Tetrahedron 68 (2012) 4292–4295

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Light-induced carbocyclization of iodoalkenes

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ARTICLE INFO

Article history:
Received 3 February 2012
Received in revised form 14 March 2012
Accepted 16 March 2012
Available online 28 March 2012

Keywords:
Iodoalkenes
Photochemistry
Carbocyclization

ABSTRACT

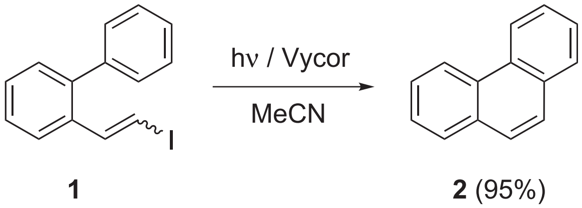
The direct irradiation of iodoalkenes leads to the formation of carbon-centered radical by homolysis of the C–I bond. The photoreaction is used in cyclizations with formation of six membered rings.

1. Introduction

The search for processes that allow useful synthetic transformations compatible with the environment should be a priority in modern chemistry. Photochemical reactions have proven to be a valid alternative in organic synthesis,[1] and are usually carried out under mild conditions. On the other hand, radical reactions are increasingly used in synthetic procedures.[2] Combining both ideas, we have recently described the use of acyloximes in the photochemical synthesis of isoquinoline derivatives by direct photolysis, avoiding the use of metals for the formation of radical species. First, the iminyl radical is easily generated by a nitrogen–oxygen bond cleavage. The cyclization of this radical with unsaturated moieties then gives the heterocyclic compounds with ease in good yields.[3] In recent years there have been several studies on radical cyclization processes induced by light, where the starting material is a halogenated derivative, such as α-iodoenones,[4] α-iodoesters,[5] iodoaromatic derivatives,[6] or α-iodoenamides.[7] Considering the mentioned examples and our experience in photolysis reactions[3,8] and synthesis of iododerivatives,[9] we found of interest to test the capacity of these systems to participate in photoinduced cyclization processes.

2. Results and discussion

Starting from 2-phenylbenzaldehyde,[10] we synthesized the 1-(2-iodovinyl)-2-phenylbenzene **1** in 82% yield (obtained as a mixture of stereoisomers *Z*:*E*=95:5) by reaction with iodomethyltriphenylphosphonium iodide in basic medium.[11] Irradiation of a solution of iodoalkene **1** in acetonitrile with a 400 W medium pressure-mercury lamp through Vycor filter for 2 h under an Ar atmosphere led to the formation of phenanthrene **2** in 95% yield after the usual work-up procedure (Scheme 1). To explore the photochemical nature of the reaction, we performed a test at room temperature in the dark. After 24 h of stirring **1** was recovered unchanged and the formation of **2** was not detected.



Scheme 1. Irradiation of **1**.

This promising result prompted us to explore the scope of this photoreaction. Building on this initial example, a variety of iodoalkenes was prepared (Table 1). First, we tried to use a naphthyl group (entry 2), what opens up the possibility of synthesizing polycycles with four rings. This was indeed the case; the irradiation of **3** for 2 h gave chrysene **4** in 80% yield. Aromatic hydrocarbons have resulted in both previous examples. The method would have added value if it were possible to include in the structure groups with different functionalities. Interestingly, we found that starting iodoalkene can accommodate several features, such as acetoxy (entry 3) or chlorine

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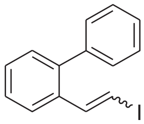
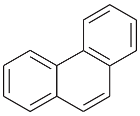
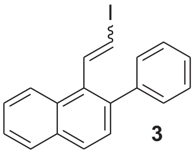
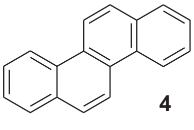
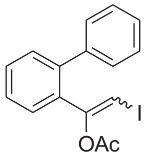
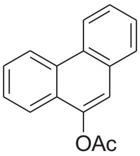
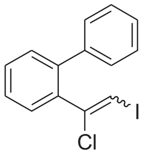
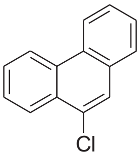
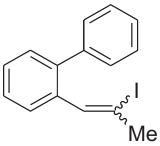
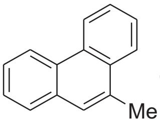
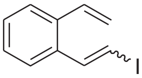
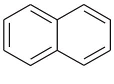
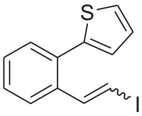
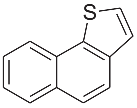
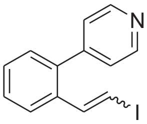
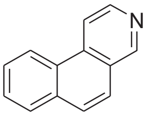
doi:10.1016/j.tet.2012.03.056

Table 1
Irradiation of iodoalkenes

Entry	Iodoalkene	Product	Yield (%)[a]
1	 **1**	 **2**	95
2	 **3**	 **4**	80
3	 **5**	 **6**	95
4	 **7**	 **8**	64
5	 **9**	 **10**	40[b]
6	 **11**	 **12**	86
7	 **13**	 **14**	62
8	 **15**	 **16**	94

[a] Yield of isolated product.

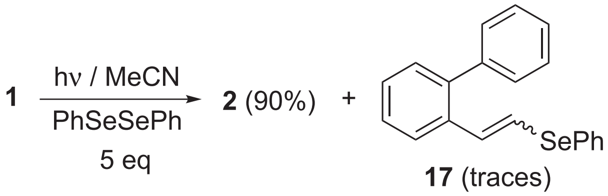
[b] Unreacted **9** was also recovered (55%).

(entry 4). After irradiation, the corresponding product, **6** or **8**, respectively, was obtained in good to excellent yields. The presence of acetoxy or chlorine on the reaction product expands tremendously the possibility of new functionalizations. Our methodology also allows for substitutions on carbon bearing the iodine atom (entry 5). However, in this particular case, in the irradiation of iodoalkene **9**, the yield of the reaction low up to 40%. This fact can be explained if it is considered that the product **10** acts as an internal filter when it is forming.[12] It is also feasible to consider that the low yield of **10** is connected with the fact that the vinyl radical derived from **9** is the only one to have a substituent (Me group) at its active site, which should provide steric hindrance to the ring closure step.

Next, we were interested in extending our methodology to other systems. Thus, we prepared and irradiated iodoalkene **11** (Table 1, entry 6). The expected **12** was formed, in 86% yield, with the involvement of a double bond in the process of cyclization. In a similar way, the photocyclization reaction with the participation of thiophene (entry 7) or pyridine (entry 8) rings led to heteropolycycles **14** or **16**, respectively, in good or excellent yields.

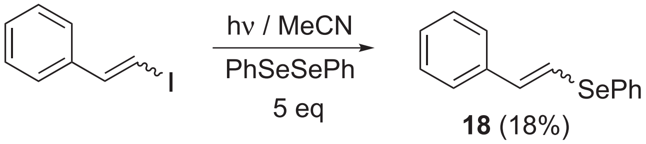
On the other hand, we have attempted to delve into the photoreaction mechanism. The rationalization of this mechanism requires the knowledge of the nature of the excited state involved in the reaction. Thus, a solution of **1** in oxygen-saturated acetonitrile was irradiated, but quenching of the reaction was not detected. This lack of quenching was also observed when a solution of **1** in degassed acetonitrile was irradiated in the presence of 10 equiv of piperylene, which is a known triplet quencher. These two experiments indicate that the triplet excited state should not be involved in the photochemical reaction. We have also determined the quantum yield for the **1**→**2** transformation. A value of $\Phi_R=0.085\pm0.005$ was obtained for a 1.6×10^{-4} M solution of **1** in deoxygenated acetonitrile at 280 nm, using *trans*-azobenzene as an actinometer.[13]

Irradiation of a C–I bond can produce a bond homolytic cleavage, generating free-radical intermediate, or an electron transfer, resulting cationic intermediate.[14] Thus, we studied the possible influence of the solvent on the cyclization. We carried out the irradiation of **1** in a variety of solvents with different polarity (e.g., hexane, toluene, acetonitrile, tetrahydrofuran, dichloromethane). The lack of influence of the solvent polarity suggests that a charged intermediate is not involved in the reaction mechanism. In addition, irradiation of **1** was performed using methanol as solvent, but the formation of methoxylated compounds was not observed, which also rules out the presence of charged intermediate species. On the other hand, when the photoreaction was performed in the presence of 5 equiv of a radical trapper, such as diphenyl diselenide it was detected a new compound in the reaction crude by ES(+) consistent with **17**, where iodine has been substituted by phenyl selenide (Scheme 2), but its isolation from the crude reaction was not possible.



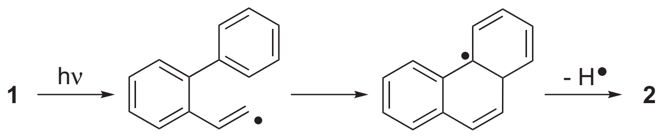
Scheme 2. Irradiation of **1** in the presence of PhSeSePh.

The intramolecular reaction should be, therefore, much faster than the intermolecular. In an attempt to confirm the formation of radicals by irradiation of aryl iodoalkenes, we synthesized β-iodostyrene,[11] where the intramolecular reaction cannot take place. Indeed, its irradiation in the presence of diphenyl diselenide (Scheme 3) led to the formation of the selenylated alkene **18** in 18% yield (*E*:*Z* ratio=1:1).



Scheme 3. Irradiation of β-iodostyrene in the presence of PhSeSePh.

Therefore, these results support a mechanism through a C–I bond homolytic cleavage with formation of a carbon-centered radical. Subsequent addition of this radical to the phenyl group should generate a cyclohexadienyl radical, from which a hydrogen atom may be abstracted by another radical to gain aromaticity (Scheme 4).[15] In fact, after irradiation, the solution took on the characteristic color of iodine species and had a strongly acid character, which agrees with the formation of HI.[16]



Scheme 4. Mechanistic proposal to obtain **2**.

3. Conclusions

In summary, the direct irradiation of iodoalkenes has proven its ability to generate radicals by homolysis of the C–I bond. The reaction can be used in cyclization with formation of six membered rings. A systematic and extensive study of the scope and limitations of this process is currently under investigation in our laboratory and will be reported in due course.

4. Experimental section

4.1. General

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as internal standard. Melting points are uncorrected. All solvents were purified by standard procedures. Reagents were of commercial grades.

4.2. Methods for the preparation of iodoalkenes

Iodoalkenes **1**, **3**, **11**, **13**, and **15** were prepared from aldehydes[17] by reaction with iodomethyltriphenylphosphonium iodide in basic medium.[11]

2-Ethynylbiphenyl[18] was used to prepare iodoalkenes **5** and **7** by iodofunctionalization with IPy_2BF_4 in the presence of a nucleophile (AcOH or LiCl, respectively) and HBF_4.[9a]

2-Phenylbenzaldehyde was also used to prepare a 1,1-diodoalkene,[19] which yields **9** by subsequent reaction with *sec*-butyl lithium and methyl iodide.[20]

*4.2.1. 2-(2-Iodovinyl)biphenyl[21] (**1**).* Yellow oil. Yield: 82%. ^{1}H NMR: δ 7.85–7.82 (m, 1H), 7.50–7.42 (m, 8H), 7.16 (d, 1H, *J*=8.37 Hz), 6.60 (d, 1H, *J*=8.37 Hz) ppm ^{13}C NMR: δ 141.1, 140.3, 139.5, 135.4, 129.8, 129.6, 128.8, 128.3, 128.0, 127.2, 126.8, 82.2 ppm. UV: λ 219, 238, 262 nm (ε=22,735, 26,147, 17,206 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{14}H_{11}I$+Ag): calculated 412.9905, measured 412.8951.

*4.2.2. 1-(2-Iodovinyl)-2-phenylnaphthalene (**3**).* Yellow solid. Yield: 70%. Mp: 95–98 °C ^{1}H NMR: δ 8.21 (d, 1H, *J*=8.02 Hz), 7.92–7.87 (m, 2H), 7.67 (d, 1H, *J*=8.15 Hz), 7.55 (t, 2H, *J*=7.64 Hz), 7.50–7.39 (m, 6H), 6.40 (d, 1H, *J*=8.15 Hz) ppm ^{13}C NMR: δ 142.3, 141.3, 137.7, 133.5, 132.9, 131.1, 130.1, 128.2, 128.1, 128.0, 127.1, 126.7, 126.0, 125.4, 83.2 ppm. UV: λ 217, 249, 297 nm (ε=50,256, 62,180, 14,359 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{18}H_{13}I$+Ag): calculated 463.0062, measured 462.9107.

*4.2.3. 2-(1-Acetoxy-2-iodovinyl)biphenyl (**5**).* Yellow solid. Yield: 37%. Mp: 91–95 °C ^{1}H NMR: δ 7.66 (d, 1H, *J*=7.62 Hz), 7.47–7.40 (m, 8H), 6.40 (s, 1H), 1.79 (s, 3H) ppm ^{13}C NMR: δ 168.0, 151.9, 141.1, 140.6, 132.34, 130.1, 129.7, 128.4, 128.1, 127.4, 126.9, 70.8, 20.5 ppm. UV: λ 210, 242 nm (ε=18,300, 12,700 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{16}H_{13}IO_2$+Na): calculated 386.996, measured 386.9852.

*4.2.4. 2-(1-Chloro-2-iodovinyl)biphenyl (**7**).* Yellow oil. Yield: 13%. ^{1}H NMR: δ 7.49–7.40 (m, 9H), 6.63 (s, 1H) ppm ^{13}C NMR: δ 141.0, 140.1, 136.9, 134.8, 130.4, 129.9, 129.7, 128.8, 128.1, 127.5, 127.4 ppm. UV: λ 227, 281 nm (ε=26,620, 5080 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{14}H_{10}I^{35}Cl$+Ag): calculated 446.8567, measured 446.8561.

*4.2.5. 2-(2-Iodoprop-1-enyl)biphenyl (**9**).* Yellow oil. Yield: 80%. ^{1}H NMR: δ 7.78–7.76 (m, 2H), 7.69 (d, 1H, *J*=7.35 Hz), 7.59–7.39 (m, 7H), 2.05 (s, 3H) ppm ^{13}C NMR: δ 143.6, 140.9, 133.3, 129.6, 129.5, 129.4, 128.1, 128.0, 127.9, 127.5, 127.3, 127.1, 122.4, 88.9, 79.4 ppm. UV: λ 213, 233, 254 nm (ε=27,584, 237,152, 17,600 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{15}H_{12}$+Ag): calculated 298.9990, measured 298.9984.

*4.2.6. 1-(2-Iodovinyl)-2-vinylbenzene (**11**).* Yellow oil. Yield: 84%. ^{1}H NMR: δ 7.59 (d, 1H, *J*=8.335 Hz), 7.45–7.33 (m, 4H), 6.88–6.79 (dd, 1H, *J*=17.45, 17.46 Hz), 6.75 (d, 1H, *J*=8.33 Hz), 5.74 (d, 1H, *J*=17.99 Hz), 5.37 (d, 1H, *J*=11.02 Hz) ppm ^{13}C NMR: δ 138.9, 136.2, 135.8, 134.3, 128.8, 128.3, 127.4, 125.6, 116.2, 84.4 ppm. UV: λ 241 nm (ε=20,116 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{10}H_9I$+Ag): calculated 362.8800, measured 362.8794.

*4.2.7. 2-[2-(2-Iodovinyl)phenyl]thiophene[21] (**13**).* Yellow oil. Yield: 82%. ^{1}H NMR: δ 7.66–7.63 (m, 1H), 7.49–7.46 (m, 1H), 7.35–7.25 (m, 4H), 7.08–7.07 (m, 1H), 7.04–7.01 (m, 1H), 6.58 (d, 1H, *J*=8.33 Hz) ppm ^{13}C NMR: δ 141.8, 139.7, 135.6, 133.5, 130.6, 130.0, 129.5, 128.5, 127.7, 127.3, 126.1, 83.2 ppm. UV: λ 199, 247, 280 nm (ε=14,954, 13,009, 11,157 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{12}H_9IS$+Ag): calculated 525.8515, measured 418.8515.

*4.2.8. 4-[2-(2-Iodovinyl)phenyl]pyridine[21] (**15**).* Yellow solid. Yield: 58%. Mp: 70–73 °C. ^{1}H NMR: δ 8.65 (d, 3H, *J*=15 Hz), 7.59–7.36 (m, 5H), 7.10 (d, 1H, *J*=9 Hz), 6.62 (d, 1H, *J*=9 Hz) ppm ^{13}C NMR: δ 151.0, 149.7, 149.5, 138.9, 134.2, 129.5, 129.3, 128.9, 128.6, 128.2, 124.4, 124.2, 83.9 ppm. UV: λ 235, 269 nm (ε=23,227, 13,067 M^{-1} cm^{-1}). Exact mass ESI(+) ($C_{13}H_{10}IN$+H): calculated 307.9858, measured 307.9931.

4.3. Typical procedure for the irradiation of iodoalkenes

The iodoalkene was dissolved in dry acetonitrile (60 mL) and irradiated at room temperature under an Ar atmosphere with a 400 W medium pressure-mercury lamp until the iodoalkene was consumed (TLC, hexane/AcOEt, 10:1). The solvent was removed with a rotary evaporator and the products were separated by column chromatography (silica gel, hexan/AcOEt).

*4.3.1. Phenanthrene (**2**).* Obtained from irradiation of **1**, through Pyrex, for 2 h. Commercial product.

*4.3.2. Chrysene (**4**).* Obtained from irradiation of **3**, through Pyrex, for 2 h. Commercial product.

*4.3.3. 9-Phenanthrol acetate[22] (**6**).* Obtained from irradiation of **5** with a 125 W Hg lamp, through Vycor, for 2 h.

*4.3.4. 9-Chlorophenanthrene (**8**).* Obtained from irradiation of **7**, through Pyrex, for 1 h. Commercial product.

*4.3.5. 9-Methylphenanthrene (**10**).* Obtained from irradiation of **9** with a 125 W Hg lamp, through Vycor, for 24 h. Commercial product.

*4.3.6. Naphthalene (**12**).* Obtained from irradiation of **11** with a 125 W Hg lamp, through Vycor, for 2 h. Commercial product.

4.3.7. Naphthol[1,2-b]thiophene[23] (***14***). Obtained from irradiation of **13**, through Pyrex, for 16 h.

4.3.8. Benzo[f]isoquinoline[24] (***16***). Obtained from irradiation of **15**, through Pyrex, for 16 h.

4.3.9. 2-(2-(phenylselanyl)vinyl)biphenyl (***17***). Obtained from irradiation of **1** with a 125 W Hg lamp, through Vycor, for 6 h in the presence of 5 equiv of PhSeSePh. Exact mass ESI(+) ($C_{20}H_{16}Se+Ag$): calculated 442.9468, measured 442.9463.

4.3.10. (Styryl)(phenyl)selenide[25] (***18***). Obtained from irradiation of *β-iodostyrene* with a 125 W Hg lamp, through Vycor, for 6 h in the presence of 5 equiv of PhSeSePh. Exact mass ESI(+) ($C_{14}H_{12}Se+Ag$): calculated 366.9155, measured 366.9150.

4.4. Experimental procedure for irradiation of 1 in the presence of different triplet quenchers

Three 1.02×10^{-2} M solutions of iodoalkene **1** in acetonitrile were contained in three 20 ml quartz tubes. One tube was saturated with oxygen. About 10 equiv of piperylene were added to the second tube. The last tube was kept deoxygenated and triplet quencher free. The irradiation was performed for 6 h with a 125 W medium pressure-mercury lamp in a merry-go-round reactor through Vycor, which removes radiation wavelength under 250 nm. The solvent was then removed from the reaction mixtures with a rotary evaporator and the amounts of **1** and **2** were quantified by ^{1}H RMN using a solution of 1,3,5-trimethoxybenzene as an internal standard.

4.5. Experimental procedure for quantum yield determination of 1

The quantum yield of the efficiency of appearance of **2** was determined using a solution of *trans*-azobenzene actinometer, which absorbance at 358 nm was about 1. The irradiation was carried out at 280 nm using a 500 W Hg(Xe) lamp and an Oriel Cornestone 130 1/8m monochromator. *trans*-Azobenzene solution was irradiated for 15 min and the absorbance at 358 nm was measured (except during irradiation, only radiation$\geq$500 nm was admitted to the sample). Then, a solution 1.6×10^{-4} M of **1** in deoxygenated acetonitrile was irradiated at 280 nm for 4 h, the solvent was removed from the reaction mixture with a rotary evaporator and the amount of **2** were quantified by ^{1}H RMN using a solution of 1,3,5-trimethoxybenzene as an internal standard. The quantum yield value was determined by the literature method.[13]

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2012.03.056.

Acknowledgements

This work was partially supported by the Ministerio de Ciencia e Innovación of Spain (CTQ2007-64197 and CTQ2011-24800) and Universidad de La Rioja (API11/20). H.F.G. thanks the Comunidad Autónoma de La Rioja for his fellowship.

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