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Molecular Rearrangements. XXIV. Thermolysis of Phenylhydrazones

Safaa Abd El-Salam Mahgoub, Atiat Mohammed Fahmy, Morsy Mohammed Aly, and Mahmoud Zaif Amin Badr*
Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt, A.R.E.

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Synopsis. Thermolysis of acetophenone phenylhydrazone by reflux in air for 24 h gives ammonia, benzonitrile, acetophenone, biphenyl, aniline, *o*- and *p*-toluidines, together with 7-methyl-3-phenylindole, while that of benzophenone phenylhydrazone gives ammonia, benzophenone, *N*-benzhydrylideneaniline, biphenyl, aniline, benzonitrile, and 9-phenylacridine.

Thermolysis of phenylhydrazones of aldehydes and ketones was a matter of controversy, where Chattaway et al.[1] recorded the thermal breakdown of benzaldehyde phenylhydrazone into *N*-benzylideneaniline, stilbene, ammonia, benzene, and nitrogen.

Further extension of this reaction to other phenylhydrazones[2] leads to the conclusion that the reaction proceeds through a concerted fourcenter process rather than a free radical mechanism.

Repeating the above thermolysis reaction in one of our studies had resulted in different products than that recorded before. This prompted us to reinvestigate the reaction in an effort to gain further information about more generalized pyrolytic mechanism.

Thermolysis of benzophenone phenylhydrazone (**1**) by reflux in air for 24 h gives ammonia, benzophenone, biphenyl, aniline, benzonitrile, *N*-benzhydrylideneaniline (**2**), and 9-phenylacridine (**3**).

Formation of most of these products strongly points to a free radical mechanism starting by homolysis of N–N bond forming phenylaminyl and diphenylmethaniminyl radical pairs (Eq. 1) followed by H-abstraction to form aniline and diphenylmethanimine, respectively. The latter most probably on hydrolysis during working up procedure, gives rise to benzophenone and ammonia. Such a mechanism is to be expected on basis of bond energy values of the N–N and N–H bonds[3] being of the order 51 and 75 kcal mol^{-1}(1 cal=4.184 J), respectively.

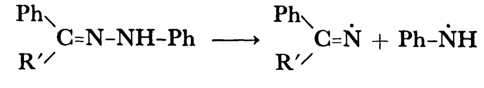
However, such mechanism can not correlate for the formation of biphenyl, **2** and **3**. Consequently we have to take into consideration an alternative pathway involving isomerization of the phenylhydrazone **1** to the corresponding phenylazoalkane **4** as observed by other workers[4] through a free radical mechanism initiated by free radicals present in the reaction medium. The isomerized phenylazoalkane undergoes nitrogen extrusion forming phenyl and diphenylmethyl free radicals. Phenyl free radical substitution on the phenylazoalkane followed by its fragmentation gives biphenyl, whereas atmospheric oxidation of diphenylmethyl free radicals gives benzophenone as described by other workers[5] in the oxidation of benzyl radicals to benzaldehyde (Scheme 1). Furthermore, coupling of phenyl and dipenylmethaniminyl radicals leads to the formation of *N*-benzhydrylideneaniline.

The **3** (a pyrolysis product of **1**) is reasonably assumed to be formed via **5** which results from C–C coupling of diphenylmethyl and phenylaminyl radicals (Scheme 2).

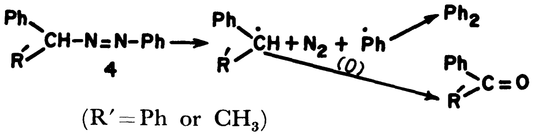
Acetophenone phenylhydrazone (**6**) behaves similarly on thermolysis under the same conditions forming ammonia, acetophenone, biphenyl, aniline, benzonitrile, *o*- and *p*-toluidines, and 7-methyl-3-phenylindole. The formation of these products can be interpreted as in the case of **1**. Moreover, the formation of benzonitrile and *o*- and *p*-toluidines is in favor of the four-center mechanism proposed earlier by Crow and Solly[2] leading to the formation of *N*-methylaniline that ultimately rearranges to *o*- and *p*-toluidines as observed in a previous work.[6] On the other hand, fragmentation of diphenylmethaniminyl radicals leads to the formation of benzonitrile and phenyl radicals.[2]

However, the *o*-toluidine so formed have been consumed in the formation of 7-methyl-3-phenylindole (**7**) through condensation with styrene which is considered to be formed along with phenylethane as a disproportionation product of 1-phenylethyl radicals, as shown in Scheme 3. Such indole structure was further confirmed by its IR spectrum which shows ν NH at 3400 cm^{-1} and its electronic spectrum which shows absorption maxima at 272 nm (ε 2680) and 285 nm (ε 1920) characteristic for indole moiety.[7]

Repeating the pyrolysis of **6** in absence of air by heating in a sealed tube filled with nitrogen leads to a great decrease in the amount of acetophenone to about one third of that obtained in the case of reflux in air in addition to a corresponding increase in the yield of **7** as expected mechanistically.



$$\mathrm{Ph(R')C{=}N{-}NH{-}Ph} \longrightarrow \mathrm{Ph(R')C{=}\dot{N}} + \mathrm{Ph{-}\dot{N}H} \qquad (1)$$



(R′=Ph or CH_3)

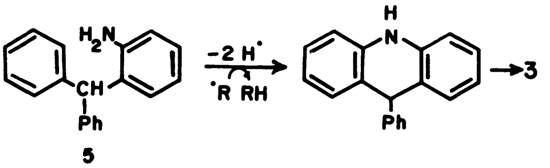
Scheme 1.

Dimerization of diphenylmethaniminyl radicals to form the corresponding azine was not observed due to the instability of the N–N bond.[8] Similarly, pyrolysis of **1** by heating in a sealed tube leads to an increase in the amount of **3** as compared with that obtained on reflux in air (cf. Table 1).

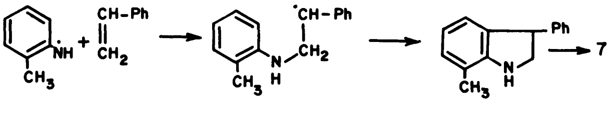
Table 1. Products of Thermolysis of Acetophenone Phenylhydrazone and Benzophenone Phenylhydrazone (20 g)

Products in g/%	Bp(θ_b/°C) 3 mm	Acetophenone phenylhydrazone		Benzophenone phenylhydrazone	
		Reflux	Seeled tube	Reflux	Seeled tube
Ammonia	—	Evolved	Evolved	Evolved	Evolved
Amine products:					
Aniline[a]	50—52	2.5(12.5)	2.3(11.5)	2.5(12.5)	1.5(7.5)
o-, *p*-Toluidine[b]	72—76	2.6(13)	1.8(9)	—	—
7-Methyl-3-phenylindole[c]	165—170	5.8(29)	7.5(37.5)	—	—
9-Phenylacridine[d]	215—220	—	—	5.6(28)	6.5(32.5)
Neutral products:					
Benzonitrile[e]	41—46	1.5(7.5)	1.3(6.5)	1.3(6.5)	1.0(5)
Acetophenone[f]	62—65	4.2(21)	1.5(7.5)	—	—
Biphenyl[g]	102—105	1.5(7.5)	1.2(6)	1.2(6)	1.0(5)
Benzophenone[h]	140—145	—	—	4.5(22.5)	4.2(21)
N-Benzhydrylideneaniline[i]	180—185	—	—	3.5(17.5)	3.0(15)
Residue	—	1.5(7.5)	3.6(16)	0.7(3.5)	2.2(11)

a) n_D^{20}: 1.5836; acetyl deriv. mp and mixed mp 113—114 °C. b) Found by GLC to consist mainly of *p*-toluidine together with traces (less than 1%) of *o*-toludine. c) MP and mixed mp 186—188 °C.[10] d) MP and mixed mp 182—183 °C, picrate mixed mp 185—186 °C.[12] e) Hydrolysis gives benzoic acid, mp and mixed mp 120—121 °C. f) D.N.P. deriv. mp and mixed mp 235—237 °C. g) MP and mixed mp 68—69 °C: 4,4′-dinitro deriv. mp and mixed mp 233 °C. h) MP and mixed mp 47—49 °C; D.N.P. deriv. mp and mixed mp 236—238 °C. i) MP and mixed mp 109—110 °C.[11]



Scheme 2.



Scheme 3.

Experimental

All mp's are uncorrected. Thin-layer chromatography was carried out on glass plates covered with silica gel (25—40 mesh) and eluted with benzene/cyclohexane (2:1 v/v). The GLC analyses were carried out on a Pye-Unicam gas chromatograph, 'Series 104', equipped with a dual flame ionization detector, Model 24. The columns used were 4 ft(1 ft=0.3048 m)X5 mm packed with 20% SE 30 on Chromosorb W (35—80 mesh) or 10% SE 30 on Celite (60—80 mesh).

Thermolysis of Phenylhydrazones. **6** (mp 105—106 °C)[9] or **1** (mp 137 °C)[9] (20 g) was heated either under reflux in air or in a sealed tube under nitrogen atmosphere at 250 °C for 24 h. The ammonia evolved was detected by means of HCl and further absorbed in a trap containing sulfuric acid forming ammonium sulfate. The pyrolysate were treated similarly where in each case was dissolved in ether and shaken several times with dil HCl to extract the amine products. The ethereal layer containing either the neutral or the amine products was dried (Na_2SO_4) and evaporated to dryness leaving an oily material (15 g) which was separated by fractional distillation under reduced pressure into its constituents and identified by elemental analyses, TLC, GLC, UV, IR spectroscopy and/or mixed mp with authentic samples whenever possible. The results are shown in Table 1.

References

1) F. D. Chattaway, C. L. Cumming, and T. Wilsden, *J. Chem. Soc.*, **99**, 1950 (1911).
2) W. D. Crow and R. K. Solly, *Aust. J. Chem.*, **19**, 2119 (1966).
3) "CRC Handbook of Chemistry and Physics," 62nd ed. ed by R. C. Weast, CRC Press, Boca Raton. FL.FL 93 (1981—1982).
4) A. J. Bellamy and R. D. Guthrie, *J. Chem. Soc.*, **1965**, 3528.
5) A. E. Woodward and R. B. Mesrobian, *J. Am. Chem. Soc.*, **75**, 898 (1957).
6) M. Z. A. Badr and M. M. Aly, *Can. J. Chem.*, **52**, 293 (1974).
7) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," ed by E. Arnold, London (1960), pp. 151—152.
8) S. W. Benson, *J. Chem. Educ.*, **42**, 503 (1969).
9) R. Criegee and G. Lohaus, *Chem. Ber.*, **84**, 219 (1951).
10) M. Z. A. Badr, M. M. Aly, G. M. El-Naggar, and A. M. Fahmy, *Z. Naturforsch.*, **34b**, 1128 (1979).
11) D. Zoeppritz, *Ber.*, **35**, 991 (1902).
12) A. Bernthren, *Justus Liebigs Ann. Chem.*, **224**, 13 (1884).