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Two Pathways of Initiation in the Intermolecular Iodine Atom Transfer Addition Reaction (I-ATRA) Initiated by AIBN

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ABSTRACT: *Detection of 4-iodo-2,2-dimethyloctanenitrile and 2-iodo-2-methylpropanenitrile proved an operation of two types (I and II) of initiation in the I-ATRA reaction. 4-Iodo-2,2-dimethyloctanenitrile, resulting from the isobutyronitrile radical attack onto 1-hexene followed by the iodine atom transfer (type II), was formed in reactions of EWG-CH(R)-I [R = H, Me; EWG = $(EtO)_2P(O)$, (−)−(MenthylO)$_2$ P(O), CN, Br-$C_6H_4C(O)$, MeO(O)C, allyl] with 1-hexene. Nitriles of analogous structures were also detected in reactions of $(EtO)_2P(O)CH(R)$-I with 1-heptene, 1-heptyne, cyclopentene, cyclohexene, and propargyl alcohol. 2-Iodo-2-methylpropanenitrile as the product of the isobutyronitrile attack onto iodine atom of the starting iodide was detected for the first time in the reaction of allyl iodide and 1-hexene and proved an operation of the cooperating pathway of initiation (type I). EPR experiments, performed directly in the spectrometer cavity, confirmed extremely low concentration of reacting radical species (for a sample of $c = 0.1$ mol/dm^3, $<10^{-8}$ mol/dm^3, or $<10^{-12}$ moles of spins in a sample) in I-ATRA reactions involving low reactive 1-iodoalkylphosphonates.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:246–253, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20116

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INTRODUCTION

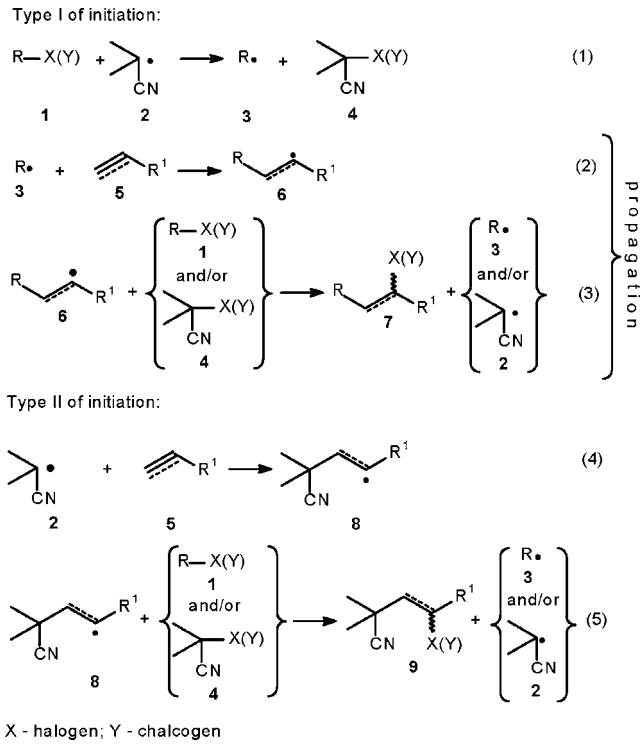
A synthetic value of atom and group transfer reactions is known both in organic synthesis and polymer chemistry [1–4]. However, mechanistic pathways of these reactions, intermediates, reactivity of reagents are recognized insufficiently, especially in the iodine atom transfer reactions (I-ATRA) initiated by AIBN [5]. One of the reasons is the use of very reactive organic iodides requiring only 1–2% (perfluorinated iodides) [6,7] or 10% (iodomalonates) [8] amounts of AIBN as an initiator. Therefore, detection and observation of products possessing isobutyronitrile groups was very difficult and therefore not done in those cases. Contribution of our laboratory to this field is connected with investigations of less reactive dialkyl 1-iodoalkyl phosphonates which required bigger amounts of AIBN. Thus, detection and isolation of the isobutyronitrile groups containing products and further mechanistic conclusions were much easier in this phosphonate series. Our recent observation that only iodine atom can be efficiently transferred from 1-iodoalkylphosphonates to alkenes and alkynes using AIBN led to elaboration of a new radical synthesis of highly functionalized phosphonates [9]. This new reaction joined another radical

synthesis of these compounds which was elaborated under reductive conditions (n-Bu_3SnH/AIBN) in our laboratory [10]. While investigating mechanistic aspects of the I-ATRA, we confirmed its radical character showing a complete reaction suppression upon addition of a radical trap TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) radical [9].

In this reaction, we assumed [11,12] a literature [6–8] mechanism of initiation for very reactive iodides in which the isobutyronitrile radical **2** derived from decomposition of catalytic amounts of AIBN, attacked halogen atom in a substrate **1** (Eq. (1), Scheme 1), and the resulting radical **3** further reacted with alkene or alkyne **5** (Eq. (2)). In the next stage, the adduct radical **6** formed, transferred halogen atom from the substrate **1** to give the corresponding atom transfer product **7** (Eq. (3)). 2-Iodo-2-methylpropanenitrile **4** has never been detected in the literature reactions since only 1–2% of AIBN was usually used. Similarly, the starting iodide **1** was considered as the only iodine donor due to the rational fact that it was used in stoichiometric amounts and **4** was not detected.

In this mechanism which we called type I, concentration of reacting radical species was extremely small (beyond the sensitivity of spectrometer) what we confirmed in our EPR investigations of the reaction of diethyl iodomethylphosphonate with 1-alkenes (for a sample of $c = 0.1$ mol/dm^3, the concentration was below 10^{-8} mol/dm^3 or 10^{-12} moles of spins) [13]. Based on competitive reactions, it was also found that diethyl iodomethylphosphonate was 2–3 orders of magnitude less reactive than other non-phosphorus containing iodides of type EWG-CH_2-I (EWG = CN, C(O)OMe, ArC(O), SMe) [14] and required bigger, at least 25% amounts of AIBN.

In the case of the PhSe-ATRA reaction from phenylselenomalononitrile **1** [R = $(NC)_2CH$, Y = PhSe] to alkenes in the presence of AIBN, Curran et al. [15] proposed in addition to the initiation mechanism of type I (Scheme 1), an additional isobutyronitrile radical **2** attack onto alkene **5** and a transfer of the phenylseleno group from **1** or **4** to give the resulting adduct radical **8** (II type of initiation, Scheme 1). In both processes (types I and II) R · radicals **3** are formed enabling further reaction steps. However, the proposed type II of initiation was not proved since the product of this transfer, i.e. 2-cyano-2-methyl-4-phenylselenoalkane **9** (Y = PhSe), was not isolated. This led to a conclusion that the AIBN initiation mechanism in the I-ATRA reaction, apparently had to be more complex than that described in the literature [6–8] and by us so far [11] (Eqs. (1)–(3), Scheme 1). In this paper, we would like to show experimental proofs for operation of the type II of initiation cooperating with the type I in the I-ATRA reaction which is a general observation, not limited only to phosphorus containing iodides.

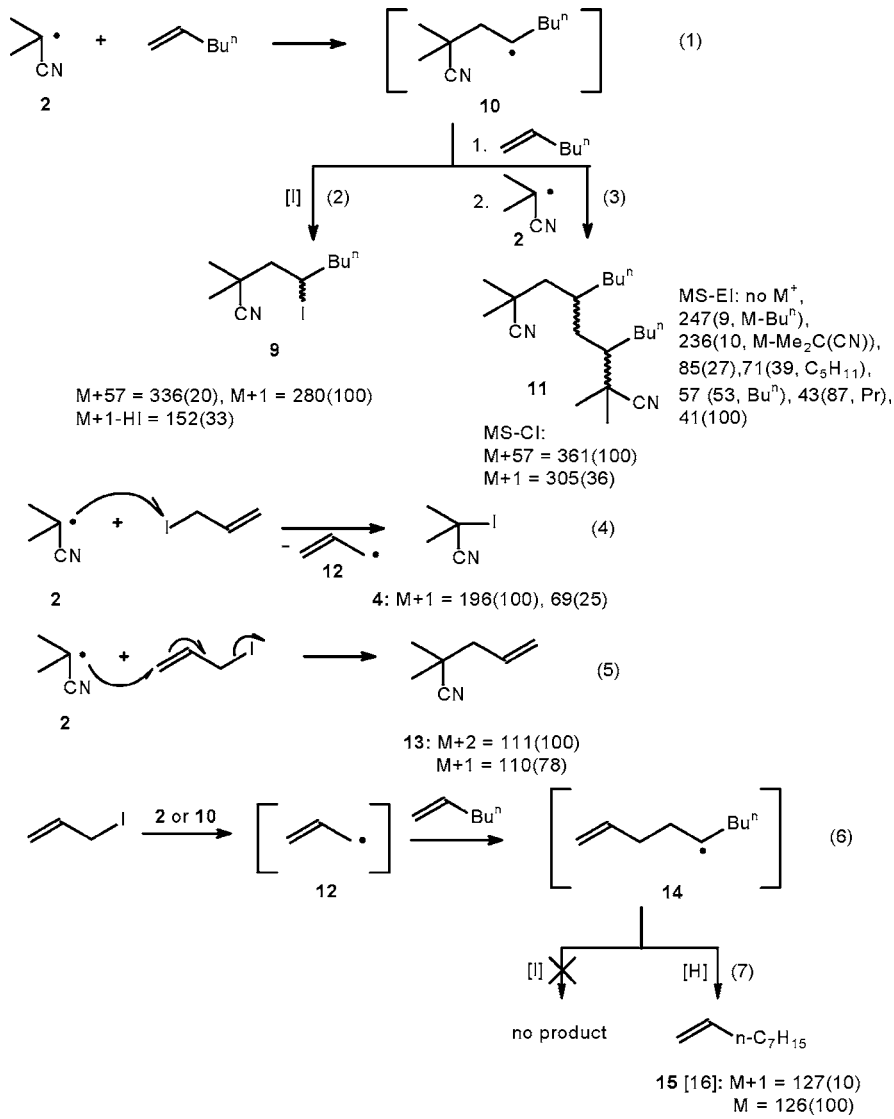


SCHEME 1 Two possible types of initiation in the I-ATRA reactions.

RESULTS AND DISCUSSION

Mechanistic Investigations

During investigation of the reaction of allyl iodide with 1-hexene, we succeeded in isolation of the new compound, 4-iodo-2,2-dimethyloctanenitrile **9** (R^1 = n-C_4H_9, X = I, Eq. (2), Scheme 2), as the product of the isobutyronitrile attack **2** onto 1-hexene to give the intermediate radical **10** followed by the iodine atom transfer (Eq. (1), Scheme 2). This was the first experimental proof of operation of the type II of initiation suggested for PhSe-ATRA reactions by Curran et al. [15]. The intermediate radical **10** also underwent addition to the second molecule of 1-hexene and recombination of the resulting radical with the isobutyronitrile radical **2** to give the product **11** (~1%, Eq. (3), Scheme 2). The isobutyronitrile radical **2** also attacked both iodine atom and the double bond of allyl iodide to give compounds **4** and **13**, respectively (~1% and 4%, Eqs. (4) and (5), Scheme 2). The latter could be also obtained via recombination of radicals **2** and **12**. Detection for the first time of



SCHEME 2 Mechanistic pathways of the free radical reaction involving allyl iodide and 1-hexene in the presence of AIBN.

the former proved an operation of the initiation of type I. The propenyl radical **12** further added to 1-hexene to form the intermediate radical **14** (Eq. (6)) which underwent rather a competitive reduction reaction to give 1-nonene **15** (3%, Eq. (7), Scheme 2) [16] than the iodine atom transfer process. This enabled building up and detection of **4**. In other reactions in which I-ATRA products **7** were formed, the iodide **4** was not detected since apparently, it was immediately consumed as a competitive iodine donor and thus remained in extremely low concentrations in reaction mixtures (Eqs. (3), (5); Scheme 1). The indirect proof of formation of **4** in these reactions showed that addition of **4** from external source to the reaction mixtures of diethyl iodomethylphosphonate with 1-hexene and 1-hexadecene caused an inhibition of the whole reaction which normally (without addition **4**) gave good yields of the I-ATRA products [11]. Two unidentified products (at a retention time of 17′86″–M + 1 = 155(100), 128(52), 69(4) and at 28′40″–316(10), 188(100), 111(35), 86(32), 71(36), 69(59) were also formed in trace quantities).

Next, knowing spectral properties of the isolated compound **9** (R = *n*-C_4H_9, X = I), we could look for it in crude reaction mixtures of all investigated reactions. Fortunately, in most cases, the characteristic multiplet at $\delta_H \approx 2.3$ ppm due to the $Me_2(CN)CCH_2$ methylene of **9** was not shielded by other signals and could be easily recognized in ^1H NMR spectra. The results are summarized in Table 1.

An inspection of these data shows that formation of **9** (R^1 = *n*-C_4H_9, X = I) was a general feature

TABLE 1 Formation of 4-Iodo-2,2-dimethyloctanenitrile **9** (X = 1, R^1 = *n*-C_4H_9) from Various Organic Iodides

Entries	*Reaction (benzene, reflux, 6--7 h)* Iodide: AIBN: n-C_4H_9 1 1 10	**9** (%)[a]
1	$(EtO)_2P(O)CH_2I$	33–38
2	$(EtO)_2P(O)CH_2I$	27[b]
3	$(EtO)_2P(O)CH(I)Me$	21
4	(-)-menthyl-O-P(O)(I)Me, 2	<56[c]
5	$CH_2{=}CHCH_2I$	35.5–48
6	$MeOC(O)CH_2I$	33
7	$N{\equiv}CCH_2I$	23–33
8	Br-C_6H_4-$C(O)CH_2I$	29
9	$CH_3(CH_2)_3I$	13–17
10	C_6H_5I	0
11	$(EtO)_2P(O)CH_2I$ + Br-C_6H_4-$C(O)CH_2I$	28[d]
12	$(EtO)_2P(O)CH_2I$ + $MeOC(O)CH_2I$	28[d]

[a]Maximum yields in relation to the total amount of AIBN as a sum of tetramethylsuccinodinitrile, **9** and the unreacted AIBN.
[b]Benzene replaced by PEG-400.
[c]In 1-hexene as the solvent.
[d]Iodides (1:1): AIBN: 1-hexene = 2:2:20.

of the I-ATRA reactions, both in the case of phosphorus (entries 1–4) and non-phosphorus containing iodides (entries 5–12, Table 1). This compound accompanied all main adducts of type **7** (Scheme 1) and could be easily separated, especially from phosphonates using column chromatography over silica gel. Average max. 30% yields of **9** (R^1 = *n*-C_4H_9, X = I) indicated that formation of this compound played an important role in the whole reaction mechanism. No iodine atom transfer was observed in the case of phenyl iodide (entry 10, Table 1) due to much worse stabilization of phenyl radical than the isobutyronitrile radical **2**. Mixtures of iodides (entries 11 and 12) also gave **9** (R^1 = *n*-C_4H_9, X = I) in an average level of 28% yield. In these reactions, the iodine atom transfer occurred sequentially according to the order of reactivity of the starting iodides [14].

4-Bromophenacylmethyl and methoxycarbonylmethyl iodides were two orders of magnitude more reactive than diethoxyphosphorylmethyl iodide and therefore the majority of **9** (R^1 = *n*-C_4H_9, X = I) was formed within first 3–4 h. Accumulations of the latter and tetramethylsuccinodinitrile (dimer of **2**) in a function of reaction time are visualized in Figs. 1–3 both for the single iodide **1** [R = $(EtO)_2P(O)$, X = I] and for its mixtures with other iodides of type **1** [R = C(O)OMe, Br-C_6H_4-C(O), X = I].

Since the compound **9** (R^1 = *n*-C_4H_9, X = I) accompanied the second I-ATRA product **17** (Scheme 3), we disclosed in Table 2 ratios of these two kinds of the iodine atom transfer products calculated in relation to the consumed 1-hexene. In the case of very reactive 4-bromophenacylmethyl iodide 24.5% of the corresponding 4-bromoacetophenone was formed.

In order to check a generality of operation of the second type of initiation, we carefully analyzed several crude reaction mixtures with the GC-MS-CI and EI techniques.

In the each investigated case (entries 1–6, Table 3), there were detected products of type **9** which arose from the isobutyronitrile radical **2** attack onto multiple bonds of unsaturated compounds. Depending on the alkene or alkyne used, they were of different characters from alicyclic (entries 1, 2), cyclic (entries 3,4) to unsaturated ones (entries 5, 6).

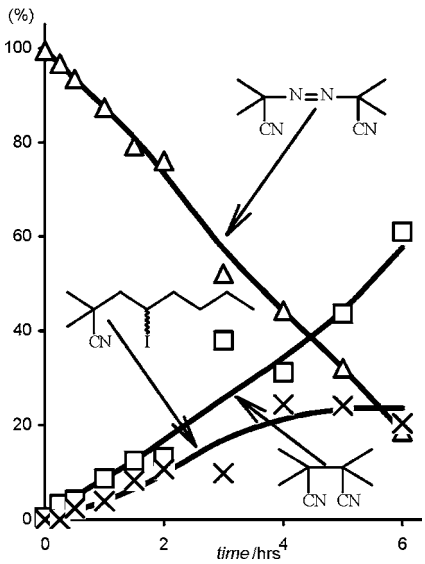


FIGURE 1 Decomposition of AIBN, formation of tetramethylsuccinodinitrile and **9** (R^1 = Bu^n, X = I) for the reaction of 1-hexene with $(EtO)_2P(O)CH_2I$.

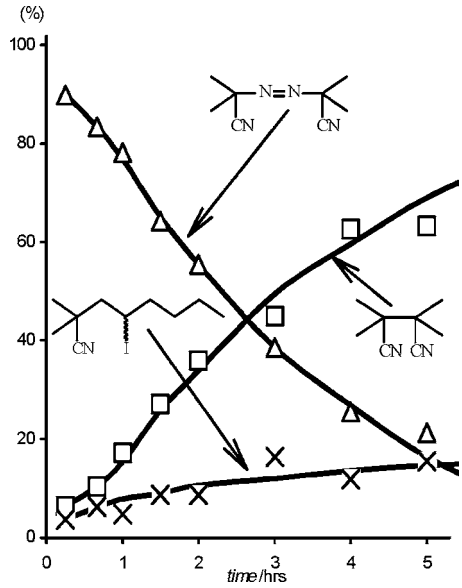


FIGURE 2 Decomposition of AIBN, formation of tetramethylsuccinodinitrile and **9** (R^1 = Bu^n, X = I) for the reaction of 1-hexene with $(EtO)_2P(O)CH_2I$ and $MeO(O)CCH_2I$.

In the latter case, ^{1}H NMR and GC spectra showed formation of the *E*/*Z* mixtures of isomers with the *Z* predominant isomer, presumably due to the beneficial N···I interactions of the hydrogen bonding type. Evidences for such interactions are reported in the literature [17–20]. For instance, for the adduct derived from 1-heptyne (entry 6, Table 3), the alkene

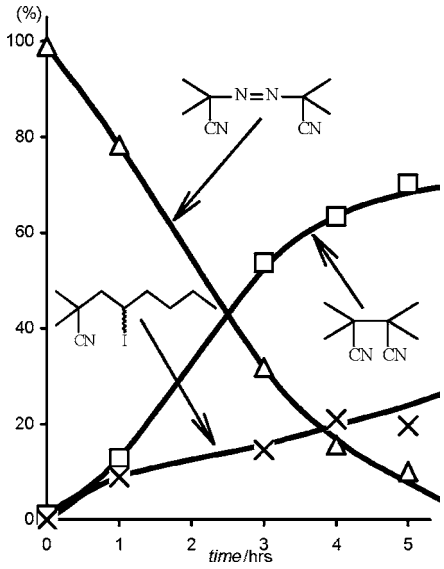


FIGURE 3 Decomposition of AIBN, formation of tetramethylsuccinodinitrile and **9** (R^1 = Bu^n, X = I) for the reaction of 1-hexene with $(EtO)_2P(O)CH_2I$ $MeO(O)CCH_2I$, and Br-$C_6H_4C(O)CH_2I$.

TABLE 2 Ratios of **9** (X = I, R^1 = *n*-C_4H_9) and **17** Formed in Competitive Reactions

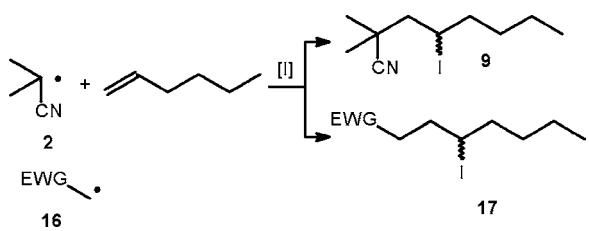
Radical **16** *EWG*	**9**	**17**
$(EtO)_2P(O)$	16.7	83.3
N≡C	39.5	60.5
4-Br-$C_6H_4C(O)$	73.5	26.5

Products **9** and **17** are calculated based on the 1-hexene consumed. All values are in per cent.

protons in the *Z*-isomer resonated at $\delta_H = 6.01$ ppm (bigger triplet, $^4J_{H,H} = 0.9$ Hz) while in the minor *E*-one, resonated at $\delta_H = 5.65$ ppm (smaller triplet, $^4J_{H,H} = 1.2$ Hz). Products of type **9** were also formed in very small quantities (see Table 3) in reactions with cyclohexene and cyclopentene (entries 3, 4) which turned out to be extremely reluctant to react in the I-ATRA reactions with diethyl iodomethylphosphonate (~5%). MS-CI spectra of saturated products (entries 1–4) showed typical M + 1-HI fragmentations. In the case of unsaturated products (entries 5, 6), the M + 1-HCN fragmentation dominated with exception of the isomer *Z* (entry 5) for which the M + 1-H_2O fragmentation was characteristic.

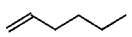
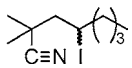
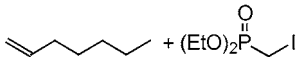
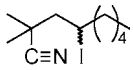
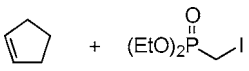
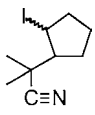
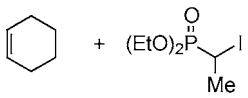
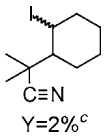
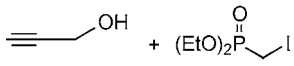
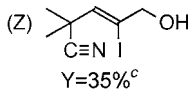
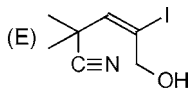
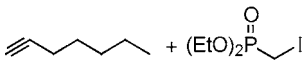
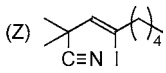
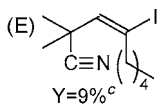
In summary of this part, one can conclude that two types (I and II) of initiation may operate in the I-ATRA reactions (Scheme 1). In both types, R· radicals are produced which enable continuation of the chain reaction.

Accumulation of **9** in relatively large quantities in comparison to **4** (X = I) proves a possible domination of the process of initiation of type II over the process of type I. Both processes may cooperate through the iodine exchange between **4** (X = I) and **8**. It also explains one of reasons for which **4** (X = I) was formed in very small quantities. Only reactions of compounds **6** or **8** with iodides **1** or **4** (Eqs. (3), (5), Scheme 1) lead to the required products **7** or **9** and R· radicals which can add to the next molecule of alkene. The competition between **4** and **1** as iodine sources was not assumed by us when only type I of initiation was known. It, among others, depends



SCHEME 3 Formation of two kinds of the I-ATRA products with 1-hexene.

TABLE 3 Formation of the Iodine Atom Transfer Products of Type **9** as a Result of the Isobutyronitrile Radical Attack onto Alkenes or Alkynes in the Given Reactions

Entry	*Reaction*	*Iodine Atom Transfer Product* [a]	*MS-CI (Isobutane) m/z (%)* [b]
1			280 (M+1, 100), 152 (M+1-HI, 33)
2		 Y=26%[c]	294 (M+1, 100) 166 (M+1-HI, 55)
3		 Y=3%[c]	264 (M+1, 73), 138 (30), 136 (M+1-HI, 30), 92 (36), 86 (88), 69 (100)
4		 Y=2%[c]	278 (M+1, 60), 150 (M+1-HI, 28), 98 (19), 96 (25), 92 (35), 86 (76), 69 (100)
5		 Y=35%[c]	252 (M+1, 100), 234 (M+1-H_2O, 30), 126 (20), 109 (69), 108 (80), 197 (40)
		 Y=14%[c] Z/E=2.8:1	252 (M+1, 100), 225 (M+1-HCN, 26), 109 (80), 108 (57)
6		 Y=36%[c]	292 (M+1, 31), 265 (M+1-HCN, 100)
		 Y=9%[c] Z/E=4:1	292 (M+1, 100), 265 (M+1-HCN, 86)

[a]Estimated yields are based on GC.
[b]In all cases peaks M+57 (Me_3C^+ from isobutane) were observed.
[c]EWG≡$(EtO)_2P(O)$, (−)-$(MenthylO)_2P(O)$, N≡C, Br-$C_6H_4C(O)$, MeO(O)C, CH_2═$CHCH_2$, *n*-C_5H_{11}, for yields see Table 1.

on the relative stabilization of the resulting isobutyronitrile radical **2** (resonance and hyperconjugation effects) and R· radical and may explain why in some reactions the product **9** and not **7** is only formed.

EPR Studies

In the previously performed EPR experiments in which we tried to observe intermediate radicals under thermal conditions employed for the decomposition of AIBN, we used the refluxing benzene solution of diethyl iodomethylphosphonate and 1-hexene [13]. The reaction was carried out in the reaction flask, and every taken sample for the EPR measurements was rapidly frozen in the liquid nitrogen. Since under these conditions we were unable to detect any EPR signal, we decided to carry out the experiment in the spectrometer cavity in order to eliminate the time before freezing the sample, in which radicals could vanish. Therefore, we had to replace the system of low boiling 1-hexene in benzene for the higher boiling 1-hexadecene in anisole in the EPR tube.

At first, we tried to use mesitylene, however, the reaction carried out in this solvent did not occur and the starting iodide was recovered quantitatively

(^{31}P NMR). In anisole, the corresponding I-ATRA product [11] was obtained in 28% yield and we decided to perform our EPR experiment in this solvent. It turned out that EPR spectra of the heated solution of diethyl iodomethylphosphonate carried out in the spectrometer cavity and recorded every 10 min, showed no signals regardless of a heating duration. This meant that at 90°C a concentration of free radicals that took part in the investigated radical reaction was below a sensitivity of the spectrometer (10^{-12} moles of spins in the sample) as in the previous experiment which was carried out in the reaction flask. This reaction, however, is a radical process as it was proved with the TEMPO radical. For a comparison, initiation with the UV or γ-irradiation generated a sufficient concentration of diethyoxyphosphorylmethyl radicals that enabled registration of the corresponding EPR spectrum [13]. These experiments explained a formation of extremely small quantities of **4** (X = I), a necessity to use larger amounts of AIBN and excess of alkene as well as a lack of improvement in yields of the I-ATRA products with a syringe pump technique to maintain a low concentration of radicals. This technique was here not advantageous because it caused a further decrease in already small concentration of reacting radicals.

The use of AIBN deserves a comment. The model reaction of diethyl iodomethylphosphonate with 1-hexene, carried out within 6–7 h in the presence of 10, 20, and 50% molar amount of AIBN, gave 21, 33, and 63% yields of the I-ATRA product [13]. The use of stoichiometric amount of AIBN had a practical meaning since it increased the yield up to 71–83% and could be applied both for reactive (iodoacetate, iodoacetonitrile) and for less reactive (1-iodoalkylphosphonates) iodides without changes in the course of these reactions. The use of 40% of molar amount of AIBN in the sequential additions (8 × 5%) generated 58% yield of the I-ATRA product, but the reaction time had to be increased from 7 to 58 h.

In a final conclusion, in this publication two types of initiations were described. The mechanism of type I, which was confirmed by detection of the product **4**, involved the isobutyronitrile radical **2** attack onto iodine of the starting iodide. The type II, which was confirmed by detection and isolation of the product **9**, involved the attack of the radical **2** onto alkene or alkyne. Extremely small concentrations of reacting radicals, which cause the above-mentioned consequences, were confirmed based on EPR measurements, carried out directly in the spectrometer cavity ($<10^{-12}$ moles of spins). The described model of two pathways of initiation in the I-ATRA reactions, which was investigated for reactions with larger amounts of AIBN (at least 25%), may be now extrapolated to the range of reactions requiring very small amounts (1–2%) of AIBN.

EXPERIMENTAL

General

The ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded using a Bruker AC-200 spectrometer. The IR and mass spectra were recorded using an ATI Mattson Infinity FTIR 60 and a Finnigan Mat 95 spectrometers, respectively.

MS-CI spectra of the crude reaction mixtures were recorded with the GC-MS hyphenated technique using 30 m DB-17 column and a 50°C(5)–250°C(10), 10°C/min. program. Measurements were carried out twice for the same sample: (a) before evaporation of the solvent (C_6H_6) in order to detect low boiling products and (b) after evaporation of the solvent for a check up. GC-MS-EI spectra of the crude reaction mixtures were recorded under the same reaction conditions as for the GC-MS-CI technique.

X-band (9.4 GHz) EPR spectra were recorded using a Bruker ER 200D-SRC spectrometer equipped with ER4102ST rectangular cavity. The spectrometer was coupled with a computer system ESP 3220-200 SH for data acquisition and equipped with a variable temperature unit (lab-made) controlled by an ITC-4 temperature controller (Oxford Instruments). Spectra were recorded using the following parameters: a magnetic field modulation of 100 kHz, a sweep width of 1000 G, a microwave power of 2 mW, and a modulation amplitude in the range of 0.5–2 G. There were up to 20 scans per spectrum acquired at the maximum gain.

Column chromatography was done using Merck silica gel (F_{254} 60, 70–230 and 270–400 mesh). Organic solvents were purified by standard procedures. Alkenes and alkynes used were of commercial purity. Organic iodides were prepared according to the following literature references.

Diethyl Iodomethylphosphonate [11,21,22]. Yield = 75%, ^{31}P NMR: $\delta = 20.5$ ppm ($CDCl_3$). Iodides of type EWG-CH_2-I [EWG = CN, C(O)OMe, p-Br-C_6H_4C(O)] were synthesized according to [14]. Other non-phosphorus containing iodides like *n*-amyl, phenyl, allyl were commercially available.

Synthesis of 4-Iodo-2,2-dimethyloctanenitrile **9** *($R^1 = n$-C_4H_9, X = I) in the Reaction of Allyl Iodide and 1-Hexene*

To a stirred solution of allyl iodide (5.95 mmol, 1 g, 544 mL) and 1-hexene (59.92 mmol, 4.99 g, 7.42 mL)

in benzene (85 mL), AIBN (976 mg, 5.95 mmol) was added in one portion and the resulting solution was stirred at room temperature at argon atmosphere until AIBN dissolved. Then the solution was refluxed for 7 h. After cooling to room temperature, benzene was evaporated and the residue was chromatographed over silica gel using *n*-hexane/acetone in a gradient as the eluent to give 0.58 g (35%) of the pure **9** (R^1 = Bu^n, X = I) as an oily substance.

^{1}HNMR (200 MHz, $CDCl_3$): $\delta = 0.93$ (t, 3H, $^3J_{H,H} = 6.8$ Hz, $C\underline{H}_3CH_2$), 1.10–1.65 [m, 4H, $CH_3(C\underline{H}_2)_2$], 1.38, 1.44 [2xs, 6H, $(C\underline{H}_3)_2C(CN)$], 1.70–1.95 [9m, 2H, $CHIC\underline{H}_2(CH_2)_2CH_3$], 2.29 [ABX, 2H, $^2J_{A,B} = 15.2$ Hz, $^3J_{A,X} = 6.5$ Hz, $^3J_{B,X} = 7.1$ Hz; $\delta_A = 2.34$, $\delta_B = 2.25$, $(CH_3)C(CN)C\underline{H}_2CHI$], 4.10–4.35 (m, 1H, CHI) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.91$ (s, $\underline{C}H_3CH_2$), 21.70 (s, $CH_3\underline{C}H_2$), 26.17, 28.08 [2xs, $[\underline{C}H_3)_2C(CN)$], 29.55 (s, CHI), 31.74 (s, $CH_3CH_2\underline{C}H_2$), 32.60 [s, $(CH_3)_2\underline{C}(CN)$], 40.67 (s, $CH_3CH_2CH_2\underline{C}H_2$), 51.08 [s, $(CH_3)_2C(CN)\underline{C}H_2CHI$], 124.41 (s, CN) ppm. IR (film): ν (cm^{-1}) = 2960, 2930, 2875, 2860, 2235, 1675, 1580, 1465, 1395, 1380, 1230, 1215, 1180, 1075, 1010, 760, 740; MS-LR-CI (isobutane): *m/z* (%) 280 ($M^+ + 1$, 100), 152 ($M^+ + 1$, -HI, 44); MS-HR-CI: $M^+ + 1$, found 280.05595; $C_{10}H_{19}NI$ requires 280.05622.

Synthesis of **9** *($R^1 = Bu^n$, X = I) in the Reaction of Diethyl Iodomethylphosphonate with 1-Hexene*

To a stirred solution of diethyl iodomethylphosphonate (1 mmol, 278 mg) and 1-hexene (10 mmol, 840 mg, 1.25 mL) in benzene (14 mL), solid AIBN (1 mmol, 164 mg) was added under argon atmosphere. Stirring was continued until AIBN was dissolved, and the resulting solution was refluxed for 6–7 h. After cooling, benzene was evaporated and the residue was purified using column chromatography with *n*-hexane/acetone in a gradient as the eluent. The compound **9** was obtained in early fractions in 24% yield and possessed identical spectral properties as those obtained in the previous preparation (vide supra).

EPR Measurements

Diethyl iodomethylphosphonate (0.045 mmol, 25.2 mg), AIBN (0.090 mmol, 14.7 mg), and 1-hexadecene (0.91 mmol, 203.8 mg, 260 μL) were dissolved in anisole (700 μL). A measurement tube was then filled with about 100 μL of the obtained solution, inserted in the EPR cavity, and thermostated at 90.0 ± 0.3°C. EPR spectra were recorded every 10 min through 2.5 h.

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