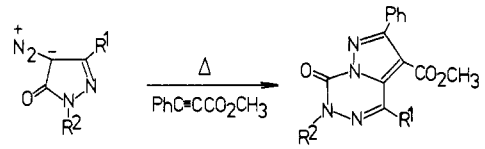
With methyl phenylpropiolate, 1,3-disubstituted diazopyrazolinones **3b** and **3c** afford single 1:1 cycloadducts in

(14) Durr, H.; Sergio, R. *Chem. Ber.* **1974**, *107*, 2027.
(15) Fisera, L.; Kovak, J.; Lesko, J.; Smanovsky, V. *Chem. Zvesti* **1981**, *35*, 93.

Scheme II



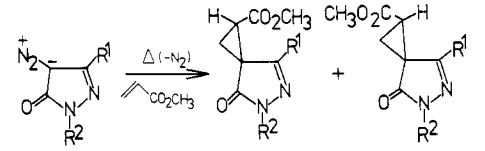
yields which consistently ranged from 45% to 50%. All attempts to effect cycloaddition between **3a** and the phenylpropiolate ester were unsuccessful. In all instances, considerable decomposition of the diazopyrazolinone was observed. The appearance in the ^1H NMR spectrum of the ester methoxy signal of **12** at δ 3.20 can be rationalized



3b; R^1=Ph, R^2=CH_3 **12**; R^1=Ph, R^2=CH_3
3c; R^1=CH_3, R^2=Ph **13**; R^1=CH_3, R^2=Ph

most satisfactorily by invoking the same shielding effect that led to the appearance in the spectrum of the ester methoxyl signal of **13** at δ 3.39. The less sterically encumbered pyrazolotriazinone **13** displays the ester methoxyl resonance, as expected, at δ 3.70.

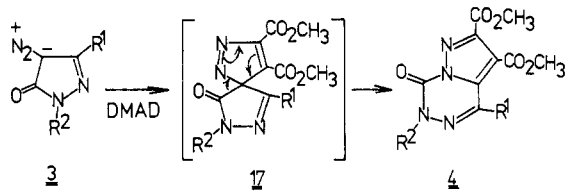
Of the electron-deficient olefinic dipolarophiles, only methyl acrylate was found to enter into cycloaddition with each of the 1,3-disubstituted diazopyrazolinones. In each case, nitrogen-deficient 1:1 adducts, the structures of which have been assigned as the spiro[cyclopropane–pyrazolinones] **14–16**, were isolated in yields in 70–80%. Whereas the reaction of diazopyrazolinone **3b** with methyl acrylate afforded a mixture of stereoisomers (i.e., **14** and **15**), **3c**



3b; R^1=Ph, R^2=CH_3 **14** **15**
3c; R^1=CH_3, R^2=Ph

afforded a single product (**16**) of indeterminate stereochemistry. That the major isomer is that in which the cyclopropyl methoxycarbonyl group is syn to the phenyl substituent (i.e., **14**, 50%) has been determined from a comparison of resonances due to the ester methoxyls. Specifically, the appearance of a high-field signal at δ 3.10 can only be rationalized by assuming a configuration (i.e. **14**) in which shielding due to the anisotropic properties of the adjacent phenyl ring is invoked. The isomer to which the anti configuration has been assigned (i.e., **15**) exhibits the same signal at δ 3.75. Because only minimal steric and anisotropic interactions are likely to be incurred with spiro adduct **16**, it is not possible to establish the stereochemistry of substitution on the cyclopropane ring. No characterizable products could be isolated from the reactions of the N(1)-unsubstituted diazopyrazolinone **3a** with methyl acrylate or in the cycloadditions of **3b** and **3c** with other olefinic dipolarophiles such as nitroethylene, acrylonitrile, or maleic anhydride.

The mechanism by which these reactions proceed is worthy of comment in view of the subtle variations in product distribution. All of the above thermally induced addition reactions with acetylenic dipolarophiles can be rationalized as proceeding by 1,3-dipolar cycloaddition of the isolated diazoalkane moiety within each of the diazopyrazolinones (**3a–c**) to give the corresponding spiro[3*H*-pyrazole-3,4′-pyrazolinone] adducts. The fate of such species is markedly dependent upon the overall pattern of substitution. Thus, cycloaddition to dimethyl acetylenedicarboxylate gives spiro 3*H*-pyrazole **17** which aro-

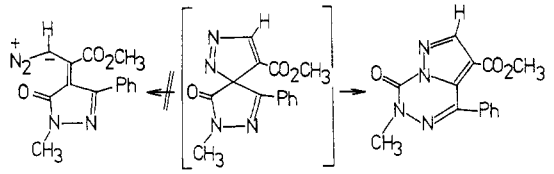


3 **17** **4**

matizes under the reaction conditions via a thermally allowed 1,5-acyl migration to the isomeric fused 1*H*-pyrazole system (i.e., **4**). Interestingly, this type of isomerization (van Alphen–Huttel rearrangement), for which ample precedence exists,[16,17] proceeds exclusively by "acyl" migration rather than by the alternative "imine" migration, in spite of the fact that both routes would lead to aromatization of the pyrazole ring. The fact that the cycloaddition reactions of the 1,3-disubstituted diazopyrazolinones display little or no regioselectivity toward additions of methyl propiolate is in accord with expectations from simple frontier MO theory. Husigen has shown that the introduction of an electron-withdrawing substituent into diazomethane shifts the dipole to type II (Sustmann's classification[18]) in methyl diazoacetate and further toward type III (dipole LUMO control) in dimethyl diazomalonate.[19] The diazopyrazolinone ring, being flanked by two electron-withdrawing residues, would be expected to exhibit type III behavior in which the dominant interaction is dictated by the LUMO (dipole), which is known to have almost equal terminal orbital coefficients.[20] Thus, cycloaddition of **3b** and **3c** to methyl propiolate proceeds to give two spiro 3*H*-pyrazole adducts (e.g., **18** and **19** Scheme II), resulting from both reactant orientations. The fate of the spiro pyrazoles is markedly dependent on the substituent groups and involves either aromatization via a 1,5-acyl migration to give the pyrazolotriazinone system or ring opening to an acyclic diazoalkane, **20**, which then rapidly loses nitrogen under these conditions to give the furopyrazoles. Diazoalkane formation is favored from **18** because of resonance stabilization of the anionic portion of the diazoalkane (e.g., **20**). A control experiment demonstrated that the diazopyrazolinone system is perfectly stable under the reaction conditions in the absence of an added dipolarophile. This observation eliminates the possibility that the observed furo[2,3-*c*]pyrazole products arise via a competitive loss of nitrogen followed by a subsequent dipolar cycloaddition of the resulting keto carbene and the activated acetylene.

(16) van Alphen, J. *Recl. Trav. Chim. Pays-Bas* **1943**, *62*, 485.
(17) Huttel, R.; Reidl, J.; Martin, H.; Franke, K. *Chem. Ber.* **1960**, *93*, 1425.
(18) Sustmann, R. *Tetrahedron Lett.* **1971**, 2721; *Pure Appl. Chem.* **1974**, *40*, 569.
(19) Bihlmaier, W.; Huisgen, R.; Reissig, H. U.; Voss, S. *Tetrahedron Lett.* **1979**, 2621.
(20) Houk, K.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301.

The substituent-dependent partitioning between the spiro adducts and the ring-opened diazoalkene is dependent upon incipient steric interactions between the group at C-3 in the pyrazolinone nucleus and C-4′ in the 3*H*-pyrazole. Thus, the unfavorable steric interaction between the phenyl group and the vinylic hydrogen leading to diazoalkene **20** (R_1 = Ph) is evidently sufficient to lead to the preferential formation of the van Alphen–Huttel product **6** rather than to the fully resonance-stabilized diazo species **20**. The same factors are responsible for the formation of the isomeric van Alphen–Huttel product **7**. Severe steric interactions leading to the formation of a relatively unstabilized diazoalkene (i.e., **21**) would account for the absence of the corresponding 1*H*-furopyrazole derived from spiro adduct **19**.

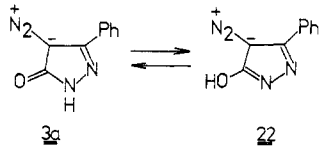


21 19 7

From a consideration of similar steric and electronic factors the formation of only products **9** and **10** from the reaction of **3c** with methyl propiolate can be rationalized. In the dimethyl acetylenedicarboxylate cycloaddition reactions to diazopyrazolinones **3a–c**, the course of each rearrangement is dictated on steric grounds in spite of the fact that diazoalkene formation (and therefore 1*H*-furopyrazole formation) would also be favorable. Similar arguments can be advanced to explain the presence of only van Alphen–Huttel rearrangement products **12** and **13** from the cycloaddition reactions of methyl phenylpropiolate.

Certain features of some of these cycloadditions require additional comment. The regiospecificity with which each of the diazopyrazolinones **3b** and **3c** interact with phenylpropiolate ester to give only the *C*(2)-phenyl-substituted pyrazolotriazinones (**12** and **13**) could well be due to either or both of the following effects. On purely steric grounds, an approach of the dipolarophile with the phenyl ring remote from the hetero ring would appear to be favored. It is also known that 1,3-dipolar addition reactions of phenylpropiolate esters give rise to products in which the ester terminus of the acetylene moiety bonds to the carbon center of the diazoalkene.[21] This regioselectivity can be adequately rationalized from a qualitative consideration of orbital coefficients.

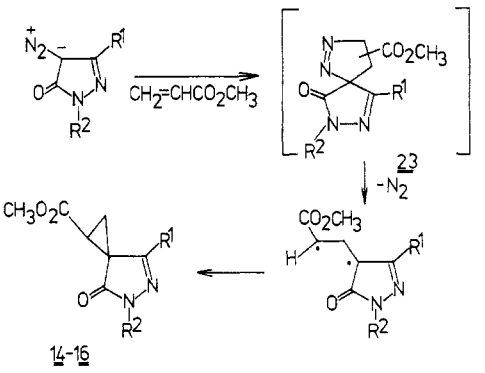
The exclusive formation of the pyrazolotriazolinone **5** from the reaction of the N(1)-unsubstituted diazopyrazolinone **3a** with phenyl propiolate is explicable in terms of the effect the free amide moiety has upon the overall diazoalkane reactivity. The electron-withdrawing capacity of the pyrazolinone carbonyl would be considerably impaired by any contribution from the enol tautomer **22**. The involvement of enol form **22** in the cycloaddition



3c 22

will promote type II behavior of the dipole, and formation of regioisomer **5** would therefore be expected on the basis of orbital coefficient considerations.

Scheme III



Finally, the formation of spirocyclopropanes **14–16** from the cycloaddition of methyl acrylate to diazopyrazolinones **3b** and **3c** can be rationalized as resulting from a thermally induced extrusion of nitrogen from intermediate spiro pyrazolinone cycloadducts **23** (Scheme III), which are presumably formed in a manner directly analogous to those derived from propiolate ester cycloadditions.

Experimental Section[22]

4-Diazo-3-phenylpyrazolin-5-one (3a). To a solution containing 10.0 g of 3-phenylpyrazolin-5-one[23] and 13.7 g of *p*-toluenesulfonyl azide in 1200 mL of methanol was added 8.0 g of triethylamine. The resulting deep red solution was stirred at ambient temperature for 3 h before being concentrated under reduced pressure. Chromatography over silica and gradient elution with acetone/hexane mixtures gave 5.3 g (46%) of the diazopyrazolinone **3a** as a yellow solid, a single recrystallization of which from benzene afforded yellow plates: mp 181 °C (lit.[23] mp 182–183 °C). Subsequent fractions gave mixtures of the diazopyrazolinone and *p*-toluenesulfonamide, the separation of which could be accomplished by careful fractional crystallization from ethyl acetate/hexane mixtures. In this manner an additional 2.79 g (69% in toto) of diazopyrazolinone **3a** was obtained.

4-Diazo-1-methyl-3-phenylpyrazolin-5-one (3b). A sample of 3.0 g of 4-diazo-3-phenylpyrazolin-5-one (**3a**) was added with vigorous stirring to a solution of 0.8 g of sodium hydroxide in 150 mL of 95% ethanol. After the mixture was stirred for 10 min, 3.0 g of methyl iodide was added in a single portion, and the resulting solution was stirred overnight at ambient temperature. Removal of the solvent and extraction of the residue with ether gave a dark oil which was filtered through a short plug of silica and concentrated to an orange oil. Trituration with cold ether gave an orange solid which was recrystallized from ethyl acetate/hexane to give 2.6 g (81%) of 4-diazo-1-methyl-3-phenylpyrazolin-5-one (**3b**) as large orange prisms: mp 78–79 °C; IR (CCl_4) 4.71, 5.95, 6.73, 6.87, 7.12, 7.30 μm; ^{1}H NMR (CCl_4, 90 MHz) δ 3.42 (s, 3 H), 7.33–7.67 (m, 5 H); MS *m/e* 200 (M^+), 129 (base), 101, 75; UV (95% ethanol) 340 nm (ε 3810), 273 sh (5950), 249 (8420). Anal. Calcd for $C_{10}H_8N_4O$: C, 59.99; H, 4.03; N, 27.99. Found: C, 59.93; H, 4.04; N, 27.94.

4-Diazo-3-methyl-1-phenylpyrazolin-4-one (3c). A solution containing 12.0 g 3-methyl-1-phenylpyrazolin-5-one, 15.1 g of *p*-toluenesulfonyl azide, and 8.0 g of triethylamine in 1200 mL of methanol was stirred at ambient temperature for 1.5 h before being concentrated under reduced pressure and subjected to chromatography over silica gel. Elution with a 20% acetone/hexane mixture furnished 7.5 g (50%) of 4-diazo-3-methyl-1-

(21) Bastide, J.; Henri-Rousseau, O.; Aspart-Pascot, L. *Tetrahedron* **1974**, *30*, 3355. Bastide, J.; Lematre, J. *Bull. Soc. Chim. Fr.* **1970**, 3543.

(22) 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. Mass spectra were determined with a Finnigan 4000 mass spectrometer at an ionizing voltage of 70 eV.

(23) Farnum, D. G.; Yates, P. *J. Am. Chem. Soc.* **1962**, *84*, 1399.

phenylpyrazolin-5-one (**3c**) as bright yellow needles: mp 93–94 °C;[24] IR (KBr) 4.56, 5.92, 6.25, 6.33, 6.67, 6.99, 7.19, 7.35, 8.85, 9.90 μm; UV (95% ethanol) 322 nm (ε 1770), 280 sh (4930), 247 (30 200); ^{1}H NMR (CCl_4, 90 MHz) δ 2.17 (s, 3 H), 6.97–7.48 (m, 3 H), 7.80–7.98 (m, 2 H); ^{13}C NMR ($CDCl_3$, 20 MHz) 162.8, 141.8, 138.3, 128.5, 126.6, 118.7, 13.5 ppm; MS, *m/e* 200 (M^+, base), 105, 77, 51. Anal. Calcd for $C_{10}H_8N_4O$: C, 59.99; H, 4.03; N, 27.99. Found: C, 60.01; H, 4.05; N, 27.96.

Cycloaddition Reactions with Dimethyl Acetylenedicarboxylate: Reaction with 4-Diazo-3-phenylpyrazolin-5-one (3a). A solution containing 0.50 g of diazopyrazolinone **3a** and 0.42 g of dimethyl acetylenedicarboxylate in 10 mL of dry toluene was heated in a sealed tube at 165 °C for 16 h. When the mixture cooled, a colorless solid (0.76 g, 86%) precipitated from solution. A single recrystallization from benzene gave dimethyl 7-oxo-4-phenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazine-2,3-dicarboxylate (**4a**) as shiny cream needles: mp 192–194 °C; IR ($CHCl_3$) 2.92, 3.29, 5.75, 7.55, 7.78, 8.33, 8.77, 9.09, 9.39 μm; UV (95% ethanol) 282 nm (ε 11 000), 232 (12 000); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.43 (s, 3 H), 3.98 (s, 3 H), 7.53 (s, 5 H); MS, *m/e* 328 (M^+), 265, 209, 153, 139, 137, 105, 77 (base), 59. Anal. Calcd for $C_{15}H_{12}N_4O_5$: C, 54.88; H, 3.68; N, 17.07. Found: C, 54.79; H, 3.72; N, 17.05.

Reaction with 4-Diazo-1-methyl-3-phenylpyrazolin-5-one (3b). A solution containing 0.40 g of diazopyrazolinone **3b** and 0.30 g of dimethyl acetylene dicarboxylate in 10 mL of dry toluene was heated in a sealed tube at 165 °C for 16 h. After cooling, the solution was concentrated, applied to a short plug of silica, and eluted with a 10% acetone/hexane mixture. Concentration of the forerun of 2 L, followed by trituration with cold ether, afforded 0.46 g (67%) of a colorless solid. Recrystallization from acetone/hexane furnished dimethyl 6-methyl-7-oxo-4-phenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazine-2,3-dicarboxylate (**4b**) as colorless crystals: mp 119–121 °C; IR (KBr) 5.81, 6.33, 6.43, 6.80, 6.92, 7.04, 7.25, 7.49, 7.69, 9.09, 8.58, 10.42, 12.05, 12.50, 1274 μm; UV (95% ethanol) 288 nm (12 000), 232 (13 000); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.42 (s, 3 H), 3.95 (s, 3 H), 3.98 (s, 3 H), 7.53 (s, 5 H). Anal. Calcd for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.12; N, 16.37. Found: C, 56.69; H, 4.07; N, 16.53.

Reaction with 4-Diazo-3-methyl-1-phenylpyrazolin-5-one (3c). A solution containing 0.50 g of diazopyrazolinone **3c** and 0.39 g of dimethyl acetylenedicarboxylate in 10 mL of dry toluene was heated in a sealed tube at 165 °C for 16 h. The solid (0.79 g, 87%) which precipitated upon cooling was removed by filtration and washed with cold toluene. A single recrystallization from benzene gave dimethyl 4-methyl-7-oxo-6-phenyl-6*H*-pyrazolo-[1,5-*d*][1,2,4]triazine-2,3-dicarboxylate (**4c**) as off-white plates: mp 142–143 °C; IR (KBr) 5.62, 5.65, 6.29, 6.45, 6.76, 7.19, 7.41, 7.69, 8.06, 8.47, 9.17, 10.31 μm; UV (95% ethanol) 292 nm (ε 10 700); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.57 (s, 3 H), 3.95 (s, 3 H), 3.97 (s, 3 H), 7.31–7.77 (m, 5 H); MS, *m/e* 342 (M^+), 311, 310, 231, 119, 105, 91, 78 (base), 77. Anal. Calcd for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.09; N, 16.37. Found: C, 56.27; H, 4.15; N, 16.29.

Cycloaddition Reactions with Methyl Propiolate: Reaction with 4-Diazo-3-phenylpyrazolin-5-one (3a). A solution containing 0.54 g of diazopyrazolinone **3a** and 0.27 g of methyl propiolate in 10 mL of dry toluene was heated in a sealed tube at 165 °C for 16 h. The solid which precipitated upon cooling (0.59 g, 73%) was removed by filtration, washed with toluene, and dried. Slow recrystallization from methanol gave methyl 7-oxo-4-phenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazin-2-carboxylate (**5**) as colorless prisms: mp 235–236 °C; IR (KBr) 5.85, 6.49, 6.76, 6.85, 7.04, 7.30, 7.55, 7.75, 8.06, 9.01, 10.00, 10.64, 13.16 μm; UV (95% ethanol) 282 nm (ε 13 000), 238 (16 000); ^{1}H NMR (Me_2SO-d_6, 90 MHz) δ 3.94 (s, 3 H), 7.39 (s, 1 H), 7.52–7.76 (m, 3 H), 7.81–7.98 (m, 2 H); MS, *m/e* 271, 270 (M^+), 211, 140, 78 (base). Anal. Calcd for $C_{13}H_{10}N_4O_3$: C, 57.77; H, 3.73; N, 20.73. Found: C, 57.73; H, 3.86; N, 20.72.

Methyl 7-Oxo-6-methyl-4-phenyl-6*H*-pyrazolo[1,5-*d*]-[1,2,4]triazine-2-carboxylate (6). A sample of 0.07 g of sodium hydride was added in a single portion to a stirred solution containing 0.38 g of pyrazolotriazinone **5** in anhydrous dimethyl formamide. After 1 h at ambient temperature, 0.35 g of methyl iodide was added, and the solution was stirred overnight. The solution was then diluted with water and extracted thoroughly with ether. The ethereal phase was washed once with water, dried, and concentrated to a homogeneous buff-colored solid (0.25 g). A single recrystallization from benzene/hexane gave methyl 7-oxo-6-methyl-4-phenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazine-2-carboxylate (**6**) as colorless needles: mp 180–181 °C; IR (KBr) 5.71, 5.78, 6.90, 7.46, 7.69, 8.00, 8.20 μm; UV (95% ethanol) 290 nm (ε 12 390), 255 sh (903), 236 (14 510); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.97 (s, 3 H), 4.00 (s, 3 H), 7.32 (s, 1 H), 7.44–7.69 (m, 3 H), 7.71–7.95 (m, 2 H); MS, *m/e* 284 (M^+), 253, 225, 198, 196, 182, 168, 156, 155, 154, 140, 95 (base). Anal. Calcd for $C_{14}H_{12}N_4O_3$: C, 59.15; H, 4.26; N, 19.71. Found: C, 59.25; H, 4.30; N, 19.66.

Crystals of **6** were monoclinic with space group $P2_1$ and with a = 7.215 (4) Å, b = 12.217 (5) Å, c = 15.074 (7) Å, β = 94.36 (4)°, and d_{calcd} = 1.425 g cm^{-3} for Z = 4. The intensity data were measured on a Hilger-Watts diffractometer using nickel-filtered Cu Kα radiation by the θ–2θ scan technique with pulse-height discimination. A total of 1887 independent reflections were measured for θ < 57°, of which 1599 were considered to be observed with $I > 2.5\sigma(I)$. The structure was solved by a multiple-solution procedure and was refined by full-matrix least-squares methods.[25] In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not defined. The final discrepancy indices are R = 0.092 and R_w = 0.101 for the 1599 observed reflections. The final difference map has no peaks greater than ±0.5 e Å^{-3}.

Reaction with 4-Diazo-1-methyl-3-phenylpyrazolin-5-one (3b). A solution containing 0.50 g of diazopyrazolinone **3b** and 0.25 g of methyl propiolate in 10 mL of dry toluene was heated as described above for 16 h. After cooling, the solution was concentrated to a dark oil and subjected to column chromatography over silica. Elution with a 5% ethyl acetate/hexane mixture furnished two principle components which were isolated as colorless solids. The more mobile fraction was recrystallized once from benzene/hexane to give methyl 1-methyl-3-phenyl-1*H*-furo[2,3-*c*]pyrazole-5-carboxylate (**8**): 0.18 g (28%); colorless needles; mp 137–138 °C; IR (KBr) 5.87, 6.21, 7.19, 7.55, 8.20, 11.11, 13.79 μm; UV (95% ethanol) 302 nm (ε 24 800), 252 (12 410), 221 (8230); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.93 (s, 3 H), 3.96 (s, 3 H), 7.51 (s, 1 H), 7.34–7.59 (m, 3 H), 7.87–7.99 (m, 2 H); MS, *m/e* 256 (M^+), 172, 128, 91, 66 (base). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.67; H, 4.74; N, 10.89.

The solid isolated as the major fraction was shown to contain two compounds, the separation of which could be accomplished by trituration with cold acetone. The acetone-insoluble solid was purified by crystallization from ethyl acetate/hexane to give methyl 7-oxo-6-methyl-4-phenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazin-2-carboxylate (**6**): 0.30 g (40%); mp 180–181 °C; the spectral characteristics which were identical in all respects with those reported above; ^{13}C NMR ($CDCl_3$, 20 MHz) 161.3, 147.9, 142.9, 139.7, 135.9, 132.3, 130.4, 128.8, 127.2, 106.5, 52.4, 39.6 ppm. The filtrate obtained after removal of **6** from the major component mixture was concentrated to dryness and triturated with a small volume of cold ether. The resulting solid was removed by filtration, washed with additional ether, and finally recrystallized from benzene/hexane to give methyl 7-oxo-6-methyl-4-phenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazine-3-carboxylate (**7**): 0.25 g (34%); mp 137–138 °C; IR (KBr) 5.78, 6.99, 7.22, 7.30, 7.43, 8.00, 8.85, 9.48, 12.82, 13.89 μm; UV (95% ethanol) 299 nm (ε 10 300), 259 sh (10 000), 242 (11 240); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.39 (s, 3 H), 3.97 (s, 3 H), 7.50 (s, 5 H), 8.47 (s, 1 H); MS, *m/e* 284 (M^+, base), 253, 226, 105, 84, 77; ^{13}C NMR ($CDCl_3$, 20 MHz) 161.3, 146.3, 143.0, 140.4, 133.8, 132.4, 129.5, 128.9, 127.9, 111.8, 51.6, 39.5 ppm. Anal. Calcd for $C_{14}H_{12}N_4O_3$: C, 59.15; H, 4.26; N, 19.71. Found: C, 59.20; N, 4.26; N, 19.67.

Reaction with 4-Diazo-3-methyl-1-phenylpyrazolin-5-one (3c). A solution containing 0.50 g of diazopyrazolinone **3c** and 0.24 g of methyl propiolate in 10 mL of dry toluene was heated as described above for 16 h. After cooling, the solution was concentrated to a dark oil and subjected to preparative thin-layer chromatography, eluting with a 20% acetone/hexane mixture.

(24) Balli, H.; Gipp, R. *Justus Liebigs Ann. Chem.* **1966**, *699*, 133.

(25) Germain, G.; Main, P.; Woolfson, M. M. *Acta. Crystallogr., Sect. A* **1971**, *A27*, 368.

The two prominent species were extracted with methylene chloride and concentrated to colorless solids. The major component (R_f 0.45) was recrystallized from hexane to give methyl 3-methyl-1-phenyl-1*H*-furo[2,3-*c*]pyrazole-5-carboxylate (**9**): 0.33 g (44%); colorless needles; mp 119–120 °C; IR (KBr) 5.78, 6.39, 6.69, 6.97, 7.84, 8.37, 8.55, 9.39, 10.36, 11.17, 11.83, 13.07, 13.25 μm; UV (95% ethanol) 279 nm (sh, ε 15 410), 263 sh (22 930), 256 (23 640); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.39 (s, 3 H), 3.90 (s, 3 H), 7.22 (s, 1 H), 7.08–7.55 (m, 5 H); MS, *m/e* 256 (M^+), 225, 215, 169, 128, 103, 91, 77 (base); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 159.2, 155.4, 146.0, 141.0, 137.3, 129.2, 125.3, 116.9, 112.4, 111.8, 51.8, 13.51 ppm. Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.62; H, 4.73; N, 10.93.

Crystals of **9** were monoclinic, space group $P2_1/C$, with a = 7.393 (3) Å, b = 10.618 (3) Å, c = 16.065 (5) Å, β = 99.52 (3)°, and d_{calcd} = 1.368 g cm^{-3} for Z = 4. A total of 1166 independent reflections were measured for $\theta < 48°$, of which 936 were considered to be observed [$I > 2.50\sigma(I)$]. The structure was derived by using direct methods and refined by least-squares methods to give an R value of 0.042 for all the data.

The less mobile and minor species was recrystallized from benzene/cyclohexane to give methyl 7-oxo-4-methyl-6-phenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazin-3-carboxylate (**10**): 0.23 g (31%); colorless needles; mp 142–143 °C; IR (KBr) 5.65, 6.25, 6.67, 6.94, 7.30, 7.52, 7.69, 8.20, 8.47, 9.35, 10.99, 12.99 μm; UV (95% ethanol) 288 nm (ε 14 320); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.84 (s, 3 H), 3.94 (s, 3 H), 7.33–7.78 (m, 5 H), 8.48 (s, 1 H); MS, *m/e* 284 (M^+), 222, 159, 144, 119, 77 (base); ^{13}C NMR ($CDCl_3$, 20 MHz) 161.1, 146.8, 142.5, 139.7, 139.1, 135.4, 128.6, 128.0, 124.9, 111.5, 51.9, 21.0 ppm. Anal. Calcd for $C_{14}H_{12}N_4O_3$: C, 59.15; H, 4.26; N, 19.71. Found: C, 59.04; H, 4.29; N, 19.67.

Cycloaddition Reactions with Methyl Phenylpropiolate: Reaction with 4-Diazo-1-methyl-3-phenylpyrazolin-5-one (3c). A solution containing 0.50 g of diazopyrazolinone **3c** and 0.44 g of methyl phenylpropiolate in 10 mL of dry toluene was heated as described above for 16 h. After cooling, the solution was concentrated to a dark oil and triturated with a small volume of cold ether. The resulting off-white solid was removed by filtration and recrystallized from benzene/hexane to give methyl 7-oxo-4-methyl-2,6-diphenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazin-3-carboxylate (**13**): 0.41 g (45%); colorless plates; mp 207–208 °C; IR (KBr) 5.73, 5.83, 6.29, 6.35, 6.92, 7.19, 7.72, 8.03, 8.62, 9.39, 9.66, 9.80, 11.56, 12.42, 13.16 μm; UV (95% ethanol) 294 nm (ε 14 760), 240 (29 900); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.57 (s, 3 H), 3.70 (s, 3 H), 7.21–7.62 (m, 10 H); MS, *m/e* 360 (M^+), 329, 328, 302, 139, 129, 105, 91, 86, 84, 77 (base). Anal. Calcd for $C_{20}H_{16}N_4O_3$: C, 66.66; H, 4.48; N, 15.55. Found: C, 66.65; H, 4.51; N, 15.55. No evidence for the presence of the regioisomeric cycloadduct could be obtained.

Reaction with 4-Diazo-3-methyl-1-phenylpyrazolin-5-one (3b). A solution containing 0.34 g of diazopyrazolinone **3b** and 0.54 g of methyl phenylpropiolate in 10 mL of dry toluene was heated as described above for 36 h. After cooling, the solution was concentrated to a dark oil, applied to a column of silica, and eluted with a 5% acetone/hexane mixture. The major fraction isolated was a white solid which was recrystallized from benzene/hexane to give 0.31 g (51%) of methyl 7-oxo-6-methyl-2,4-diphenyl-6*H*-pyrazolo[1,5-*d*][1,2,4]triazin-3-carboxylate (**12**) as colorless needles: mp 182–183 °C; IR (KBr) 5.80, 6.90, 6.97, 7.22, 7.41, 7.84, 8.37, 8.62, 9.43, 12.90, 12.99, 14.29 μm; UV (95% ethanol) 291 nm (ε 11 490), 248 (33 560); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.20 (s, 3 H), 3.95 (s, 3 H), 7.37–7.66 (m, 8 H), 7.76–7.97 (m, 2 H); MS, *m/e* 360 (M^+), 329, 284, 225, 202, 127, 105, 77 (base). Anal. Calcd for $C_{20}H_{16}N_4O_3$: C, 66.66; H, 4.48; N, 15.55. Found: C, 66.75; H, 4.52; N, 15.49.

Cycloaddition Reactions with Methyl Acrylate: Reaction with 4-Diazo-1-methyl-3-phenylpyrazolin-5-one (3b). A solution containing 0.15 g of diazopyrazolinone **3b** and 0.13 g of freshly distilled methyl acrylate in 10 mL of dry toluene was heated as previously described for 12–16 h. The cooled solution was concentrated to a dark oil and subjected to column chromatography over silica, eluting with a 3% acetone/hexane mixture. The more mobile species was recrystallized from ether/hexane to give 0.11 g (50%) of methyl spiro[1-methyl-3-phenylpyrazolin-5-one-4,1′-cyclopropane]-2′-carboxylate (**14**) as colorless plates: mp 89–90 °C; IR (KBr) 5.73, 5.88, 6.99, 7.38, 7.87, 8.33, 8.51, 9.76, 10.36, 13.16, 13.79, 14.29 μm; UV (95% ethanol) 278 nm (ε 8024), 223 (4248); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.03 (m, 1 H), 2.67 (m, 2 H), 3.10 (s, 3 H), 3.48 (s, 3 H), 7.38 (s, 5 H); ^{13}C NMR ($CDCl_3$, 20 MHz) 171.4, 166.2, 156.0, 131.1, 129.3, 127.9, 127.3, 51.5, 36.2, 31.7, 34.0, 19.4 ppm; MS, *m/e* 258 (M^+, base), 226, 199, 185, 155, 128, 115, 77. Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 64.97; H, 5.47; N, 10.85.

The less mobile species was obtained as a homogeneous colorless oil (0.07 g) which slowly solidified. Recrystallization from hexane gave methyl spiro[1-methyl-3-phenylpyrazolin-5-one-4,1′-cyclopropane]-2′-carboxylate (**15**): 32% yield; colorless needles; mp 109–110 °C; IR (KBr) 5.78, 5.92, 6.94, 7.46, 7.94, 9.01, 9.71, 12.99, 13.79, 14.39 μm; UV (95% ethanol) 301 nm (ε 9450), 222 (7810); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.15–2.43 (m, 2 H), 3.00 (t, 1 H, J = 8.7 Hz), 3.44 (s, 3 H), 3.73 (s, 3 H), 7.43 (s, 5 H); MS, *m/e* 258 (M^+, base), 226, 199, 185, 155, 128, 115, 77; ^{13}C NMR ($CDCl_3$, 20 MHz) 170.0, 166.3, 155.0, 130.05, 129.0, 125.9, 52.5, 35.5, 31.9, 32.4, 21.22 ppm. Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 65.09; H, 5.46; N, 10.85.

Reaction with 4-Diazo-3-methyl-1-phenylpyrazolin-5-one (3c). A solution containing 0.50 g of diazopyrazolinone **3c** and 0.43 g of methyl acrylate in 10 mL of dry toluene was heated as described above for 16 h. The cooled solution was concentrated to a dark oil which was purified by preparative thin-layer chromatography (20% acetone/hexane) and recrystallized from hexane to give 0.52 g (72%) of methyl spiro[3-methyl-1-phenylpyrazolin-5-one-4,1′-cyclopropane]-2′-carboxylate (**16**) as shiny colorless needles: mp 69–70 °C; IR (KBr) 5.76, 5.83, 6.27, 6.64, 6.71, 7.17, 7.43, 7.84, 8.23, 8.40, 10.53, 10.99, 13.07 μm; UV (95% ethanol) 262 nm (ε 3432), 232 (17 510); NMR ($CDCl_3$, 90 MHz) δ 1.93 (dd, 1 H, J = 8.7 Hz), 2.04 (s, 3 H), 2.28 (dd, 1 H, J = 8.7 Hz), 2.74 (t, 1 H, J = 8.7 Hz), 3.76 (s, 3 H), 7.06–7.51 (m, 3 H), 7.83–8.01 (m, 2 H); ^{13}C NMR ($CDCl_3$, 20 MHz) 170.0, 168.2, 157.0, 138.3, 128.7, 124.9, 118.5, 52.4, 39.0, 33.3, 20.9, 14.9 ppm; MS, *m/e* 258 (M^+), 226, 199, 185, 118, 105, 91, 77 (base). Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 65.12; H, 5.47; N, 10.84.

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Registry No. 3a, 84752-10-3; **3b**, 82937-04-0; **3c**, 1781-33-5; **4a**, 84752-11-4; **4b**, 84752-12-5; **4c**, 84752-13-6; **5**, 84752-14-7; **6**, 82937-05-1; **7**, 82937-06-2; **8**, 82937-07-3; **9**, 82937-08-4; **10**, 82937-09-5; **12**, 84752-15-8; **13**, 84752-16-9; **14**, 84752-17-0; **15**, 84752-18-1; **16**, 84752-19-2; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; methyl phenylpropiolate, 4891-38-7; methyl acrylate, 96-33-3; *p*-toluenesulfonyl azide, 941-55-9; 3-phenylpyrazolin-5-one, 4860-93-9; 3-methyl-1-phenylpyrazolin-5-one, 89-25-8.

Supplementary Material Available: Tables of the final atomic parameters, bond lengths, and bond angles and structures for compounds **6** and **9** (10 pages). Ordering information is given on any current masthead page.