TABLE II
DISTRIBUTION OF ISOMERS[a] AND NMR[b] DATA FOR ENAMINE PHOSPHONATES 2a–i

Compd	Isomer % cis	Isomer % trans	Cis PCH δ	Cis PCH J, Hz	Trans PCH δ	Trans PCH J, Hz	NH, δ cis	NH, δ trans	CH_2OP, δ, qn (J = 7.5, 15 Hz)	Other proton chemical shifts, δ
2a	50	50	3.60	13	3.76	10.5	7.32	5.59	4.05	3.08 (m, NCH_2), 2.55 (m, allyl), 1.34 (m, containing t, J = 7 Hz, 20 H)
2b	55	45	3.50	13	3.72	10.5	7.28	5.12	4.03	3.04 (m, NCH_2), 2.45 (m, allyl), 1.28 (m containing t, J = 7 Hz, 24 H)
2c	80	20	3.82	13			7.51	5.22	4.08	7.42 (C_6H_5), 2.92 (m, NCH_2), 1.30 (m, 13 H)
2d	15	85	3.62	13	3.75	11	7.36	4.46	4.02	2.42 (m, allyl), 1.32 (m containing t, J = 7 Hz, 22 H)
2e	10	90	3.67	13	3.74	11	7.42	4.36	4.05	2.43 (m, allyl), 1.36 (m containing t, J = 7.5 Hz, 26 H)
2f	15	85	3.79	13			7.23	4.54	4.11	7.42 (C_6H_5), 1.32 (t, J = 7.5 Hz, CH_3CO), 1.43 and 1.10 (two s, *tert*-butyl)
2g	30	70	3.63	13	4.15	11	7.12	4.39		7.35 (C_6H_5), 2.15 and 2.08 (two d, J = 2 Hz, allyl), 1.28 and 1.26 (two s, *tert*-butyl)
2h		100			3.75	8.5			4.05	3.25 (q, J = 7.5 Hz, NCH_2), 2.65 (m, allyl), 1.31 (m containing two t, J = 7, 7.5 Hz, 19 H)
2i		100			3.87	8.5			4.10	7.32 (C_6H_5), 3.25 (q, J = 7.5 Hz, NCH_2), 2.90 (s, allyl and benzyl), 1.25 (t, J = 7 Hz, CH_3CO), 1.15 (t, J = 7 Hz, CH_3CN)

[a] Configuration cis and trans refer to the amino and the phosphonate groups being cis or trans to each other. [b] In the nmr description, s, d, t, q, qn, and m represent a singlet, doublet, triplet, quartet, quintet, and multiplet, respectively.

isomer rapidly isomerized to the trans product.[6] Conceivably, the trans addition of amines to 1-alkynylphosphonates **1** results in the cis isomers, which, on heating, isomerize to the trans products. Under the reflux conditions employed in this investigation, a different mode of addition may also be taking place.[5,6]

The isomerization of the cis to the trans isomers is in accordance with the concept that the electron-withdrawing substituents on one end and electron-releasing substituents on the other end of the double bond favor cis–trans isomerization.[5,6,8] The excess of amine in the reaction mixture may also be playing some role in the cis–trans isomerization.

A comparison of the amounts of cis and trans isomers in adducts **2a–c** (N-*n*-C_4H_9) and **2d–g** (N-*t*-C_4H_9) shows that the greater steric requirements of the *N*-alkyl group result in the increasing amount of the trans product. In compound **2c** (R = C_6H_5), the cis isomer predominates because the phenyl ring is probably in conjugation with the ring formed through hydrogen bonding of the amino proton to the oxygen atom of the phosphonate group. However, in adduct **2f** (R = C_6H_5), resulting from the addition of *tert*-butylamine to **1** (R = C_6H_5), this effect is found to be offset by the bulkiness of the *tert*-butyl group and the trans isomer predominates.

Experimental Section

The amines were dried over potassium hydroxide pellets and the starting 1-alkynylphosphonates **1** were redistilled before use. The nmr spectra were determined on a Varian A-60 and 100 MHz spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Chemical analyses were performed by Geller Microanalytical Laboratories, Saddle River, N. J.

Preparation of Enamine Phosphonates 2a–i. General Procedure.—The 1-alkynylphosphonates **1** were refluxed with a 10–12 molar excess of the amines. The reflux was continued for 3–6 days until the ir spectra of a test portion of the reaction mixture showed almost complete disappearance of the absorption band in the region of 4.5–4.6 μ (C≡C). The excess amines were evaporated *in vacuo* at aspirator pressure. The resulting adducts were short path distilled at reduced pressure from anhydrous potassium carbonate.

Registry No.—**1a**, 3450-61-1; **1b**, 3450-66-6; **1c**, 3450-67-7; **1g**, 3095-09-8; **1i**, 30238-19-8; *cis*-**2a**, 37692-17-4; *trans*-**2a**, 37692-18-5; *cis*-**2b**, 37692-19-6; *trans*-**2b**, 37692-20-9; *cis*-**2c**, 37692-21-0; *trans*-**2c**, 37692-22-1; *cis*-**2d**, 37692-23-2; *trans*-**2d**, 37692-24-3; *cis*-**2e**, 37692-25-4; *trans*-**2e**, 37692-26-5; *cis*-**2f**, 37692-27-6; *trans*-**2f**, 37692-28-7; *cis*-**2g**, 37692-29-8; *trans*-**2g**, 37692-30-1; *trans*-**2h**, 37755-04-7; *trans*-**2i**, 37692-31-2; butylamine, 109-73-9; diethylamine, 109-89-7; *tert*-butylamine, 109-73-9.

Acknowledgment.—We wish to acknowledge the National Institutes of Health for support of this work under Grant GM-16828 and the National Science Foundation under Grant GP-10739. We also wish to thank Hoffmann-La Roche, Inc., Nutley, N. J., for their unrestricted grant which helped us to complete this work.

Reductive Cleavage of Phenylhydrazones of α-Keto Acids to Amino Acids

NASEEM H. KHAN* AND AKHLAQ R. KIDWAI

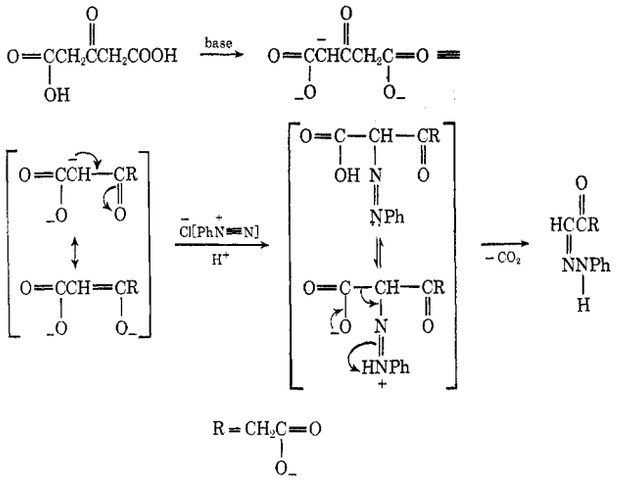
Department of Chemistry, Aligarh Muslim University, Aligarh, India

Received June 6, 1972

Reductive cleavage of phenylhydrazones of α-keto acids is an important method for the synthesis of α-amino acids, because of the easy availability of these phenylhydrazones by the Japp–Klingemann reaction.[1] This reaction, which takes place between a phenyl-

(1) R. F. Japp and F. Klingemann, *Ber.*, **20**, 2942, 3284, 3398 (1887).

diazonium salt and a reactive methylene group, may be exemplified with reference to β-oxoglutaric acid.



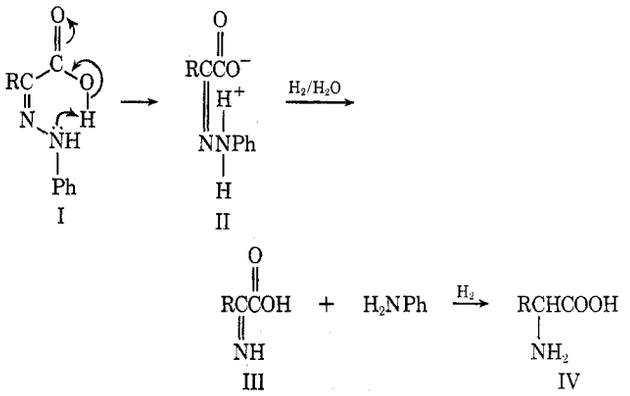
The phenylhydrazones are thus obtained in good yields and in a one-step operation.

Phenylhydrazones thus obtained were subsequently reduced by Feofilaktov and his associates[2-9] to the corresponding amino acids by means of zinc dust in acidic medium at 0°. Our attempts at following this procedure[4] were not successful. The isolation of the amino acid from the reaction mixture was unsatisfactory, as it involved several operations. Another undesirable feature of the procedure is that the conditions employed also favor Fischer cyclization to the corresponding indoles.[10]

In view of these facts we have attempted different methods of reductive cleavage of phenylhydrazones of α-keto acids to the corresponding amino acids. Sodium hydrosulfite and sodium sulfite have been successfully used in the reduction of diazonium compounds,[11] but these reagents proved ineffective in the reduction of phenylhydrazones of α-keto acids.

Zinc dust in 75% alcohol in the presence of mercuric chloride was quite satisfactory and gave glycine, valine, and phenylalanine in 43, 74, and 55% yields, respectively. Mercuric chloride could be replaced by calcium chloride without any loss in the yields of the amino acids. Zinc dust in alkaline medium (sodium hydroxide or ammonium hydroxide) did not reduce pyruvic acid phenylhydrazone satisfactorily. By using zinc dust in acetic acid, alanine, valine, and phenylalanine could be obtained in 50, 53, and 48% yields, respectively. Formic acid alone did not effect reductive cleavage of phenylhydrazones to amino acids, but cyclized them to indoles.[12] Sodium and ammonium formates were useful neither for cyclization nor for the reductive cleavage of the phenylhydrazones. Catalytic reduction of α-oximino acids to amino acids has been successful in an acidic medium.[13,14] In the case of phenylhydrazones of α-keto acids, acidic conditions had to be avoided lest Fischer indole cyclization take place.

Nitrogen attached to the aromatic nucleus has a great tendency to undergo protonation, thus making it a potential electron-withdrawing group, necessary for the cleavage of the N–N linkage as represented. It was felt, however, that in the six-membered transition state the proton migrates to nitrogen so as to form the inner salt II which could provide the driving force for



cleavage of the N–N bond and hydrogenation under neutral conditions should thus also lead to amino acids.

This expectation was fully realized when it was found that alcoholic solutions of phenylhydrazones of α-keto acids, when subjected to reduction with palladium over carbon, platinum, or palladium at room temperature and pressure, took up hydrogen readily with precipitation of the amino acid formed.

Reduction in alcoholic medium had one disadvantage. The phenylhydrazone is soluble in alcohol while its reduction product, the amino acid, in many cases is not. The result is that, as reduction proceeds, the precipitated amino acid sticks to the catalyst and makes it ineffective. Fortunately, it has been found that aqueous suspensions of phenylhydrazones can be advantageously used for catalytic reduction. As reduction proceeds, the phenylhydrazones go into solution and the amino acid produced also remains in solution in most cases. When reduction is complete, the catalyst is filtered off and the filtrate is washed with ether. The concentration of the aqueous layer afforded the desired pure amino acid in high yield.

Table I shows the amino acids obtained by catalytic reduction of phenylhydrazones of α-keto acids.

Experimental Section

Phenylhydrazones used in this work were prepared by the Japp–Klingemann reaction. Only pyruvic acid phenylhydrazone and levulinic acid phenylhydrazones were prepared from their respective keto acids. Satisfactory analyses were obtained for all the reported compounds. Melting points were taken on a Gallenkamp melting point apparatus in open capillaries and are uncorrected. Hydrogenation was conducted in a

(2) V. V. Feofilaktov and V. N. Zaitseva, *J. Gen. Chem. USSR*, **10**, 258, 1391 (1940).
(3) V. V. Feofilaktov, *C. R. Acad. Sci. URSS*, **24**, 755 (1939); *J. Gen. Chem. USSR*, **10**, 247 (1940).
(4) V. V. Feofilaktov and E. Vinogradova, *C. R. Acad. Sci. URSS*, **24**, 759 (1939); *J. Gen. Chem. USSR*, **10**, 225, 258 (1940); **21**, 399, 1684 (1951); **23**, 463, 699 (1953).
(5) V. V. Feofilaktov and N. K. Semenova, *J. Gen. Chem. USSR*, **23**, 887 (1953).
(6) V. V. Feofilaktov, *Bull. Acad. Sci. URSS, Cl. Sci. Chem.*, 521 (1941); *Chem. Abstr.*, **37**, 2347 (1943).
(7) V. V. Feofilaktov and F. Blanko, *J. Gen. Chem. USSR*, **11**, 859 (1941).
(8) V. V. Feofilaktov and A. Onischenko, *C. R. Acad. Sci. URSS*, **20**, 133 (1938).
(9) V. V. Feofilaktov and T. N. Ivanova, *Zh. Obshch. Khim.*, **21**, 1684 (1951); *J. Gen. Chem. USSR*, **21**, 1851 (1951).
(10) R. R. F. Manske, E. Robinson, and W. H. Perkin, Jr., *J. Chem. Soc.*, 1 (1927).
(11) J. B. Conant, R. E. Lutz, and B. B. Corson, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1946, p 49.
(12) A. R. Kidwai and N. H. Khan, *C. R. Acad. Sci.*, **256**, 3709 (1963).
(13) K. E. Hamlin and W. H. Hartung, *J. Biol. Chem.*, **145**, 349 (1942).
(14) D. Shemin and R. M. Herbst, *J. Amer. Chem. Soc.*, **60**, 1951 (1938).

TABLE I

Registry no.	Phenylhydrazone of	Catalyst	Solvent[b]	Conditions of reduction[a]	Amino acid obtained	Registry no.	Yield, %	Time, hr	Remarks
6000-60-8	Glyoxylic acid	Pd/C	A	X	Glycine	56-40-6	96	6	
10475-63-5	Ethyl α,β-diketobutyrate	Zn, $HgCl_2$	B	Y	Glycine		43	4	
5330-70-1	Pyruvic acid	Pd/C	A	X	Alanine	302-72-7	92	6	
		PdO	A	X	Alanine		98	6	
		PtO	A	X	Alanine		42	6	
		Zn, $CaCl_2$	B	Y	Alanine		60	4	
		Zn, AcOH	B	Y	Alanine		50	4	
36963-34-5	α-Ketoisovaleric acid	Pd/C	A	X	Valine	516-06-3	85	6	
		PtO	A	X	Valine		17		
		Zn, $HgCl_2$	B	Y	Valine		74		
		Zn, $CaCl_2$	B	Y	Valine		75		
		Zn, AcOH	B	Y	Valine		53		
36963-35-6	α-Ketocaproic acid	Pd/C	A	X	Norleucine	616-06-8	94	5	
		PdO	D	X	Norleucine		92	6	
36963-36-7	α-Ketoisocaproic acid	Pd/C	A	X	Leucine	328-39-2	87	6	
36963-37-8	α-Keto-*sec*-caproic acid	Pd/C	A	X	Isoleucine	443-79-8	83	6	
36963-38-9	Phenylpyruvic acid	Pd/C	A	X	Phenylalanine	150-30-1	88	6	
		PtO	A	X	Phenylalanine		80	6	
		PtO	C	X					Not completely hydrogenated
		Zn, $HgCl_2$	B	Y	Phenylalanine		55	4	
		Zn, $CaCl_2$	B	Y	Phenylalanine		58	4	
		Zn, AcOH	B	Y	Phenylalanine		48	4	
		Zn, NaOH	B	Y					No reduction
		Am, Formate	B	Y					No reduction
		Na, Formate	B	Y					No reduction
		HCOOH		Y	3-Phenylindole-2-carboxylic acid[c]				
36963-39-0	*p*-Methoxyphenylpyruvic acid	Pd/C	A	X	*O*-Methyltyrosine	7635-29-2	95	6	
		PtO	A	X	*O*-Methyltyrosine		91	6	
123-76-2	Levulinic acid	Pd/C	A	X	γ-Aminovaleric acid	627-61-2	94	6	

[a] X = room temperature and pressure; Y = reflux temperature and pressure. [b] A = water; B = aqueous alcohol (78%); C = absolute alcohol; D = alcohol (95%). [c] Reference 12.

semimicro Tower's hydrogenation apparatus at room temperature and pressure. Yields and melting points reported in this work are of analytically pure products.

DL-**Valine.**—Powdered α-ketoisovaleric acid phenylhydrazone[15] (0.5 g) was suspended in 50 ml of water in a hydrogenation flask containing 0.5 g of 5% Pd/C. Absorption was complete in 6 hr. The catalyst was filtered off. The filtrate on evaporation on a water bath under reduced pressure gave a residue which was thrice washed with 10-ml portions of ether and then thrice with 10-ml portions of cold alcohol. The alcohol-insoluble residue on drying weighed 0.25 g (89%), mp 276° dec on rapid heating. The crude amino acid was dissolved in 5 ml of hot water and subsequently diluted with 15 ml of alcohol. This was allowed to stand overnight in a refrigerator. The crystalline amino acid obtained on filtration weighed 0.245 g, mp 286° dec with rapid heating, mmp 286° with an authentic sample (lit.[16a] mp 293°, lit.[16b] mp 280–282°).

N-Benzoyl-DL-valine was prepared from 0.25 g of DL-valine, 4 ml of 1 *N* sodium hydroxide solution, and 0.5 ml of benzoyl chloride by the usual Schotten–Baumann reaction. The crude derivative after recrystallization from benzene–petroleum ether (bp 40–60°) melts at 131.5° (lit.[17] mp 132°).

N-(*p*-Toluenesulfonyl)-DL-valine was obtained by usual method, mp 166.5° (lit.[18] mp 166–167°), mmp 166.5° with an authentic sample.

DL-**Phenylalanine.**—Phenylpyruvic acid phenylhydrazone[19] (2.5 g) was reduced using 5% Pd/C to give 1.4 g of amino acid, mp 265° dec,[4] benzoyl derivative mp 181.5°,[20] *p*-toluenesulfonyl derivative mp 134–135°.[21,22]

γ-**Aminovaleric Acid. Levulinic Acid Phenylhydrazone.**—Levulinic acid (10.2 ml, 0.1 mol) was dissolved in 80 ml of water. Phenylhydrazine (9.8 ml) containing acetic acid (1 ml) was added with stirring. In a few minutes straw-colored phenylhydrazone was obtained. This was washed and dried, mp 102°, yield 20.8 g (100%). On recrystallization from benzene–petroleum ether, the melting point was raised to 106.5° (lit.[23] mp 108°).

DL-γ-**Aminovaleric Acid.**—Levulinic acid phenylhydrazone (1.6 g) on hydrogenation over 5% Pd/C (0.6 g) for 5 hr gave DL-γ-aminovaleric acid, mp 191° dec, yield 0.85 g (93.6%) (lit.[16a] mp 193°).[24]

N-Benzoyl-DL-aminovaleric acid was prepared from DL-γ-aminovaleric acid (0.5 g) and benzoyl chloride (0.5 ml). Recrystallization twice from benzene–petroleum ether yielded *N*-benzoyl-DL-γ-aminovaleric acid, mp 135.5° (lit.[16a] mp 132°).

DL-α-**Alanine. A.**—A mixture of pyruvic acid phenylhydrazone (1 g) dissolved in alcohol (30 ml, 78%), zinc dust (8 g), and calcium chloride (0.2 g) was heated under reflux for 4 hr and then filtered hot. The zinc sludge was washed with two 20-ml portions of boiling water. The combined filtrate and washings were saturated with water-washed hydrogen sulfide gas, boiled, and filtered. This process of passing hydrogen sulfide was repeated to ensure complete removal of zinc. The filtrate obtained was concentrated to dryness under reduced pressure. The residue was dissolved in water (15 ml) and extracted with ether. The aqueous layer was boiled with active carbon (1 g) and filtered. The filtrate was concentrated to 5 ml under reduced pressure and then diluted with alcohol (15 ml, 95%). The contents were cooled overnight in a refrigerator. The crystalline amino acid was filtered, dried, and weighed, 0.3 g, mp 285° dec, yield 60%. The ether layer was extracted with sodium bicarbonate solution (5%). The alkaline solution thus obtained was heated on a steam bath to remove dissolved ether, treated with active carbon, and filtered. The clear filtrate on acidification with hydrochloric acid (10%) gave 0.1 g of unreduced product, mp 168–170°.

B.—Pyruvic acid phenylhydrazone (10 g) was dissolved in alcohol (300 ml, 75%) in a 1-l. flask. To this zinc dust (75 g) and mercuric chloride (1 g) were added and the mixture was heated under reflux on a steam bath for 8 hr and filtered hot. Zinc dust was washed with three 20-ml portions of hot water. The filtrate and aqueous washings were combined and saturated with hydrogen sulfide gas (water washed), boiled, and filtered. The filtrate was evaporated to dryness under reduced pressure on a steam bath. The dry substance thus obtained was washed

(15) V. V. Feofilaktov and V. N. Zaitseva, *J. Gen. Chem. USSR*, **10**, 1391 (1940).

(16) (a) L. Senfter and J. Tafel, *Ber.*, **27**, 2313 (1894); (b) C. S. Marvel, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 848.

(17) M. D. Slimmer, *Ber.*, **35**, 402 (1902).

(18) A. E. Beecham, *J. Amer. Chem. Soc.*, **79**, 3257 (1957).

(19) W. Wislecenus, *Ber.*, **20**, 593 (1887).

(20) E. Erlenmeyer, Jr., *Justus Liebigs Ann. Chem.*, **275**, 15 (1893).

(21) W. E. McChesney and W. K. Swan, Jr., *J. Amer. Chem. Soc.*, **59**, 1116 (1937).

(22) T. Oseki, *Bull. Chem. Soc. Jap.*, **41**, 8 (1920).

(23) E. Fischer, *Justus Liebigs Ann. Chem.*, **236**, 146 (1886).

(24) J. Tafel, *Ber.*, **19**, 2415 (1886).

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.

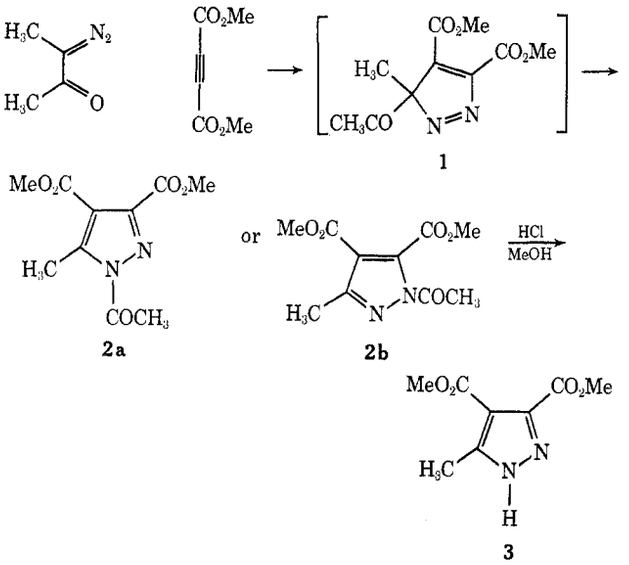
The Reactions of 2-Diazo-3-butanone and 2-Diazocyclopentanone with Dimethyl Acetylenedicarboxylate

A. S. KATNER

The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana 46206

Received August 30, 1972

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).