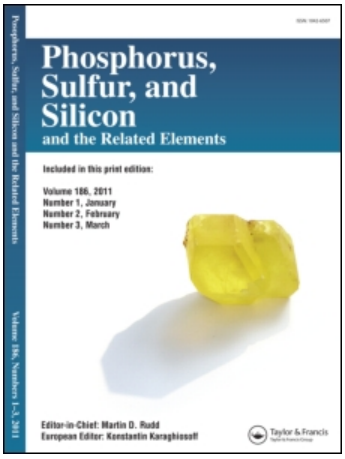

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Recent Progress in Synthetic and Mechanistic Aspects of Phosphonate C-Radical Chemistry

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Recent Progress in Synthetic and Mechanistic Aspects of Phosphonate C-Radical Chemistry

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Progress in radical chemistry of C—C bond formation reactions as well as C-heteroatom (halogen, O, S, Se) and C—C bonds cleavage reactions under reductive conditions, involving phosphonate C-centered radicals, is reviewed with special emphasis on the achievements during the past seven years in iodine atom transfer addition (I-ATRA) and cyclization (I-ATRC) reactions, which were developed in this laboratory.

Keywords I-ATRA and I-ATRC reactions; phosphonate; radical; radical asymmetric induction; radical C—C and C-heteroatom (halogen, S, Se) bonds scission; radical C—C bond formation

INTRODUCTION

Phosphonates, as is commonly known, play a vital role in various fields of chemistry; they are important as biologically and pharmacologically active substances, synthetic targets, ligands, advanced materials, and building blocks.[1–5] The synthesis of phosphonates, which sometimes have complex structures, requires the development of new procedures for the functionalization of simple molecules, which are available via classical reactions in phosphorus chemistry. In contrast to the continuing development of α-carbanion chemistry of phosphonates as a method

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

Together with the representative of the young generation (A.B.), I (P.B.) would like to wish Professor Marian Mikołajczyk long years of further activity as a scientist and thank him for accompanying me in all stages of my scientific carrier. I also thank my collaborators A. Szadowiak (PhD), T. Białas (M.Sc.), and W. M. Pietrzykowski (M.Sc.) for their contribution to the radical chemistry of phosphonates.

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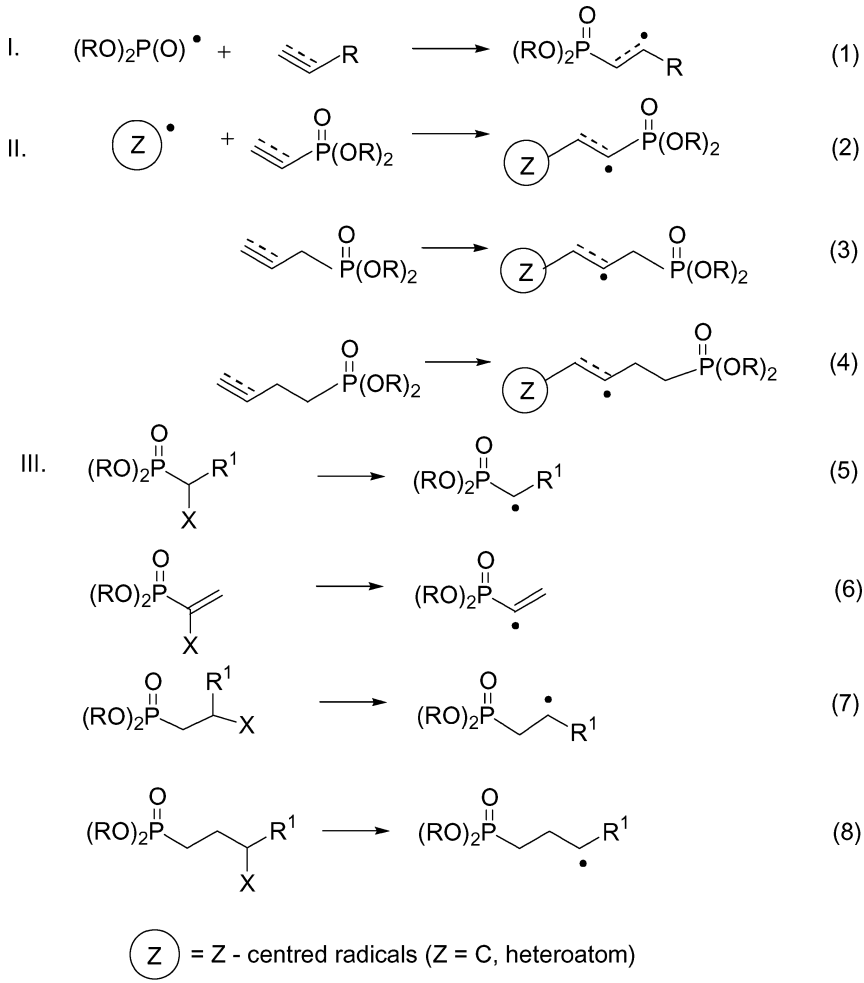
of their functionalization, the chemistry of phosphonate *C*-centered radicals has been less often considered for many years despite the potential capabilities for stabilization of phosphonate carbanions, carbocations, and radicals by the phosphoryl P(=O) group.[6] Most synthetic methods for the formation of phosphonate C-radicals are based on three approaches: (I) addition of *P*-radicals to alkenes or alkynes (Scheme 1, Eq. 1), (II) addition of *Z*-centered radicals to vinyl-, allyl-, and homoallyl phosphonates and their alkyne analogs (Scheme 1, Eqs. 2–4), and (III)



SCHEME 1

direct synthesis from radical precursors (Scheme 1, Eqs. 5–8). Not all concepts concerning the alkyne approaches have been realized so far.

The first chain reaction in phosphorus chemistry was the reaction of type I between PCl_3 and 1-octene in the presence of acetyl peroxide, carried out by Kharash et al.[7] Addition of radicals $(RO)_2P(O)^{\cdot}$ to alkenes developed in the 1960s and 1970s proceeded according to an analogous chain mechanism[8,9] and was intensively investigated with ESR spectroscopy.[10] The transiently formed 2-*C*-radical (Scheme 1, Eq. 1) was reduced in this reaction in the final step by the starting dialkyl phosphite. The synthetic value of this reaction, initiated by peroxides (100–130°C), azo compounds, or UV light, depended on the ratio of the starting reagents. Adducts 1:1 could be obtained with an excess of the phosphite over the alkene, otherwise telomers were obtained.[8,9,11] The reaction with alkadienes,[12] alkynes,[13,14] aromatic compounds,[15,16] unsaturated silanes,[17] and nitriles[18] proceeded analogously. In the case of nitriles, three phosphoryl moieties were attached to give the 1-*C*-radical $RC[P(O)(OEt)_2]N[P(O)(OEt)_2]_2$ while alkynes gave products of mono or bis addition depending on stoichiometry.[13,14] The corresponding acid $(HO)_2P(O)H$ and its salts as well as dialkyl thiono-$[(RO)_2P(=S)H]$ and dialkyl thiolophosphites $[(RS)_2P(=O)H]$ also reacted with alkenes and alkynes by a radical mechanism.[9,19]

The addition of carbon or heteroatom *Z*-centered radicals to vinyl, allyl, and homoallyl phosphonates and their alkyne derivatives according to the concept (II) represents a source for the corresponding *C*-radicals in positions 1, 2, or 3 to the P(=O) group and proceeds at different rates (Scheme 1, Eqs. 2–4). Analysis of the reaction rate constants showed that, for instance, the phenyl radical added three times faster to vinylphosphonate than to allylphosphonate.[20] The addition reaction of alkyl radicals to vinylphosphonates was investigated with ESR by Baban and Roberts.[21,22] Other interesting examples of radical generation from *N*-hydroxy-2-thiopyridone esters via photolytic or thermal decomposition[23,24] and from alkyl anisyl telluride via radical exchange[25–27] in the presence of vinylphosphonate motif, were delivered by Barton et al. Addition reactions of *C*-radicals to vinyl and allyl phosphonates (Scheme 1, Eqs. 2 and 3) were realized by Denieul et al. using *S*-trifluoroacetonyl *O*-neopentyl dithiocarbonates in the presence of lauroyl peroxide as a source of radicals[28] and by Hu and Chen, who added the $(EtO)_2P(O)CF_2^{\cdot}$ radical to alkenes.[29] In 1995, a first stereoselective (>92% d.e.) intramolecular addition of alkyl radicals to vinylphosphonates to give phosphonate analogs of 2-deoxyriboso-3-phosphates was carried out by Yokomatsu et al.[30] The iodine atom

transfer radical addition reaction (I-ATRA) of iododifluoroacetates to vinylphosphonates was carried out by Yang and Burton.[31] Finally, Binot and Zard[32] used homoallyl phosphonates as acceptors of cyclobutanone radicals according to the concept (ii) (Scheme 1, Eq. 4).

Realization of the concept (III), i.e., a direct synthesis of radicals from precursors via homolysis of C—H, C—C, and C—heteroatom bonds began in the 1970s during intensive development of ESR spectroscopy; however radicals obtained for the ESR investigations were not used in further addition reactions to unsaturated bonds to obtain other synthetic targets. Thus, the radical $(RO)_2P(O)CMe_2^{\cdot}$ was obtained via thermal decomposition of diazophosphonates $(RO)_2P(O)CMe_2\text{-}N{=}N\text{-}CMe_2P(O)(OR)_2$[33] or via the reduction of 1-nitroalkylphosphonates $(RO)_2P(O)C(NO_2)Me_2$ with *n*-Bu_3SnH.[34] The radicals $(RO)_2P(O)C(R^1)(R^2)CH_2^{\cdot}$ were synthesized either by thermal decomposition of the perester $(RO)_2P(O)(CH_2)_2C(O)OO\text{-}t\text{-}Bu$[35] or by deformylation of 3-formylphosphonates $(RO)_2P(O)C(R^1)C(R^2)CH_2CH(=O)$ with *t*-$BuO^{\cdot}$.[36] γ-Radiolysis of crystalline bisphosphonic acid $(HO)_2P(O)CH_2P(O)(OH)_2$ gave radicals $(HO)_2P(O)CH_2^{\cdot}$ and $(HO)_2P(O)CHP(O)(OH)_2^{\cdot}$ as the result of C-H and C-P cleavage.[37] In the beginning of the 1990s, Yang and Burton (1992)[38] and Hu and Chen (1993)[29] investigated the addition of the radical $(RO)_2P(O)CF_2^{\cdot}$ to simple alkenes. In 1995, Byers et al.[39] performed a Se-ATRA reaction, adding the radical $(EtO)_2P(O)CHP(O)(OEt)_2^{\cdot}$, obtained via a photolytic C-Se cleavage, to alkenes.

In the same year (1995), our group joined these investigations, utilizing for the first time reductive conditions (*n*-Bu_3SnH or $(Me_3Si)_3SiH$/AIBN) for a direct generation of 1-diethoxyphosphorylalk-1-yl radicals from diethyl 1-halo, 1-sulfenyl, and 1-selenylalkyl phosphonates according to the concept (III) (Scheme 1, Eq. 5) via cleavages of C-halogen (Cl, Br, I), C-S and C-Se bonds and their further reaction with electron-rich and -poor alkenes or alkynes.[40,41] Ten years later, in 2005, Ageno et al. synthesized for the first time 1-diethoxyphosphorylvinyl radical in a direct synthesis from the corresponding bromo- and iodoprecursors (Scheme 1, Eq. 6).[42]

The aim of this article is to summarize the contribution of our laboratory to the development of C—C bond formation as well as C-heteroatom (halogen, O, S, Se) and C—C bonds scission reactions via 1-diethoxyphosphorylalk-1-, -2-, and -3-yl radicals under reductive conditions (Scheme 1, Eqs. 5, 7, 8).[43] A special emphasis will be put on synthetic and mechanistic aspects of I-ATRA (addition) and I-ATRC (cyclization) reactions originating from this laboratory.

RESULTS AND DISCUSSION

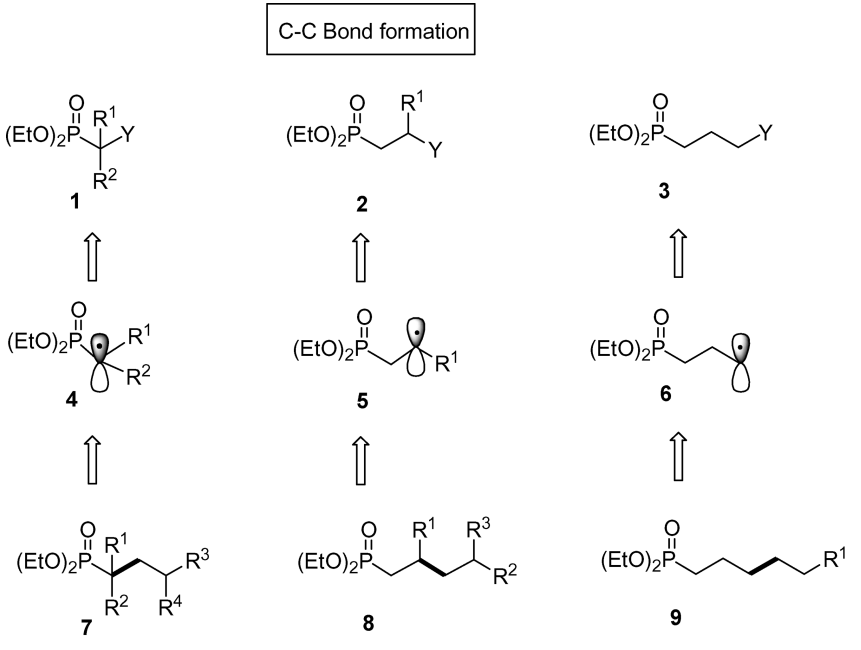
Radical C–C Bond Formation Under Reductive Conditions

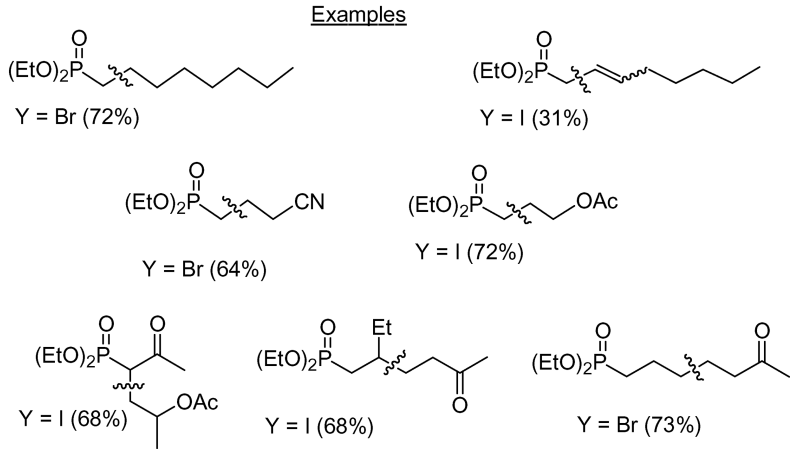
The above brief outline of the development of investigations in the radical chemistry of phosphonates showed that, before 1995, there was no general approach to a direct functionalization of the phosphonate carbon chain that might constitute an alternative to classical reactions in phosphorus chemistry, such as Arbuzov or Michaelis–Becker reactions, which did not allow the synthesis of complex phosphonate structures. However, the progress made in selective methods of radical chemistry allowed at that time the possibility of this functionalization for the use of neutral *C*-radicals, which tolerated a broad spectrum of solvents and did not require protection of many functional groups (OH, NH_2, and C=O), as it was necessary in the case of reactive ionic species, such as carbanions and carbocations. Therefore, starting from easily available 1-, 2-, and 3-heterosubstituted (Y = Cl, Br, I, SR, SeR) phosphonates **1–3** as radical **4–6** precursors, we realized such a general approach to the functionalization of phosphonates **7–9** (Scheme 2).[40,41,44] This approach tolerated a variety of functional groups R^1-R^4 and utilized stoichiometric amounts of $(Me_3Si)_3SiH$ or *n*-Bu_3SnH/AIBN,[40,41,44] *n*-$Bu_3SnH/Et_3B/O_2$,[41,45] or catalytic amounts of *n*-Bu_3SnCl, Me_3SnBr, or $Ph_3SnCl/NaBH_4$/AIBN[40,41,44] and *n*-$Bu_3SnCl/NaBH_4/Et_3B/O_2$[41,45] reductive initiation systems. In all investigated reactions, the main product was accompanied by a small amount (a few to several percent) of the reduced substrate, and only 1:1 adducts were formed using standard procedures. The adducts 1:2 could only be formed in special cases, when a large excess (50 eqs) of the alkene was employed.[46]

Radical C–C and C–Heteroatom (Halogen, O, S, Se) Bonds Scissions Under Reductive Conditions

From a synthetic point of view, a selective bond scission is an important process, but much more difficult to accomplish than a selective bond formation. In our investigations, we found a few interesting examples of such transformations (Scheme 3).[41,47]

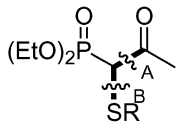
A subtle difference between PhS and MeS groups was observed in α-sulfenylated β-ketophosphonates as a result of oxo-/carbophilic or thiophilic attack of the tri-*n*-butylstannyl radical. Thus, in the case of the PhS group, a C–C bond cleavage occurred due to the better stabilizing properties of the $(EtO)_2P(O)CHSPh^{\cdot}$ radical in comparison to the $(EtO)_2P(O)CHSMe^{\cdot}$ radical (**10**, pathway **A**). The expected thiophilic attack of the stannyl radical was observed in the case of the MeS group





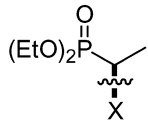
SCHEME 2

C-C versus C-S bond scission



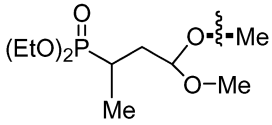
10 A: R=Ph
B: R= Me

C-Cl, C-S, C-Se bonds scissions



11: X=Cl, SR, SeR, $SC(=S)NMe_2$

C-O bond scission



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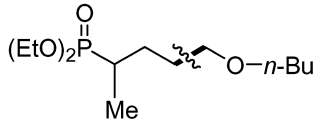
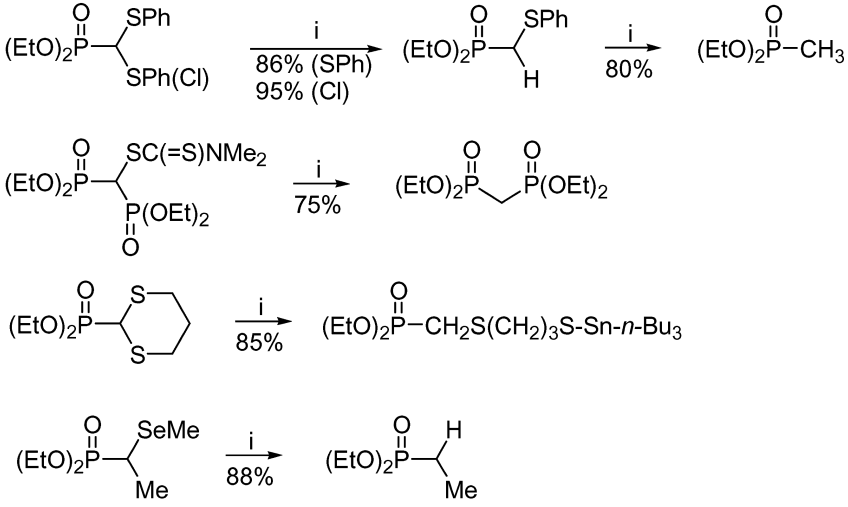


13

Examples of C-heteroatom bond scissions



i: n-Bu_3SnH/AIBN

SCHEME 3

(**10**, pathway **B**). Other examples of the selective desulfenylation and deselenylation of α-thio- and α-selenosubstituted phosphonates **11** allowed the elaboration of a general method for the selective removal of heteroatoms under radical conditions. This reaction could be carried out in the presence of α-phosphoryl sulfoxide and sulfone moieties, which were tolerated in this type of reaction. Selected examples are depicted in Scheme 3.

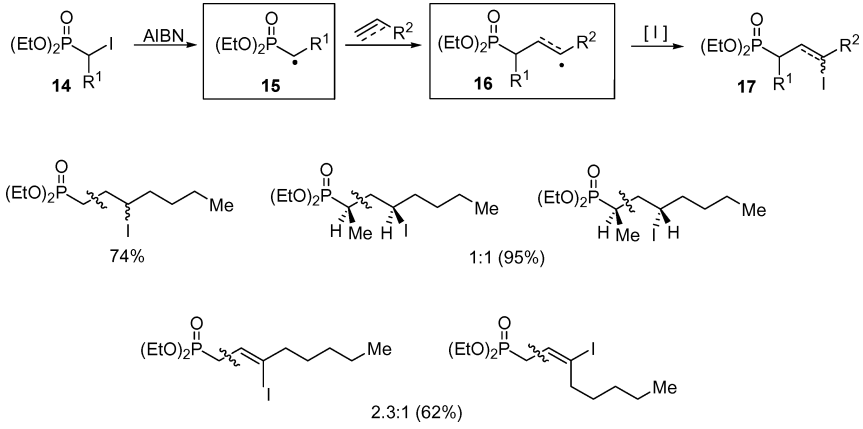
Two other interesting examples of radical C—O bond scission were observed in compounds **12** and **13** (Scheme 3)[41] during the reaction of diethyl 1-methylselenylethylphosphonate with ketene *O*, *O*-dimethyl acetal and diethyl 1-phenyl (or methyl) selenylbenzylphosphonate with *n*-butoxyethene, respectively. A cleavage of C-heteroatom bonds in 1-hetero (Cl, Br, SMe) substituted β-ketophosphonates leading to the corresponding *C*-radicals was applied in the synthesis of antibacterial antibiotic Methylenomycin B.[48]

Radical C—C Bond Formation Under I-ATRA Reaction Conditions

The general progress in iodine of atom transfer radical reactions[49—51] enabled a further functionalization of phosphonates with iodine, which in radical C—C bond formation reactions was removed as a tin iodide waste. Before our group joined this research area in 2000,[52,53] two contributions on I-ATRA reactions of iodofluoromethyl phosphonate[54] and iododifluoromethylphosphonate[55] were reported in the literature. These reactions, for which a SET radical mechanism was proposed, were carried out in the presence of Cu(0) or $Pd(PPh_3)_4$; we found that these initiators failed in the case of non-fluorine-containing phosphonates, however. For these group of compounds, we employed α, α'-azobisisobutyronitrile (AIBN) as a radical initiator. It is noteworthy that bromine atom transfer from bromodifluoromethyl phosphonate[54] and chlorine atom transfer from trichloromethyl phosphonate onto olefins were also reported; these reactions proceed via two different non-chain catalytic and redox chain mechanisms, however, depending on the initiator system used.

The radical character of our reaction, which led to the formation of iodo-substituted phosphonates **17** from iodides **14** (Scheme 4) was confirmed by the use of a radical trap TEMPO-2,2,6,6-tetramethyl-1-piperidinyloxy radical, which caused a complete suppression of the reaction.

Although direct attempts to show the presence of radicals **15** or **16** at 80°C with ESR techniques failed due to low concentration or



SCHEME 4

short lifetime, we were successful in observing **15** upon γ-irradiation or UV-photolysis of **14**.[58] Analysis of the stability of this radical showed disappearance of the corresponding ESR signals above 170–190 K. In contrast to C-C bond formation reactions occurring under reductive conditions (n-Bu_3SnH/AIBN) with various 1-heterosubstituted phosphonates (Cl, Br, I, SR, SeR), the ATRA reactions employing AIBN as an initiator proceeded only with 1-iodo-substituted phosphonates. In these reactions, neither chlorine nor bromine could be efficiently transferred.

Negative results were also achieved while attempting MeS and PhS radical transfers with AIBN. Alternatively, a successful transfer reaction of a PhSe group was reported under photolytic conditions.[39] The mechanism of the I-ATRA reactions involving reactive iodides, reported in the literature, assumes that the isobutyronitrile radicals derived from the decomposition of catalytic amounts of AIBN (usually 1–10%) produce *C*-radicals, capable of reacting with alkenes or alkynes via homolytic C-iodine bond cleavage.[59–61] In these reactions, detection and observation of products containing isobutyronitrile groups was not possible due to the catalytic amount of AIBN used. Although, Curran et al.[61] proposed this type of initiation for an additional mechanism involving the isobutyronitrile attack onto alkene, followed by a transfer of the PhSe group from phenylselenomalononitrile to the radical adduct, they did not prove it by isolation or detection of the corresponding PhSe group transfer product.

An occasion to obtain a deeper insight in the I-ATRA mechanism initiated by AIBN appeared during our investigation of reactions

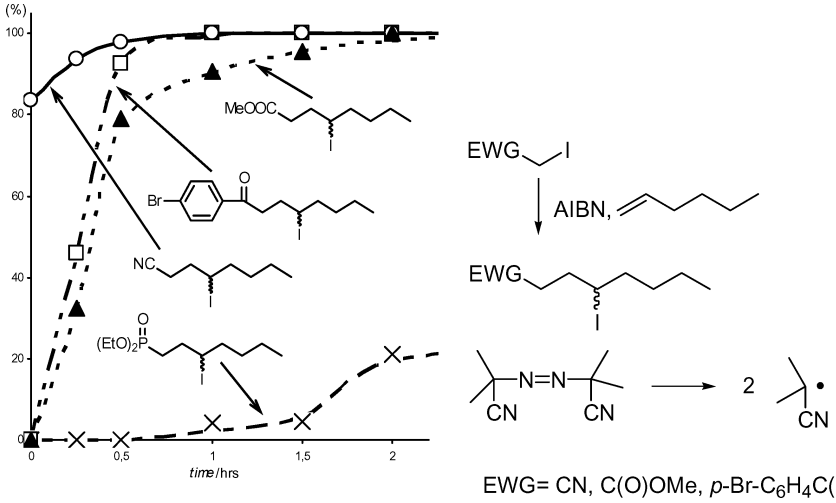


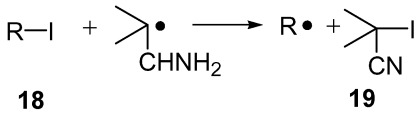
FIGURE 1 The difference in reactivity between iodoalkyl phosphonates and other non-phosphorus containing iodides of type EWG-CH_2I [EWG = CN, C(O)OMe, ArC(O)] in the I-ATRA reaction.[63]

between 1-iodo-substituted phosphonates and alkenes or alkynes.[53,64,65] It turned out that iodoalkylphosphonates were a few orders of magnitude less reactive than other non-phosphorus containing iodides of type EWG-CH_2I [EWG = CN, C(O)OMe, ArC(O)] and required at least a 25% amount of AIBN to make spectroscopic observation and chemical isolation of isobutyronitrile containing species possible (Figure 1).[63,65]

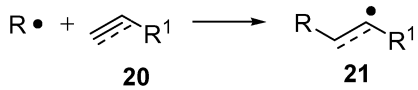
Thus, we proved the presence of a more complex mechanism of initiation for the I-ATRA reaction than that described in the literature so far. The new mechanism assumed two possibilities of initiation, involving attack of the isobutyronitrile radical on the iodine atom in the iodide **18** to give 2-iodo-2-methylpropionitrile **19** (type I) and radical R, which was capable of reacting react with alkenes or alkynes leading to the main I-ATRA product **22** via the intermediate radical **21** (Scheme 5).

The second type of initiation (type II) involved the addition reaction of the isobutyronitrile radical to the double or triple bond to give another I-ATRA product **24** via the intermediate radical **23** (Scheme 5). Both transfer products **22** and **24** were either observed spectroscopically or isolated. The source of iodine could be the starting iodide **18** or 2-iodo-2-methylpropionitrile **19**, which, however, has never been observed for this reaction in the literature due to only catalytic amounts

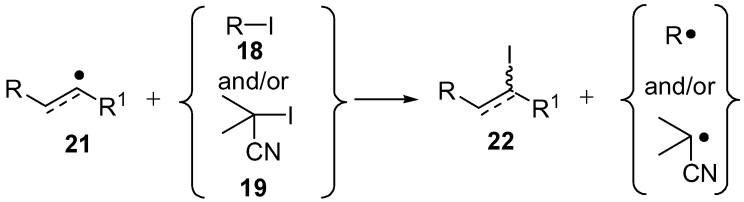
Type I of initiation and propagation:



18 **19** (1)

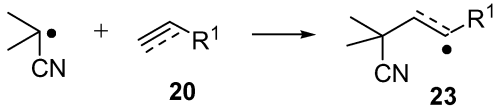


20 **21** (2)

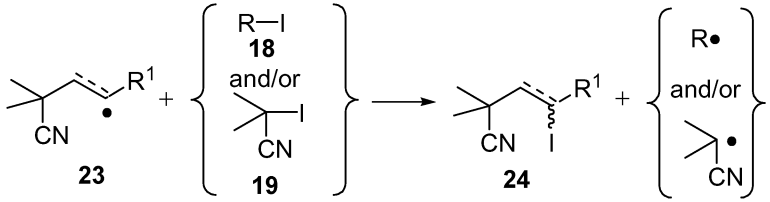


21 **22** (3)

Type II of initiation and propagation:

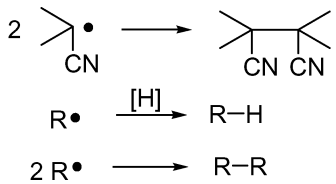


20 **23** (4)



23 **24** (5)

Termination



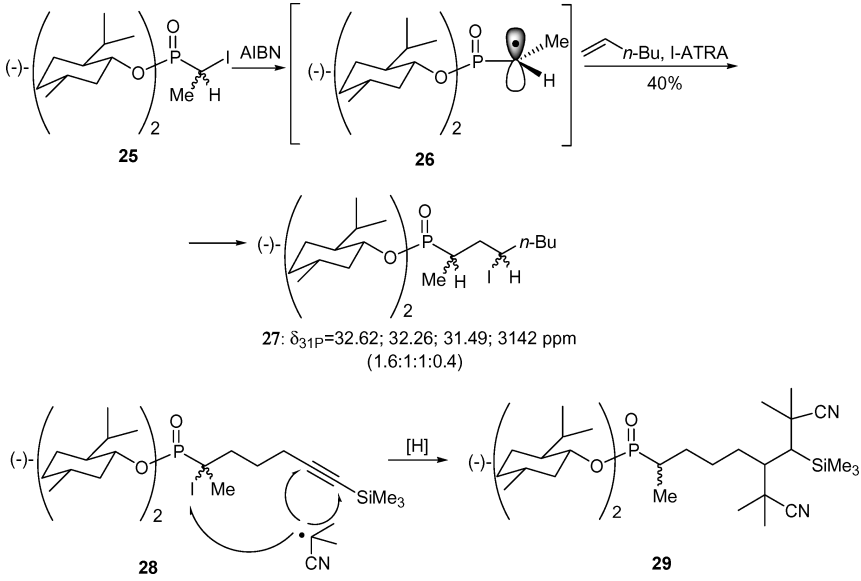
SCHEME 5

of AIBN used. We synthesized this compound in an independent way[53] and showed that its addition to the reaction mixture suppressed the reaction. Thus, we also proved the reversibility of the first step of the initiation of type (I). In the termination step, all three reactions depicted in Scheme 5 were observed. A very small amount of bisphosphonates (0–2%) formed in the radical–radical type reaction proved once again that the I-ATRA reactions proceed via extremely small concentrations of the reacting radicals, which was shown in the EPR investigations carried out directly in the spectrometer cavity ($<10^{-12}$ moles of spins).[58,63]

The described model of two pathways of initiation, which could be investigated due to the low reactivity of 1-iodoalkyl phosphonates and the necessity to use larger amounts of AIBN, may now be extrapolated to reactions requiring smaller amounts (1–10%) of AIBN.

Use of I-ATRA and I-ATRC Reactions in Asymmetric Induction

Following our interest in the iodine transfer reactions initiated by AIBN, we synthesized (-)-dimenthyl 1-iodoalkyl phosphonates **25** and **28** as first model phosphonates in a radical asymmetric induction reaction (Scheme 6).[66]



SCHEME 6

We found that the two menthoxyl groups in these phosphonates created a very strong steric hindrance around the P(O)CH moiety both in the crystal (X-ray) and in solution, making carbanionic and radical reactions much more difficult than in analogous diethyl alkylphosphonates.[52,53,58,63–66] The radical reactions proceeded with lower yields, needed longer reactions times, and required much more alkene (as a solvent) and AIBN than reactions involving diethyl phosphonates.[66] Diastereoselectivity was not high, and column chromatography over silica gel allowed separation of four diastereomers **27** into two pairs from the reaction of **25** with 1-hexene (Scheme 6).

The increase of the steric hindrance by introduction of the additional alkyne-containing substituent in **28** prevented the intramolecular cyclization reaction, thus allowing a sterically much easier intermolecular attack of the isobutyronitrile radical on the iodine atom and the triple bond to give **29** instead of the expected five-membered product (Scheme 6). Replacement of AIBN with the Et_3B/O_2 initiating system favored unexpectedly the termination step and the formation of (-)-tetramenthyl ethylenebisphosphonate in 48% yield starting from **25**, as the result of the easier formation of **26** with ethyl (from Et_3B, irreversible reaction) than isobutyronitrile radicals (from AIBN, reversible reaction) and consequently the bigger concentration of **27**. For comparison, in the analogous reaction with 1-hexene, diethyl iodomethyl phosphonate gave the corresponding tetraethyl ethylenebisphosphonate in 0–2% yield only.[53] The above results show that the strategy of using bulky cycloalkoxy ester substituents around the P(=O)CH moiety should be replaced by other strategies involving either sterically less demanding chiral ester groups or a chiral phosphorus atom with ester substituents with reduced steric hindrance.

REFERENCES

[1] A. Vioux, J. Le Bideau, P. M. Mutin, and D. Leclereq, *Top. Curr. Chem.*, **232,** 145 (2004).
[2] *The Merck Index: An Encyclopedia for Chemicals Drugs and Biologicals* (Merck & Co., Inc, Rahway, NY, USA, 1989), 11th ed., pp. 370, 665, 666, 709, 1108, 1514, 2369, 4169, 4409, 6954, 9536.
[3] M. Mikołajczyk and P. Bałczewski, *Top. Curr. Chem.*, **223,** 161 (2002).
[4] M. Mikołajczyk and P. Bałczewski, α-Phosphoryl Substituted Organosulfur Compounds, In: *Advances in Sulfur Chemistry*, E. Block, Ed. (JAI Press, 1994), Vol. 1, pp. 41–96.
[5] V. M. R. Santos, C. L. Donnici, J. B. N. Da Costa, and J. M. R. Caixeiro, *Quim. Nova*, **30,** 159 (2007).
[6] X. Creary, M. E. Mehrsheikh-Mohammadi, and J. P. Bays, *Tetrahedron Lett.*, **26,** 2383 (1985).

[7] M. S. Kharash, E. V. Jensen, and W. H. Urry, *J. Am. Chem. Soc.*, **67,** 1864 (1945).
[8] A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74,** 3282 (1952).
[9] Ch. Walling and M. S. Pearson, *Radical Reaction of Organophosphorus Compounds, Topics in Phosphorus Chemistry*, (Wiley, New York, 1966).
[10] A. G. Davies, D. Griller, and B. P. Roberts, *J. Am. Chem. Soc.*, **95,** 1782 (1972).
[11] R. Sasin, W. F. Olszewski, J. R. Russell, and D. Swern, *J. Am. Chem. Soc.*, **81,** 6275 (1959).
[12] H. J. Callot and C. Benezra, *Can. J. Chem.*, **49,** 500 (1971).
[13] A. N. Pudovik, I. W. Konovalova, and O. S. Durova, *Zh. Obshch. Chim.*, **31,** 2656 (1961).
[14] A. N. Pudovik and O. S. Shuylinolina,*Zh. Obsch. Khim.*, **39,** 1014 (1969).
[15] S. Gauapathy, B. B. V. Soma Sekhar, S. M. Cairus, K. Akutagawa, and W. G. Bentrude, *J. Am. Chem. Soc.*, **121,** 1085 (1999).
[16] E. F. Jason and E. K. Fields, *J. Org. Chem.*, **27,** 1402 (1962).
[17] G. H. Barnes Jr. and M. P. David, *J. Org. Chem.*, **25,** 1191 (1960).
[18] R. A. Kaba, D. Griller, and K. V. Ingold, *J. Am. Chem. Soc.*, **96,** 6202 (1974).
[19] C. Lopin, A. Gautier, G. Gouhier, and S. R. Piettre, *Tetrahedron Lett.*, **41,** 10195 (2000).
[20] J. A. Levin, A. G. Abulkhanov, W. P. Nefedov, M. S. Skorobogatova, and B. J. Ivanow, *Dokl. Akad. Nauk SSSR*, **235,** 629 (1977).
[21] J. A. Baban and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 373 (1979).
[22] J. A. Baban and B. P. Roberts, *J. Chem. Soc., Perkin Trans. II*, 161 (1981).
[23] D. H. R. Barton, S. D. Gero, B. Quiclet-Sire, and M. Samadi, *J. Chem. Soc., Chem. Commun.*, 1000 (1989).
[24] D. H. R. Barton, S. D. Gero, B. Quiclet-Sire, and M. Samadi, *Tetrahedron*, **48,** 1627 (1992).
[25] D. H. R. Barton, N. Ozbalik, and J. C. Sarma, *Tetrahedron Lett.*, **29,** 6581 (1988).
[26] D. H. R. Barton and M. Ramesh, *J. Am. Chem. Soc.*, **112,** 891 (1990).
[27] D. H. R. Barton, S. D. Gero, P. Holliday, and B. Quiclet-Sire, *Tetrahedron*, **52,** 8233 (1996).
[28] M.-P. Denieul, B. Quiclet-Sire, and S. Z. Zard, *Chem. Comm*., 2511 (1996).
[29] Ch.-M. Hu and J. Chen, *J. Chem. Soc., Perkin Trans. 1*, 327 (1993).
[30] T. Yokomatsu, T. Shimizu, Y. Yuasa, and S. Shibuya, *Syn. Lett.*, 1280 (1995).
[31] Z.-Yu. Yang and D. J. Burton, *J. Org. Chem.*, **56,** 5125 (1991).
[32] G. Binot and S. Z. Zard, *Tetrahedron Lett.*, **44,** 7703 (2003).
[33] J. A. Levin, P. Gozman, A. G. Abulkhanov, and B. J. Ivanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 983 (1975).
[34] N. Ono, H. Miyake, and A. Kamimura, *Tetrahedron*, **41,** 4013 (1985).
[35] A. G. Davies, D. Griller, and B. P. Roberts, *J. Am. Chem. Soc.*, **94,** 1782 (1972).
[36] T. Hoz, Z. Shachrai, and M. Sprecher, Book of Abstracts, 5th Int. Conf. of Org. Phosphorus Comps., Gdańsk, Poland, p. 59 (1976).
[37] M. Geoffroy, L. Ginet, and E. A. C. Leucken, *Mol. Phys*, 1289 (1974).
[38] Z.-Y. Yang and D. J. Burton, *J. Org. Chem.*, **57,** 4676 (1992).
[39] J. H. Byers, J. G. Thissell, and M. A. Thomas, *Tetrahedron Lett.*, **36,** 6403 (1995).
[40] P. Bałczewski and M. Mikołajczyk, *Synthesis*, 392 (1995).
[41] P. Bałczewski, W. M. Pietrzykowski, and M. Mikołajczyk, *Tetrahedron*, **51,** 7727 (1995).
[42] T. Ageno, T. Okauchi, T. Minami, and M. Ishida, *Org. Biomol. Chem.*, **3,** 924 (2005).
[43] P. Bałczewski and M. Mikołajczyk, *Revs. Heteroatom Chem.*, **18,** 37 (1998).
[44] P. Bałczewski and W. M. Pietrzykowski, *Tetrahedron*, **52,** 13681 (1996).

[45] P. Bałczewski and W. M. Pietrzykowski, *Tetrahedron*, **53,** 7291 (1997).
[46] P. Bałczewski, *Tetrahedron,* **53**, 7199 (1997).
[47] P. Bałczewski, *Phosphorus, Sulfur, and Silicon,* **104,** 113 (1995).
[48] P. Bałczewski, *Heteroatom Chem*., **8,** 67 (1997).
[49] D. P. Curran, *Synthesis,* 489 (1988).
[50] D. P. Curran and G. Thoma, *J. Am. Chem. Soc.*, **114,** 4436 (1992).
[51] D. P. Curran and C. M. Seong, *Tetrahedron*, **48,** 2157 (1992).
[52] P. Bałczewski, T. Białas, and M. Mikołajczyk, *Tetrahedron Lett.*, **41,** 3687 (2000).
[53] P. Bałczewski and M. Mikołajczyk, *New J. Chem*., **25,** 659 (2001).
[54] X. Zhang, W. M. Qin, and D. J. Burton, *J. Fluorine Chem.*, **89,** 39 (1998).
[55] Z. Y. Yang and D. J. Burton, *J. Org. Chem.*, **57,** 4676 (1992).
[56] D. Villemin, F. Sauvaget, and M. Hayek, *Tetrahedron Lett.*, **35,** 3537 (1994).
[57] H. Rosin and M. Asscher, *J. Org. Chem.*, **40,** 3298 (1975).
[58] T. Białas, A. Szadowiak, and P. Bałczewski, *Heteroatom Chem.*, **15,** 127 (2004).
[59] N. O. Brace, *J. Org. Chem*., **31,** 2879 (1966).
[60] N. O. Brace, *J. Fluorine Chem.*, **93,** 1 (1999).
[61] D. P. Curran, M. H. Chen, E. Spletzer, C. N. Seong, and C. T. Chang, *J. Am. Chem. Soc.*, **111,** 8872 (1989).
[62] D. P. Curran, E. Eichenberger, M. Collis, M. Roepel, and G. Thoma, *J. Am. Chem. Soc.*, **116,** 4279 (1994).
[63] P. Bałczewski, A. Szadowiak, and T. Białas, *Heteroatom Chem.*, **16,** 246 (2005).
[64] P. Bałczewski, A. Szadowiak, and T. Białas, *Heteroatom Chem.*, **17,** 22 (2006).
[65] P. Bałczewski, T. Białas, and A. Szadowiak, *Heteroatom Chem.*, **14,** 186 (2003).
[66] P. Bałczewski, A. Szadowiak, A. Bodzioch, T. Białas, and W. M. Szyrej, *J. Organomet. Chem.*, **692,** 997 (2007).