

Benzimidoyl Radicals: Free-radical Reactions of Benzaldimines

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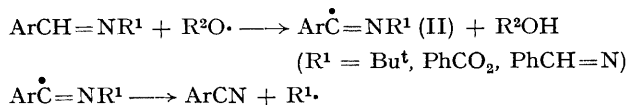
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Summary Benzaldimines, $\text{ArCH}=\text{NR}$ ($\text{R} = \text{Bu}^t$ or PhCO_2), on treatment with di-isopropyl peroxydicarbonate in warm benzene, generates benzimidoyl radicals, $\text{Ar}\dot{\text{C}}=\text{NR}$, which subsequently decompose to give benzonitrile together with the radical $\text{R}\cdot$.

WE present evidence for the formation of benzimidoyl radicals, $\text{Ar}\dot{\text{C}}=\text{NR}$, from reaction of benzaldimines with peroxides.

In a typical experiment, di-isopropyl peroxydicarbonate (I) (0.02 mole) and *N*-benzylidene-*t*-butylamine (0.01 mole) were kept at 60° under nitrogen in benzene (50 ml) until decomposition of (I) was complete. The products were benzonitrile (69% based on the imine), benzaldehyde (6%), *t*-butyl isopropyl carbonate (48%), together with small amounts of *t*-butylbenzene and *N*-*t*-butylbenzamide. Acetone and isopropyl alcohol were also formed. Similar reactions with *p*-methoxy- and *p*-chloro-benzylidene-*t*-butylamine gave the nitriles, 77 and 90%, respectively. In the presence of 2,2-diphenyl-1-picrylhydrazyl no benzonitrile or *t*-butyl isopropyl carbonate was formed, which indicates a radical pathway for the reactions.

The following mechanism is possible:



Oxy-radicals generated from the peroxide abstract the imidoyl hydrogen atom giving the imidoyl radical (II; $\text{R} = \text{Bu}^t$) which subsequently fragments to give benzonitrile and a *t*-butyl radical.¹ This radical reacts with

benzene giving *t*-butylbenzene, or induces the decomposition of (I)² affording *t*-butyl isopropyl carbonate.

Likewise, with benzaldoxime benzoate under the same conditions, benzonitrile (65%) was obtained, together with phenyl isopropyl carbonate (8%), benzoic acid (14%), and biphenyl (7%). These products are consistent with the formation of an intermediate benzoyloxy-radical which subsequently decarboxylates to give a phenyl radical. Benzalazine under the same conditions afforded benzonitrile (30%), which suggests loss of the radical $\text{PhCH}=\text{N}\cdot$ from the imidoyl radical (II; $\text{R} = \text{PhCH}=\text{N}$).

Benzylideneaniline, in contrast, gave no benzonitrile (through loss of a phenyl radical) but instead gave isopropyl *N*-benzoyl-*N*-phenylcarbamate, $\text{PhCO}\cdot\text{NPh}\cdot\text{CO}\cdot\text{OPr}^i$ (40%). This compound is probably formed by induced decomposition of (I) by *N*-phenylbenzimidoyl radical (II; $\text{R} = \text{Ph}$), formed by abstraction as above. The failure of the *N*-phenylbenzimidoyl radical to lose a phenyl radical is undoubtedly due to the strong N-Ph bond, and accords with the failure of other systems such as alkoxy-radicals, in which an alkyl rather than an aryl radical is lost preferentially,³ to lose phenyl groups.

The ready abstraction of imidoyl hydrogen by oxy-radicals makes an interesting contrast with the fact that abstraction of vinylic hydrogen atoms from olefins has not been observed.

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¹ Participation of aliphatic imidoyl radicals as intermediates in the homolytic isomerization of isonitriles to the corresponding nitriles has been postulated. [D. H. Shaw and H. O. Pritchard, *Canad. J. Chem.*, 1967, **45**, 2749; T. Saegusa, Y. Ito, N. Yasuda, and S. Kobayashi, presented at the 9th Symposium on Free-radical Reactions, Kiryu (Oct., 1968)].

² H. C. McBay and O. Tucker, *J. Org. Chem.*, 1954, **19**, 869.

³ C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, 1963, **85**, 1593.