Oxidative Halo-Decarboxylation of α,β-Unsaturated Carboxylic Acids

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A procedure for oxidative halo-decarboxylation of α,β-unsaturated carboxylic acids using iodosylbenzene, or iodosylbenzene diacetate, and *N*-chloro-, *N*-bromo-, or *N*-iodosuccinimide is presented. Good yields of the corresponding bromoalkenes are obtained when the α,β-unsaturated carboxylic acids are substituted with an aromatic substituent in the β-position and *N*-bromosuccinimide is used as the halogenation reagent. The scope of mainly the oxidative bromo-decarboxylation reaction is presented, and a tentative mechanism is proposed.

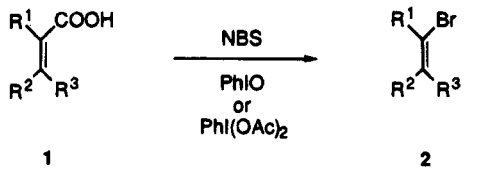
Introduction

The decarboxylation of organic carboxylic acids accompanied by a simultaneous replacement by a halogen under radical conditions is an extremely useful and selective reaction in organic chemistry for the synthesis of halogenated organic substances. The original method for oxidative halo-decarboxylation, known as the Hunsdiecker reaction, is the reaction of a silver salt of carboxylic acid with mainly bromine as the halogen.[2] This procedure has been further developed, and today different methods are available for the oxidative halo-decarboxylation of organic carboxylic acids.[3] The latter methods are known as the modified-Hunsdiecker reaction and probably also involve radical intermediates as radical initiators or photochemical reaction conditions are required.[3] Many functional groups may be present in the Hunsdiecker and modified-Hunsdiecker reactions, *but* if the substrate is an α,β-unsaturated carboxylic acid, the reaction seldom gives good results;[2b,4] the Hunsdiecker bromo-decarboxylation of both *trans*- and *cis*-cinnamic acid gives a yield of less than 15% of β-bromostyrene.[2b]

This paper presents a new synthetic procedure for oxidative bromo-decarboxylation of α,β-unsaturated carboxylic acids under nonradical conditions by which a bromine atom replaces the carboxylic acid substituent, using iodosylbenzene (IB),[5] or iodosylbenzene diacetate (IBDA),[5] and *N*-bromosuccinimide (NBS).[6] The replacement of the carboxylic acid substituent by chlorine and iodine atoms is also presented. The usefulness of the method will be presented for different substrates and an attempt to explain the mechanism of the reaction is made.

Results and Discussion

α,β-Unsaturated carboxylic acids (**1**) undergo an oxidative bromo-decarboxylation by reaction with IB or IBDA and NBS (eq 1). Reaction of *trans*-cinnamic acid (**1a**) (1.0



1 2 (1)

mmol) with 1.0 mmol of NBS and 0.5 mmol of IB, or IBDA, in CH_3CN/H_2O at 60 °C for 0.5 h affords β-bromostyrene in 73% yield. The results of the oxidative bromo-decarboxylation of a series of α,β-unsaturated carboxylic acids (**1**) using IB and NBS are presented in Table 1 (for details see Experimental Section).

The results in Table 1 show that **1** having an aromatic substituent in the β-position are the best substrates for the oxidative bromo-decarboxylation. It is seen that substrates having an aromatic substituent in the β position containing electron-donating groups (entries 2, 4; **1b,d**) give a higher yield of the bromoalkene (**2b,d**) compared with one having an electron-withdrawing substituent (entry 3; **1c**). The stereochemistry at the double bond is to a high extent retained during the reaction, as *trans*-α,β-unsaturated carboxylic acids (**1a–d**) mainly yield *trans*-bromoalkenes (entries 1–4; **2a–d**), while a *cis*-α,β-unsaturated carboxylic acid (**1e**) produces mainly the corresponding *cis*-bromo compound (entry 5; **2e**). For the bromo-decarboxylation it is found that the introduction of a substituent at the α carbon leads to a decrease of the yield of the corresponding bromoalkene and that the yield decreases as the size/electron-donating properties of the substituent at the α carbon increase (entries 6,7; **1f,g**). The method is also efficient for substrates having both an aryl- and an aryl/alkyl substituent at the β carbon (entries 8,9; **1h,i**), whereas substrates with an alkyl substituent only at the β carbon are not very reactive in the present

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Table 1. Results for the Oxidative Bromo-Decarboxylation of α,β-Unsaturated Acids (1) Using Iodosylbenzene and NBS

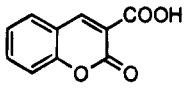
entry	compd	R^1	R^2	R^3	**2** yield (%) (t:c)[a]
1	**1a**	H	C_6H_5	H	73 (96:6)
2	**1b**	H	p-$CH_3OC_6H_5$	H	67[b] (100:0)
3	**1c**	H	p-ClC_6H_4	H	51[b] (96:4)
4	**1d**	H	p-$CH_3C_6H_4$	H	65[b] (100:0)
5	**1e**	H	H	o-$CH_3OC_6H_4$	60[b] (12:88)
6	**1f**	CH_3	C_6H_5	H	32[c]
7	**1g**	C_6H_5	H	C_6H_5	<7[c]
8	**1h**	H	C_6H_5	CH_3	77[c]
9	**1i**	H	p-ClC_6H_4	m,p-$(CH_3O)_2C_6H_3$	89[b,c]
10	**1j**	H	C_4H_9	H	<5

[a] (t:c) amount of the *trans* and *cis* isomer. [b] Isolated yields. [c] Stereochemistry not assigned.

oxidative bromo-decarboxylation reaction (entry 10, **1j**, only one example is presented).

A similar attempt to perform the chloro- and iodo-decarboxylation of **1** using *N*-chlorosuccinimide (NCS), *N*-iodosuccinimide (NIS), and IB, or IBDA, leads to a lower yield of the corresponding chloro- and iodoalkenes, compared with NBS as the halogenation agent. Chlorination of **1b–e,i** using IB and NCS gave the following yield of the β-chloroalkenes (**3b–e,i**), with the amount of *trans* and *cis* isomers in the brackets: **3b**, 39% (t:c = 89:11); **3c**, 13% (t:c = 93:7); **3d**, 18% (t:c = 93:7); **3e**, 24% (t:c = 40:60); and **3i**; 85% (t:c not assigned). For the oxidative iodo-decarboxylation of **1b,d,e,i** using IB and NIS the following results were obtained for the β-iodoalkenes (**4b,d,e,i**), with the amount of *trans* and *cis* isomers in the brackets: **4b**, 30% (t:c = 100:0); **4d**, 25% (t:c = 88:12); **4e**, 29% (t:c = 16:84); and **4i**, 82% (t:c not assigned).

The oxidative bromo-decarboxylation has also been tested for some other substrates, such as *e.g.*, **5–7**, but no significant amount of the corresponding bromoalkene was formed in the reaction with IB and NBS.



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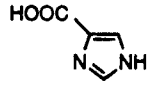

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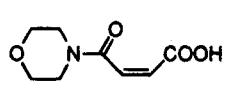

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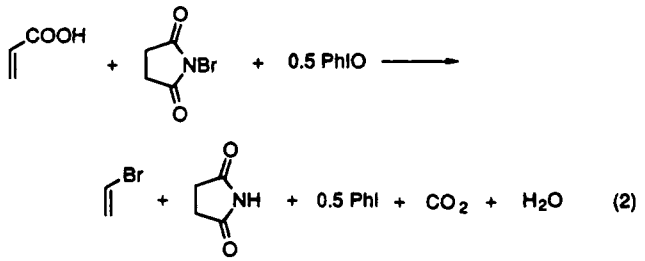
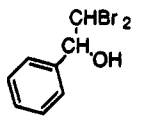
Other products formed in the bromo-decarboxylation of **1** with IB and NBS are CO_2 (identified by precipitation with $Ba(OH)_2$), PhI (identified by GC/MS and ^1H NMR), succinimide (identified by GC/MS and ^1H NMR), and H_2O (or AcOH in the reactions with IBDA). The yield of PhI is, on the basis of the amount of IB, comparable with the yield of the bromoalkene formed. The identification of these products could indicate the following main reaction:



(2)

Other minor byproducts, formed in the reaction of **1a** with IB and NBS, have been identified as:



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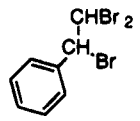

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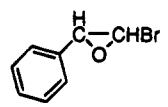

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The compounds **8–10** are shown, by independent synthesis, to be formed by reaction of the β-bromostyrene (**2a**) with the brominating agents and H_2O present in the reaction mixture.

In the reactions of **1b,d,e,i** with IB and NIS the conversion of the substrate is higher than the yields of **4b,d,e,i** given above. The reason is that the iodoalkene formed is very reactive toward the iodination reagent(s) present in the reaction mixture, as the iodo analogues to **8–10** are formed in relatively high amounts compared with the isolated yields of the iodoalkenes.

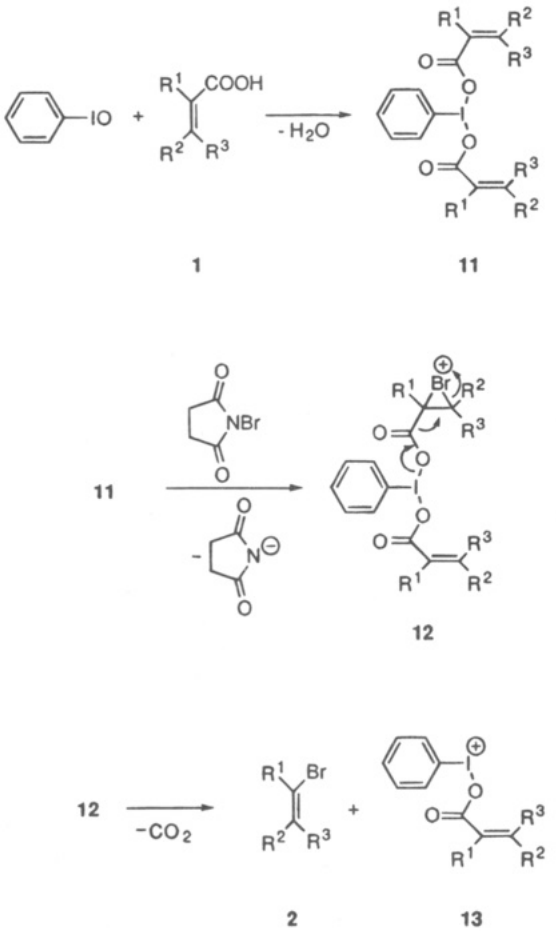
The oxidative bromo-decarboxylation of **1** can also be performed using Bu_4NBr and excess IB, but the yield of the bromoalkenes formed and the stereochemical course of the reaction are not as good as those given in Table 1. The reactive decarboxylating intermediate in these reactions is probably a species formed in an ionic reaction involving the bromide ion being indirectly oxidized by IB. In relation to this, attempts to brominate cyclohexene under similar reaction conditions by Bu_4NBr and IB were not feasible, indicating that the bromination reagent is probably not bromine. It should also be noted that attempts to perform bromo-decarboxylation of **1a** (1 mmol) by IBDA (0.5 mmol) and Br_2 (1 mmol) were unsuccessful under the same reaction conditions as those used in Table 1. The latter reactions are related to the halo-decarboxylation of carboxylic acids using iodine and IBDA under photochemical reaction conditions.[3m]

Several attempts have been made to elucidate the mechanism for the oxidative bromo-decarboxylation of **1**. Reaction of **1a** with IB and NBS in the presence of a nitrone [$(PhCH{=}N(O)C(CH_3)_3$] as a radical trap causes no significant reduction in the yield and stereochemical outcome of β-bromostyrene formed, which indicates that radicals are probably not involved in this reaction, in contrast to the Hunsdiecker and modified-Hunsdiecker reaction.

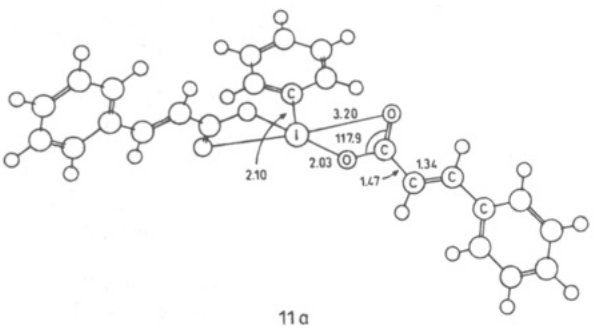
A mechanism for bromo-decarboxylation of **1** is tentatively proposed in Scheme 1. It is observed by ^1H NMR that the reaction proceeds via an intermediate, presumably of the structure **11**, formed by reaction of IB with **1**. It has been observed that the formation of **11** leads to an activation of **1** toward addition of the bromination reagent. The next step is reaction of **11** with NBS probably leading to a bromonium intermediate (**12**) from which the bromoalkene (**2**), CO_2, and a polyvalent iodine intermediate (**13**) is formed as outlined in Scheme 1. The polyvalent iodine intermediate formed might then react with another molecule of the **1** or decompose. In the case of IBDA, the acetate groups are substituted with the α,β-unsaturated carboxylate.

In an attempt to support the mechanism for the oxidative bromo-decarboxylation of **1** outlined in Scheme 1 and the stereochemical course of the reaction (which takes place mainly with retention of the stereochemistry at the alkene) a series of theoretical calculations have

Scheme 1



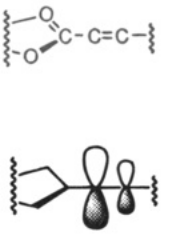
been performed using AM1 calculations.[7] The structure of the intermediate proposed to be formed by reaction of IB with **1a** has been optimized and is shown in **11a**, along with some of the structural data obtained.



11a

It appears from **11a** that **1a** binds to the iodine atom by both oxygens of the carboxylic acid: one is a primary interaction with an iodine–oxygen bond length of 2.03 Å, while the other is a secondary interaction with a iodine–oxygen bond lenght of 3.20 Å. This type of binding of the carboxylic acid to the iodine atom resembles the X-ray structure of IBDA.[8] Comparing the obtained results for the intermediate **11a** with the X-ray structure of IBDA, it is observed that the calculated primary iodine–oxygen bond length is about 0.1 Å shorter, while the calculated secondary iodine–oxygen bond length is about 0.3 Å longer compared with the same bonds in the IBDA.[8] The calculated ∠OCO– and ∠OIC bond angles and the iodine–carbon(phenyl) bond length for **11a** are similar to those found for IBDA.[8]

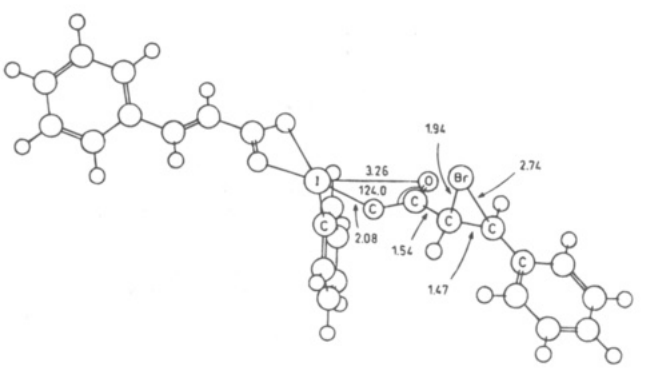
The electronic structure of **11a** has been investigated, with the main attention drawn to the α,β-unsaturated carboxylic acid part of the system. The HOMO of **11a**, a degenerate set of orbitals, is located primarily at the alkene as $\pi_{C=C}$, perpendicular to the plane of the α,β-unsaturated carboxylic acid, with the largest amplitude at the α-carbon as shown in **13** (where only the α,β-unsaturated carboxylic acid part attached to iodine is shown). The energy of the HOMO is calculated to be −9.22 eV. The next occupied MOs are found as a degenerated set of orbitals at the phenyl substituent at the cinnamic part of **11a** at −9.85 eV. The LUMO of **11a** is the $\sigma^*_{I-C(phenyl)}$ orbital at −1.77 eV, while the next lowest unoccupied MO is the σ^*_{I-O} orbital, calculated to be −1.37 eV. At −0.44 eV is the $\pi^*_{C=C}$ of the α,β-unsaturated carboxylic acid part, with an equal distribution of the amplitude at the two carbon atoms.



13

The charge at the carbon atoms at the alkene part of the α,β-unsaturated carboxylic acid is calculated to be −0.19 at the α-carbon and −0.05 at the β-carbon. The elctronic structure of **11a** indicates that an electrophilic attack of the bromonium ion of NBS at the alkene part of the α,β-unsaturated carboxylic acid of **11a** is not an unlikely process because the HOMO is located at this part of the molecule and the two carbon atoms possess a negative charge. The bromonium ion will probably prefer to attack the α-carbon atom of the α,β-unsaturated carboxylic acid part because of its higher amplitude in the HOMO and its higher negative charge, compared with the β-carbon atom.

The geometry of **12a** has also been optimized and is shown below along with some of the bond lengths and bond angles:



12a

It is seen from **12a** that the bromonium ion adds to the alkene, with a significant preference for the α-carbon,

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(8) Alcock, N. W.; Countryman, R. M.; Esperås, S.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* **1979**, 854.

compared with the β-carbon, as the C_α—Br bond length is 1.94 Å, relative to 2.74 Å for the C_β—Br bond length. The former bond length corresponds to a C_{sp^3}—Br bond length. By the formation of **12a** several other changes are also observed (with the values for **11a** in the brackets): I—O, 2.08 Å (2.03 Å); I—O, 3.26 Å (3.20 Å); C—C_α, 1.54 Å (1.47 Å); C_α—C_β, 1.47 Å (1.34 Å); and ∠OCO, 124.0° (117.9°). The changes when moving from **11a** to **12a** indicate that the I—O and C—C_α bond strengths are weakened and the CO_2 part of **12a** is more "opened", indicating that the CO_2 part of **12a** is more weakly bound to the rest of the system in **12a**, compared with **11a**, and might be on its way to be liberated. Moving the bromine atom toward the carboxylic acid part of **12a** leads to a more stable system compared with a movement toward the hydrogen atom. This preference for the movement of the bromine atom accounts for the stereochemical outcome of the reaction.

The present work has shown that α,β-unsaturated carboxylic acids can undergo an oxidative halo-decarboxylation reaction using iodosylbenzene or iodosylbenzene diacetate and *N*-bromo-, *N*-chloro-, or *N*-iodosuccinimide by which the carboxylic acid substituent is exchanged with a halogen atom. The reaction works best for the halogen being bromine. This reaction is not feasible under the Hunsdiecker or the modified-Hunsdiecker reaction conditions. The present method is efficient for α,β-unsaturated carboxylic acids having an aromatic substituent in the β-position.

Experimental Section

Apparatus. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$ with $SiMe_4$ as internal standard. GC/MS was recorded on an OV-101 column.

Chemicals. Iodosylbenzene (IB) was prepared according to the literature,[9] while iodosylbenzene diacetate (IBDA), and *N*-bromo- (NBS), *N*-chloro- (NCS), and *N*-iodosuccinimide (NIS) are commercially available and were used without further purification. The α,β-unsaturated carboxylic acids are either commercially available or were received as a gift from Cheminova A/S and were used without further purification.

Bromo-Decarboxylation of α,β-Unsaturated Carboxylic Acids. The α,β-unsaturated carboxylic acid (**1**) (1.0 mmol) and IB (or IBDA) (0.5 mmol) was dissolved in 10 mL of CH_3CN and H_2O (2:1) at 60 °C. This mixture was stirred for 10 min, 1.0 mmol of NBS was added, and the reaction mixture was stirred for 0.5 h at 60 °C. After the reaction was complete the solvent was evaporated. The aqueous phase was washed three times with 10 mL of ether. The ether phases were dried over $MgSO_4$ and evaporated. The crude reaction mixture was separated using flash chromatography using petroleum ether as the eluent.

The chloro and iodo halo-decarboxylations of the the α,β-unsaturated carboxylic acids (**1**) were performed in a similar manner using NCS and NIS.

^{1}H NMR for **2a** (*trans*) δ: 6.76 (1H, d, J = 14.0 Hz), 7.10 (1H, d, J = 14.0 Hz), 7.23–7.37 (5H, m).

^{1}H NMR for **2b** (*trans*) δ: 3.81 (3H, s), 7.03 (1H, d, J = 14.0 Hz), 6.61 (1H, d, J = 14.0 Hz), 6.85 (2H, d, J = 8.9 Hz), 7.24 (2H, d, J = 10.6 Hz). MS m/z: 215 (94), 213 (100), 199 (41), 197 (37), 171 (22), 169 (24), 133 (44), 118 (42), 90 (74), 89 (100), 77 (37).

^{1}H NMR for **2c** (*trans*) δ: 6.77 (1H, d, J = 14.0 Hz), 7.06 (1H, d, J = 14.0 Hz), 7.23 (2H, d, J = 8.5 Hz), 7.30 (2H, d, J = 8.7 Hz). MS m/z: 220 (54), 218 (100), 216 (86), 139 (42), 137 (92), 102 (50), 101 (66), 75 (69).

^{1}H NMR for **2d** (*trans*) δ: 2.33 (s, 3H), 6.71 (1H, d, J = 13.95 Hz), 7.07 (1H, d, J = 14.0 Hz), 7.14 (2H, d, J = 8.0 Hz), 7.20 (2H, d, J = 8.2 Hz). MS m/z: 198 (78), 196 (70), 117 (100), 115 (84), 102 (14), 91 (78).

^{1}H NMR for **2e** (*cis*) δ: 3.83 (s, 3H), 6.46 (1H, d, J = 8.1 Hz), 6.83–7.02 (2H, m), 7.23–7.38 (1H, m), 7.28 (1H, d, J = 8.1 Hz), 7.89 (1H, dd, J = 7.6 Hz, J = 1.5 Hz). *MS* m/z: 214 (26), 212 (24), 133 (43), 118 (44), 105 (45), 102 (45), 90 (46), 78 (100).

^{1}H NMR for **2f** δ: 2.46 (s, 3H), 6.97 (s, 1H), 7.19–7.38 (m, 5H). MS m/z: 198 (80), 196 (74), 127 (65), 125 (100), 91 (25).

^{1}H NMR for **2g** δ: 7.12–7.42 (m, 11H). MS m/z: 260 (34), 258 (32), 179 (28), 178 (100), 176 (36), 158 (31), 157 (22), 108 (22), 89 (50), 76 (34).

^{1}H NMR for **2h** δ: 2.22 (s, 3H), 6.45 (s, 1H), 7.25–7.35 (m, 5H). MS m/z: 198 (96), 196 (98), 117 (86), 115 (100), 102 (17), 91 (46), 77 (18).

^{1}H NMR for **2i** (mixture of *cis* and *trans* isomers) δ: 3.81 (s, 3H), 3.82 (s, 3H), 3.85 (s, 3H), 3.88 (s, 3H), 6.69–6.88 (m, 3H), 7.14–7.39 (m, 4H). MS m/z: 356 (14), 354 (82), 352 (56), 273 (25), 215 (16), 165 (28), 151 (100).

^{1}H NMR for **3b** (*trans*) δ: 3.81 (3H, s), 6.50 (1H, d, J = 13.6 Hz), 6.77 (1H, d, J = 13.8 Hz), 6.85 (2H, d, J = 8.9 Hz), 7.23 (2H, d, J = 9.9 Hz).

^{1}H NMR for **3b** (*cis*) δ: 3.83 (3H, s), 6.16 (1H, d, J = 7.0 Hz), 6.85 (2H, d, J = 4.5 Hz), 6.91 (2H, d, J = 4.8 Hz), 6.91 (2H, d, J= 7.0 Hz). MS m/z: 170 (74), 168 (100), 155 (30), 153 (78), 137 (18), 135 (48), 99 (10), 89 (43).

^{1}H NMR for **3c** (*trans*) δ: 6.63 (1H, d, J = 13.8 Hz), 6.78 (1H, d, J = 13.6), 7.23–7.65 (4H, m).

^{1}H NMR for **3d** (*trans*) δ: 2.33 (s, 3H), 6.58 (1H, d, J = 13.7 Hz), 6.79 (1H, d, J = 13.7 Hz), 7.01–7.20 (3H, m). MS m/z: 154 (37), 152 (89), 117 (100), 115 (88), 102 (19), 91 (42), 89 (23).

^{1}H NMR for **3e** (*cis*) δ: 3.84 (s, 3H), 6.29 (1H, d, J = 8.1 Hz), 6.88–7.05 (2H, m), 7.26–7.34 (1H, m), 7.92 (1H, dd, J = 7.7, 1.7 Hz). MS m/z: 169 (51), 132 (48), 126 (52), 119 (47), 106 (89), 99 (23), 90 (63), 78 (100).

^{1}H NMR for **3i** (mixture of *cis* and *trans* isomers) δ: 3.82 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 3.93 (s, 3H), 6.52 (s, 1H), 6.69 - 7.39 (m, 7H). MS m/z: 310 (78), 308 (100), 293 (12), 230 (18), 215 (28), 198 (13), 165 (25), 115 (84), 74 (32).

^{1}H NMR for **4b** (*trans*) δ: 3.81 (3H, s), 6.63 (1H, d, J = 14.9 Hz), 7.35 (1H, d, J = 14.9 Hz), 6.85 (2H, d, J = 8.9 Hz), 7.23 (2H, d, J = 8.5 Hz). MS m/z: 260 (77), 133 (70), 127 (35), 118 (34), 90 (38), 89 (66), 77 (28).

^{1}H NMR for **4d** (*trans*) δ: 2.32 (s, 3H), 6.74 (1H, d, J = 14.9 Hz), 7.39 (1H, d, J = 14.0 Hz), 7.12 (2H, d, J = 8.4 Hz), 7.19 (2H, d, J = 8.4 Hz). MS m/z: 244 (82), 220 (16), 127 (26), 125 (100), 117 (76), 103 (12), 91 (54), 77 (18).

^{1}H NMR for **4e** (*cis*) δ: 3.83 (s, 3H), 6.57 (1H, d, J = 8.5 Hz), 6.86–7.04 (2H, m), 7.28–7.34 (1H, m), 7.39 (1H, d, J = 8.1 Hz), 7.74 (1H, dd).

^{1}H NMR for **4e** (*trans*) δ: 3.85 (s, 3H), 6.91 (1H, d, J = 14.8 Hz), 7.68 (1H, d, J = 14.9 Hz), 6.84–6.96 (3H, m), 7.22–7.30 (1H, m).

^{1}H NMR for **4i** (mixture of *cis* and *trans* isomers) δ: 3.81 (s, 3H), 3.88 (s, 3H), 3.91 (s, 3H), 3.92 (s, 3H), 6.52–6.89 (m, 3H), 7.07–7.29 (m, 2H), 7.35–7.46 (m, 1H). MS m/z: 400 (60), 281 (14), 279 (48), 241 (15), 152 (100), 122 (14), 97 (15), 77 (38).

Supplementary Material Available: Copies of ^{1}H NMR spectra of **2b,d–g,i**, *cis*- and *trans*-**3b**, *trans*-**3c**, *trans*-**3d**, *cis*- and *trans*-**3i**, *trans*-**4b**, *trans*-**4d**, *cis*-**4e**, and *cis*- and *trans*-**4i** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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