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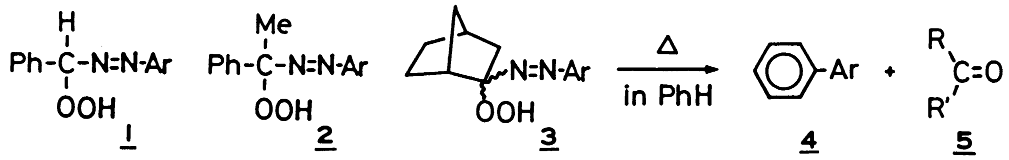
Novel Thermal Deoxygenation in Bornyl α-Azohydroperoxide to Give Camphor Hydrazone. A Retro-ene Reaction Assisted by the Steric Compression Effect

Takahiro TEZUKA* and Takashi OTSUKA
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

Camphor hydrazone, its dimer, and oxygen are generated from bornyl α-azohydroperoxide by thermal reaction accompanied by several other products. The retro-ene elimination mechanism is proposed.

The retro-ene decomposition reaction in α-azohydroperoxide is not known, while the retro-ene reaction in some hydrotrioxides and/or hydroperoxides is known to give several important species including singlet oxygen.[1,2] We wish to report a new thermal decomposition reaction of sterically crowded α-azohydroperoxide (6), that yields camphor hydrazone (7) and its dimer (8) accompanied by oxygen via the retro-ene elimination pathway, in which the steric compression effect by the methyl groups assists the reaction.

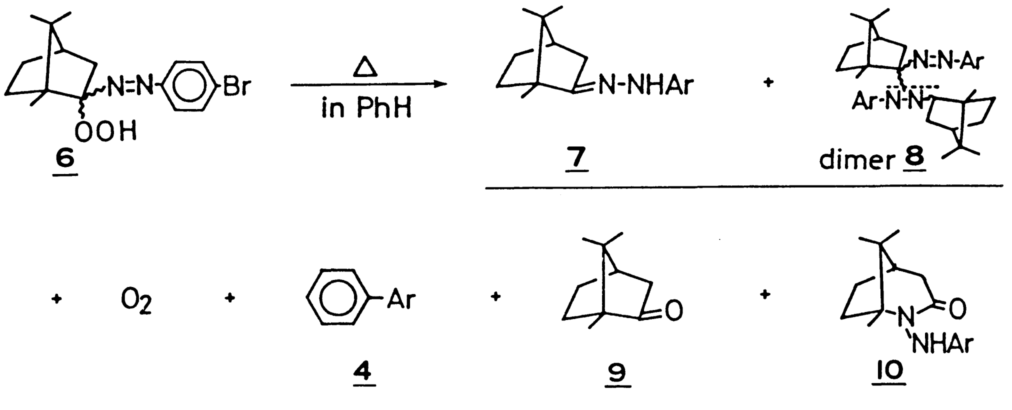
α-Azohydroperoxides 1 - 3 gave biaryl (4) and the parent carbonyl compound (5) as the main reaction products accompanied by a small amount of phenol when refluxed in benzene under inert gas (Scheme 1).[3] In contrast, the α-azohydroperoxide 6 exhibited a different thermal reactivity.



Scheme 1.

When bornyl α-azohydroperoxide (6) (a 3:2 mixture of endo- (6a) and exo- (6b) hydroperoxides)[1,3-6] (10^{-2} M) was refluxed in benzene under inert gas until all of 6 decomposed, both camphor hydrazone (7) (11%) and its dimer (8)[7,8] (11%) were formed together with oxygen (35%), 4-bromobiphenyl (4) (25%), camphor (9) (40%), lactam (10) (22%),[9] and phenol (5%) (Scheme 2). The formation of the hydrazone 7 and its dimer 8 from α-azohydroperoxide (6) is of no precedent and has an important bearing on the mechanism of the reaction.

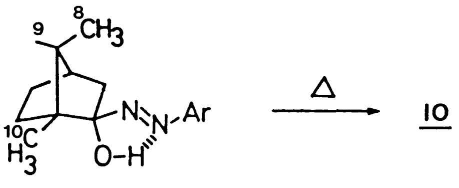
The results are rationalized by the mechanism indicated in Scheme 3. The thermal homolytic cleavage of the O-O bond in 6 generates an oxy radical (11) which decomposes to give 9 and aryl radical, from which 4 is formed by the reaction with benzene. Upon abstraction of a hydrogen atom from 6 by 11, endo- (12a) and exo- (12b) alcohols and a peroxy radical (13) are generated. Thermolysis of the endo-alcohol 12a yields the lactam 10, while the exo-alcohol 12b gives both camphor (9) and aryl radical which yields 4 by the reaction with benzene. These reactions in-



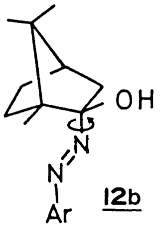
Scheme 2.

cluding the rearrangement of 12a into 10 are known.[3,9]

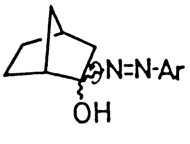
On the other hand, the peroxy radical 13 generates both oxygen and 11 by the decomposition via a tetroxide intermediate formed by the dimerization of 13.[10]



12a



12b



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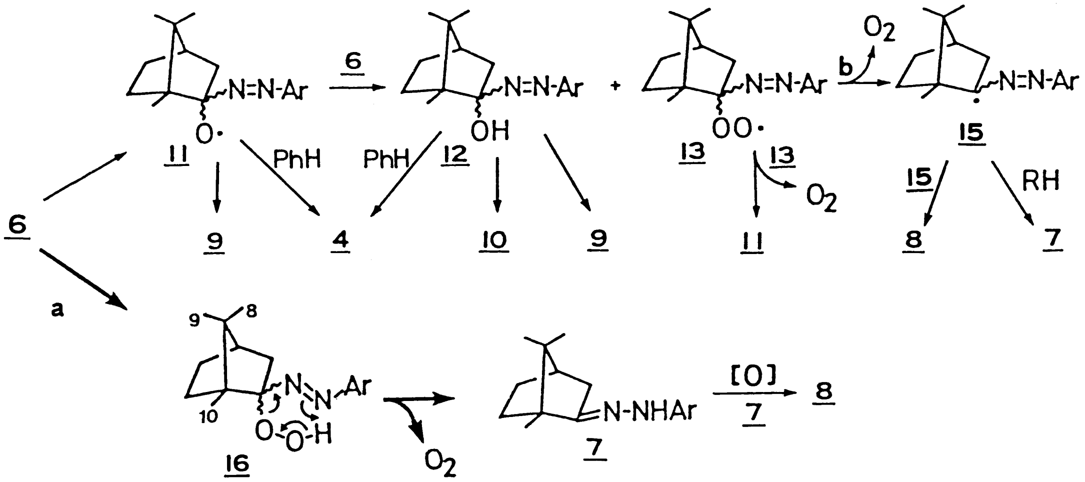
The analogy of the oxygen exchange or migration in allyl peroxy radicals suggests the possibility that the peroxy radical 13 gives off oxygen and the radical 15,[11] which yields the hydrazone 7 and dimer 8 by abstraction of a hydrogen atom and by the coupling, respectively (Scheme 3, path b).

However, the radical mechanism for the formation of the hydrazone 7 via 15 (path b) is not consistent with the following observations. The addition of the radical scavenger such as 2,6-di-tert-butyl 4-methyl phenol (BHT) and/or triphenyl methane did not inhibit the formation of 7. The formation of 8, on the other hand, was suppressed by the addition of these scavengers. The photo reaction of 6, which is expected to produce the oxy radical 11 as one of the important intermediate species,[4] did not give 7. The yield of the dimer 8 increased when the thermal reaction of 6 was carried out in the presence of 7 (1 mol eq), suggesting that the dimer 8 is a secondary product arising from 7 by the oxidative coupling. Thus the radical pathway for the formation of 7 via 15 is concluded not to be likely.

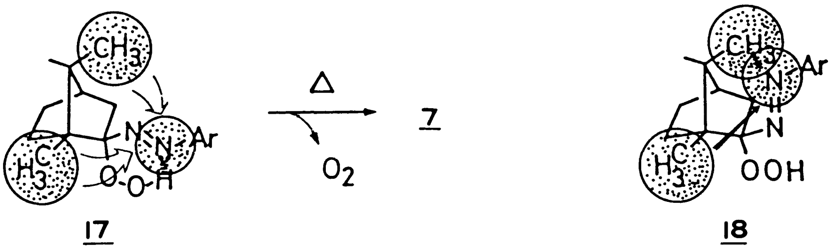
The retro-ene elimination mechanism involving a six-membered transition state (16 or 17) well accounts for the formation of the hydrazone 7 from 6 (Scheme 3, path a, or Scheme 4), and is consistent with the following observations. The favorable thermal formation of the hydrazone 7 from 6 as compared with 1 - 3[12] indicates that the steric hindrance or steric compression effect by the 8- and 10-methyl groups in 6 plays an important role in the formation of the hydrazone. The molecular model indicates that in the endo-hydroperoxide 6a, the steric hindrance by the 8- and 10-methyl groups toward the exo-arylazo group fixes the conformation



Scheme 3.

in the manner indicated by 17 in which the free rotation of the arylazo group is inhibited, because the rotamer 18 is of higher energy. This results in the formation of the strong intramolecular hydrogen bonding, which provides readily the retro-ene transition state 17, leading to the formation of the hydrazone 7 by the thermal reaction (Scheme 4).[13]

The steric effect mentioned above is supported by the analogy in the rearrangement of the endo-alcohol 12a into the lactam 10, in which the steric hindrance by the 8- and 10-methyl groups fixes the arylazo group in the conformation indicated by 12a that brings about the favorable rearrangement into the lactam 10. In contrast, the arylazo group rotates freely in the exo-alcohol 12b and norbornyl azo alcohols (both endo- and exo-alcohols). This renders the rearrangement of these alcohols into the lactam unfavorable.[9]



Scheme 4.

The existence of the strong intramolecular hydrogen bonding in 6a in benzene is supported by the fact that the hydroperoxy hydrogen of 6a shifted to the extremely low field (9.9 ppm in C_6D_6) as compared with that of 6b in the ^{1}H NMR spectra.[14,15] The six-membered hydrogen bonding in 6a is supported by the X-ray crystallographic study of a cyclohexyl azohydroperoxide derivative by Bozzini et al.[16] and by MO calculation.[17]

It is worthy to note that in the formation of 7 from 6a via 17 by the retro-ene reaction[18] and the rearrangement of 12a into 10, the steric hindrance by the 8- and 10-methyl groups fixes first the conformation of the arylazo substituent and the steric compression thus substantiated induces the specific reaction when the molecule is thermally activated. The reaction may be classified as a steric compression-assisted reaction.[18-20]

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7) The dimer structure was assigned by the comparison with the authentic sample obtained by the MnO_2 oxidation of camphor p-bromophenylhydrazone (Ref. 8).

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12) The precise search in the reaction mixture suggested the possibility for the formation of a very small or trace amount of the corresponding hydrazones from 1 - 3.

13) This suggests the preference for the endo-hydroperoxide 6a to undergo the retro-ene elimination reaction rather than the exo-one 6b.

14) In the ^{1}H NMR spectrum of 6 (endo and exo mixture) in d_6-benzene (around 10^{-2} M), two kinds of hydroperoxy hydrogen absorption due to 6a and 6b appeared at 9.9 and 9.0 ppm, respectively.

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18) Details of the mechanism of the retro-ene reaction and/or the steric compression-assisted reaction described in this paper will be reported in our forthcoming paper.

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