

914. *Alicyclic Compounds. Part I. The Formation of cycloPropanes in the Kishner-Wolff Reduction of $\alpha\beta$ -Unsaturated Carbonyl Compounds.*

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The decomposition of 3:5-diphenyl- and 3-methyl-5-phenyl- Δ^2 -pyrazolines into nitrogen and *cyclopropanes*, with various catalysts, is investigated. On pyrolysis over potassium hydroxide, 5-phenyl- Δ^2 -pyrazoline is rapidly isomerised to 3-phenyl- Δ^2 -pyrazoline, which then slowly gives nitrogen, phenyl*cyclopropane*, some olefinic material, and a tar. Some of the factors involved in the formation of Δ^2 -pyrazolines, azines, and unsaturated hydrazones from $\alpha\beta$ -unsaturated carbonyl compounds and hydrazine are examined. In the preparation of 5-phenyl- Δ^2 -pyrazoline from cinnamaldehyde and hydrazine, cinnamaldehyde hydrazone is often obtained. Δ^2 -Pyrazolines are *N*-acetylated in hot glacial acetic acid; the acetyl compounds are converted into *cyclopropanes* on pyrolysis over potassium hydroxide (>1 equiv.). The mechanism of the Kishner-Wolff reaction, and the formation of *cyclopropanes* by this and the Buchner-von Pechmann synthesis, are discussed.

HYDRAZONES may be pyrolysed by several methods, usually with an alkaline catalyst, collectively known as the Kishner-Wolff reaction (Todd, *Org. Reactions*, 1948, **4**, 378):

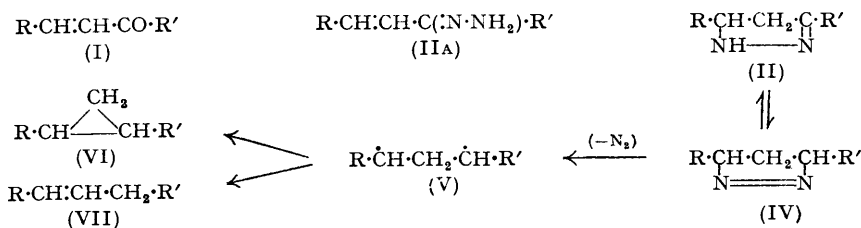
$$\text{>C:O} \longrightarrow \text{>C:N}\cdot\text{NH}_2 \longrightarrow \text{>CH}_2 + \text{N}_2$$
 Many $\alpha\beta$ -unsaturated carbonyl compounds (e.g., I; R = Ph, R' = H, Me, or Ph) are abnormal in this reaction; their hydrazones often cyclise to Δ^2 -pyrazolines (II), which then may decompose into *cyclopropanes* (VI) and nitrogen (Kishner, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 849; 1913, **45**, 949; 1915, **47**, 1102; 1918, **50**, 1). Kishner's catalyst (potassium hydroxide and platinised porcelain) has been employed usually by the few later workers who have followed this attractive route to *cyclopropanes* (e.g., Davidson and Feldman, *J. Amer. Chem. Soc.*, 1944, **66**, 488; Rogers, *ibid.*, 1947, **69**, 2544). Although Kishner's method gave a *cyclopropane* in the reduction of pulegone, Wolff's procedure (catalyst, sodium ethoxide) yielded an olefin (Semmler and Feldstein, *Ber.*, 1914, **47**, 385). Recent studies on the reduction of $\alpha\beta$ -unsaturated carbonyl compounds, mainly by Wolff's procedure, have shown that olefins usually accompany the *cyclopropanes* formed and are often the sole products (Lardelli and Jeger, *Helv. Chim. Acta*, 1949, **32**, 1817; Fischer, Lardelli, and Jeger, *ibid.*, 1950, **33**, 1335; 1951, **34**, 1577).

With a view to improving the preparation of *cyclopropanes* and elucidating further the mechanism of their formation in Kishner-Wolff reactions, catalytic effects in the pyrolysis of selected Δ^2 -pyrazolines, and aspects of the formation of pyrazolines from $\alpha\beta$ -unsaturated carbonyl compounds, have been studied. Further publications will deal with various aspects of alicyclic chemistry, with particular reference to terpenes and steroids.

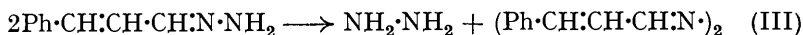
Experiments (see Table) on the decomposition of 3:5-diphenyl- Δ^2 -pyrazoline (II; R = R' = Ph), obtained from benzylideneacetophenone and hydrazine, confirmed the superiority of basic catalysts: the activity of strong acids (KHSO₄ and H₃PO₄) is of considerable theoretical interest. Organic bases had appreciable activity, and very small amounts of potassium hydroxide were sufficient, suggesting the possibility of reducing the large amount of alkali customarily used in Kishner-Wolff reactions (cf. Todd, *op. cit.*, p. 385). The 1:2-diphenyl*cyclopropane* (presumably a mixture of stereoisomers) obtained in these experiments contained only 3–6% of the isomeric olefin. The ultra-violet absorption curve of purified diphenyl*cyclopropane* indicated appreciable interaction between the *cyclopropane* and the benzene ring.

The pyrazoline (II; R = Ph, R' = Me) from benzylideneacetone was decomposed in a few similar experiments (see Table). A typical product from crude pyrazoline contained 7% of olefin; the ultra-violet absorption data showed that the olefin content was considerably reduced when the pyrazoline had been purified. The same observation was made by Lardelli and Jeger (*loc. cit.*), who employed different pyrolysis conditions.

Interesting results were expected from a study of the pyrolysis of 3- and 5-phenyl- Δ^2 -pyrazolines (von Auwers and Heimke, *Annalen*, 1927, **458**, 186), which are potential tautomers. Unexpected complications arose in the preparation of the latter (II; R = Ph



R' = H) from cinnamaldehyde and hydrazine. The hydrazone was abnormally stable, and cyclisation to the pyrazoline was often incomplete. The hydrazone was easily detected by the quantitative precipitation of cinnamaldazine (III) on treatment with alcoholic cinnamaldehyde or, better, on shaking with dilute hydrochloric acid :



Any pyrazoline also present dissolved in the acid and, after recovery, was identical with von Auwers and Heimke's material. 3-Phenyl- Δ^2 -pyrazoline (II; R = H, R' = Ph) can be made from phenyl vinyl ketone and hydrazine (Freudenberg and Stoll, *Annalen*, 1924, **440**, 36), but β -dimethylaminopropiophenone was a more accessible source. Reaction of this Mannich base with hydrazine gave the pyrazoline in excellent yield; in a previous study of this reaction (Jacob and Madinaveitia, *J.*, 1937, 1929), the sole product was a yellow solid, believed to be polymeric. Both 3- and 5-phenyl- Δ^2 -pyrazoline were characterised as their nitroso-derivatives (von Auwers and Heimke, *loc. cit.*).

In preliminary experiments, 5-phenyl- Δ^2 -pyrazoline isomerised rapidly to the 3-phenyl-isomer (which has a more extended conjugated system) over potassium hydroxide at 200°. The ultimate pyrolysis products from either pyrazoline were phenylcyclopropane, some olefin, and much tar, possibly due to polymerisation of the olefin. Direct isomerisation of a Δ^2 -pyrazoline had not been recorded, although such changes have been encountered during the preparation of *N*-substitution products (von Auwers and Heimke, *loc. cit.*; von Auwers and Ludewig, *Ber.*, 1936, **69**, 2347), and sometimes occur spontaneously during the preparation of Δ^2 -pyrazolines. Although it is established that 5-phenylpyrazoline can be made from cinnamaldehyde, spontaneous isomerisation to 3-phenylpyrazoline probably occurred during the preparation by Freudenberg and Stoll (*loc. cit.*), and possibly also during Lardelli and Jeger's experiments (*loc. cit.*), as their product had m. p. 41–42°.

The initial product from an $\alpha\beta$ -unsaturated carbonyl compound and hydrazine will be the hydrazone, which can subsequently cyclise to the pyrazoline, or form an azine by reacting with a second carbonyl molecule. Consequently, the ease of azine formation will vary inversely with the rate of cyclisation of the unsaturated hydrazone. Cinnamaldehyde hydrazone is stable enough to be isolated, and both cinnamaldehyde and benzylideneacetone readily formed azines in acetic acid; no azine could be obtained from benzylideneacetophenone. The rates of cyclisation of the unsaturated hydrazones (IIA; R = Ph) are therefore in the order R' = Ph > Me > H. Boiling glacial acetic acid cyclises unsaturated phenylhydrazones (von Auwers and Voss, *Ber.*, 1909, **42**, 4412; Raiford and Petersen, *J. Org. Chem.*, 1937, **1**, 544; Nisbet, *J.*, 1945, 126). The ketones (I; R = Ph, R' = Ph or Me) and excess of hydrazine in boiling acetic acid gave crystalline *N*-acetylpyrazolines; hydrazine alone in boiling acetic acid gave 1:2-diacetylhydrazine. Pyrolysis of *N*-acetylpyrazolines over potassium hydroxide (>1 equiv.) (see Table) gave hydrocarbons similar to those obtained from the parent pyrazolines; indeed, the latter are no doubt formed intermediately by deacetylation.

Discussion.—Two main stages are believed to be involved in the Kishner–Wolff decomposition of hydrazones :



(Balandin and Vaskevitch, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 1878; Todd, *J. Amer. Chem. Soc.*, 1949, **71**, 1356; Seibert, *Ber.*, 1947, **80**, 494; 1948, **81**, 266). A simple extension of this mechanism (Barton, Holness, and Klyne, *J.*, 1949, 2457) explains bond migration

	Catalyst ¹	Solvent	Temp.	Time, hr.	B. p./mm. (and n_D^{25})	Olefin content, %	Yield, %
<i>Pyrolysis of 3 : 5-diphenyl-Δ^2-pyrazoline.</i>							
Ph·CH:CH·COPh ₂ , g.					1 : 2-Diphenylcyclopropane ²		
4	KOH (1 g.)	(·CH ₂ ·OH) ₂ (10 c.c.)	200 ³	8	152—154°/10	—	77·5
12	KOH (0·2 g.)	(·CH ₂ ·OH) ₂ (30 c.c.)	200 ³	1·5	158—160/12 (1·5947)	3	86·5 ⁴
4	KOH (1 g.)	None	200	2	170/16	—	89
12	KOH (0·2 g.)	None	200	1	156—159/12 (1·5950)	4	92·5
4	Na ₂ CO ₃ (1 g.)	None	200	24	148—154/8	—	36
4	NaOAc (1 g.)	None	200	24	148—154/8	—	32·4
4	Quinoline (20 c.c.)		230 ²	24	152—156/8	—	21
4	NBu ₃ (20 c.c.)		200	24	145/8	—	21
4	N(CH ₂ ·CH ₂ ·OH) ₃ (20 c.c.)		200	24	152—157/8	—	66
12	K ₂ HPO ₄ (4 g.)	None	200	25·5	166—170/12	—	83
12	H ₃ PO ₄ (0·15 c.c.)	None	200	26	166—172/12 (1·5935)	6	30
4	KHSO (1 g.)	None	200	24	160/11	—	34 ⁵
<i>Pyrolysis of 3-methyl-5-phenyl-Δ^2-pyrazoline.</i>							
COMe, g.					1-Methyl-2-phenylcyclopropane. ⁶		
4	KOH (1 g.)	(·CH ₂ ·OH) ₂ (15 c.c.)	200°	12	80°/12	7	75 ⁷
4	KOH (2 g.)	None	200	4	72—74/10	—	61
4	N(CH ₂ ·CH ₂ ·OH) ₃ (6 c.c.)		200	24	78/11	—	10
<i>Pyrolysis of 1-acetyl-3 : 5-diphenyl-Δ^2-pyrazoline.</i>							
Acetyl cpd., g.					1 : 2-Diphenylcyclopropane.		
10	KOH (5 g.)	None	200°	2	149—154°/8	—	73
6	KOH (3 g.)	Diethylene glycol (25 c.c.)	200	24	156—158/9	—	79

¹ Yields were zero with the following catalysts at 200°: none (24 hr.), Na₂PO₄ (0·33 pt.; 24 hr.), KH₂PO₄ (0·33 pt.; 27 hr.), ultra-violet irradiation, ethereal solution (30°; 15 hr.)⁸, Pt foil (24 hr.), Pt black (0·025 pt.; 24 hr.), Cu bronze (8 hr.). ² Kishner, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1104, gives b. p. 145°/9·5 mm.; n_D^{20} 1·5960—1·5967; Lespiau and Wakelin, *Bull. Soc. chim.*, 1932, **51**, 384, give b. p. 164—166°/13 mm.; n_D^{21} 1·5897. ³ Acetophenone-vapour heating-bath not used; solvent refluxed. ⁴ The product from this experiment, after being treated with bromine in carbon tetrachloride, washed with sodium thiosulphate solution, and refractionated, had the following ultra-violet absorption (in EtOH): λ_{max} 234 m μ (ϵ 12,600); inflexion at 275 m μ (ϵ 900). ⁵ 3 : 5-Diphenylpyrazole (50%) also isolated; the KHSO₄ became reduced and the reaction product gave SO₂ and H₂O with acids. ⁶ Lardelli and Jeger, *Helv. Chim. Acta*, 1949, **32**, 1817, give b. p. 80—85°/11 mm. ⁷ Ultra-violet absorption (in EtOH): λ_{max} 254 (ϵ 1000) and 275 m μ (ϵ 320), and absorption at 230 m μ (ϵ >2500). For hydrocarbon samples similarly obtained from redistilled pyrazoline: λ_{max} 268 (ϵ 420) and 275 m μ (ϵ 290), and absorption at 230 m μ (ϵ >2500); no max. at 254 m μ (ϵ 480).

during formation of olefins from certain $\alpha\beta$ -unsaturated carbonyl compounds (in these cases the hydrazone probably does not cyclise) (Fischer, Lardelli, and Jeger, *loc. cit.*). Since pyrazolines may be regarded as cyclic hydrazones, the mechanism (II) \rightleftharpoons (IV) \longrightarrow (V) \longrightarrow (VI) for the transformation* of Δ^2 -pyrazolines into cyclopropanes is at once suggested. In this scheme, the rate-controlling step is the prototropic rearrangement (II) \rightleftharpoons (IV); substances which have catalytic activity in the pyrolysis of pyrazolines (*e.g.*, Table) are those which would facilitate prototropy (cf. Ossorio and Hughes, *J.*, 1952, 426). Triethanolamine is both a proton acceptor and a potential donor, and is a more effective catalyst than tributylamine or quinoline, which are solely proton acceptors. Among the phosphates used, only K₂HPO₄ had catalytic activity; it is tempting to attribute this to the amphoteric nature of the HPO₄⁼ ion; the PO₄⁼ ion is a stronger proton acceptor, but is not amphoteric, and Na₂PO₄ is inactive. The alkali-catalysed conversion of 5- into 3-phenyl- Δ^2 -pyrazoline is believed to be a two-stage prototropic rearrangement, in which

the Δ^1 -pyrazoline (IV; R = Ph, R' = H) is formed transitorily. The equilibrium (II) \rightleftharpoons (IV) is therefore a reasonable postulate; only a small concentration of Δ^1 -pyrazoline (IV) is necessary to account for hydrocarbon formation. The equilibrium will favour (II), as Δ^1 -pyrazolines, isolated from activated olefins and aliphatic diazo-compounds, can be rapidly isomerised to (substantially pure) Δ^2 -pyrazolines by mineral acids (von Auwers and Cauer, *Annalen*, 1929, **470**, 305; von Auwers and König, *ibid.*, 1932, **496**, 27; von Auwers and Ungemach, *Ber.*, 1933, **66**, 1198).

There are many analogies for the decomposition of Δ^1 -pyrazolines (IV) into nitrogen and 1 : 3-diradicals (V) (e.g., Overberger and Berenbaum, *J. Amer. Chem. Soc.*, 1951, **73**, 4883); the diradicals should cyclise readily to cyclopropanes (VI), but their rearrangement to isomeric olefins (VII) is also possible. Olefins may also arise by rearrangement of previously formed cyclopropanes (e.g., Davidson and Feldman, *loc. cit.*; Kelso, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1952, **74**, 291). In the Buchner-von Pechmann synthesis of cyclopropanes from activated olefins and aliphatic diazo-compounds, the intermediate Δ^1 -pyrazolines probably lose nitrogen before isomerisation to Δ^2 -pyrazolines can occur. Later work on the Buchner-von Pechmann synthesis has shown that olefins are frequently formed instead of cyclopropanes, particularly from less heavily substituted Δ^1 -pyrazolines (von Auwers and König, *Annalen*, 1932, **496**, 252); catalysts do not appear to be essential for the reaction, although copper bronze or platinum is sometimes added (e.g., Owen and Simonsen, *J.*, 1932, 1424; Campbell and Harper, *J.*, 1945, 283; Kohler and Steele, *J. Amer. Chem. Soc.*, 1919, **41**, 1093). The behaviour of known Δ^1 -pyrazolines is therefore consistent with the view that they are formed intermediately, by the action of prototropic catalysts, during the pyrolysis of Δ^2 -pyrazolines.

A few conclusions of practical value may be stated. In making cyclopropanes from $\alpha\beta$ -unsaturated compounds, pyrazoline formation should be complete before pyrolysis. In some cases the isolation and purification of *N*-acetylpyrazolines may be useful. Often, however, even pure pyrazolines give some olefin on pyrolysis. Useful innovations are the use of dipotassium hydrogen phosphate, triethanolamine, or small amounts of potassium hydroxide, as the catalyst. The extension of some of these procedures to the normal Kishner-Wolff reduction of saturated carbonyl compounds is giving promising results.

EXPERIMENTAL

A nitrogen atmosphere was employed in all experiments (including those recorded in the Table) involving pyrazolines. An acetophenone-vapour bath was used, unless otherwise stated, for maintaining temperatures of 200°. Olefins were determined with perbenzoic acid in benzene (Koltzoff, Lee, and Mairs, *J. Polymer Sci.*, 1947, **2**, 199).

3 : 5-Diphenyl- Δ^2 -pyrazoline.—Recrystallised benzylideneacetophenone (*Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 78) (12 g.), 90% hydrazine hydrate (7.5 c.c.), and ethanol (30 c.c.) were refluxed for 20 minutes, then evaporated, finally at 100° (bath-temp.)/12 mm. The waxy residue was used in pyrolysis experiments without distillation; it had m. p. 84–86°, b. p. 174–178°/0.02 mm. (without decomp.) (Kishner, *loc. cit.*, gives m. p. 88°).

1-Acetyl derivative. Refluxing of a solution of benzylideneacetophenone (8 g.) and 90% hydrazine hydrate (5 c.c.) in acetic acid (25 c.c.) for 1 hour, evaporation, and fractional crystallisation of the residue from ethanol, gave the acetyl derivative (68%), m. p. 125.5–126° (Found: C, 77.9; H, 6.15. Calc. for C₁₇H₁₆ON₂: C, 77.25; H, 6.1%), and 1 : 2-diacetylhydrazine (6 g.), m. p. 138–139°. A 92% yield of the acetylpyrazoline, m. p. 125°, was obtained from the purified pyrazoline and acetic anhydride (Freudenberg and Stoll, *loc. cit.*). Hydrazine hydrate (5 c.c.; 90%) and acetic acid (25 c.c.) were refluxed for 1 hour; the product, recrystallised from dioxan, was 1 : 2-diacetylhydrazine (43%), m. p. 135–137° (Guha and Chakraborty, *J. Indian Chem. Soc.*, 1928, **6**, 102, give m. p. 139°).

3-Methyl-5-phenyl- Δ^2 -pyrazoline.—Redistilled benzylideneacetone (4.0 g.), 90% hydrazine hydrate (2.5 c.c.) and ethanol (10 c.c.) were refluxed for 1 hour, and the product was heated at 120° (bath-temp.)/12 mm., to remove water and ethanol. The crude pyrazoline was used without distillation in most pyrolysis experiments; it had b. p. 166°/35 mm. (without decomp.) (von Auwers and Heimke, *loc. cit.*, give b. p. 143–144°/12 mm.).

1-Acetyl derivative. A mixture of benzylideneacetone (4 g.), 90% hydrazine hydrate (2 c.c.), and glacial acetic acid (10 c.c.) was refluxed for 1 hour, evaporated to a syrup, and diluted with ether. 1 : 2-Diacetylhydrazine (0.7 g.; m. p. 134–136°) was filtered off; the ethereal solution

was distilled, and the fraction of b. p. 179°/10 mm. recrystallised from ether, giving the 1-acetylpyrazoline (63%), m. p. 77—79° (Found: C, 71.1; H, 6.85. Calc. for C₁₂H₁₄ON₂: C, 71.2; H, 7.0%) (von Auwers and Heimke, *loc. cit.*, give m. p. 76°).

Experiments on the Formation of Azines.—Benzylideneacetone (4 g.) was added to a cold mixture of 90% hydrazine hydrate (1 c.c.) and acetic acid (3 c.c.). After 15 minutes, the azine (3.7 g., 70%), m. p. 159°, was filtered off (Knopfer, *Monatsh.*, 1909, 30, 38, gives m. p. 160°). An azine could not be obtained from benzylideneacetophenone by this procedure, but cinnamaldazine was very readily formed.

3-Phenyl-Δ²-pyrazoline.—3-Dimethylamino-1-phenylpropan-1-one (29.7 g.; from the hydrochloride, prepared as in *Org. Synth.*, 1943, 23, 30), 90% hydrazine hydrate (25 c.c.), and ethanol (60 c.c.) were refluxed for 3 hours: dimethylamine was evolved. Distillation afforded 3-phenyl-Δ²-pyrazoline (81%), b. p. 150—152°/10 mm., m. p. 44°; a solution of the base in cold dilute hydrochloric acid with sodium nitrite gave the nitroso-compound, m. p. 151—152° after recrystallisation (von Auwers and Heimke, *loc. cit.*, give b. p. 164°/17 mm., m. p. 44—45°, and m. p. 152.5—153.5°, respectively). The colourless pyrazoline rapidly darkened and evolved nitrogen on exposure to air, but was stable in the absence of air.

Pyrolysis of 3-Phenyl-Δ²-pyrazoline.—A solution of the pyrazoline (19.8 g.) and potassium hydroxide (0.5 g.) in ethylene glycol (30 c.c.) was slowly distilled; fresh glycol (40 c.c.) was added to maintain the volume over a total period of 7.5 hours. The distillate was diluted with water, and the oil (32%) isolated by ether; it was mainly phenylcyclopropane containing β-methylstyrene (8.1%), and had b. p. 172—174°, *n*_D²⁰ 1.5298 (Lespieau, *Compt. rend.*, 1930, 190, 1129, for example, gives for phenylcyclopropane, b. p. 170.5°/760 mm., *n*_D²⁰ 1.5291; for β-methylstyrene, b. p. 173°/760 mm., *n*_D²⁰ 1.550). The pyrolysis residue was extracted with dilute hydrochloric acid, and sodium nitrite added to precipitate 1-nitroso-3-phenyl-Δ²-pyrazoline (10%). A dark brown neutral tar (6.3 g.) was also obtained from the residue. Pyrolysis of 3-phenyl-Δ²-pyrazoline over potassium hydroxide at 200° without a solvent gave similar results. Reduction of the reaction time decreased the yield of hydrocarbon, and increased the amount of undecomposed pyrazoline.

5-Phenyl-Δ²-pyrazoline.—(a) Freshly distilled cinnamaldehyde (13.2 g.) was added to a mixture of 90% hydrazine hydrate (12 c.c.) and ethanol (40 c.c.); alteration of this order of addition causes precipitation of a large amount of azine. The mixture was refluxed for 1 hour, ethanol distilled off, and the residue dissolved in ether and washed with water. Distillation gave a colourless oil (6.6 g.), b. p. 146—148°/9 mm., which was a mixture of 5-phenyl-Δ²-pyrazoline (≥50%) and cinnamaldehyde hydrazone (≥23%). The oil (1.00 g.) was suspended in cold water (5 c.c.), and 2N-hydrochloric acid (10 c.c.) added; the precipitate of cinnamaldazine (23%), m. p. 161—163°, was filtered off. The filtrate with sodium nitrite (0.5 g.) precipitated 1-nitroso-5-phenylpyrazoline (50%), m. p. 71°. Treatment of the oil with cinnamaldehyde in ethanol gave a copious precipitate of cinnamaldazine (von Auwers and Heimke, *loc. cit.*, give b. p. 152.6—152.8°/15 mm. for the pyrazoline, and m. p. 74.5° for the nitroso-derivative).

(b) In a further experiment, the mixture was refluxed for 3 hours, and the solvent distilled off, finally at 180° (bath-temp.; maintained for 5 minutes). The product was not distilled; analysis as in (a) showed it to be mainly hydrazone, containing about 25% of pyrazoline.

(c) Cinnamaldehyde (26.4 g.) was converted, as in (a), into a product (19.15 g.), b. p. 140—145°/9 mm. Redistillation gave pure 5-phenyl-Δ²-pyrazoline (60%), b. p. 135—138°/9 mm., *n*_D²⁴ 1.5750, which gave no precipitate with ethanolic cinnamaldehyde. The pyrazoline (0.99 g.) was dissolved in cold dilute hydrochloric acid (no precipitate), and sodium nitrite added; the nitroso-compound (74%) had m. p. 70—71°.

Pyrolysis of 5-Phenylpyrazoline.—The pure pyrazoline (15.6 g.) from (c) was heated under reflux at 200° with potassium hydroxide (0.1 g.) for 1.5 hours. The product was shaken with dilute hydrochloric acid; the neutral fraction gave phenylcyclopropane (32.5%), b. p. 172—174°, *n*_D²⁵ 1.5311 (which contained 3% of β-methylstyrene), and much non-volatile tar. The acid solution with sodium nitrite gave 1-nitroso-3-phenyl-Δ²-pyrazoline (39%), m. p. 144—145°, undepressed on admixture with an authentic specimen.

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