A. N. Kost, G. A. Golubeva, Corresponding Member of the Academy of Sciences of the USSR A. P. Terent’ ev, and I. I. Grandberg

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Abstract

Full Text

Chemistry

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Cleavage of the Pyrazoline Ring with Rupture of the Nitrogen–Nitrogen Bond

In one of N. M. Kishner' s papers (1) it was noted that heating 5-methyl-5-isohexenylpyrazoline with platinized alkali leads to the formation, along with the corresponding cyclopropane hydrocarbon, of acetonitrile and methylheptenone imine. Recently it was found (2) that 4-ethyl-5-propylpyrazoline hydrochloride, when heated to 230°, undergoes cleavage, giving the nitrile of α-ethyl-β-aminocaproic acid.

While studying the hydrogenation and dehydrogenation of pyrazolines, we assumed that these compounds are capable of transformation according to the scheme of N. D. Zelinsky' s irreversible catalysis. On treatment of 5-phenylpyrazoline I (140°) with colloidal platinum, instead of the expected mixture of pyrazole and pyrazolidine, β-phenyl-β-aminopropionitrile was isolated in 65% yield; its structure was established from the IR spectrum, by reactions of the amino group, and by conversion into cinnamic acid.

$$\text{[5-phenylpyrazoline]} \xrightarrow{\text{Pt}} \mathrm{NC{-}CH_2{-}CH(NH_2){-}C_6H_5}$$

It turned out that other pyrazolines having no substituents in position 3 are also capable of this reaction. Thus, from 4-isopropyl-5-isobutylpyrazoline, under the action of platinum at 120–140°, α-isopropyl-β-amino-δ-methylcapronitrile was obtained.

$$\text{[4-isopropyl-5-isobutylpyrazoline]} \xrightarrow{\text{Pt}} \mathrm{NC{-}CH(CH(CH_3)_2){-}CH(NH_2){-}CH_2CH(CH_3)_2}$$

However, at the same time the greater part of the substance was converted into high-boiling condensation products. In the case of 4-ethyl-5-propylpyrazoline the process proceeds exothermically, a considerable amount of ammonia is liberated, and the main reaction products prove to be resin-like substances (probably due to polymerization of the unsaturated nitrile formed).

When a substituent is present in position 3 of the pyrazoline ring, the rearrangement found by us does not occur. 3-Methyl-5-phenylpyrazoline, when heated for 20-30 hours with platinum black at 135-140° in the absence of oxygen, is dehydrogenated in 45% yield to the corresponding pyrazole.

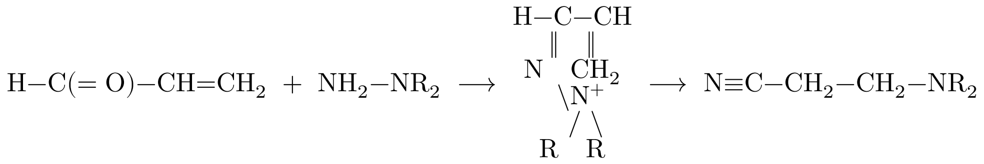
$$\text{[3-substituted 5-phenylpyrazoline]} \xrightarrow{-\mathrm{H}_2} \text{[corresponding pyrazole]}$$
$$R = CH_3,\ C_6H_5$$

1,3,5-Triphenylpyrazoline, in which the 1-position is occupied, was recovered unchanged from the reaction.

It might have been supposed that the catalytic hydrogenation of the pyrazoline ring to 1,3-diamines over skeletal catalyst, which we studied earlier, ···

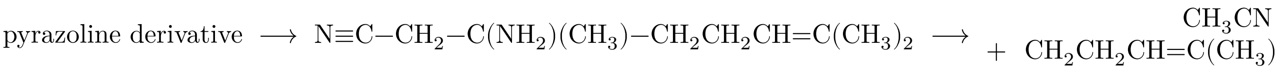
with nickel (3) may initially be reduced to the indicated rearrangement with subsequent reduction of the aminonitrile to the 1,3-diamine. However, we were unable to subject 5-phenylpyrazoline and 4-isopropyl-5-isobutylpyrazoline to an analogous rearrangement over skeletal nickel. They either returned from the reaction unchanged, or under more severe conditions (170—180°) underwent cleavage with the formation of a mixture of high-boiling substances. With a series of substrates we succeeded in carrying out the cleavage of pyrazolines (not having a substituent in position 3) by heating with hydrogen chloride; this is the subject of a special communication.

The transformation of pyrazolines into β-aminonitriles that we have found, occurring under the influence of acidic agents or a catalyst, is part of a more general property of hydrazones to undergo cleavage with rupture of the N—N bond. Indeed, as early as 1913 A. E. Arbuzov (4) found that phenylhydrazones of aliphatic aldehydes, on heating (180—200°) with Cu_2Cl_2, $PtCl_2$, or $ZnCl_2$, form aniline and the corresponding nitrile. C. Robev, in a series of works (see, for example, (5)), showed that phenylhydrazones of aldehydes, when heated with alkaline agents (for example, with $NaNH_2$), also undergo rearrangement with rupture of the N—N bond and formation of amidines. Recently B. V. Ioffe and K. N. Zelenin (6) discovered that acrolein, when heated with 1,1-dimethylhydrazine, is converted under the action of acidic agents into β-dimethylaminopropionitrile; diethylhydrazine behaves analogously in this reaction. All these processes are close to the Beckmann rearrangement of oximes, although for an objective assessment of the generality or specificity of the mechanisms of these reactions we still do not have sufficient information. The example described by Ioffe and Zelenin apparently reduces to the formation of a dialkylhydrazone, which then undergoes cleavage; moreover, it is probable that the dimethylamino group can migrate without formation of a kinetically independent entity.



$$\mathrm{H{-}C(=O){-}CH{=}CH_2} + \mathrm{NH_2{-}NR_2} \longrightarrow \begin{array}{c} \mathrm{H{-}C{-}CH} \\ \| \quad \| \\ \mathrm{N} \quad \mathrm{CH_2} \\ \backslash \mathrm{N^+} \\ / \ \backslash \\ \mathrm{R} \quad \mathrm{R} \end{array} \longrightarrow \mathrm{N{\equiv}C{-}CH_2{-}CH_2{-}NR_2}$$

The anomalous reaction described by Kizhner may likewise be thought to proceed through the stage of formation of a β-aminonitrile, which under the severe reaction conditions is cleaved similarly to what is known, for example, for Mannich bases (7)



$$\text{pyrazoline derivative} \longrightarrow \mathrm{N{\equiv}C{-}CH_2{-}C(NH_2)(CH_3){-}CH_2CH_2CH{=}C(CH_3)_2} \longrightarrow \begin{array}{r} \mathrm{CH_3CN} \\ +\ \mathrm{CH_2CH_2CH{=}C(CH_3)} \end{array}$$

It should be noted that benzylhydrazones of ketones, when heated with acidic agents, undergo complex transformations; but among the reaction products benzylamine was isolated, which could have formed only through cleavage of the *N*—*N* bond (8).

Thus, along with the rather well-studied reaction of the formation of indoles from arylhydrazones, there is an entire group of reactions of hydrazones (or their analogues) that proceed with rupture of the *N*—*N* bond.

Experimental part

Rearrangement of 5-phenylpyrazoline. Into a flask with a reflux condenser were placed 43 g of 5-phenylpyrazoline, b.p. 137—141°/11 mm, n_D^{20} 1.5784 (9), and 1.5 g of platinum black prepared according to Willstätter. To avoid contact with atmospheric oxygen, 5 ml of heptane was added. Heating was carried out on a metal bath with

with Wood' s alloy, controlled by a contact thermometer. The initial reaction temperature was 110°, then the temperature was raised to 140°. Heating was continued for 25 h. Bubbles of gas continuously came from the platinum; the flask smelled faintly of ammonia. After the heating was completed, the reaction mixture was treated with 500 ml of 1.5 N HCl. The catalyst was separated, and the resulting solution was extracted several times with benzene. The acidic layer was separated, made alkaline with a concentrated aqueous solution of sodium hydroxide, and extracted twice with benzene. The benzene was distilled off, and the residue was distilled in vacuo. This gave 28 g (65%) of β-phenyl-β-aminopropionitrile, b.p. 151-154°/10 mm, 127-129°/3 mm, n_D^{20} 1.5570, d_4^{20} 1.0541. MR_D found 44.58, calculated 44.70. The IR spectrum (IKS-12, in Vaseline oil) showed the presence of valence vibrations in the regions 2250 cm^{-1} (nitrile group) and 3460 cm^{-1} (amino group).

Found, %: C 73.80, 74.09; H 7.19, 7.06
$C_9H_{10}N_2$. Calculated, %: C 73.94; H 6.82

Picrate, m.p. 212-213° (from alcohol).

Found, %: C 48.21, 48.41; H 3.58, 3.75
$C_9H_{10}N_2 \cdot C_6H_3N_3O_7$. Calculated, %: C 48.01; H 3.49

Acetyl derivative, m.p. 105-108° (from alcohol).

Found, %: C 70.20, 69.98; H 6.55, 6.46
$C_{11}H_{12}N_2O$. Calculated, %: C 70.20; H 6.32

Benzoyl derivative (by Schotten-Baumann), m.p. 140° (from alcohol).

Found, %: C 76.80, 76.86; H 5.87, 5.74
$C_{16}H_{14}N_2O$. Calculated, %: C 76.77; H 5.64

13 g of the β-phenyl-β-aminopropionitrile obtained and 0.3 g of fused potassium hydroxide were heated in a Wurtz flask. At 150° a vigorous exothermic reaction began, accompanied by evolution of ammonia and strong resinification. The temperature rose spontaneously to 190-200°; at 210-230° part of the substance distilled off. On redistillation, 2.9 g of cinnamic acid nitrile was obtained, b.p. 215-222°/760 mm.

1.5 g of the resulting oil was heated for 2 h with 25 ml of 10% aqueous sodium hydroxide and 15 ml of alcohol. After cooling, the alcohol was distilled from the reaction mixture and it was extracted three times with ether. The aqueous layer was acidified with 20% sulfuric acid; the oil that separated was extracted with ether and dried over anhydrous magnesium sulfate. The ether was distilled off; the remaining oil, on standing in the refrigerator, crystallized, m.p. 67-68°, which corresponds to cis-cinnamic acid. The crystals obtained were heated on a water bath for 25 min with a fivefold amount of conc. H_2SO_4 and, after cooling, extracted with ether. After the ether was distilled off, an oil remained which did not crystallize after standing in the refrigerator for 14 days. The isolated oil was identified by paper chromatography as trans-cinnamic acid, with an authentic sample of trans-cinnamic acid as witness (solvent: methanol, 10% aqueous formic acid in a ratio of 1:1). Development was carried out by irradiation with ultraviolet light on a UFS-1 apparatus, BUV-15 lamps.

Rearrangement of 4-isopropyl-5-isobutylpyrazoline. Under analogous conditions, the reaction was carried out with 40 g of 4-isopropyl-5-isobutylpyrazoline. Upon addition of 2 g of platinum black to this pyrazoline, vigorous evolution of ammonia was observed. After 28 h of heating at 125°, the appropriate workup gave 10.2 g (26%) of α-isopropyl-β-amino-δ-methylcapronitrile, b.p. 105-108°/10 mm, n_D^{20} 1.4502, d_4^{20} 0.8793, MR_D found 51.45, calculated 51.62.

The IR spectrum (IKS-12) in Vaseline oil showed the presence of stretching vibrations in the region of 2236 cm^{-1} (CN group) and 3405 cm^{-1} (NH group).

Found, %:	C 71.99, 71.84;	H 11.54, 11.69
$C_{10}H_{20}N_2$. Calculated, %:	C 71.44;	H 11.97

Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.