several times with 20-ml portions of dry ether until the ether washings were colorless. The ether-insoluble residue was dissolved in 10 ml of hot water to which 35 ml of alcohol (95%) was added and the contents were cooled in a refrigerator overnight. Next morning this was filtered and the crystalline amino acid was dried, 2.8 g, mp 285° dec. Mother liquor was concentrated to 6 ml, diluted with alcohol (20 ml, 95%), and cooled. A further amount of alanine (0.9 g) was obtained, yield 74%. The amino acid obtained in this manner was recrystallized from aqueous alcohol when pure alanine (3.5 g), mp 288° dec, was obtained, yield 70%. A mixture melting point with DL-α-alanine (BDH) showed no depression.

The Reactions of 2-Diazo-3-butanone and 2-Diazocyclopentanone with Dimethyl Acetylenedicarboxylate

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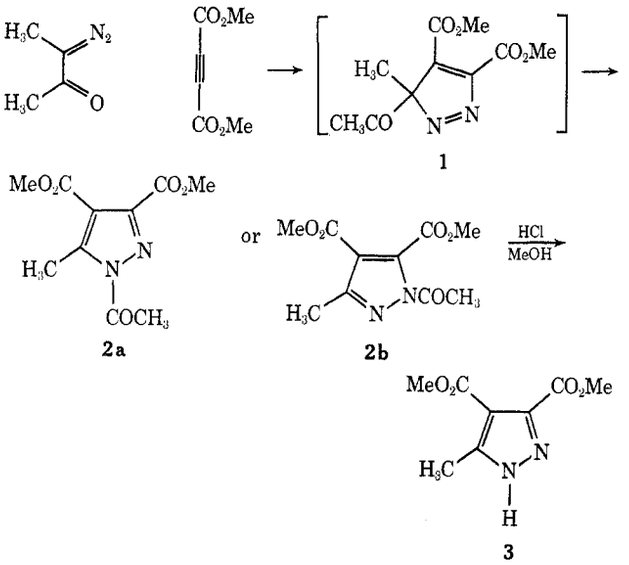
The product from the reaction of 2-diazo-3-butanone with dimethyl acetylenedicarboxylate (DMAD) was first assigned a dimethyl 3-acetyl-3-methyl-3*H*-pyrazole-4,5-dicarboxylate structure (**1**) by Diels and König.[1] Franck–Neumann and Buchecker report that this product is, in fact, an *N*-acetylpyrazole (**2a** or **2b**) resulting from thermal rearrangement of **1** with isomer **2a** being preferred on mechanistic grounds.[2,3]



We had also investigated this reaction and reached the same conclusions as Franck–Neumann and Buchecker. However, in view of the fact that *N*-acylpyrazoles are known to undergo thermal isomerization,[4,5] we felt that additional evidence was needed to confirm that **1** rearranged to **2a** and not to **2b**.

(1) O. Diels and H. König, *Chem. Ber.*, **71**, 1179 (1938).
(2) M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, 937 (1972).
(3) Similar rearrangements of diazocyclopentadiene–acetylene adducts have been reported recently: H. Düss and R. Sergio, *ibid.*, 3479 (1972).
(4) R. H. Wiley, Ed., in "Chemistry of Heterocyclic Compounds," Vol. 22, A. Weissberger, Ed., Interscience, New York, N. Y., 1967, p 137, and references cited therein.
(5) J. Castells, *Chem. Commun.*, 709 (1972).

Treatment of the 2-diazo-3-butanone–DMAD product with hot methanolic HCl gave dimethyl 3(5)-methylpyrazole-4,5(3,4)-dicarboxylate (**3**).[6] Acetylation of **3** under different conditions permitted the isolation of pure **2a** and **2b**. Treatment of **3** with acetic anhydride gave isomer A (identical with the 2-diazo-3-butanone–DMAD product) as the major product, whereas with acetyl chloride and pyridine in ether at room temperature the other isomer (B) was formed almost exclusively.

The results of thermal isomerization studies on A and B (Tables I and II) show A to be the more thermodynamically stable isomer. The data suggest, however, that B would not isomerize appreciably to A under the conditions used in the 2-diazo-3-butanone–DMAD reaction (refluxing ether, 2 hr). Thus, the presence of only A in the product indicates that the intermediate 3*H*-pyrazole (**1**) rearranges directly and entirely to A.

TABLE I

	N-acetyl isomer mixture (by vpc) %A	%B
Ac_2O, 24°, 2 hr	72	28
Ac_2O, reflux, 2 hr	80	20
AcCl, pyridine	8	92
Et_2O, 22°, 2.5 hr		

	A (2-Diazo-3-butanone–DMAD product)	B
Mp, °C	66–67	51–53
ν_{max} ($CHCl_3$), cm^{-1}	1742 (broad, ester, amide)	1739 (broad, ester, amide)
Nmr ($CDCl_3$), δ, ppm	2.75 (3 H, s)	2.50 (3 H, s)
	2.81 (3 H, s)	2.70 (3 H, s)
	3.88 (3 H, s)	3.87 (3 H, s)
	3.97 (3 H, s)	4.02 (3 H, s)

TABLE II

THERMAL ISOMERIZATION OF A AND B

Isomer	Temp, °C	Time	Product[a] % A	% B
A	Ambient	15 months	100	0
B	Ambient	15 months	>99[b]	<1
A	53	16 hr	100	0
B	53	16 hr	5	95
A	90	16 hr	100	0
B	90	16 hr	73	27
A	250	30 min	73	27
B	250	30 min	71	29
A	Reflux, ether	24 hr	100	0
B	Reflux, ether	24 hr	5	95

[a] By vpc analysis. [b] Melting point changed from 51–53° to 66–67°.

Unlike the spectroscopic properties listed above, the ultraviolet spectra of A and B were significantly different (Table III). The assignment of structures to A and B on the basis of this difference is discussed below.

Franck–Neumann and Buchecker referred to an investigation of the reactions of cyclic α-diazo ketones with DMAD but presented no results.[2] We have

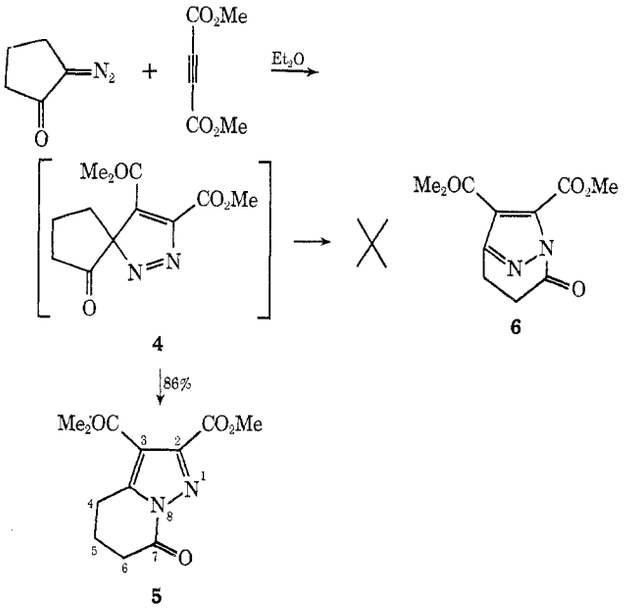
(6) H. Reimlinger, *Chem. Ber.*, **93**, 1857 (1960).

TABLE III

Compd	λ_{max}, nm (ϵ)[a]
A (2a)	237 (8700)
5	240 (8200)
B (2b)	251 (13,400)

[a] In 95% EtOH.

studied the reaction of 2-diazocyclopentanone[7] with DMAD.[8] Physical data confirmed that the product was dimethyl-4,5-dihydro-7(6*H*)-oxopyrazolo[1,5-*a*]pyridine-2,3-dicarboxylate (**5**) (rearrangement of the intermediate 3*H*-pyrazole **4** to **6** would violate Bredt's rule).



The similarity between the uv spectra of **5** and A (Table III) provides considerable support for the assignment of the dimethyl 1-acetyl-5-methylpyrazole-3,4-dicarboxylate (**2a**) structure to the 2-diazo-3-butanone–DMAD product (isomer A) and the dimethyl 1-acetyl-3-methylpyrazole-4,5-dicarboxylate (**2b**) structure to isomer B.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. Nmr spectra were recorded on Varian A-60A and HA60 instruments at 60 MHz in 5–10% deuteriochloroform solution with tetramethylsilane as an internal standard. Infrared spectra were obtained with a Perkin-Elmer Model 21 in chloroform solution, and ultraviolet spectra were determined in 95% ethanol solution on a Carey Model 15. Vpc analyses were performed on a Hewlett-Packard Model 402 instrument equipped with a flame ionization detector. A 4 ft × 4 mm, 3% OV-1 on Chromosorb W (HP) 80/100 mesh column at 125° and a He flow rate of 60 ml/min were used. Mass spectral data were obtained on a CEC Model 110 spectrometer.

Dimethyl 3(5)-Methylpyrazole-4,5(3,4)dicarboxylate (3).—A solution of 2.5 g (10.4 mmol) of the 2-diazo-3-butanone–DMAD adduct[1] in 140 ml of methanol and 0.5 ml of concentrated HCl was heated under reflux for 20 min and poured into 500 ml of water. The mixture was extracted with 3 × 50 ml of CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and concentrated. The residual oil was crystallized from benzene–hexane to give 1.7 g (82%) of **3** as tan crystals: mp 104–106° alone and mixed with an authentic specimen prepared from the reaction of diazoethane with DMAD;[6] ir 3425, 3180 (broad, NH), 1724 cm^{-1} (broad, C=O); nmr δ 2.52 (s, 3 H), 3.87 (s, 3 H), 3.91 (s, 3 H); mass spectrum *m/e* 198 (M^+).

Anal. Calcd for $C_8H_{10}N_2O_4$: C, 48.49; H, 5.09; N, 14.14. Found: C, 48.70; H, 5.34; N, 14.33.

Dimethyl 1-Acetyl-5-methylpyrazole-3,4-dicarboxylate (2a, Isomer A).—A solution of 0.7 g (3.54 mmol) of **3** in 20 ml of acetic anhydride was heated under reflux for 2 hr and then concentrated at 50° under reduced pressure. The residual oil was shown by vpc to contain isomers A (retention time 16 min) and B (retention time 12 min) in an 80:20 ratio (Table I). Crystallization from ether/Skelly B gave 0.5 g (59%) of **2a** (isomer A) (homogeneous by vpc) as colorless needles, mp 64–66° alone and mixed with 2-diazo-3-butanone–DMAD adduct.[1] Ir and nmr are presented in Table I and uv in Table III.

Acetylation of **3** in acetic anhydride at 24° for 24 hr gave a 72:28 mixture of isomers A and B (vpc, Table I).

Dimethyl 1-Acetyl-3-methylpyrazole-4,5-dicarboxylate (2b, Isomer B).—A mixture of 1 g (5.05 mmol) of **3**, 0.75 g of pyridine, 0.75 g of acetyl chloride, and 50 ml of ether was stirred for 2.5 hr at 22°. Water (40 ml) was added and after stirring for 0.5 hr the ether layer was separated, washed with water (2 × 50 ml) and brine (50 ml), and dried (Na_2SO_4). Removal of solvent under reduced pressure at <25° left a pale yellow oil which crystallized on standing. Vpc indicated that the product was a mixture of isomers A and B in the ratio 8:92 (Table I). Recrystallization from ether–hexane gave 0.5 g (41%) of **2b** (isomer B), mp 51–53°. This material was homogeneous by vpc. Ir and nmr are shown in Table I and uv in Table III; mass spectrum *m/e* 240 (M^+).

Anal. Calcd for $C_{10}H_{12}N_2O_5$: C, 50.00; H, 5.04; N, 11.66. Found: C, 49.90; H, 5.21; N, 11.79.

Dimethyl 4,5-Dihydro-7(6*H*)oxopyrazolo[1,5-*a*]pyridine-2,3-dicarboxylate (5).—A solution of 2.8 g (25.5 mmol) of 2-diazocyclopentanone[7] and 3.7 g (26.0 mmol) of DMAD in 70 ml of ether was warmed to boiling and then allowed to stand at ambient temperatures for 72 hr. The crystalline product (5.5 g, 86%) was separated and washed with a little ether: mp 108–110°; ir 1739 cm^{-1} (broad, C=O); nmr δ 2.28 (m, 2 H), 2.95 (t, 2 H, J = 6.25 Hz), 3.29 (t, 2 H, J = 6.25 Hz), 3.87 (s, 3 H), 3.94 (s, 3 H); uv 240 nm (ϵ 8200); mass spectrum *m/e* 252 (M^+).

Anal. Calcd for $C_{11}H_{12}N_2O_5$: C, 52.38; H, 4.80; N, 11.11. Found: C, 52.17; H, 5.02; N, 10.96.

Registry No.—**1**, 37387-70-5; **2a**, 37387-71-6; **2b**, 37387-72-7; **3**, 37387-73-8; **5**, 37387-74-9; 2-diazo-3-butanone, 14088-58-5; 2-diazocyclopentanone, 14088-61-0; dimethyl acetylenedicarboxylate, 762-42-5.

(7) M. Regitz and J. Rüter, *Chem. Ber.*, **101**, 1263 (1968).

(8) NOTE ADDED IN PROOF.—Additional examples of the reactions of acetylenes with five-membered ring α-diazo ketones have recently been described by T. Yamazaki and H. Shechter, *Tetrahedron Lett.*, 4533 (1972).

(1) P. Youseízadeh and C. K. Mann, *J. Org. Chem.*, **33**, 2716 (1968).

(2) (a) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949); (b) H. M. Walborsky, *ibid.*, **36**, 1251 (1953); (c) F. G. Bordwell, B. M. Pitt, and M. Knell, *J. Amer. Chem. Soc.*, **73**, 5004 (1951).

Sulfur–Oxygen Bond Cleavage in the Condensation of Cinnamyl Tosylate with Carbonium Ions

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The enormous utility of tosyl esters as substrates in nucleophilic substitution reactions arises from the extreme readiness with which the tosyl residue departs as an anion, after cleavage of the C–O bond. Cleavage of the S–O bond in tosylates has been reported, but only in special cases, as for example during electrolytic reduction,[1] or where the tosylate carbon atom is not susceptible to nucleophilic attack for steric or other reasons,[2] or where loss of the tosylate anion would lead