Reactivity in the formation of lactones from aromatic carboxylic acids with organohypervalent iodine compounds in the Suárez system

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The reactivity of various iodanes, such as (diacetoxyiodo)arenes, the Dess–Martin reagent, and (arylsulfonyloxy)-benziodoxolones, with (*o*-alkyl)- and (*o*-phenyl)arenecarboxylic acids in the presence of iodine (Suárez system) was studied to give the corresponding lactones *via* oxygen-centered radicals. (Diacetoxyiodo)arenes gave the lactones in good yields, while 1-(arylsulfonyloxy)benziodoxolones gave lactones together with the iodinated lactones. The Dess–Martin reagent also showed the same reactivity as (diacetoxyiodo)arenes to give the lactones. Among them, (diacetoxyiodo)toluene showed the best reactivity for the conversion of these carboxylic acids to the corresponding lactones.

Introduction

Recently, the study and synthetic use of organohypervalent iodine compounds have been widely carried out.[1] For example, in ionic reactions, (diacetoxyiodo)benzene (**1A**) and [bis(trifluoroacetoxy)iodo]benzene (**1E**) have been used extensively as oxidants,[1,2] and the trivalent iodine compound having a sulfonyloxy group, [hydroxy(tosyloxy)iodo]benzene (Koser's reagent, **1I**), has been used as a powerful carbon–carbon bond forming reagent.[1] Furthermore, a typical organopentavalent iodine compound, the Dess–Martin periodane (DMP, **1G**), is a very useful oxidation reagent of alcohols.[3] In radical reactions,[1f,i] iodane **1A** has been often used as the precursor of alkyl radicals[4] and oxygen-centered radicals (*i.e.*, the Suárez system).[5,6] Thus, in the Suárez system, a mixture of a trivalent iodine compound, iodine, and alcohol or carboxylic acid is exposed to light to generate the corresponding alkoxyl[5] or carbonyloxyl radicals,[5j] and used for organic synthesis. In this system (diacetoxyiodo)benzene and iodosylbenzene (**1H**) have been commonly used.[7] However, the reactivity with various organohypervalent iodine compounds has been never studied. Thus, we planned to compare the reactivities with various organohypervalent iodine compounds, as shown in Fig. 1, in the formation of lactones from arenecarboxylic acids. Since there are many kinds of natural products and bioactive compounds containing γ- and δ-lactones, direct synthetic methods for these skeletons are very important.[8]

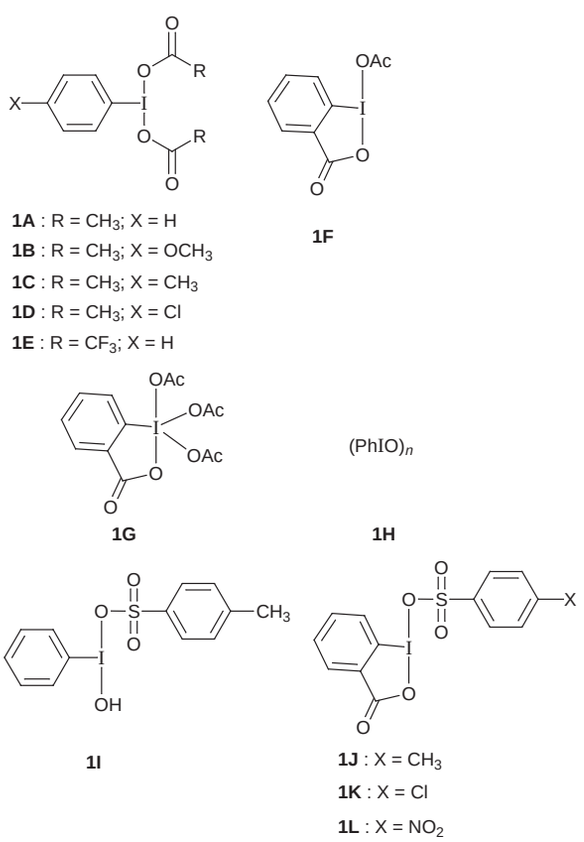


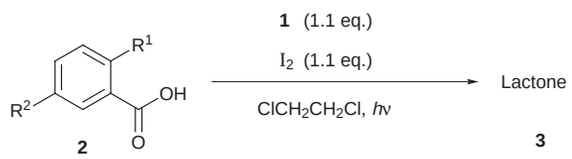
Fig. 1 Various organohypervalent iodines **1**.

Results and discussion

We have already reported on the lactonization of *ortho*-substituted benzoic acids with [bis(trifluoroacetoxy)iodo]-benzene (**1E**) and iodine.[5j] There, we used four types of arenecarboxylic acids, 2-ethylbenzoic acid (**2a**), 2,5-diisopropylbenzoic acid (**2b**), 2-benzylbenzoic acid (**2c**), and 2-phenylbenzoic acid (**2d**), as typical 2-substituted benzoic acids. Here, the lactonization of acids **2a–2d** with iodanes **1A–1H** is shown in Table 1, and a plausible reaction mechanism is shown in Scheme 1.

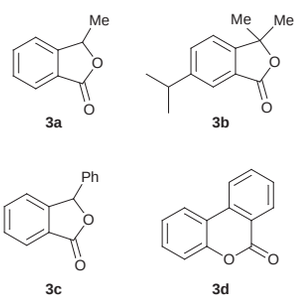
In *para*-substituted (diacetoxyiodo)benzenes **1A–1D**, a large difference in the formation of lactones was not observed, *i.e.*, *para*-substituents do not affect significantly these lactonizations. However with [bis(trifluoroacetoxy)iodo]benzene (**1E**), the yields of lactones **3a** and **3b** were decreased. The cyclic trivalent iodine compound **1F** gave the corresponding lactones in poor yields. Interestingly, the Dess–Martin reagent **1G** converted benzoic acid derivatives to the corresponding lactones in moderate to good yields. In iodosylbenzene (**1H**), lactones were formed in poor yields, because of the poor solubility of iodane **1H**. When the reactivities of (diacetoxyiodo)benzene (**1A**),

Table 1 Cyclization of acids **2a**–**2d** with iodanes **1A**–**1H**

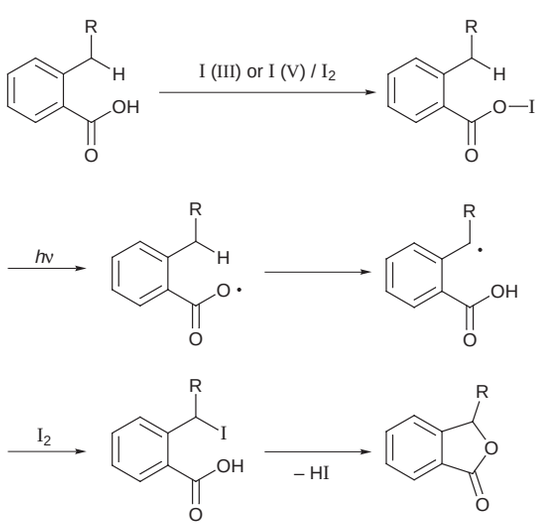


	Yields of lactones (%)[a]			
Iodanes	**3a**[b]	**3b**[c]	**3c**[c]	**3d**[d]
1A	53	83	72	89
1B	49	82	61	74
1C	56	91	68	99
1D	56	91	68	86
1E	40	36	70	90
1F	6	10	13	12
1G	44	61	58	83
1H	22	37	27	41

[a] Structure of lactones:



[b] Irradiation with a high-pressure Hg lamp at rt for 5 h in $ClCH_2CH_2Cl$ (5 ml). [c] Irradiation with a high-pressure Hg lamp at rt for 5 h in $ClCH_2CH_2Cl$ (10 ml). [d] Irradiation with a tungsten lamp at 60–70 °C for 2 h in $ClCH_2CH_2Cl$ (10 ml).

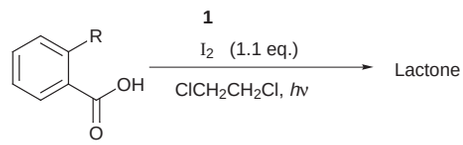


Scheme 1 Plausible reaction mechanism.

1-(acetoxy)benziodoxolone (**1F**), and the Dess–Martin reagent (**1G**) are compared, the yields of lactones **3a–3d** decreased in the order of **1A > 1G > 1F**. From the structural point of view, the benziodoxole skeleton retarded reactions such as the acyloxy exchange reaction and the formation of hypoiodite species because of their rigid structure, and so iodane **1F** gave the lactones in poor yields. DMP **1G** overcame this disadvantage owing to its powerful oxidation ability derived from the pentavalent iodine atom. Then trivalent iodine compounds having sulfonyloxy groups **1I–1L** were used in this reaction system to give the corresponding lactones (Table 2).

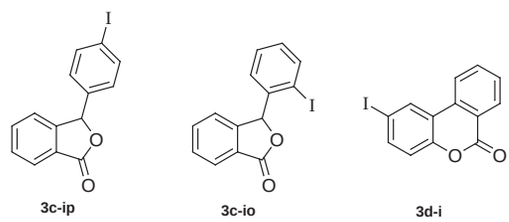
2-Benzylbenzoic acid (**2c**) and 2-phenylbenzoic acid (**2d**) were

Table 2 Cyclization of 2-substituted benzoic acids with trivalent iodine compounds having sulfonyloxy groups



Entry	1	2	Lactones[a]	Yields (%)
1	**1I**	**2c**	**3c/3c-ip**	15/15[b]
2	**1J**	**2c**	**3c/3c-ip**	13/38[b]
3	**1K**	**2c**	**3c/3c-ip**	3/39[b]
4	**1L**	**2c**	**3c/3c-ip**	2/30[b]
5	**1K**	**2c**	**3c/3c-ip/3c-io**	2/19/11[c]
6	**1I**	**2d**	**3d**	27[d]
7	**1J**	**2d**	**3d/3d-i**	36/5[d]
8	**1K**	**2d**	**3d/3d-i**	39/10[d]
9	**1L**	**2d**	**3d/3d-i**	41/6[d]
10	**1K**	**2d**	**3d-i**	49[e]

[a] Structure of lactones:



[b] Ratio of 1:2 is 1.1:1.0 and irradiation with a high-pressure Hg lamp for 5 h at rt. [c] Ratio of 1:2 is 2.2:1.0 and irradiation with a high-pressure Hg lamp for 5 h at rt. [d] Ratio of 1:2 is 1.1:1.0 and irradiation with a tungsten lamp for 2 h at 60–70 °C. [e] Ratio of 1:2 is 2.2:1.0 and irradiation with a tungsten lamp for 2 h at 60–70 °C.

converted to the corresponding lactones, in moderate yields. Furthermore, iodinated lactones **3c-ip**, **3c-io**, and **3d-i** were also obtained, and these compounds were not obtained using iodanes bearing acyloxy groups (**1A–1G**). Probably, this is due to the powerful iodination ability of aromatic rings with iodanes **1I–1L** as compared with iodanes **1A–1E**, in the presence of iodine.[9] Thus, iodinated lactones **3c-ip**, **3c-io**, and **3d-i** were produced through the formation of lactone skeletons as shown in Scheme 1 and iodination of the aromatic rings by the arenesulfonyl hypoiodite species *via* the ionic pathway. Actually, under the dark conditions, iodane **1J** iodinated benzo[*c*]-chromen-6-one (**3d**) to give iodinated lactone **3d-i** in 24% yield in the presence of iodine at room temperature. The large difference in reactivity between acyloxy and sulfonyloxy groups in iodanes **1** probably comes from the facts that sulfonyloxy groups have better leaving ability than acyloxy groups, and that the sulfonyl hypoiodite species formed *in situ* are more powerful iodination reagents for aromatic rings than acyl hypoiodite species. Here, since lactones **3c** and **3c-ip** could not be separated by preparative TLC (silica gel), the yields were determined by the integral ratio obtained from ^1H NMR. However, yields were lower than those with iodanes **1A–1E** and **1G**, and so improvement of reaction conditions was attempted. In benziodoxolones, the amount of iodane **1K** was increased to 2.2 equiv. (Entries 5 and 10, Table 2). Thus, in entry 10, lactone **3d-i** was obtained in 49% yield as the sole product and benzo[*c*]-chromen-6-one (**3d**) completely disappeared. This result again confirms that benziodoxolones **1J–1L** are more powerful iodination reagents than **1A–1F**.[9] The lactonization of acids **2a** and **2b** with **1I–1L** did not occur because of decomposition of the iodanes in the presence of iodine. Thus, for the lactonization of arenecarboxylic acids, iodane **1A–1E** and **1G** should be used. The reactivities are shown in Fig. 2 based on Table 1.

In conclusion, (diacetoxyiodo)arenes gave the lactones in

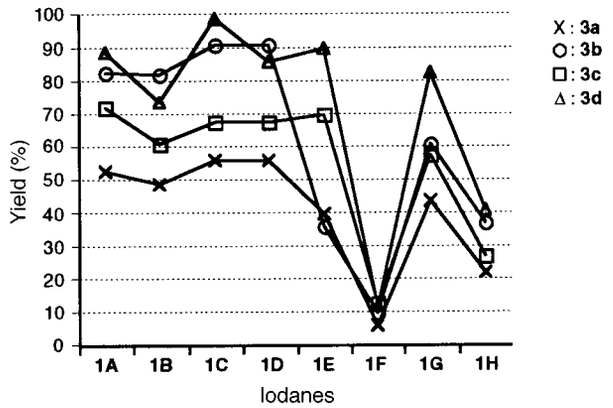


Fig. 2 Reactivity map of iodanes **1A**–**1H** in the Suárez system.

high yields; in particular, (diacetoxyiodo)toluene showed the best reactivity for the cyclization of aromatic carboxylic acids. 1-(Acetoxy)benziodoxolone (**1F**) gave the lactones in poor yields because of their rigid structure. The Dess–Martin reagent also reacted in this system. Only trivalent iodine compounds having sulfonyloxy groups gave the iodinated lactones, since these iodanes have powerful iodination ability.

Experimental

General

^{1}H NMR spectra were recorded on 400 MHz and 500 MHz spectrometers and ^{13}C NMR spectra were recorded on 100 MHz and 125 MHz spectrometers; p, q and t indicate primary, quaternary and tertiary centres, respectively. Chemical shifts are reported as ppm downfield from tetramethylsilane (TMS) in δ units. *J*-Values are given in Hz. The matrix of high resolution mass spectra (FAB) used 3-nitrobenzyl alcohol. Melting points were determined on an electrothermal apparatus in open capillary tubes and are uncorrected. Wakogel C-200 was used for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

Materials

The iodanes **1A**, **1E**, **1H**, **1I** and aromatic carboxylic acids **2c** and **2d** are commercially available. The other (diacetoxyiodo)arenes were prepared by the oxidation of the corresponding iodoarenes with $NaBO_4 \cdot 4H_2O$ in acetic acid.[10] Benziodoxolone derivatives **1F**,[11] **1G**,[3] and **1J**[12] were prepared based on the literature method. Iodanes **1K** and **1L** were prepared with the same method of iodane **1J**.

Typical procedures

To a solution of iodine (1.1 mmol) were added iodane (1.1 mmol) and the appropriate aromatic carboxylic acid (1.0 mmol). The solution was irradiated with a high-pressure mercury lamp (400 W) for 5 h at rt (or irradiated with a tungsten lamp (500 W) for 2 h at 60–70 °C). Then the reaction mixture was poured into sat. aq. $NaHCO_3$ solution and extracted with chloroform three times. The organic layer was poured into sat. aq. Na_2SO_3 solution and extracted with chloroform. Finally, the organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residual oil was purified by preparative TLC on silica gel using hexane–EtOAc (4 : 1) (or toluene–EtOAc = 30 : 1) as an eluent.

1-(*p*-Chlorophenylsulfonyloxy)-1λ^3,2-benziodoxol-3(1*H*)-one (1K). Mp 172–173 °C (decomp.); IR (KBr) 3080, 1610, 1230, 1180, and 760 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.36 (2H, d, *J* = 8.5 Hz), 7.59 (2H, d, *J* = 8.2), 7.68 (1H, td, *J* = 7.3, 1.0 Hz), 7.83 (1H, d, *J* = 7.5 Hz), 7.94 (1H, td, *J* = 7.3, 1.7 Hz), 8.00 (1H, dd, *J* = 7.6, 1.5 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 120.37 (q), 126.25 (t), 127.42 (t), 127.64 (t), 130.31 (t), 131.04 (t), 131.48 (q), 132.93 (q), 134.42 (t), 147.16 (q), 167.68 (q); Found: C, 35.72; H, 1.92%. Calcd. for $C_{13}H_6ClIO_5S$: C, 35.60; H, 1.84%.

1-(*p*-Nitrophenylsulfonyloxy)-1λ^3,2-benziodoxol-3(1*H*)-one (1L). Mp 180–181 °C (decomp.); IR (KBr) 3080, 1610, 1510, 1240, 1120, and 740 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.68 (1H, t, *J* = 7.1 Hz), 7.81–7.85 (3H, m), 7.94 (1H, td, *J* = 7.5, 1.5 Hz), 7.99 (1H, dd, *J* = 7.5, 1.3 Hz), 8.18 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 120.41 (q), 123.33 (t), 126.28 (t), 126.90 (t), 130.36 (t), 131.03 (t), 131.48 (q), 134.47 (t), 147.27 (q), 154.22 (q), 167.74 (q); Found: C, 34.55; H, 2.01; N, 2.97%. Calcd. for $C_{13}H_8INO_7S$: C, 34.76; H, 1.80; N, 3.12%.

3-Methylphthalide (3a). Oil; IR (neat) 2940, 1740, 1590, 1450, 1210, 760, and 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.64 (3H, d, *J* = 6.7 Hz, CH_3), 5.57 (1H, q, *J* = 6.7 Hz, 3-H), 7.45 (1H, dd, *J* = 7.3, 0.9 Hz, 4-H), 7.53 (1H, t, *J* = 7.7 Hz, 6-H), 7.68 (1H, td, *J* = 7.3, 0.9 Hz, 5-H), 7.89 (1H, d, *J* = 7.7 Hz, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.38 (p, CH_3), 77.85 (t, 3-C), 121.57 (t, 4-C), 125.72 (t, 7-C), 129.10 (t, 6-C), 134.12 (t, 5-C), 151.23 (q, Ar), 170.63 (q, CO); Found: C, 73.13; H, 5.27%. Calcd. for $C_9H_8O_2$: C, 72.96; H, 5.44%; HRMS (FAB) Found: $(M + H)^+$ = 149.0627. Calcd. for $C_9H_9O_2$: M + H = 149.0603.

3,3-Dimethyl-6-isopropylphthalide (3b). Oil; IR (neat) 2930, 1750, 1580, 1490, 1190, 800, and 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29 (6H, d, *J* = 7.0 Hz, isopropyl-CH_3), 1.65 (6H, s, CH_3), 3.02 (1H, septet, *J* = 7.0 Hz, isopropyl-CH), 7.31 (1H, d, *J* = 8.1 Hz, 4-H), 7.53 (1H, dd, *J* = 8.1, 1.7 Hz, 5-H), 7.72 (1H, d, *J* = 1.7 Hz, 7-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 23.92 (p, isopropyl-CH_3), 27.40 (p, CH_3), 33.98 (t, isopropyl-CH), 85.32 (q, 3-C), 120.47 (t, 4-C), 123.07 (t, 7-C), 125.48 (q, Ar), 133.09 (t, 5-C), 150.25 (q, Ar), 152.75 (q, Ar), 170.17 (q, CO); Found: C, 76.20; H, 7.77%. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%; HRMS (FAB) Found: $(M + H)^+$ = 205.1229. Calcd. for $C_{13}H_{17}O_2$: M + H = 205.1229.

3-Phenylphthalide (3c). Mp 113.0–114.0 °C; IR (KBr) 3000, 1740, 1580, 1455, 1280, 970, and 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.41 (1H, s, 3-H), 7.26–7.28 (2H, m, phenyl), 7.33 (1H, d, *J* = 7.6 Hz, 4-H), 7.36–7.37 (3H, m, phenyl), 7.56 (1H, t, *J* = 7.3 Hz, 6-H), 7.65 (1H, t, *J* = 7.3 Hz, 5-H), 7.97 (1H, d, *J* = 7.7 Hz, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 87.73 (t, 3-C), 122.90 (t, 4-C), 125.64 (t, 7-C), 126.98 (t, Ph), 128.99 (t, Ph), 129.31 (t, 6-C), 129.38 (q, Ar), 134.34 (t, 5-C), 136.46 (q, Ar), 149.71 (q, Ar), 170.52 (q, CO); Found: C, 79.81; H, 4.92%. Calcd. for $C_{13}H_8O_2$: C, 79.98; H, 4.79%; HRMS (EI) Found: M^+ = 210.0678. Calcd. for $C_{14}H_{10}O_2$: M = 210.0681.

3-(4′-Iodophenyl)phthalide (3c-ip). IR (KBr) 3060, 1760, 1600, 1480, 1000, and 800 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.34 (1H, s, 3-H), 7.03 (2H, d, *J* = 8.6 Hz, 2′, 6′-H), 7.32 (1H, d, *J* = 7.6 Hz, 4-H), 7.57 (1H, t, *J* = 7.3 Hz, 6-H), 7.66 (1H, td, *J* = 7.6, 1.1 Hz, 5-H), 7.72 (2H, d, *J* = 8.2 Hz, 3′, 5′-H), 7.96 (1H, d, *J* = 7.7 Hz, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 81.94 (t, 3-C), 95.19 (q, 4′-C), 122.75 (t, 4-C), 125.80 (t, 7-C), 128.71 (t, 2′ 6′-C), 129.59 (t, 6-C), 134.47 (t, 5-C), 136.20 (q, Ar), 138.16 (t, 3′, 5′-C), 149.15 (q, Ar), 170.20 (q, CO); HRMS (FAB) Found: $(M + H)^+$ = 336.9721. Calcd. for $C_{14}H_{10}O_2I$: M + H = 336.9726.

3-(2′-Iodophenyl)phthalide (3c-io). Mp 121.0–122.0 °C; IR (KBr) 2920, 1770, 1610, 1480, 1280, 1060, 760, and 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.83 (1H, s, 3-H), 6.95 (1H, dd, *J* = 8.0, 1.5 Hz, 6′-H), 7.06 (1H, td, *J* = 7.9, 1.7 Hz, 4′-H), 7.28 (1H, td, *J* = 7.3, 1.2 Hz, 5′-H), 7.55–7.59 (2H, m, 4, 6-H), 7.65 (1H, td, *J* = 7.3, 0.9 Hz, 5-H), 7.93 (1H, dd, *J* = 8.0, 1.3 Hz,

3′-H), 7.97 (1H, d, J = 7.3 Hz, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 85.60 (t, 3-C), 98.02 (q, 2′-C), 123.06 (t, 4-C), 125.38 (q, Ar), 125.84 (t, 7-C), 127.62 (t, 6′-C), 128.91 (t, 5′-C), 129.60 (t, 6-C), 130.83 (t, 4′-C), 134.49 (t, 5-C), 139.23 (q, Ar), 139.98 (t, 3′-C), 149.42 (q, Ar), 170.45 (q, CO); Found: C, 49.79; H, 2.51%. Calcd. for $C_{14}H_9O_2I$: C, 50.03; H, 2.70%; HRMS (FAB) Found: $(M + H)^+$ = 336.9715. Calcd. for $C_{14}H_{10}O_2I$: M + H = 336.9726.

Benzo[*c*]chromen-6-one (3d). Mp 91.0–92.0 °C; IR (KBr) 1720, 1600, 1480, 1300, 900, and 730 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31–7.36 (2H, m, 2, 4-H), 7.46 (1H, tt, J = 7.8, 1.2 Hz, 3-H), 7.56 (1H, td, J = 7.7, 1.2 Hz, Ar), 7.80 (1H, td, J = 7.7, 1.1 Hz, Ar), 8.03 (1H, dd, J = 7.8, 1.4 Hz, 1-H), 8.09 (1H, d, J = 8.0 Hz, Ar), 8.38 (1H, dd, J = 7.9, 1.2 Hz, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 117.75 (t, 4-C), 118.02 (q, Ar), 121.23 (q, Ar), 121.67 (t, Ar), 122.76 (t, 1-C), 124.54 (t, 2-C), 128.86 (t, Ar), 130.42 (t, 3-C), 130.54 (t, Ar), 134.74 (q, Ar), 134.83 (t, Ar), 151.27 (q, Ar), 161.16 (q, CO); Found: C, 79.63; H, 3.98%. Calcd. for $C_{13}H_8O_2$: C, 79.58; H, 4.11%; HRMS (FAB) Found: $(M + H)^+$ = 197.0610. Calcd. for $C_{13}H_9O_2$: M + H = 197.0603.

2-Iodobenzo[*c*]chromen-6-one (3d-i). Mp 148.0–149.0 °C; IR (KBr) 3070, 1740, 1600, 1480, 1220, 1040, and 815 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.12 (1H, d, J = 8.5 Hz, 4-H), 7.62 (1H, td, J = 7.6, 1.1 Hz, Ar), 7.74 (1H, dd, J = 8.5, 1.5 Hz, 3-H), 7.84 (1H, tt, J = 7.3, 0.6 Hz, Ar), 8.05 (1H, d, J = 7.9 Hz, Ar), 8.34 (1H, d, J = 1.5 Hz, 1-H), 8.39 (1H, dd, J = 7.6, 0.6 Hz, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 87.85 (q, 2-C), 119.80 (t, 4-C), 120.32 (q, Ar), 121.25 (q, Ar), 121.79 (t, Ar), 129.60 (t, Ar), 130.76 (t, Ar), 131.75 (t, 1-C), 133.35 (q, Ar), 135.09 (t, Ar), 139.07 (t, 3-C), 150.96 (q, Ar), 160.51 (q, CO); Found: C, 48.13; H, 2.10%. Calcd. for $C_{13}H_7O_2I$: C, 48.48; H, 2.19%; HRMS (FAB) Found: $(M + H)^+$ = 322.9562. Calcd. for $C_{13}H_8O_2I$: M + H = 322.9569.

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