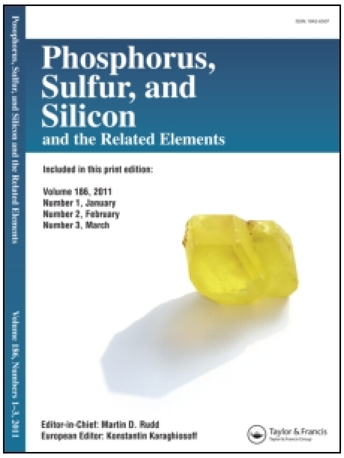

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A New View of the Mechanistic Pathways in the Iodine Atom Transfer Addition Reaction Involving 1-Iodoalkylphosphonates and Related Nonphosphorus Systems

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A NEW VIEW OF THE MECHANISTIC PATHWAYS IN THE IODINE ATOM TRANSFER ADDITION REACTION INVOLVING 1-IODOALKYLPHOSPHONATES AND RELATED NONPHOSPHORUS SYSTEMS†

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The title reaction in the initiation step proceeds via two mechanistic pathways involving attack of the isobutyronitrile radical either on the starting iodide or on the starting alkene or alkyne followed by the reaction of the adduct radical with the iodide.

Keywords: α,α'-Azaisobutyronitrile (AIBN); iodine atom transfer addition reaction; organic iodide; phosphonate; reaction mechanism

INTRODUCTION

In a series of papers,[1–9] we have demonstrated a synthetic utility of 1-diethoxyphosphorylalkan-1,2- and -3-yl radicals that are phosphorus-containing intermediates, enabling in our research further functionalization of the phosphonate chain under reductive conditions (Scheme 1, $X = H$). Recently,[10,11] we have extended a scope of utilization of these radicals onto the iodine atom transfer addition reactions involving 1-iodoalkyl-phosphonates (Scheme 1, $X = H$). The mechanistic pathways of this and related reactions, until now, have not been fully proved.[12]

[†] Part X of the series: Phosphorus containing radicals. For Part IX see.[10]

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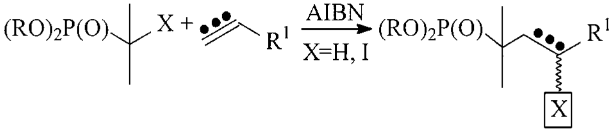
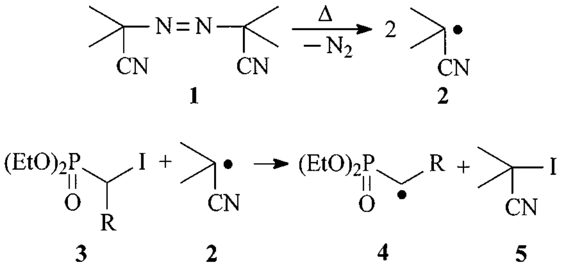


SCHEME 1 Synthesis of functionalized phosphonates.

RESULTS AND DISCUSSION

According to the reaction mechanism of the heteroatom or heterogroup transfer reactions, 1-iodoalkylphosphonate **3** must be attacked in the initiation step by the isobutyronitrile radical **2** obtained by the thermal decomposition of α,α'-azaisobutyronitrile (AIBN) **1** to form 1-diethoxyphosphorylalkan-1-yl radical **4** capable of reacting with alkene or alkyne and 2-iodo-2-methylpropio-nitrile **5** (Scheme 2).



SCHEME 2 Initiation step of the iodine atom transfer reaction.

However, considering the above mechanism, two additional and fundamental questions arose:

1. Is the iodide **5** an additional (to the iodide **3**) iodine donor in the next transfer reaction step?
2. Is this the only mechanism of initiation?

For the first question the answer is negative.[11] Addition of **5** either in catalytic or stoichiometric amounts from the external source caused a total inhibition of the reaction. On the other hand, careful GC-MS analyses of crude reaction mixtures of various organic iodides with alkenes or alkynes showed trace amounts of **5** only in one case. It was consistent with the EPR experiments, which revealed a lack of radical species in refluxing benzene in measurable quantities. All of these observations led to a conclusion that the title reaction proceeds via very short reaction chains and with extremely small concentrations of radical species.

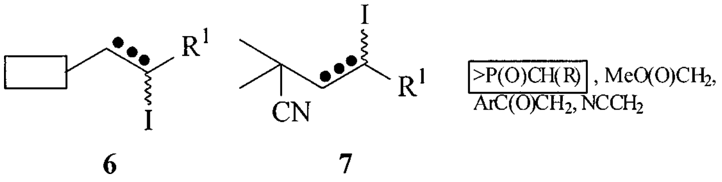
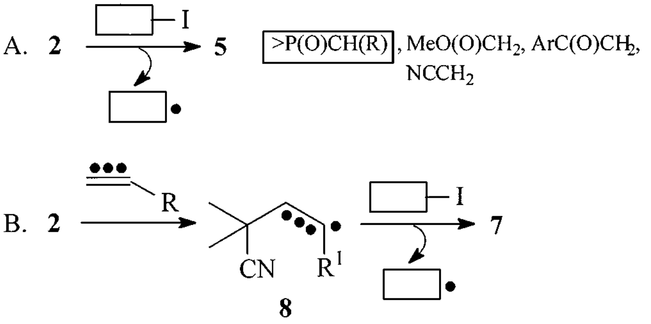


FIGURE 1 Two types of the iodine atom transfer products.

However, other experiments with the free radical TEMPO showed that this reaction possesses a radical character. Such a conclusion suggested the second question: Is this the only mechanism of the initiation for the title reaction involving the α-phosphoryl iodide **3** and for other reactions involving nonphosphorus-containing organic iodides?

The positive answer for this question came from a careful analysis of both types of reactions, which showed that in addition to main products **6**, a second type of the iodine atom transfer products **7** was formed in 14–66% yields (based on the AIBN used).

The products **7** were formed as the result of the competitive attack of the radical **2** onto alkene or alkyne to give adduct radicals **8** undergoing the iodine atom transfer reaction (Scheme 3).



SCHEME 3 Two types (A & B) of the initiation stage.

CONCLUSIONS

1. The title reaction possesses a radical character (TEMPO). However, it proceeds with short reaction chains and with extremely small concentrations of radical species.
2. The initiation step proceeds via two mechanistic pathways (A & B) of which the latter seems to be predominant (Scheme 3)
3. In the iodine atom transfer stage, the iodide **5** is not an iodine donor but an inhibitor.

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