Benzimidoyl Radicals: Free-radical Reactions of Benzaldimines

By HIROYUKI OHTA and KATSUMI TOKUMARU*

(Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo, Japan)

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

WE present evidence for the formation of benzimidoyl radicals, $\mathrm{Ar\dot{C}{=}NR}$, 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:

$$\mathrm{ArCH{=}NR^1 + R^2O\cdot \longrightarrow Ar\dot{C}{=}NR^1\ (II) + R^2OH}$$

$$(\mathrm{R^1 = Bu^t,\ PhCO_2,\ PhCH{=}N})$$

$$\mathrm{Ar\dot{C}{=}NR^1 \longrightarrow ArCN + R^1\cdot}$$

Oxy-radicals generated from the peroxide abstract the imidoyl hydrogen atom giving the imidoyl radical (II; $\mathrm{R = Bu^t}$) 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 $\mathrm{PhCH{=}N\cdot}$ from the imidoyl radical (II; $\mathrm{R = PhCH{=}N}$).

Benzylideneaniline, in contrast, gave no benzonitrile (through loss of a phenyl radical) but instead gave isopropyl *N*-benzoyl-*N*-phenylcarbamate, $\mathrm{PhCO{\cdot}NPh{\cdot}CO{\cdot}OPr^i}$ (40%). This compound is probably formed by induced decomposition of (I) by *N*-phenylbenzimidoyl radical (II; R = 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.

We thank Professor O. Simamura for his interest in, and support of, this work and also Professor J. I. G. Cadogan for his hospitality, as a result of which one of us (K.T.) began part of this work at the University of St. Andrews.

(Received, September 2nd, 1970; *Com.* 1485.)

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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.