ether. After drying, the solvent was evaporated to a yellow solid. Recrystallization from ethanol–water gave 64 mg (22%) of yellow needles of **20**: mp 114–115°; ν^{KBr} 2120, 1690, 1378 cm^{-1}; λ_{max}^{MeOH} 238 mμ (ε 25,500), 278 (15,300), 355 (1290); δ^{CDCl_3} 2.20 (s, 3), 7.50 (s, 5).

Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.93; H, 3.73; N, 13.03.

Reaction of 18 and 19 in Acetic Acid.—To a solution of 2.0 g of the mixed alcohols **18** and **19** in 50 ml of glacial acetic acid was added about 100 mg of copper powder. The solution was stirred at 45° until gas evolution became very slow (1 hr). The mixture was filtered and the acetic acid was evaporated. The residual greenish-brown syrup was dissolved in CH_2Cl_2 and washed with water to remove copper salts. The organic phase was dried and concentrated and the residue (1.47 g) was chromatographed on 40 g of silicic acid. The first two fractions, eluted with chloroform, gave 190 mg of dark yellow oil which was distilled in short-path apparatus to give 140 mg (10%) of yellow crystals of methylphenylcyclopentene-1,3-dione (**21**): mp 117–118°; ν^{KBr} 1740, 1705, 1385 cm^{-1}; λ_{max}^{MeOH} 224 mμ (ε 10,000), 286 (7800); δ^{CDCl_3} 2.18 (s, 3), 3.03 (s, 2), 7.49 (s, 5).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.34; H, 5.47.

Conversion of 21 to 20.—To a solution of 61 mg (0.33 mmol) of dione **21** and 71 mg (0.35 mmol) of *p*-toluenesulfonyl azide in 2 ml of acetonitrile was added 0.15 ml of triethylamine. The yellow solution darkened rapidly and tlc examination after 30 min showed no starting material remaining. The orange solution was diluted with 20 ml of ether, washed with water, dried, and concentrated to a dark, noncrystalline residue. Chromatography over a short silicic acid column (85:15 chloroform–benzene eluent) gave 39 mg of an orange oil which crystallized on addition of a few drops of benzene. Recrystallization from benzene–hexane gave 30 mg (43%) of orange needles, mp 112–114°, mixture melting point with **20** prepared by oxidation, 112–114°. The ir spectra of the two samples matched in all peaks.

Registry No.—**2**, 40704-62-9; **4**, 40704-63-0; **5**, 40704-64-1; **6**, 1706-26-9; **7a**, 40704-65-2; **7b**, 40704-66-3; **8**, 24302-15-6; **9**, 40704-14-1; **10**, 40704-68-5; **11**, 40704-69-6; **12**, 24302-17-8; **13a**, 40704-16-3; **13b**, 40704-17-4; **18**, 40704-18-5; **19**, 40704-19-6; **19** acetate, 40704-20-9; **20**, 40674-82-6; **21**, 40704-21-0; (*Z*)-α-methylcinnamic acid, 15250-29-0; diazomethane, 334-88-3; bis(*N*-methyl-*N*-nitroso)terephthalamide, 133-55-1; 3-methyl-4-phenylpyrazole, 13788-84-6.

Heterocyclic Studies. 41. The Conversion of 3-Diazoacetylpyrazolines to Pyrazoles *via* Pyrazolo[1,5-*c*]-*v*-triazines[1]

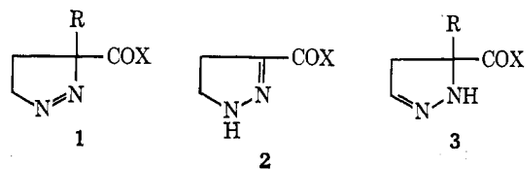
F. BARTOW CULP, AIKO NABEYA, AND JAMES A. MOORE*

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received December 12, 1972

3-Diazoacetyl-4-methoxycarbonyl-3-methyl-1-pyrazoline (4) is converted by base to the pyrazolotriazinone **6**. Further reaction of **6** with base leads to the pyrazole **8** and methyl glyoxylate hydrazone (**9**). The hydrazone was also isolated, together with pyrazoles, from the reaction of several related diazoacetylpyrazolines in base, but triazinone intermediates were not detected. *cis*- and *trans*-3,4-di(methoxycarbonyl)-3-methyl-1-pyrazolines (**17** and **18**) were found to epimerize at C-4 on conversion to the 5-pyrazolines, suggesting that the triazinone **6** is isolable because of the rapid isomerization of the double bond in the presumed intermediate **7**.

The 1-pyrazolines **1** (R = H) that are initially formed in the 1,3-dipolar addition of diazomethane to α,β-unsaturated carbonyl systems containing no α substituent are highly labile and rapidly isomerize to the conjugated 2-pyrazoline **2**. With a 3-alkyl or aryl substituent (**1**, R ≠ H) the 1-pyrazolines are more stable, but isomerization with acid or base under mild conditions leads to the 5-pyrazoline **3**.[2] In the preparation of diazabicyclo[3.2.0]heptenones from 3-diazoacetylpyrazolines (**1** X = CHN_2), milder acid conditions can be used for the cyclization if base-catalyzed isomerization to **3** is carried out prior to the



cyclization step.[3] It has been found, however, that longer exposure of a 3-diazoacetyl-5-pyrazoline to base leads to formation of a pyrazole.[2a] The reactions of these compounds with base have now been further examined, and the nature of this unusual elimination reaction has been clarified.

In the attempted tautomerization of the 4-methoxycarbonylpyrazoline **4**[3] with base, an isomer was obtained which was not the diazoacetyl-5-pyrazoline. The ir spectrum contained no diazo band; the nmr spectrum contained peaks for two NH protons and two singlet vinyl protons at δ 6.61 and 6.81 as well as CH_3 signals at δ 1.31 and 3.88 (OCH_3). The uv spectrum had λ_{max} 330 nm (ε 6000). The mass spectrum contained a small parent ion peak at *m/e* 210 and two more intense peaks at *m/e* 141 and 109, corresponding to loss of a C_2HN_2O fragment and further loss of CH_3O. These data, particularly the nmr values, define the bicyclic triazinone structure **6**, resulting from isomerization of the pyrazoline, nucleophilic attack of N-2 at the terminus of the diazocarbonyl group, and tautomerization (Chart I).

A number of reactions have been observed in which the diazo group in $COCHN_2$ and $COCN_2CO$ systems coordinates various nucleophiles, including HSO_3^-, CN^-, amines, phosphines, and hydrazine.[4] In the last case, the intermediate tetrazene breaks down to give an azide.[5] A chain of four contiguous nitrogen atoms has previously been obtained in this type of coupling only with arenediazonium ions and hydrazines or pyrazoles,[6] and with these products the coupling is reversed in acid. The pyrazolotriazinone **6** was relatively stable in acid, and did not give the 1,2-

(1) Supported in part by Grant G.P. 5219 from the National Science Foundation.

(2) (a) J. A. Moore and R. W. Medeiros, *J. Amer. Chem. Soc.*, **81**, 6026 (1959); (b) J. A. Moore, F. J. Marascia, R. W. Medeiros, and R. L. Wineholt, *J. Org. Chem.*, **31**, 34 (1966).

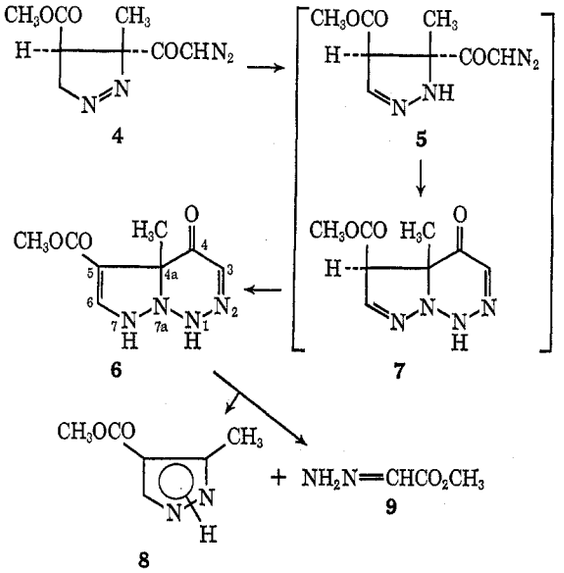
(3) A. Nabeya, F. B. Culp, and J. A. Moore, *ibid.*, **35**, 2015 (1970).

(4) R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

(5) T. Curtius, A. Darapsky, and A. Bockmuhl, *Ber.*, **41**, 344 (1908).

(6) E. Koenigs and J. Freund, *ibid.*, **80**, 143 (1947).

CHART I

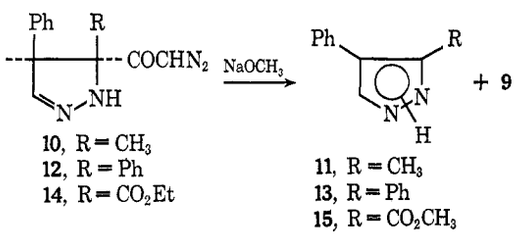


diazepinone which arises[3] from protolysis of the 1-pyrazoline **4**.

The yield of the triazinone **6** in the reaction of **4** with methanolic sodium methoxide was very low because of the rapid further conversion of **6** to the pyrazole **8**. A better procedure for preparing **6** is the reaction of **4** with triethylamine as the base. When solutions of **4** or **6** and a catalytic amount of methoxide stood for several days at 0°, another product was isolated. This material was identified as methyl glyoxylate hydrazone (**9**) by comparison with a sample prepared from α-methoxycarbonyltriphenylphosphazine.[7]

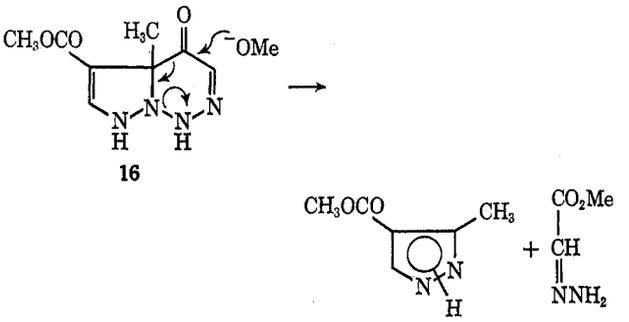
The formation of **8** and **9** from reactions of **4** with base prompted further examination of the products arising from the phenylpyrazoline **10** and also the diphenyl- and 3-ethoxycarbonyl-4-phenylpyrazolines **12** and **14** (Chart II). Conversion of the 3-methyl-4-

CHART II



phenyl-5-pyrazoline **10** (or the Δ^1 isomer) to pyrazole **11** was found to occur under much milder conditions than were previously used,[2] and the hydrazone **9** was isolated under conditions comparable to those used with **4**. Similarly, the *cis*-diphenylpyrazoline **12**[8] and the *c*-4-phenyl-*r*-3-carboxylate **14** were converted to pyrazoles **13** and **15**, respectively; hydrazone **9** was isolated from the same reaction mixture with **13**.

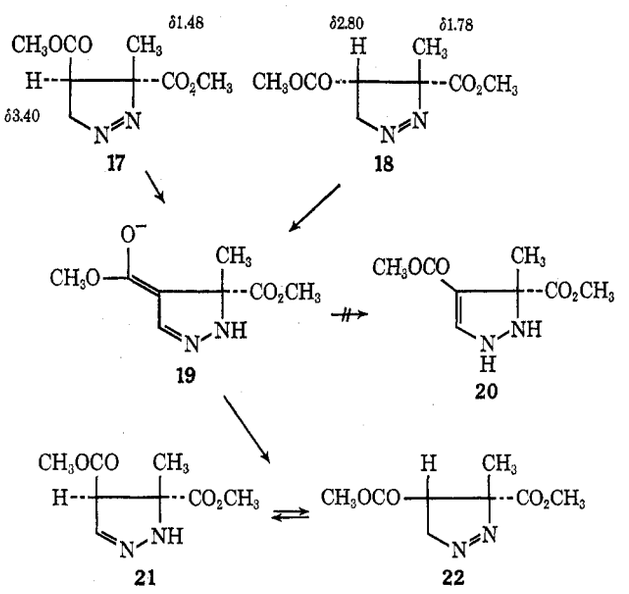
The formation of pyrazole **11** was previously depicted as a β elimination of the $COCHN_2$ group from the pyrazoline **10**.[2] Although this represents the overall reaction, there is no basis for investing the $COCHN_2$ anion with the role of a leaving group. The bicyclic triazine **6** (Chart I) provides a much more satisfactory picture of the process in the case of the 4-methoxycarbonylpyrazoline **1**. The pyrazole and hydrazono ester can arise directly by nucleophilic addition to the carbonyl group and vinylogous elimination as shown in **16**.



Questions remain, however, as to whether a triazinone intermediate is involved in the reactions of the 4-phenylpyrazolines, and why the 5-pyrazoline is not observed in the methoxycarbonyl case. The contrasting behavior of the two series obviously stems from the nature of the C-4 substituent. To probe these points, the pyrazoline diesters **17** and **18** and the 4-phenyl ester **23** were examined as models for the diazo ketones.

The pyrazolines **17** and **18** were described by von Auwers,[9,10] and these preparations were repeated (Chart III). The crude 1-pyrazoline **17** from dimethyl

CHART III



mesaconate was >95% pure by nmr; **18**, from dimethyl citraconate, contained an impurity and was distilled. Treatment of either **17** or **18** with sodium methoxide gave the same mixture of 5-pyrazolines **21** and **22**, in

(7) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 619 (1919); H. Staudinger and G. Lüscher, *ibid.*, **5**, 75 (1922).

(8) The reaction of the 3,4-*trans*-diphenylpyrazoline is discussed in the accompanying paper: A. Nabeya, K. Kurita, and J. A. Moore, *J. Org. Chem.*, **38**, 2954 (1973).

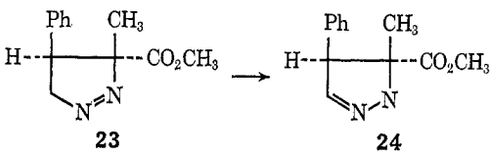
(9) K. von Auwers and E. Cauer, *Justus Liebigs Ann. Chem.*, **470**, 284 (1929).

(10) K. von Auwers and E. Koenig, *ibid.*, **496**, 97 (1932).

a ratio of 1.1:1.0.[11] The reaction of either pyrazoline with anhydrous HCl gave a salt whose nmr spectrum in D_2O showed the same mixture of **21** and **22**, with the H-4 proton signals absent. Isomerization of **17** to **21** and **22** was also observed on heating; after 22 hr at 110°, conversion to the same mixture of **21** and **22** was 60% complete.

The rapid conversion of the Δ^1-pyrazoline esters **17** and **18** to the same mixture of epimeric 5-pyrazolines demonstrates the ease of enolization with the 4-carboxylate substituent (*cf.* **19**). However, the Δ^4-pyrazoline **20** is not present in detectable amounts in the equilibrium mixture. Monocyclic pyrazolines with this tautomeric structure have been observed only when N-1 is substituted, and apparently the conjugated enamino ester system in **20** is insufficient to stabilize this structure. In the diazoacetylpyrazoline, however, cyclization of the side chain (**5** → **7** in Chart I) apparently tips the equilibrium in favor of the conjugated tautomer **6**, perhaps owing to relief of steric repulsion between the ester and bridgehead methyl groups in **7**.

In the 4-phenyl series, the pyrazoline ester **23** was prepared by addition of diazomethane to methyl α-methylcinnamate during a period of several weeks; this reaction had previously been reported to give the α,β-dimethyl ester.[9] Treatment of **23** with base under conditions which led to a mixture of the epimeric diesters **21** and **22** gave the 5-pyrazoline **24**, without



23 **24**

deuterium exchange or epimerization. The diazoacetyl-Δ^5-pyrazoline **10** was unaffected by similar conditions. At a higher base concentration, sufficient to cause conversion to the pyrazole **11**, slow deuterium exchange of H-4 in **10** did occur; when the formation of **11** was 50% complete, the area of the H-4 signal in the remaining **10** indicated approximately 25% exchange.

These qualitative observations suggest the possibility that the pyrazoles may be formed by the same mechanism from both the methoxycarbonyl and phenylpyrazolines, with the contrasting behavior in the two series owing simply to differences in the rates of the several steps. With this in mind, pseudo-first-order rate constants in excess 1.65×10^{-3} *M* methanolic sodium methoxide were determined spectrophotometrically for the 1-pyrazoline and the intermediate in each series. These values are given in Charts IV and V.

In the methoxycarbonyl series (Chart IV) the conversion of **6** to the pyrazole **8** plus hydrazone **9** was followed by the decrease in absorbance of **6** at λ_{max} 330 nm; an isosbestic point (associated with the formation of **9**) occurred at 292 nm. The disappearance of the 1-pyrazoline **4** could not be measured at its absorbance maximum because the further reaction of **6** interfered; the rate constant for **4** was obtained by assuming that **4**, **6**, **8**, and **9** are the only species present and following the change in **4** at 292 nm, the isosbestic point for the reaction of **6**.

CHART IV

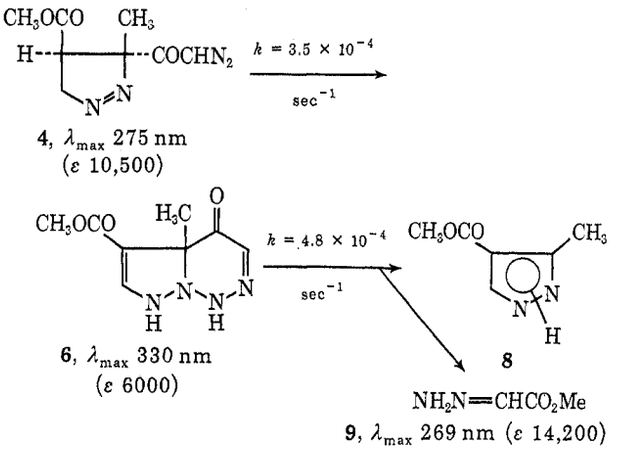
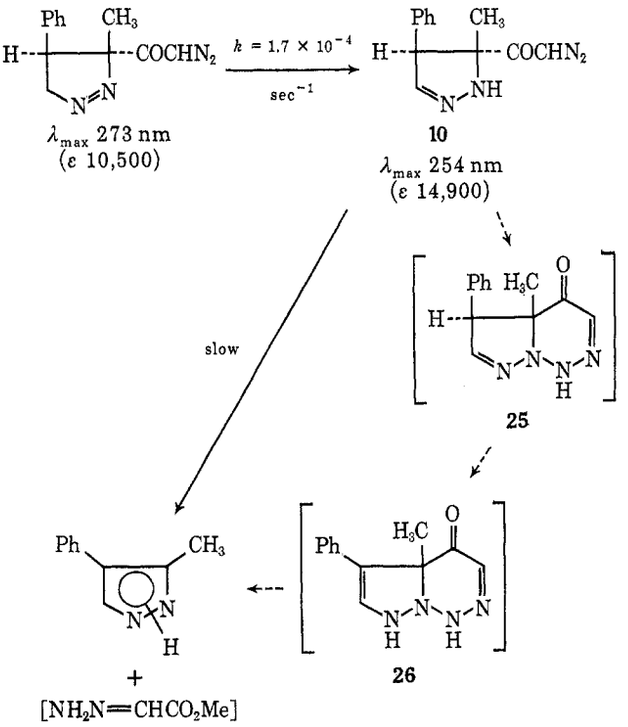


CHART V



In the 4-phenyl series (Chart V) the rate of isomerization of the 1-pyrazoline to the Δ^5 isomer was straightforward. However, the conversion of the 5-pyrazoline **10** to pyrazole plus hydrazone required 10^3-fold stronger base to obtain a comparable rate, and under these conditions the hydrazone **9** undergoes a further reaction which complicated the kinetics and prevented accurate measurement of the rate of reaction of **10**.

These kinetic data establish that the initial isomerization of the 1-pyrazolines in both series occurs at very nearly the same rate. In the methoxycarbonyl case, the conversion of the "missing" 5-pyrazoline

(11) The ratio is based on the nmr spectrum of the mixture of **21** and **22**. Although peaks for the CCH_3 and H-4 protons in each isomer were well resolved, the relative chemical shifts *vis-à-vis* those for the 1-pyrazolines of known configuration did not permit unequivocal assignment of signals to **21** and **22**, and it is not known which was present in the larger amount.

(5, Chart I) to 6 must be a much faster step, as borne out by the very rapid epimerization of the esters 17 and 18, and the fact that the kinetic plots show no detectable intermediate between 4 and the triazinone 6. The rate data show also that conversion of 6 to the pyrazole is actually slightly faster than its rate of formation in NaOMe. If the triazinone 26 is an intermediate in the phenyl series, its fragmentation should occur at a rate similar to that of 6, since this step involves the same six-membered ring in both cases, and a transition state of comparable stability. At the relatively high base concentration required for the reaction of the 5-pyrazoline 10, the triazinone 26 would not be detectable.

A final point is the sequence of enolization and N–N bonding steps in the formation of the triazinones 6, and presumably 26, from the 5-pyrazolines. From circumstantial evidence in related work[8] we are inclined to the sequence indicated in Charts I and V, with initial coupling to give the species 7 and 25, but there is no direct support for these intermediates.

Experimental Section

Methyl 1,4,4a,7-Tetrahydro-4a-methyl-4-oxopyrazolo[1,5-*c*]-*v*-triazine-5-carboxylate (6).—To an ice-cold solution of 1.05 g (5 mmol) of pyrazoline 4 in 40 ml of methanol was added 0.2 ml (0.4 mequiv) of freshly prepared 5% methanolic sodium methoxide. The yellow color of the solution deepened immediately and a new compound appeared in the tlc. After 2 hr at 0° the solution was neutralized by addition of Dry Ice and was concentrated and then diluted with chloroform. After removal of inorganic salts the resulting oil was chromatographed on silicic acid. Elution with alcohol-free chloroform gave in initial fractions 240 mg of unreacted 4. The second band eluted with chloroform gave 140 ml of yellow solid, mp 136–139°. This material sublimed to a yellow glass on the cold finger; this glass crystallized on rubbing to give cream-colored crystals of the triazinone 6: mp 140–142°; ν^{KBr} 3350, 1160, 1590 cm^{-1}; for nmr and uv, see text.

Anal. Calcd for $C_8H_{10}N_4O_3$: C, 45.71; H, 4.80; N, 26.66. Found: C, 45.96; H, 4.82; N, 26.27.

A more satisfactory preparation of 6 was effected by refluxing a methanolic solution of 206 mg of pyrazoline 4 and 0.5 ml of triethylamine. After 30 min, evaporation and chromatography of the mixture gave 116 mg (70%) of the triazinone 4.

Hydrazone 9 from 6.—A solution of the oxotriazine 6 (750 mg) in 15 ml of methanol containing 0.26 mequiv of sodium methoxide was allowed to stand for 4 days at 0°. After neutralization with Dry Ice the solution was concentrated and the residue was chromatographed on silicic acid. Elution with chloroform gave initially fractions from which 512 mg of unreacted 6 crystallized. Later fractions crystallized to give 21 mg of the hydrazone 9, mp 120–123°, mmp with synthetic material (below), 119–123°.

Methyl 3(5)-Methylpyrazole-4-carboxylate (8).—A cold solution of 2.0 g of the methoxycarbonylpyrazoline 4 in 75 ml of methanol was treated with 50 ml (47 mequiv) of 0.95 *N* methanolic sodium methoxide. After a few minutes, tlc indicated complete disappearance of the starting pyrazoline. The red solution was neutralized with Dry Ice and the solvent was evaporated. The residue was extracted with chloroform; after washing and drying, the chloroform was evaporated to a residue (300 mg) which crystallized on standing, mp 88–95°. Recrystallization from benzene–hexane gave tiny white needles of the pyrazole 8: mp 89–90°; ν^{KBr} 3050, 1722, 1582 cm^{-1}; λ_{max}^{MeOH} 223 nm (ϵ 9700); δ ($CDCl_3$) 12.24 (broad, exchanged in D_2O), 7.98 (s, 1), 3.84 (s, 3), 2.57 (s, 3).[12]

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 19.99. Found: C, 51.32; H, 6.04; N, 20.17.

To obtain an authentic specimen of this pyrazole ester, a sample of dimethyl 3-methyl-1-pyrazoline-3,5-dicarboxylate was prepared by addition of excess diazomethane to 10 g of dimethyl mesaconate. The resulting crude pyrazoline was treated in chloroform with bromine until an orange color persisted and the solution was then concentrated to a brown semisolid residue. This material was then heated for 2 hr with 30 ml of concentrated hydrochloric acid. A small amount of white solid which separated from this solution was removed and discarded, and the dark filtrate was then neutralized with KOH, filtered, and concentrated. The gummy residue was extracted with chloroform to give a solid; recrystallization from ethanol–water gave a white powder, mp 220–230°; further recrystallization from chloroform gave 3(5)-methylpyrazolecarboxylic acid, mp 228° (lit.[13] mp 228–229°).

Treatment of this acid in methanol solution with diazomethane gave a yellow oil which was taken up in benzene. After filtration to remove unreacted acid the solution was evaporated and crystallized by adding hexane. The gray solid was sublimed at 70° to give colorless crystals of methyl ester 8, mp 86–88°; the ir spectrum (16 peaks) corresponded to that of the ester obtained from 4.

3-Methyl-4-phenylpyrazole (11).[2a]—3-Diazoacetyl-*c*-3-methyl-*r*-4-phenyl-1-pyrazoline[2] (700 mg, 4.4 mmol) was dissolved in 20 ml of methanol. After the solution was flushed with nitrogen, 7 ml (8.8 mequiv) of 1.25 *N* methanolic sodium methoxide was added dropwise and the solution was then stored at 0° for 2 days. The solution was then neutralized with HCl and evaporated to a dark semisolid residue which was extracted with methylene chloride. After washing andd rying, the organic layer was evaporated to give 470 mg of pyrazole 11 as a yellowish solid, mp 140–145°.

Methyl Gloxylate Hydrazone.—A solution of 3 g of the 4-phenyl-1-pyrazoline in 85 ml of methanol was treated with 1.2 ml of 1.3 *N* methanolic sodium methoxide. After standing at 0° for 10 days the solution (two spots by tlc) was neutralized with Dry Ice and concentrated *in vacuo*. Addition of water caused a large crop of the 5-pyrazoline 10[2] to precipitate. After pyrazoline was removed the aqueous residue was evaporated to a red-brown solid which was extracted with hot benzene. Concentration of the benzene solution gave a tan solid which was recrystallized from benzene–hexane to give 40 mg of the hydrazone 9, mp 120–123°. Sublimation gave colorless crystals: mp 124–125°; ν^{KBr} 3350–3150, 1700, 1540 cm^{-1}; δ ($CDCl_3$) 7.07 (s, 1, –CH=N), 6.5 (broad, 2, exchanges with D_2O), 3.83 (s, 3).

Anal. Calcd for $C_3H_6N_2O_2$: C, 35.29; H, 5.92; N, 27.44. Found: C, 35.12; H, 6.02; N, 27.23.

An authentic sample of 9 was synthesized as follows:[7] Methoxycarbonyltriphenylphosphazine was prepared by combining ether solutions of 8.0 g of methyl diazoacetate[14] and 35 g of triphenylphosphine. The solution became warm and, on cooling, a mass of crystals separated which were collected and washed with ether to give 23 g of pale yellow needles of the phosphazine, mp 107–110°. A solution of 10 g of the phosphazine in 40 ml of methanol–water (8:2) was refluxed for 30 min and then concentrated at reduced pressure. The resulting suspension was extracted with benzene to remove triphenylphosphine oxide and the aqueous solution was evaporated to a white solid residue. Sublimation [80° (0.1 mm)] gave 2.05 g of the hydrazone 9, mp 125–126°. The ir spectrum was identical with that of the sample isolated from 6 and from 10.

3,4-Diphenylpyrazole (13) from 12.—To a solution of 890 mg of 12[3] in 15 ml of methanol was added 3 ml of 1 *N* KOH. After 1 hr at room temperature the reaction mixture was neutralized with acetic acid and extracted with ether. After washing and drying, the ether was evaporated to a yellow gum which crystallized on addition of chloroform and petroleum ether (bp 30–60°). This solid, a mixture of hydrazone 9 and pyrazole 13, was placed in a sublimer. At a bath temperature of 100° (0.3 mm), the hydrazone sublimed as white crystals: mp 120°; ir nearly identical with spectra of earlier samples; the nmr spectrum showed a trace of 13.

Sublimation was continued at 150–160°, and 300 mg (45%) of the pyrazole 13 was collected: mp 150°; ν^{KBr} 3300, 3000 (broad), 1600 cm^{-1}; δ ($CDCl_3$) 12.2 (s, 1), 7.58 (s, 1, H-5), 7.4–7.2 (m, 10). Resublimation gave white crystals: mp 152–153°;[15] mass

(12) D. E. McGreer and Y. Y. Wigfield, *Can. J. Chem.*, **47**, 2095 (1969), report for 8 mp 93–94°, δ 7.95 (1), 3.83 (3), 2.54 (3).

(13) H. V. Pechmann and E. Burkard, *Ber.*, **33**, 3597 (1900).

(14) "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 424.

(15) W. E. Parham and W. R. Hasek, *J. Amer. Chem. Soc.*, **76**, 799 (1954), report mp 155° for 3,4-diphenylpyrazole.

spectrum apparent molecular ion m/e 220, base peak (M − 1) m/e 219.0922 (calcd for $C_{15}H_{11}N_2$, 219.0922).

Methyl 4-Phenylpyrazole-3-carboxylate (15).—A solution of 570 mg of ethyl 3-diazoacetyl-*c*-4-phenyl-1-pyrazoline-*r*-3-carboxylate (**14**)[3] in 10 ml of methanol was treated with 2 ml of 1 *N* KOH. After 1 hr at 30° tlc showed three new components in the reaction. The solution was diluted with water, neutralized with acetic acid, and extracted with methylene chloride. After washing and drying, the organic phase was concentrated to give 60 mg (14%) of crystalline residue, mp 180°. Recrystallization from methanol–water gave white crystals of the pyrazole **15**, mp 185°,[16] identical (mixture, melting point, ir) with authentic **15** prepared by reaction of (*Z*)-α-bromocinnamic acid with diazomethane; after a solution of the crude bromopyrazoline was concentrated, HBr was evolved and the pyrazole was isolated by crystallization from methanol. (Extensive ester exchange occurred in the reaction of the ethyl ester **14** in methanol.)

***trans*-3,4-Di(methoxycarbonyl)-3-methyl-1-pyrazoline (17)** was prepared from dimethyl mesaconate (3 g) and about 3 equiv of ethereal diazomethane. After 3 days the solution was evaporated to a nearly colorless oil: δ 1.48 (s, 3), 3.40 (three lines, J = 7.6 Hz, H-4), 3.69 (s, 3), 3.80 (s, 3), 4.90 (d, J = 7.6 Hz, 5-CH_2).

***cis*-3,4-Di(methoxycarbonyl)-3-methyl-1-pyrazoline (18)** was similarly prepared from dimethyl citraconate. The crude oil was distilled and **18** was obtained in the first fraction, bp 130–136° (7 mm) (65% yield), as a colorless oil which crystallized at 0°: δ 1.78 (s, 3), 2.80 (three lines, J = 8.2 Hz), 3.68 (s, 3), 3.72 (s, 3), 4.87 (d, J = 8.2 Hz, 5-CH_2).

Isomerization of 1-Pyrazolines 17 and 18.—One gram of the pyrazoline was dissolved in 30 ml of 0.15 *N* methanolic sodium methoxide. After 5 min, tlc showed absence of the starting pyrazoline. The solution was neutralized with Dry Ice and evaporated to a semisolid residue, which was extracted with CH_2Cl_2. After washing, drying, and evaporation the residue was a pale yellow oil. A typical nmr spectrum (from trans isomer **17**) contained the following peaks (δ, neat): two CCH_3 singlets at 1.41 and 1.65 with area ratio 23:21; four $-OCH_3$ singlets at 3.65–3.88, total area 100 (corresponding to two OCH_3 each in **21** and **22** plus H-4 of one isomer); a doublet (J = 1.8 Hz) at 4.38, area 9 (H-4 of one isomer); an exchangeable singlet at 6.29, area 16 (NH of both isomers); multiplet at 6.7, area 15 (C-5 of both isomers).

In a typical acid-catalyzed isomerization, a solution of **18** in ether was treated at 20° with a stream of HCl gas. The resulting white precipitate of hydrochloride was then extracted into water. The aqueous solution was treated with excess Na_2CO_3 and extracted with several portions of CH_2Cl_2, and the solution was dried and evaporated to an oil. The nmr spectrum in $CDCl_3$ closely resembled that described above. In DMSO-d_6 the H-4 signals from both isomers were resolved. The relative peak areas permitted matching the H-4 and CCH_3 peaks of the two isomers, which are designated A and B[11] (A/B = 1.1): δ 1.17 (s, 3-CH_3 of A), 1.43 (s, 3-CH_3 of B), 3.6–3.8 (four s, OCH_3), 4.0 (d, J = 1.8 Hz, H-4 of B), 4.5 (d, J = 1.7 Hz, H-4 of A), 5.3–5.7 (broad, NH), 6.9 (m, C-5 of A and B). In a 100-MHz spectrum ($CDCl_3$), the signal for the H-5 peaks was resolved into two doublets, J = 2 Hz.

***r*-3-Methoxycarbonyl-3-methyl-*t*-4-phenyl-1-pyrazoline (23).**—A solution of 3.75 g of freshly distilled methyl α-methylcinnamate in 20 ml of ether–methanol (1:1) was added to 250 ml of 0.3 *M* ethereal diazomethane. After standing for 3 weeks at 25° the pale yellow solution was filtered and evaporated. The resulting oil crystallized at 0°. Recrystallization from ether–pentane gave white crystals: mp 55–56°; δ ($CDCl_3$) 1.21 (s, 3), 3.45–3.8 (m, 1, H-4), 3.80 (s, 3), 4.83–4.98 (m, 2, H-5), 6.8–7.3 (m, 5).

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 66.27; H, 6.23; N, 13.03.

A solution of **23** in $CDCl_3$ and CD_3OD containing 0.1 equiv of NaOD was allowed to stand for some time. The nmr spectrum showed only peaks for the Δ^5 isomer **24**: δ 1.03 (s, 3), 3.8 (s, 3), 4.52 (d, J = 1.7 Hz, H-4), 6.8 (d, J = 1.7 Hz, H-5), 7.0–7.4 (m, 5); the areas of the δ 1.03 and 4.52 ppm peaks were in the ratio 3.0:1.0.

Rate Measurements.—The kinetic runs were carried out in a Cary Model 14 spectrophotometer with thermostated cell holders. Temperature was controlled at 25 ± 0.5° with a circulating bath; the cell temperature was monitored with a Model 42SC Telethermometer. Compounds were freshly sublimed or recrystallized and dried *in vacuo* before each series of measurements.

A 2.0-ml portion of the substrate in methanol was placed in a cuvette and equilibrated in the cell compartment for 30 min. One milliliter of standardized methanolic NaOMe was then added, the contents were mixed, and the spectrum was scanned for several half-lives. The reference cell contained 2 ml of methanol and 1 ml of the NaOMe solution. Values of k_1 were obtained from the slope of plots of log A at the appropriate wavelength *vs.* time.

Acknowledgment.—We are particularly grateful to Professor D. L. Dalrymple for helpful discussions and advice on the kinetic determinations.

Registry No.—**4**, 24302-22-5; **6**, 40711-65-7; **8**, 23170-45-8; **8** free acid, 40704-11-8; **9**, 19501-77-0; **10**, 5109-24-0; **11**, 13788-84-6; **12**, 24302-15-6; **13**, 24567-08-6; **14**, 40704-54-9; **15**, 5932-28-5; **17**, 40704-55-0; **18**, 40704-56-1; **23**, 40704-57-2; **24**, 40704-58-3; dimethyl 3-methyl-1-pyrazoline-3,5-dicarboxylate, 40704-10-7; diazomethane, 334-88-3; dimethyl mesaconate, 617-53-8; 3-diazoacetyl-*c*-3-methyl-*r*-4-phenyl-1-pyrazoline, 5109-38-6; 4-phenyl-1-pyrazoline, 40704-12-9; methyl α-methylcinnamate, 21370-57-0.

(16) K. von Auwers and O. Ungemacht, *Chem. Ber.*, **66**, 1205 (1933), report mp 184–187° for **15**.