OXIDATION OF HYDRAZONES. I.   HYDRAZONYL FREE RADICALS

FROM α,α'-BIS(PHENYLAZO)BIBENZYLS.   AN INEFFECTIVE CAGE

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We should like to report some observations on the formation and properties of hydrazonyl

free radicals of the general structure 1. The corresponding dimers 3 and 4 are obtained by oxi-

dation of hydrazones 2 with a variety of oxidizing agents.[1] The interesting bis-azo compounds

3 can be isolated in dl and meso forms. Their structures[1d,2] are supported by that fact, as

well as by spectral data, elemental analyses, and clean conversion in base to the corresponding

osazones 5. Nmr spectra of dl- and meso-3 are clearly distinguishable. (We have assumed,

although it is not crucial to our discussion, that the markedly more soluble compounds are the

racemic mixtures.)

Production of radicals 1 by thermal decomposition of bis-azo compounds 3 is indicated by

the following: (a) Crossing experiments can be performed; thus, after a mixture of 3a and 3c is

heated in benzene solution, 6 is recovered in addition to the starting materials. Conversely,

when 6 is heated in benzene, 3a, 3c, and 6 are recovered. (b) Heating compounds 3 in benzene in

the presence of free radical trapping agents such as thiophenol, hydroquinone, and tri n-butyl

tin hydride leads to hydrazones 2. Experiments with hydroquinone-d_2 demonstrate the interesting

fact that hydrogen is captured directly at the nitrogen site in at least 90% of the abstractions.

We do not observe any of the methine-d hydrazone whose formation would be expected if deuterium

were captured at the carbon site, followed by tautomerization of the resulting azo compound.

(c) Dl- and meso-3 can be equilibrated. The equilibrium ratio [dl]/[meso] at 80° in benzene is,

for 3a, 1.30; for 3c, 1.45. Similar cases of equilibration of dl and meso forms via radical

intermediates are few, but have been observed.[2,3] It should be noted that the Cope rearrange-

ment cannot be invoked to account for the equilibration unless it is assumed that both four-

center and six-center transition states[4] are involved. "Head-to-tail" dimers 4, heated in

benzene, yield the more thermodynamically stable bis-azo dimers 3; when 3 are heated, 4 are not

observable (by nmr spectroscopy). We attribute to thermodynamic instability the fact that we do

TABLE I. Rates of Trapping by Thiophenol, k_t,[a] and of Epimerization, k_e,[b] Min^{-1} [c]

°C	dl-3a		meso-3a		dl-3c		dl-3b[d]
	$10^3 k_t$	$10^3 2k_e$	$10^3 k_t$	$10^3 2k_e$	$10^3 k_t$	$10^3 2k_e$	$10^3 k_t$
70	4.06		5.61		6.64[f]	4.85	
75	6.91					8.58	
80	10.9[f]	8.30[f]	13.0[f]	10.8[f]	21.3[f]	15.3	
85	19.3		22.0[f]				5.15[d]

a First order rates from nmr integrals. Concentrations: 0.1 m dimer, 2 m thiophenol, in benzene.

b Calculated from the equations $k_{dl} + k_{meso} = k_{obs}$ and $k_{dl}/k_{meso} = K$, where K = 1.30 for 3a, 1.45 for 3c; k_{obs} are first order rates of approach to equilibrium based on nmr integrals. Concentrations: 0.1 m dimer in benzene.

c Values of $\Delta H^{\ddagger}$, kcal per mole: from dl-3a k_t, 26.2 ± 2.8; from meso-3a k_t, 24.0 ± 2.0; from dl-3c k_t, 28.2; from dl-3c k_e, 27.6 ± 1.0; from dl-3b[d] k_t, 26.4 ± 2.8.
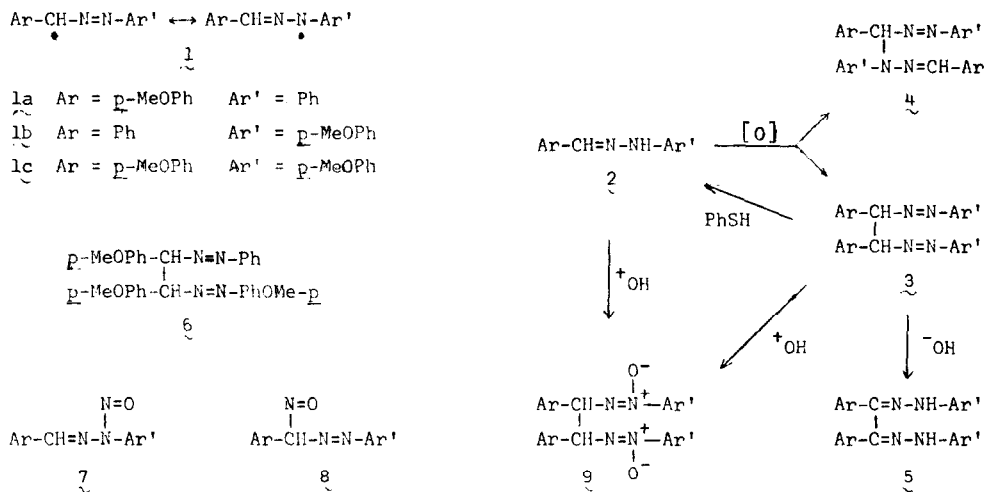
d Other measurements for dl-3b $10^3 k_t$: 90°, 9.48; 95°, 13.1; 100°, 24.1.

f Average of several measurements.

not observe N-to-N dimerization products. (The N-to-N structure was incorrectly assigned to compounds 3 for many years.)[1d,2]

We have reproduced the work of Bamberger and Pemsel[5] on oxidation of hydrazones 2 with amyl nitrite to form compounds of the molecular formula (Ar-CH-N$_2$-Ar')(NO). Although there remains some question as to whether these compounds should be formulated as 7 or 8, our observation is unambiguous that, when 7 (8) are dropped into boiling hexane, there occurs a clean reaction to form 3, 4, and nitric oxide. We have found amyl nitrite oxidation to be the most useful preparation of dimers 3. It is not necessary to isolate the sensitive intermediates 7 (8).

We have measured the trapping rates (rates of production of two molecules of 2 from one molecule of 3) in benzene in the presence of excess thiophenol for 3a-c at several temperatures (Table I). Controls, run with added di-t-butylperoxyoxalate, establish the fact that induced decomposition of the dimers by thiophenoxy radicals does not take place. We have also established, by varying the thiophenol concentration, that at concentrations of 2 m thiophenol and 0.1 m 3 (our usual conditions) thiophenol is trapping all of the free radicals as they are formed from the dimers. We find that $\Delta H^{\ddagger}$ for breaking the central bond in 3a-c is about 27 kcal per mole (Table I, note c). It is interesting to compare this figure with that of 14 kcal per

Ar-CH-N=N-Ar' ⟷ Ar-CH=N-N-Ar'
    •   •

                    1

la Ar = p-MeOPh   Ar' = Ph
lb Ar = Ph   Ar' = p-MeOPh
lc Ar = p-MeOPh   Ar' = p-MeOPh

p-MeOPh-CH-N=N-Ph
    |
p-MeOPh-CH-N=N-PhOMe-p

          6

        N=O   N=O
         | |
Ar-CH=N-N-Ar'   Ar-CH=N=N-Ar'

        7   8

Ar-CH=N-NH-Ar'   [O]
                         ↗
      2   Ar-CH-N=N-Ar'
                               |
                               Ar'-N-N=CH-Ar
              PhSH   4
                      ↘
                        Ar-CH-N=N-Ar'
                        |
                        Ar-CH-N=N-Ar'

                               3

      │ ⁺OH   │ ⁻OH
      ↓   ⁺OH   ↓
              O⁻
               |
Ar-CH=N-N⁺—Ar'   Ar-C=N-NH-Ar'
         | |
Ar-CH-N=N⁺—Ar'   Ar-C=N-NH-Ar'
         |
         O⁻
         9   5

mole for the breaking of the central bond in a dimer of the structure 9, where the radical

formed is a nitroxide in addition to being hydrazonyl. (Compounds of the general structure 9

are obtained by treatment of hydrazones 2 with peracids.[6] Their structures had been widely

misassigned,[7] before being firmly established as 9.[2] Treatment of compounds 3 with peracids

also leads to compounds 9.[2] These compounds will be the subject of a future paper.)

No epimerization (dl ⇌ meso) of 3a-c is observable in the presence of thiophenol, except at

concentrations of thiophenol lower than 1 m. However, we have measured the rates of epimeriza-

tion in benzene in the absence of thiophenol (Table I). These rates give a similar value for

$\Delta H^{\ddagger}$ for breaking the central bond. One might have expected that twice the rate of conversion of

dl-3 to meso-3 (or of meso-3 to dl-3) would be equal to the rate of production of two radicals

from 3 as measured in the thiophenol experiment at the same temperature and dimer concentration.

That is, a radical, once formed, would have an even chance of returning to a dl or to a meso

dimer. However, our results (Table I) show that epimerization, both of meso- and of dl-3, is

somewhat slower than expected. Thus, the radicals (known from the corresponding thiophenol

experiment to be present) have some memory of the dimer which spawned them.

We feel that this interesting effect is most simply attributed to the fact that one of a

pair of radicals, once formed, must still "turn over" before epimerization can take place. For

radicals as bulky as are these, it is not unreasonable to suppose that direct return to the

spawning dimer might be a somewhat favored process.

An alternative but essentially equivalent view is of a cage reaction R-R ⇌ [R··R] ⇌ R··R,

where the cage is completely penetrated by thiophenol at our concentrations, and where epimerization does not occur within the cage. Preliminary observations indicate that there are differences, depending on the substituents on 3, in the cut-off points for thiophenol concentration below which not all of the radicals are trapped and epimerization can occur concurrently with trapping. While the cut-off for 3c is at about 1 m thiophenol, 0.1 m thiophenol suffices for complete penetration in the case of 3a. These facts are in contrast to some reported cases[8] of the cage effect, where the cage cannot be scavenged even with 3 m thiophenol. It is surprising that such low concentrations of thiophenol are effective in our cases. While we cannot rule out a complex between thiophenol and 3, uv spectra taken in the presence of thiophenol show no evidence of such an association.

The ambient nature of hydrazonyl radicals may provide an explanation for the relative ineffectiveness of the cage in our cases, since trapping can, and does, take place on nitrogen, well removed from the bond which is being broken. We feel that a spectrum of return phenomena in free radical chemistry, comparable to that observed in carbonium ion chemistry, may be suggested by these results.[9-11]

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