[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AMHERST COLLEGE]

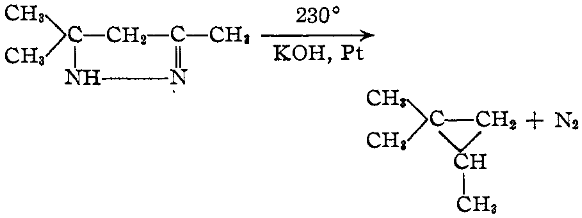
The Wolff–Kishner Reduction. II. The Effect of Alkali on N-Substituted Hydrazones

BY DAVID TODD

The net change in the Wolff–Kishner reduction is a shift of two hydrogen atoms from nitrogen to carbon and simultaneous loss of a molecule of nitrogen

$$R_2C{=}N{-}NH_2 \longrightarrow R_2CH_2 + N_2$$

That monoalkylhydrazones might undergo the same reaction with loss of N_2 and formation of a new carbon–carbon bond would seem not unlikely in view of the fact that alkylpyrazolines, when heated to 230° in the presence of potassium hydroxide and platinum, have been found to lose nitrogen with the formation of a cyclopropane ring



A glance at the formula of the above pyrazoline will show that such compounds are cyclic N-alkylhydrazones. By the same analogy, since N-substituted pyrazolines are stable to hot alkali, it would be expected that dialkylhydrazones would also be stable.

The observed facts are in good accord with expectations. Three methylhydrazones have been found to lose close to the theoretical amount of nitrogen under the influence of hot alkali. Benzaldehyde methylhydrazone lost nitrogen in the presence of potassium hydroxide and platinum at 220–230°. Among the products of the reaction there were identified ethylbenzene (about 10% yield), benzoic acid and stilbene. When *p*-isopropylbenzaldehyde methylhydrazone was treated in a similar fashion, a 25% yield of *p*-ethylisopropylbenzene was obtained, as well as a small amount of *p*-isopropylbenzoic acid. No diisopropylstilbene could be detected. The *p*-ethylisopropylbenzene was identified by conversion to 2-ethyl-5-isopropylbenzenesulfonamide. The structure of the latter was proved by oxidation to the known 3-sulfonamido-4-ethylbenzoic acid.

Furfural methylhydrazone lost nitrogen at 170–190° in the presence of alkali and platinum but no products could be isolated from the reaction mixture.

Cyclohexanone methylhydrazone distilled unchanged from alkali and platinum at about 200°, but when the mixture of reagents was heated in a sealed tube at 250° there was obtained a colorless crystalline product of unknown structure. It is apparently a tertiary amine of the empirical formula $C_9H_{15}N$. There was no methylcyclohexane detected.

The dimethyl and diethylhydrazones of benzaldehyde, *p*-isopropylbenzaldehyde and furfural were all stable to alkali at 250°. The dialkylhydrazones of cyclohexanone, however, were largely decomposed to tarry products under these conditions.

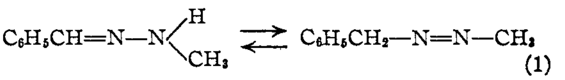
Discussion of Results

The fact that some N-monoalkylhydrazones, but not N,N-dialkylhydrazones, can be made to lose nitrogen in the presence of hot alkali with the formation of a product analogous to that formed in the Wolff–Kishner reduction of simple hydrazones makes it appear plausible that these processes go by a similar mechanism at least in the absence of solvent. It has been suggested[1] that the Wolff–Kishner reduction proceeds by a preliminary shift of the double bond to form a diimine, which then loses nitrogen in the manner characteristic of compounds containing the N=N linkage

$$R{-}CH{=}N{-}NH_2 \xrightarrow{OH^-} RCH_2{-}N{=}N{-}H \longrightarrow RCH_3 + N_2$$

Balandin and Vaskevitch[2] have reported kinetic data on the decomposition of cyclohexanone hydrazone that indicate an intermediate is formed in the process, and suggest that the only reasonable intermediate is the diimine.

If this mechanism is applied to the decomposition of benzaldehyde methylhydrazone it is difficult to avoid the conclusion that the diimine decomposes into two free radicals and a molecule of nitrogen. The free radicals then combine with each other to form ethylbenzene. The three steps in the reaction are then



$$C_6H_5CH{=}N{-}N\begin{matrix}H \\ CH_3\end{matrix} \rightleftarrows C_6H_5CH_2{-}N{=}N{-}CH_3 \qquad (1)$$

$$C_6H_5CH_2{-}N{=}N{-}CH_3 \longrightarrow C_6H_5CH_2\cdot + CH_3\cdot + N_2 \qquad (2)$$

$$C_6H_5CH_2\cdot + CH_3\cdot \longrightarrow C_6H_5CH_2CH_3 \qquad (3)$$

There is a considerable amount of evidence that points to the existence of the reversible reaction (1).[3] The hydrazone is evidently always favored in this equilibrium though there are cases known in which the diimine form exhibits considerable stability. Phenyl ethyl diimine can be distilled at

---

[1] Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," New York, N. Y., 1938, p. 384.

[2] Balandin and Vaskevitch, *J. Gen. Chem. U.S.S.R.*, **6**, 1878 (1936); [*C. A.*, **31**, 4575 (1938)].

[3] Sidgwick, "Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1937, p. 432.

180° without isomerizing to acetaldehyde phenylhydrazone, and is stable to dilute alkali.[4] Phenyl benzyl diimine and dibenzyl diimine have been prepared, and are converted to the corresponding hydrazones by the action of either acid or base.[5] Surprisingly enough, diisopropyl diimine is so stable that the action of alkali at 180° for three to five hours converts it only partially into the hydrazone form.[6] It is evident that not only are the diimine forms characterized by considerable stability, but that alkali is a catalyst for the diimine-hydrazone equilibrium.

The evidence for step (2) is equally impressive. The thermal decomposition of dimethyl diimine in the gas phase into nitrogen and ethane at 275 to 320° has been carefully studied,[7] and shown to proceed almost certainly by a free radical mechanism.[8] Substitution of the hydrogens of one or both methyls in dimethyl diimine by alkyl groups leads to a slight decrease in thermal stability of the compound, whereas substitution by aromatic groups leads to a far more pronounced decrease in thermal stability. Thus, the temperatures of roughly comparable rates of decomposition are: dimethyl diimine, 320°; methyl isopropyl diimine, 300°[9]; diisopropyl diimine, 280°[10]; dibenzyl diimine,[5] 160–170°. It would then be expected that methyl benzyl diimine formed by isomerization of benzaldehyde methylhydrazone, would decompose at a temperature between 170° and 280°. The observed temperature is 220–230°.

If the reaction proceeds by a free radical mechanism, it could be expected that the particles might recombine partly with themselves and partly with each other. Therefore a search was made for dibenzyl among the reaction products of the benzaldehyde methylhydrazone decomposition but none could be detected. It was thought likely that the small amount of stilbene formed in the reaction might have arisen by platinum dehydrogenation of dibenzyl produced. But dibenzyl was found to be completely stable under the reaction conditions, and the formation of stilbene remains unexplained. However Wolff[3] found some symmetrical tetraphenylethane among the reaction products when benzophenone phenylhydrazone was heated with sodium ethoxide at 190° or slowly distilled in the absence of alkali. In this case the relatively high stability of the diphenylmethyl radical can explain the formation of this product though it is difficult to see why triphenylmethane was not also formed.

Similarly, it seems highly likely that the thermal decomposition of pyrazolines proceeds by initial isomerization to the Δ'-form, which loses nitrogen to form a di-free radical. This becomes stabilized by forming a cyclopropane derivative. Further work on appropriately substituted pyrazolines is now in progress.

Experimental

Attempted Alkaline Decomposition of the Dialkylhydrazones.—The procedure used involved simply heating the compound in question, with a pellet of sodium or potassium hydroxide and a small platinum spiral, in a Woods metal bath to 250° for about half an hour. The apparatus was connected with a gas buret.

The dimethyl- and diethylhydrazones of benzaldehyde, *p*-isopropylbenzaldehyde and furfural were all found to be stable under the above conditions. There was little or no net evolution of gas and the hydrazones could be recovered virtually quantitatively, as shown by the boiling points, indices of refraction, and preparation of solid derivatives.

Because of their low boiling point, the dimethyl- and diethylhydrazones of cyclohexanone had to be heated in sealed tubes. Considerable pressure had developed when the tubes were cooled and opened, and a strong amine odor was evident. In both cases very little dialkylhydrazone could be recovered from the dark tarry mass, and it was evident that almost complete decomposition had occurred.

Alkaline Decomposition of Benzaldehyde Methylhydrazone.—In a 50-ml. modified Claisen flask equipped with a receiver and connected to a gas buret were placed 5.0 g. of the hydrazone, a pellet of sodium hydroxide and several pieces of platinized porous plate. The flask was heated in a Woods metal-bath. Gas began to evolve rapidly at 235° (bath temp.). The bath was heated to 254° and maintained there for one-half hour, when gas evolution had virtually ceased. The gas evolved corresponded to 83% of the theoretical amount of nitrogen expected.

In the receiver there was found a mixture of two liquids. This turned out to consist of a few drops of methylhydrazine and 0.5 g. of ethylbenzene. The former was identified by its rapid positive Fehling test and conversion to the picrate. The ethylbenzene was removed with a pipet, washed with 1 ml. of water, dried over potassium carbonate. The material has b. p. (micro) 137°, n^{20}_{D} 1.4943 (ethylbenzene has b. p. 136.2, n^{20}_{D} 1.4959). Several hundred milligrams of this material was converted to 2,4-diacetaminoethylbenzene,[11] m. p. 223–225° (no depression with an authentic specimen of m. p. 224–227°).

The residue in the flask was taken up in ether, washed with water and 5% hydrochloric acid and dried. (From the aqueous washings there was recovered a little benzoic acid.) The ether residue was distilled at 16 mm. to give 0.3 g. of material coming over below 100° (odor of benzaldehyde, positive DNP test), 0.73 g. of a fraction boiling at 160–180° (A), and 0.60 g. of a fraction of b. p. 213° (B). The residue weighed 0.88 g.

Fraction A was partially crystalline. After seven crystallizations from ethanol–water there was isolated about 20 mg. of slightly impure stilbene, m. p. 116–121°, mixed m. p. with stilbene (m. p. 120–124°) showed no depression.

Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.17; H, 7.27.

Fraction B was almost entirely crystalline, but was evidently a mixture since it could not be obtained crystalline from ethanol–water. The ethanol solution on treatment with trinitrobenzene gave a yellow precipitate that after two more crystallizations gave yellow needles, m. p. 110.0–111.5°. The analysis indicates this compound is still impure.

Anal. Found: C, 38.04; H, 2.11.

Alkaline Decomposition of *p*-Isopropylbenzaldehyde Methylhydrazone.—The decomposition was carried out as described in the previous case. From 13.4 g. of the hydrazone there was obtained 119% of the theoretical amount of gas. A sample of this gas was cooled to −193°

---

(4) Fischer, *Ann.*, **199**, 328 (1879); *Ber.*, **29**, 793 (1896).

(5) Thiele, *ibid.*, **376**, 267 (1910).

(6) Lochte, Bailey and Noyes, This Journal, **44**, 2556 (1922).

(7) Ramsperger, *ibid.*, **49**, 912 (1927).

(8) Leermakers, *ibid.*, **55**, 3499 (1933); Rice and Evering, *ibid.*, **55**, 3898 (1933).

(9) Ramsperger, *ibid.*, **51**, 2134 (1929).

(10) Ramsperger, *ibid.*, **50**, 714 (1928).

(11) Ipatieff and Schmerling, This Journal, **59**, 1056 (1937).

and pumped off with a mercury pump. No significant portion of the gas remained after this treatment. Evidently no detectable amount of ethane is formed in the reaction.

The distillate produced during the reaction was combined with the few drops of material that could be distilled *in vacuo* (bath to 180°), worked up in ether as usual and finally distilled from sodium. There was obtained 2.8 g. (25%) of *p*-ethylisopropylbenzene. Micro b. p. is 194°, n^{23}_{D} 1.4858, d^{23}_{4} 0.8530 (the literature values are: b. p. 196°, n^{16}_{D} 1.4928, d^{16}_{4} 0.8606); MR_{obs} 49.90; $MR_{calcd.}$ 49.40.

2-Ethyl-5-isopropylbenzenesulfonanilide.—One gram of the hydrocarbon was dissolved in 5 ml. of chloroform, cooled to 0°, and while stirred in an ice-bath was treated dropwise with 5 ml. of chlorosulfonic acid. The solution was held at 0° for ten minutes, allowed to warm to room temperature and poured on ice. The chloroform solution was separated, washed and dried. One-half of the chloroform solution of sulfonyl chloride was evaporated to dryness and to the oil was added 2 ml. of aniline. The solution was boiled for two minutes, and the product was worked up by extraction from ether with 1% of sodium hydroxide. There was obtained 0.74 g. (72%) of the crude anilide of m. p. 104–107°. Crystallization from ethanol–water gave the pure material as tiny serrated needles melting constantly at 108.0–109.0°.

The same material was prepared from authentic hydrocarbon. It had the same melting point and a mixture of the two showed no melting point depression.

This material is probably identical with the compound (position of sulfonanilide group unknown), prepared by Klages and Keil,[12] reported to melt at 110°.

The position of the entering sulfonyl chloride group was demonstrated as follows:

Authentic *p*-ethylisopropylbenzene was treated as described above, and the chloroform solution of the acid chloride was divided into two parts. One of these was converted to the anilide as described. The other was evaporated, heated with ammonium carbonate on the steam-bath for one-half hour, the solid washed well with cold water, and the residue crystallized from ethanol to give 64% of crude 2-ethyl-5-isopropylbenzenesulfonamide. Two crystallizations from ethanol gave a product melting at 69.0–70.5°.

Anal. Calcd. for $C_{11}H_{17}NO_2S$: C, 58.12; H, 7.54. Found: C, 58.11; H, 6.92.

3-Sulfonamido-4-ethylbenzoic acid.—Two-tenths of a gram of the above sulfonamide was refluxed with 1.2 g. of potassium dichromate, 1 ml. of concentrated sulfuric acid, and 3 ml. of water for four hours. The acid fraction was crystallized from ethanol–water several times to give the pure acid which has a constant, though wide, melting range. It begins to soften at 235°, and melts at 248–257°, mostly at 253–257°. Widman[13] reported that this compound melted at 259–260°.

An authentic specimen of this material was prepared by the same series of reactions applied to *p*-diethylbenzene. The acid so formed was obtained as colorless needles that begin to soften at about 235°, and melts at 248–259°, mostly at 253–259°. A mixture of the two materials shows exactly the same melting characteristics.

Alkaline Decomposition of Furfural Methylhydrazone.—This material was decomposed in the usual way. It was found that the decomposition temperature was considerably lower than in the other cases. At about 140° the compound begins a very rapid evolution of gas. The temperature was carried up to 200° to ensure complete reaction. There was collected 91% of the theoretical volume of gas.

On working up the reaction mixture nothing but tar could be obtained. Evidently little or no ethylfuran was formed.

Alkaline Decomposition of Cyclohexanone Methylhydrazone.—This material was found to distill unchanged at about 200° from potassium hydroxide and platinum. The hydrazone (3.45 g.) one pellet of potassium hydroxide and a platinum spiral were heated in a sealed tube at 250° for two hours. On being cooled the tube's contents were found to be a solid mass of crystals. On being worked up this material was found to contain no trace of methylcyclohexane. The solid material was crystallized from ethanol to give 0.40 g. of colorless plates, m. p. 88.0–89.5°. A second crop of 0.39 g. of less pure material was obtained. Recrystallization of the first crop from ethanol gives platelets of m. p. 90.5–91.0°.

Anal. Found: C, 81.90, 81.57; H, 9.63, 9.51; N, 7.95, 8.32. Calcd. for $C_{11}H_{15}N$: C, 81.9; H, 9.3; N, 8.8.

This material is a very weak base (soluble in 6 *N* HCl, insoluble in 1.3 *N* HCl), and is probably a tertiary amine (forms no derivative in the Hinsberg process). It does not form a picrate or a chloroplatinate.

Summary

The stability of some N-alkyl and N,N-dialkylhydrazones to alkali has been investigated. The results indicate that the decomposition of monoalkylhydrazones, of unsubstituted hydrazones, and of pyrazolines may all proceed by the same mechanism in the absence of solvent: *i. e.*, preliminary isomerization of the hydrazone to the diimine, and loss of nitrogen from the diimine to give two free radicals (a di-free radical in the case of pyrazolines) that rapidly combine to give the observed products.

RECEIVED OCTOBER 18, 1948

---

[12] Klages and Keil, *Ber.*, **36**, 1641 (1903).

[13] Widman, *ibid.*, **23**, 3086 (1890).