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N-(*ortho*-Aryloxyphenyl)arylimidoyl Radicals: Novel 1,5-Aryl Radical Translocation from Oxygen to Carbon

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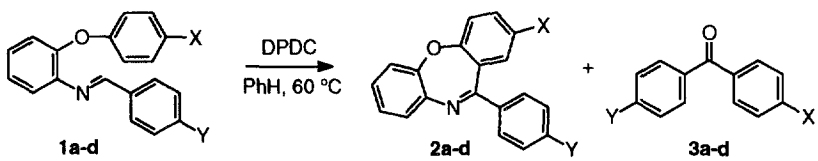
Abstract: Imidoyl radicals **4a-d**, obtained by hydrogen abstraction from imines **1a-d**, give 7-membered cyclisation leading to oxazapines **2a-d**. The intermediate spirocyclohexadienyl radicals of the competitive 6-membered ring closure (**6a-d**) rearrange to aryloxy radicals, giving benzophenones **3a-d**: the whole process entails a novel 1,5-aryl radical translocation from an oxygen to a carbon atom.

Our group has been studying for several years the reactivity of arylimidoyl radicals, which were generated by hydrogen abstraction from aromatic imines by means of di-*iso*-propyl peroxydicarbonate (DPDC). These radicals have proved to be synthetically useful intermediates in annulation reactions leading to quinolines[1] or benzotriazines;[2] very recently, they have been generated by radical addition to isonitriles and have been involved in the first example of 4 + 1 homolytic annulation.[3] As far as cyclisation reactions are concerned, imidoyl radicals can add intramolecularly to carbon-carbon double bonds[4] and aromatic rings,[5] and they can also give rise to homolytic substitutions at the sulfur atom of a sulfide moiety leading to benzothiazoles.[6] Here we report the reactivity of the imidoyl radicals obtained by hydrogen abstraction from N-arylidene-2-phenoxyanilines **1a-d**. When these imines (1 mmol) were allowed to react with DPDC (2 or 4 mmol) at 60 °C in benzene solution they gave complicated mixtures of compounds among which dibenzoxazepines **2** and benzophenones **3** could be identified as the major products (Scheme 1 and Table 1).[7]

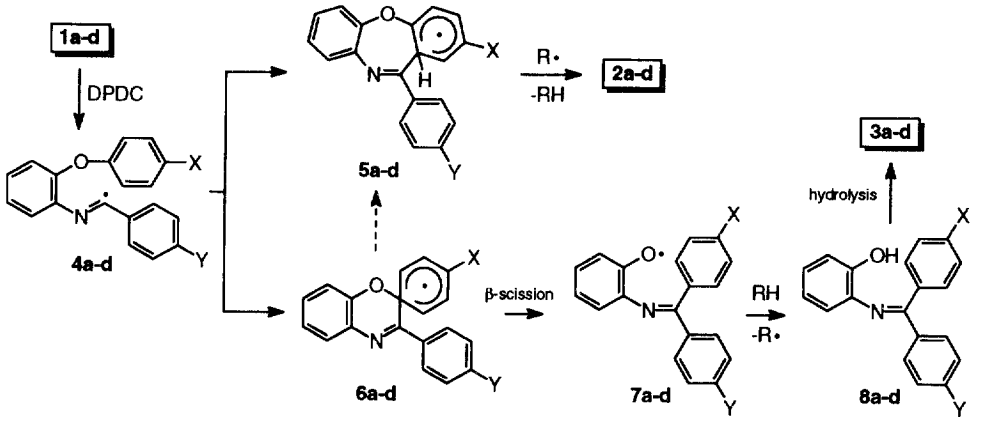


Scheme n. 1. Main products of the reaction of imines **1a-d** with DPDC.

Comp.	X	Y	t (h)[a]	**2** (%)[a]	**3** (%)[a]	t (h)[b]	**2** (%)[b]	**3** (%)[b]
1a	H	H	47	12	11	25	10	9
1b	H	Cl	70	17	11	48	8	8
1c	H	OMe	24	19	14	6	17	18
1d	Cl	Cl	54	11	16	30	14	13

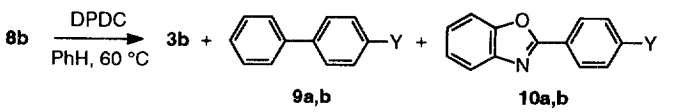
Table n. 1. All yields are for the starting imines and were determined by GC analysis using indole as an internal standard and authentic specimens of the reaction products prepared according to reported procedures.
a) Reactions carried out with 2 mmol of DPDC. b) Reactions carried out with 4 mmol of DPDC.

The reaction products **2** and **3** can be rationalised by assuming the initial formation of imidoyl radicals **4a-d**. These radicals can give oxazepines **2** through 7-membered cyclisation on the benzenic ring of the phenoxy group followed by aromatisation of the intermediates **5**: they can also lead to ketones **3** through competitive 6-membered ring closure on the same aromatic ring followed by β-fragmentation of the spiro-radicals **6**: the resulting phenoxy radicals **7** can furnish ketimines **8** by hydrogen abstraction and then benzophenones **3** through hydrolysis of **8** in the reaction mixture (Scheme 2).



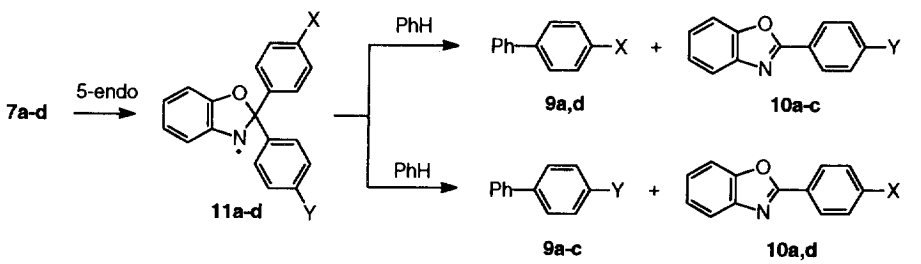
Scheme n. 2. Reaction mechanism of imidoyl radicals **4a-d**.

Ketimines **8** were not detected in the reaction mixtures, as one should expect on the basis of their reported great instability toward hydrolysis.[8] Actually, ketimine **8b** was synthesised and kept in benzenic solution in the presence of DPDC: under these conditions it disappeared quickly giving benzophenone **3b** (25%) and trace amounts of biphenyls **9a,b** and benzoxazoles **10a,b** (Scheme 3).[9] Trace amounts of compounds **9** and **10** were also detected in all the reactions of imines **1a-d** with DPDC and this confirmed the intermediacy of ketimines **8** in the reaction mechanism of imidoyl radicals **4a-d**.



Scheme n. 3. Reaction of ketimine **8b** with DPDC.

The formation of **9** and **10** is ascribable to a 5-endo ring closure of the phenoxy radicals **7** on the carbon-nitrogen double bond: the resulting radicals **11** can aromatise to benzoxazoles **10** by loss of either Y- or X-substituted aryl radicals that, in turn, attack the solvent yielding the corresponding biphenyls **9** (Scheme 4).



Scheme n. 4. Mechanism of formation of compounds **9** and **10**.

The mechanism of Scheme 4 is supported by the previously reported lead-tetraacetate-mediated cyclisation of N-arylidene-2-aminophenols to benzoxazoles, which probably entails a radical pathway.[10] Furthermore, when imine **1a** was allowed to react in chlorobenzene we found small quantities of the three isomeric chlorobiphenyls in the same ratio obtained in the homolytic phenylation of chlorobenzene.[11] It is worth pointing out that the reaction path leading from **4** to **7** entails a homolytic rearrangement that appears to be the first example of 1,5 radical translocation of an aryl group from an oxygen to a carbon atom.[12]

The reaction of Scheme 1 also afforded variable amounts of the compounds reported in Figure 1.[7]

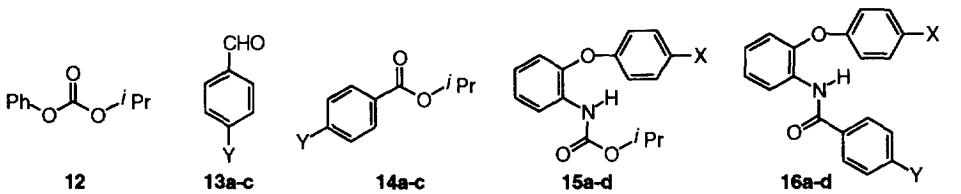
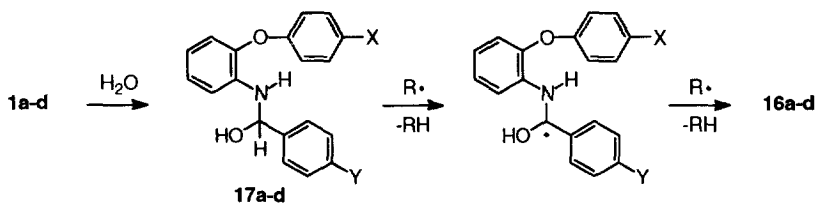


Figure n. 1. By-products of the reaction of imines **1a-d** with DPDC.

Carbonate **12**, detected by GC-MS analysis, has no relation with our study and arises from attack of *iso*-propoxycarbonyloxy radicals to benzene, in accordance with the low kinetic constant reported for the loss of carbon dioxide from these radicals.[13] Aldehydes **13** (3-17%) are the result of hydrolysis of the starting imines **1** occurring in the reaction medium; trace amounts of esters **14** are likely to be formed through hydrogen abstraction from **13** followed by coupling with *iso*-propoxy radicals.[14] Carbamates **15** (1-10%) were not completely rationalised. Variable amounts of these compounds were detected in other reactions involving imines and DPDC[1c] and they probably arise from a non-radical reaction between DPDC and the aryloxyanilines derived from hydrolysis of **1**.[15] The formation of amides **16** (1-3%) involves a radical pathway because it was affected by the presence of a radical scavenger. A mechanism entailing attack of imidoyl radicals **4** to dioxygen molecules is not likely because the yields of **16** did not lower significantly by carrying out the reaction in a carefully degassed solution in a sealed vial. Therefore, we suggest that **16** arise from oxidation of **17**, that are the intermediate species in hydrolysis of **1** (Scheme 5).



Scheme n. 5. Suggested mechanism of formation of amides **16**.

Studies are still in progress to find out other 1,5-aryl migrations from heteroatom to carbon in **4**-like imidoyl radicals.

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7. All new compounds gave satisfactory microanalytical and ^{1}H-NMR, MS, and HRMS spectral data, which will be published in a subsequent paper. For preparation and handling of DPDC see ref. 1b.
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9. 2-Aminophenol should be formed as well as a result of the hydrolysis of **8**. Nevertheless, it was not detected neither in the reactions of imines **1**, nor starting from ketimine **8b**: it was probably destroyed by the oxidant medium to give tarry materials.
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14. When aldehyde **13b** was allowed to react with DPDC at 60 °C it gave small amounts of **14b**.
15. This hypothesis is supported by the reaction between 2-phenoxyaniline and DPDC giving **15a** (33%). Furthermore, when imine **1a** was allowed to react with DPDC in the presence of 2,6-di-*tert*-butylphenol as a radical scavenger it afforded **15a** (53%), exclusively.

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