

Reactivity of [bis(1-adamantylcarbonyloxy)iodo]arenes in substitution and addition reactions

Hideo Togo,^{*a} Rie Taguchi, Kentaro Yamaguchi^b and Masataka Yokoyama^{*a,b}

^a Department of Chemistry, Faculty of Science, and ^b Chemical Analysis Center, Chiba University, Yayoi-cho 1-33, Inage-Ku, Chiba 263, Japan

The reactivity of [bis(1-adamantylcarbonyloxy)iodo]arenes with 4-methylquinoline (substitution) as a typical heteroaromatic base and phenyl vinyl sulfone (addition) as a typical activated olefin has been studied under thermal and irradiation conditions. The results suggest that electron-withdrawing groups on the aromatic ring in [bis(1-adamantylcarbonyloxy)iodo]arenes are detrimental to reactions. The crystal structures of [bis(1-adamantylcarbonyloxy)iodo]arenes **1b** and **1e** are reported.

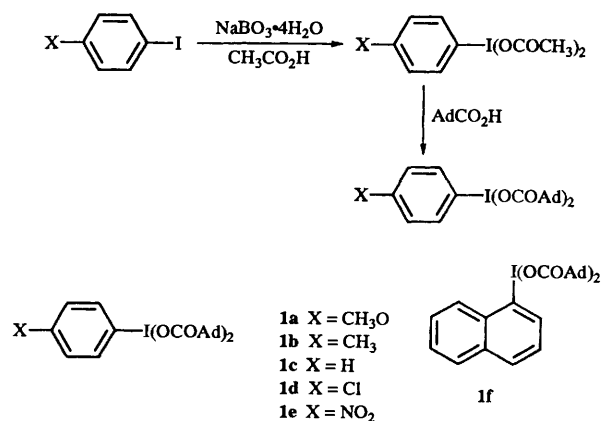
Radical reactions are one of the most useful synthetic methods for the formation of carbon-carbon bonds.¹ Thus, many reagents which form carbon radicals, such as tributyltin hydride^{1a} and *N*-hydroxy-2-thiopyridone,^{1b} have been extensively developed. Recently, the chemistry of hypervalent iodine compounds has been widely studied,² and it has been found that some of them show a radical character.³ We have directed our studies with (diacyloxyiodo)benzenes towards the alkylation of heteroaromatic bases,⁴ additions to olefins,⁵ and conversions into sulfides⁶ via radical pathways. Of the (diacyloxyiodo)benzenes studied, those derived from (diacetoxyiodo)benzene and tertiary carboxylic acids such as adamantane-carboxylic acid and 1-methylcyclohexanecarboxylic acid were the most reactive. However, there has been no study on the effect of the nature of the aromatic group in (diacyloxyiodo)arenes on the formation of the corresponding alkyl radicals, which can be subsequently trapped with heteroaromatic bases and olefins to give the corresponding alkylated products. In this paper, we report the effect of the aromatic group of (diacyloxyiodo)arenes on carbon-carbon bond formation with aromatic compounds (substitution) and olefins (addition).

Results and discussion

For our study on the effect of the substituent on the aromatic ring of (diacetoxyiodo)arenes, reactive substrates were selected, namely, 4-methylquinoline for the substitution reaction and phenyl vinyl sulfone for the addition reaction. (Diacetoxyiodo)arenes were prepared from the oxidation of iodobenzenes with a variety of substituent groups (CH₃O, CH₃, H, Cl, NO₂) by treatment with sodium perborate tetrahydrate in acetic acid based on the reported method in the literature.⁷ The [bis(1-adamantylcarbonyloxy)iodo]arenes were obtained from an acyloxy exchange reaction between (diacetoxyiodo)arene and adamantane-1-carboxylic acid (Scheme 1).

The study on the substituent effect was carried out as follows. A mixture of [bis(1-adamantylcarbonyloxy)iodo]arene and 4-methylquinolinium trifluoroacetate was refluxed in benzene or irradiated with a high-pressure mercury lamp in dichloromethane. The results are shown in Table 1.

Interestingly, the most effective [bis(1-adamantylcarbonyloxy)iodo]arene for adamantylation was the unsubstituted one **1c**, both in thermal and photochemical reactions. The addition reaction was then carried out under photochemical conditions. A mixture of [bis(1-adamantylcarbonyloxy)iodo]arene and phenyl vinyl sulfone in the presence of cyclohexa-1,4-diene as a hydrogen donor was irradiated with a high-pressure mercury lamp to give 2-(1-adamantyl)ethyl phenyl sulfone. There was

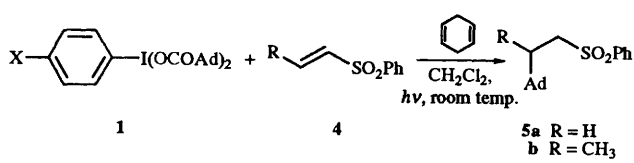


Scheme 1 Preparation of [bis(1-adamantylcarbonyloxy)iodo]arenes

Table 1 Substitution effect on the alkylation of 4-methylquinoline

Entry	1	Yield (%)	
		Heat	<i>hν</i>
1	a	57	77
2	b	80	90
3	c	80	99
4	d	64	83
5	e	28	66
6	f	29	61

little difference between the [bis(1-adamantylcarbonyloxy)iodo]arenes except with [bis(1-adamantylcarbonyloxy)iodo]nitrobenzene **1e**. The same addition reaction also proceeded under thermal conditions, however, the yield was less satisfactory owing to the direct reduction of the adamantyl radical formed by a hydrogen donor such as cyclohexa-1,4-diene, which gives adamantane in high yield.⁵ For example, the thermal reaction between [bis(1-adamantylcarbonyloxy)iodo]benzene and phenyl vinyl sulfone in refluxing 1,2-dichloroethane gave **5a** in 40% yield with cyclohexa-1,4-diene. The

Table 2 Substitution effect on addition to olefins


Entry	1	Yield (%)	
		5a	5b
1	a	94	79
2	b	96	84
3	c	93	75
4	d	93	75
5	e	34	4
6	f	92	—

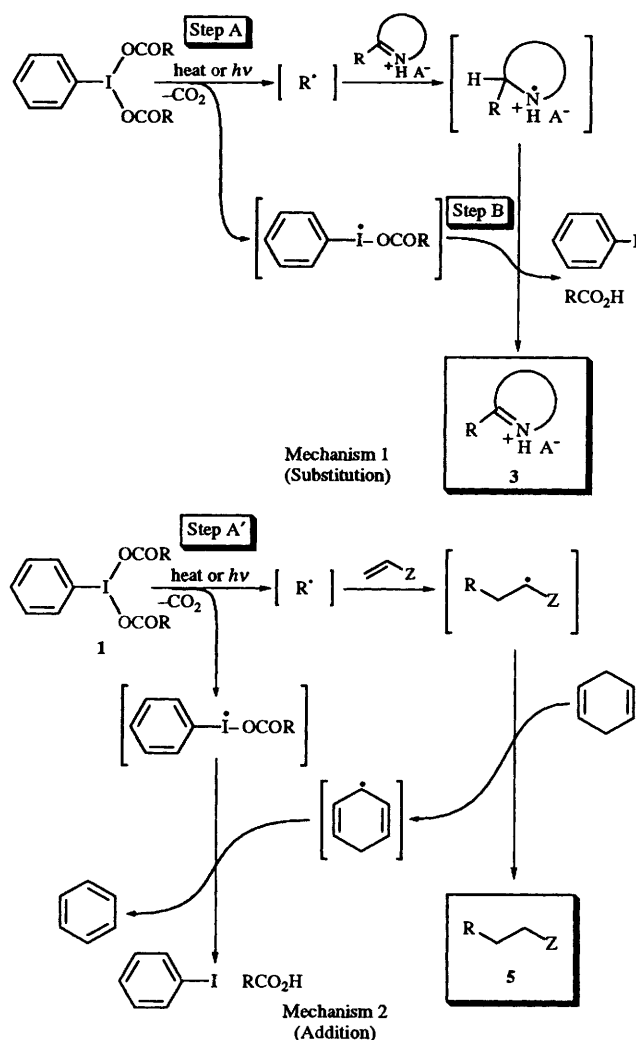
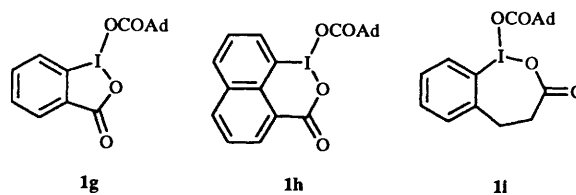
addition reaction with phenyl prop-1-enyl sulfone was then carried out (Table 2). The most effective reagent was **1b**, which has a *p*-tolyl group.

From these results, it was seen that the substituent effects for the substitution and addition reactions differed slightly, namely, **1c** was the most reactive in the former reaction, and **1b** followed by **1a** were the most reactive in the latter reaction. This result might be explained by a difference between the reaction pathways in the substitution (mechanism 1) and addition reactions (mechanism 2) (Fig. 1).

In the addition reaction shown in mechanism 2, the (diacyloxyiodo)arene takes part only in the decarboxylation (step A'). So the total reactivity depends on its ability to form a 1-adamantyl radical since the carbon radical reacts with the olefin rapidly.⁸ However, in the substitution reaction shown in mechanism 1, the (diacyloxyiodo)arene takes part not only in decarboxylation (step A), but also in the abstraction of a hydrogen atom (step B). The most effective substituent in the decarboxylative process in the substitution reaction may be the tolyl and anisyl groups. However, the oxidative ability will increase in proportion to the electron-attracting ability of the substituent group,⁹ and, therefore, a (diacyloxyiodo)arene which has an electron-withdrawing group will be more effective in the extraction of a hydrogen atom (step B). Therefore, **1c** which has a phenyl group might consequently be expected to give **3** in high yield.

Although the (diacyloxyiodo)arenes have two acyloxy groups, only one decarboxylation occurs. Thus, one acyloxy group is used for the formation of the corresponding carbon radical and CO₂, while the other is finally recovered as the carboxylic acid. We, therefore, investigated the effect of employing (monoacyloxyiodo)arenes such as **1g–1i** as radical reagents.

(Monoacyloxyiodo)arene **1g** was easily prepared from *o*-iodobenzoic acid.¹⁰ Although other iodoarenes **1h** and **1i** were formed, it was impossible to purify them because of oligomerization. Alkylation of 4-methylquinoline (Hg-*hν*) and addition to phenyl vinyl sulfone (Hg-*hν*) with **1g** were carried out under the same conditions. However, the yields of **3** and **5a** were only 29 and 10%, respectively. This result suggests that an electron-withdrawing group (carboxy group) on the aromatic ring retards the reactivity of **1g**. This result supports the data of Tables 1 and 2. Consequently, (diacyloxyiodo)arene derivatives which have an electron-donating group exhibit high reactivity. Presumably, the electron density on iodine is increased and the iodine–oxygen bond is easily broken in these compounds. However, it is difficult to observe the environment of the iodine atom directly. It was found that (diacyloxyiodo)benzene is suitable for the substitution reaction and (diacyloxyiodo)toluene for the addition reaction. X-Ray structures of **1b** and **1e**

**Fig. 1** Reaction pathways

were obtained (Figs. 2 and 3, respectively). Both molecules showed T-shaped structures similar to (diacetoxyiodo)benzene.¹¹ No big differences between **1b** and **1e** were observed.

Recently, radical addition reactions have been performed with various reagents. Among them, tributyltin hydride, *N*-acyloxy-2-thiopyridone, and a combination of metal ions and peroxides are the most popular reagents.¹ Although each of these reagents has excellent carbon-carbon bond formation ability, most of them are used for intramolecular reactions and very few have been used for intermolecular reactions. In particular, it is very difficult to obtain the C–C bond formation products in addition reactions when the substrate has a substituent at β -, addition position. For instance the yield from the reaction of compound **1b** with phenyl prop-1-enyl sulfone was slightly lower than that with phenyl vinyl sulfone owing to steric hindrance. Thus, in the case of *N*-acyloxy-2-thiopyridone, which is a well-known radical reagent, the yield of the addition product was low in spite of using optimal

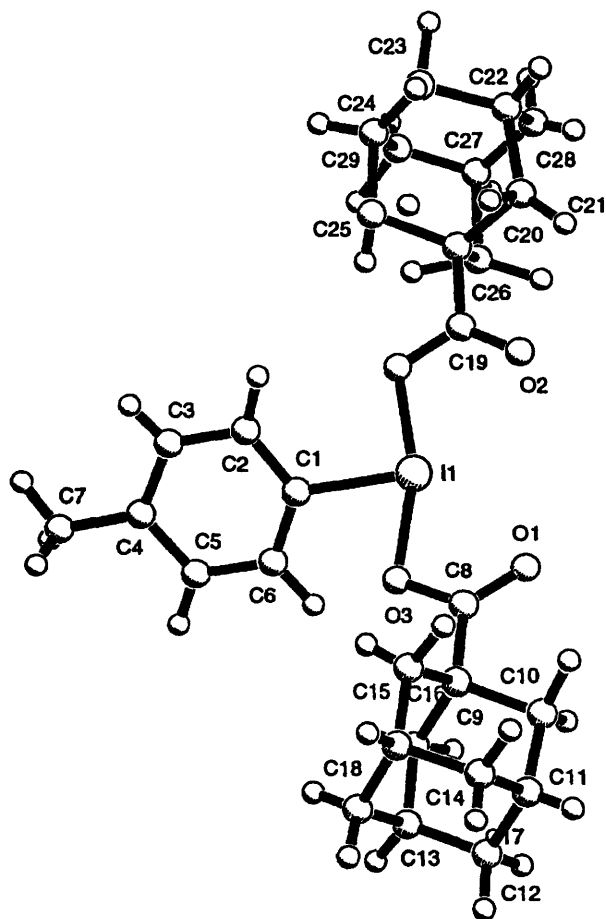


Fig. 2 X-Ray crystal structure of **1b**. Selected bond lengths (Å) and angles (°): I(1)–O(3) 2.117(9), I(1)–O(4) 2.158(9), I(1)–C(1) 2.09(1), O(1)–C(8) 1.22(2), O(2)–C(19) 1.18(2), O(3)–C(8) 1.33(2), O(4)–C(19) 1.29(2), C(8)–C(9) 1.49(2), C(19)–C(20) 1.55(2); O(3)–I(1)–O(4) 164.8(4), O(3)–I(1)–C(1) 81.5(5), O(4)–I(1)–C(1) 83.4(5), I(1)–O(3)–C(8) 111.1(9), I(1)–O(4)–C(19) 109.0(9), O(2)–C(19)–O(4) 121(1), O(1)–C(8)–O(3) 119(1), O(3)–I(1)–C(1)–C(2) 130(1), O(4)–I(1)–C(1)–C(6) 136(1).

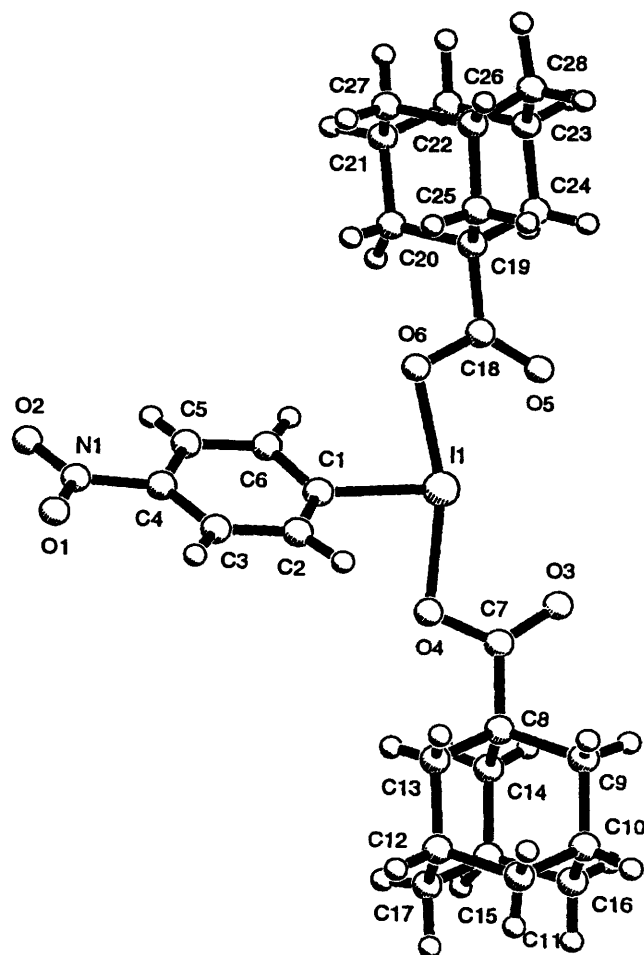


Fig. 3 X-Ray crystal structure of **1e**. Selected bond lengths (Å) and angles (°): I(1)–O(4) 2.149(10), I(1)–O(6) 2.133(9), I(1)–C(1) 2.14(1), O(3)–C(7) 1.23(2), O(4)–C(7) 1.30(2), O(5)–C(18) 1.22(2), O(6)–C(18) 1.32(2), C(18)–C(19) 1.54(2), C(8)–C(7) 1.52(2), O(4)–I(1)–O(6) 161.3(4), O(4)–I(1)–C(1) 80.8(5), O(6)–I(1)–C(1) 80.6(5), I(1)–O(4)–C(7) 107.6(9), I(1)–O(6)–C(18) 106.5(9), O(3)–C(7)–O(4) 122(1), O(5)–C(18)–O(6) 121(1), O(4)–I(1)–C(1)–C(6) 135(1), O(6)–I(1)–C(1)–C(2) 127(1).

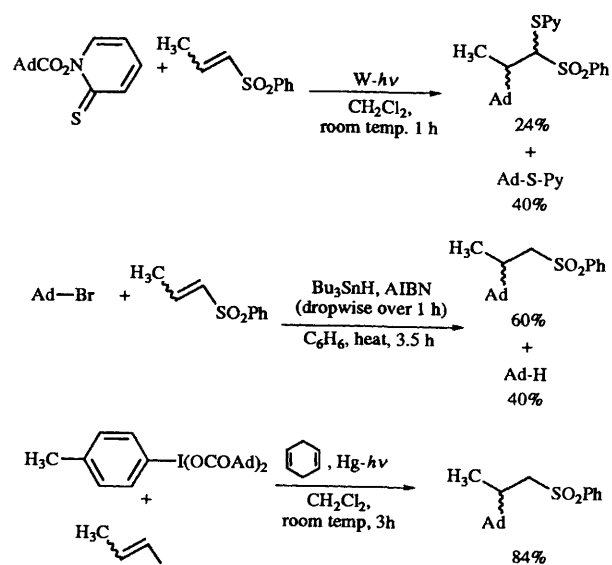
conditions with an excess of phenyl prop-1-enyl sulfone. The main product in this case was the corresponding decarboxylated product, adamantyl pyridyl sulfide. Further, in the case of tributyltin hydride, the most popular reagent, the desired compound was obtained only in moderate yield, again in spite of using optimal conditions with slow dropwise addition of Bu_3SnH (Scheme 2). Tributyltin hydride is commonly employed for this purpose, but it requires slow addition and is highly toxic. However, side reactions hardly occur in the case of (diacyloxyiodo)arenes.

In conclusion, (diacyloxyiodo)arenes are expected to be applicable to various kinds of organic syntheses because of their low toxicity and easy handling. In particular, (diacyloxyiodo)-toluene exhibited a high reactivity for addition reactions, and is recognized as a reagent which may be better than previously known radical reagents.

Experimental

General

Microanalyses were performed with Perkin-Elmer 240B and 240 elemental analysers at the Chemical Analysis Center of Chiba University. IR spectra were recorded on a Hitachi-215 spectrophotometer. ^1H and ^{13}C NMR spectra were measured with JEOL-MH-100, JEOL-JNM-FX270, JEOL-JNM-GSX-



Scheme 2

400, and JEOL-JNM-GSX-500 spectrometers at 21–22 °C. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane (TMS). J Values are given in Hz. In ^{13}C NMR spectral assignments Cp, Cs, Ct and Cq represent primary, secondary, tertiary and quaternary carbon atoms respectively. Mass spectra were measured with Hitachi M-60 (EI) and JEOL-HX 110A (FAB) mass spectrometers. Melting points were determined on a Yamato MP-21 melting point apparatus. Wakogel C-200 was used for column chromatography, Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for PTLC.

Preparation of (diacyloxyiodo)arene derivatives 1

(Diacetoxyiodo)arenes and 1-acetoxy-1,2-benziodoxol-3-one were prepared according to the procedures described in detail in the literature.⁷ 1-[Bis(1-adamantylcarbonyloxy)iodo]arenes **1** were prepared according to the method of Stang *et al.*^{12a}

1-[Bis(adamantylcarbonyloxy)iodo]-4-methoxybenzene 1a. Mp 142.1–145.5 °C (decomp.); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2870, 2830, 1620, 1240, 1180, 1080, 830 and 800; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.65–2.00 (30 H, m, Ad), 3.87 (3 H, s, CH_3O), 6.95 (2 H, dd, J 7.1, 2.2, Ar) and 7.92 (2 H, dd, J 7.1, 2.2, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 28.18 (Ct, Ad), 36.53, 39.42 (Cs, Ad), 41.10 (Cq, Ad), 55.52 (Cp, CH_3O), 112.02 (Cq, Ar), 116.21, 136.25 (Ct, Ar), 161.69 (Cq, Ar) and 182.62 (Cq, CO) [Found: C, 58.5; H, 6.1%; m/z (FAB) 593.1755. Calc. for $\text{C}_{29}\text{H}_{37}\text{IO}_5$: C, 58.79; H, 6.29%; ($M + 1$)⁺, 593.1764].

1-[Bis(adamantylcarbonyloxy)iodo]-4-methylbenzene 1b. Mp 149.0–152.5 °C (decomp.); $\nu_{\text{max}}(\text{KBr})$ 2870, 2820, 1620, 1440, 1320, 1270, 1240, 1080 and 800; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.65–2.00 (30 H, m, Ad), 2.44 (3 H, s, CH_3), 7.37 (2 H, d, J 8.2, Ar) and 7.87 (2 H, d, J 8.2, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.44 (Cp, CH_3), 28.18 (Ct, Ad), 36.53, 39.42 (Cs, Ad), 41.10 (Cq, Ad), 118.62 (Cq, Ar), 131.37, 134.20 (Ct, Ar), 141.82 (Cq, Ar) and 182.60 (Cq, CO) [Found: C, 60.2; H, 6.2%; m/z (FAB) 577.1810. Calc. for $\text{C}_{29}\text{H}_{37}\text{IO}_4$: C, 60.42; H, 6.47%; ($M + 1$)⁺, 577.1815].

[Bis(1-adamantylcarbonyloxy)iodo]benzene 1c. Mp 142.5–146.2 °C (decomp.); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2860, 2820, 1610, 1265, 1240, 1075, 800 and 735; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.65–2.01 (30 H, m, Ad), 7.58–7.45 (3 H, m, Ar) and 8.00 (2 H, dd, J 8.6, 1.3, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 28.17 (Ct, Ad), 36.52, 39.42 (Cs, Ad), 41.13 (Cq, Ad), 121.96 (Cq, Ph), 130.60, 131.17, 134.25 (Ct, Ph) and 182.65 (Ct, CO) [Found: C, 59.7; H, 6.1%; m/z (FAB) 563.1666. Calc. for $\text{C}_{28}\text{H}_{35}\text{IO}_4$: C, 59.79; H, 6.27%; ($M + 1$)⁺, 563.1658].

1-[Bis(1-adamantylcarbonyloxy)iodo]-4-chlorobenzene 1d. Mp 137.5–142.7 °C (decomp.); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2870, 2820, 1620, 1440, 1320, 1270, 1240, 1080, 1000 and 800; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.65–2.00 (30 H, m, Ad), 7.44 (2 H, dd, J 6.9, 2.0, Ar) and 7.92 (2 H, dd, J 6.9, 2.0, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 28.14 (Ct, Ad), 36.49, 39.41 (Cs, Ad), 41.16 (Cq, Ad), 119.02 (Cq, Ar), 130.88, 135.60 (Ct, Ar), 137.81 (Cq, Ar) and 182.79 (Cq, CO); [Found: C, 55.7; H, 5.6%; m/z (FAB) 597.1271 and 599.1233. Calc. for $\text{C}_{28}\text{H}_{34}\text{ClIO}_4$: C, 56.34; H, 5.74%; Calc. for $\text{C}_{28}\text{H}_{35}^{35}\text{ClIO}_4$: ($M + 1$)⁺, 597.1269; Calc. for $\text{C}_{28}\text{H}_{35}^{37}\text{ClIO}_4$: ($M + 1$)⁺, 599.1253].

1-[Bis(1-adamantylcarbonyloxy)iodo]-4-nitrobenzene 1e. Mp 150.0–151.8 °C (decomp.) $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2860, 2810, 1620, 1510, 1440, 1350, 1330, 1320, 1270, 1250, 1080, 850 and 800; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.65–2.00 (30 H, m, Ad), 8.20 (2 H, dd, J 7.1, 2.2, Ar) and 8.32 (2 H, dd, J 7.1, 2.2, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 28.10 (Ct, Ad), 36.43, 39.39 (Cs, Ad), 41.26 (Cq, Ad), 125.32 (Ct, Ar), 127.07 (Cq, Ar), 135.34 (Ct, Ar), 149.25 (Cq, Ar) and 183.04 (Cq, CO) [Found: C, 55.1; H, 5.5; N, 2.3%; m/z (FAB) 608.1509. Calc. for $\text{C}_{28}\text{H}_{34}\text{INO}_6$: C, 55.36; H, 5.64; N, 2.31%; ($M + 1$)⁺, 608.1509].

1-[Bis(1-adamantylcarbonyloxy)iodo]naphthalene 1f. Mp 133.5–137.0 °C (decomp.); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2880, 2840, 1620, 1450, 1320, 1270, 1250, 1080, 800 and 770; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.58–2.00 (30 H, m, Ad), 7.52 (1 H, t, J 7.9, Ar), 7.67 (2 H, m, Ar), 7.91 (1

H, d, J 7.9 Ar), 8.07 (2 H, dd, J 11.2, 8.6, Ar), 8.41 (1 H, d, J 7.25 Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 28.10 (Ct, Ad), 36.44 (Cs, Ad), 39.31 (Cs, Ad), 41.17 (Cq, Ad), 125.61 (Cq, Ar), 126.41, 127.42, 128.75, 128.93, 129.81 (Ct, Ar), 131.47 (Cq, Ar), 133.01 (Ct, Ar), 134.34 (Cq, Ar), 136.50 (Ct, Ar) and 182.85 (Cq, CO).

1-(Adamantylcarbonyloxy)-1,2-benziodoxol-3-one 1g. Mp 157.5–160.5 °C (decomp.); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2860, 2810, 1620, 1425, 1220, 1070, 820, and 740; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.70–2.11 (15 H, m, Ad), 7.72 (1 H, m, Ar) 7.95 (2 H, m, Ar) and 8.26 (1 H, dd, J 9.3, 1.7 Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 20.32, 27.84, 28.06 (Ct, Ad), 36.38, 38.62, 39.52 (Cs, Ad), 41.78 (Cq, Ad), 118.70, 129.27 (Cq, Ar), 129.34, 131.34, 133.19, 136.13 (Ct, Ar), 176.40 and 182.85 (Cq, CO) (Found: C, 50.5; H, 4.7. Calc. for $\text{C}_{18}\text{H}_{19}\text{IO}_4$: C, 50.72; H, 4.70%).

General procedure for the adamantylation of 4-methylquinoline

Method A. A mixture of trivalent iodine compound **1** (0.5 mmol) and 4-methylquinolinium trifluoroacetate (1.5 mmol) **2** was dissolved in dry dichloromethane (5 cm³) under an argon atmosphere. The resulting solution was irradiated with a high-pressure mercury lamp (400 W) for 3 h at about 30 °C.

Method B. A mixture of trivalent iodine compound **1** (0.5 mmol) and 4-methylquinolinium trifluoroacetate **2** (1.5 mmol) was dissolved in dry benzene (5 cm³) under an argon atmosphere. The resulting solution was refluxed for 5 h.

Each reaction mixture was poured into saturated aqueous sodium hydrogen carbonate and the water layer was extracted with chloroform three times. The combined organic layers were dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residual oil was purified by PTLC on silica gel (eluent: CHCl_3) to give 2-(1-adamantyl)-4-methylquinoline **3**, mp 120.3–122.0 °C; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3040, 2880, 2840, 1590, 1440 and 760; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.80 (6 H, br s, Ad), 2.07 (9 H, br s, Ad), 2.60 (3 H, s, CH_3), 7.15 (1 H, s, Ar 3-H), 7.30–7.60 (2 H, m, 6- and 7-H), 7.80 (1 H, d, J 9.0, 5-H) and 7.90 (1 H, d, J 9.0, 8-H); m/z (EI) M^+ 277 (Found: C, 86.4; H, 8.3; N, 5.2. Calc. for $\text{C}_{20}\text{H}_{23}\text{N}$: C, 86.59; H, 8.36; N, 5.05%).

General procedure for the addition of compound 1 to phenyl vinyl sulfone

To a solution of trivalent iodine compound **1** (0.5 mmol) and phenyl vinyl sulfone **4** (0.5 mmol) in dry dichloromethane (5 cm³) was added cyclohexa-1,4-diene (2.5 mmol) under an argon atmosphere. The obtained mixture was irradiated with a high-pressure mercury lamp (400 W) for 3 h at 30 °C. The reaction mixture was poured into saturated aqueous sodium hydrogen carbonate and the water layer was extracted with chloroform three times. The combined organic layers were dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residual oil was purified by PTLC (eluent, hexane–ethyl acetate 3:1) to give compound **5**.

2-(1-adamantyl)ethyl phenyl sulfone 5a. Mp 101.4–103.5 °C; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2860, 1440, 1295, 1145, 1085, 760, 730 and 685; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.35–1.76 (14 H, m, Ad), 1.93 (3 H, br s, $-\text{CH}_2-$ and Ad), 3.07 (1 H, d, J 9.6, $-\text{CH}_2-$), 3.05 (1 H, dd, J 9.6, 3.9 $-\text{CH}_2-$), 7.53–7.72 (3 H, m, Ph) and 7.91 (2 H, dt, J 7.0, 1.8) [Found: C, 71.3; H, 7.7%; m/z (FAB) 305.1574. Calc. for $\text{C}_{18}\text{H}_{24}\text{O}_2\text{S}$: C, 71.01; H, 7.95%; ($M + 1$)⁺, 305.1574].

2-(1-adamantyl)propyl phenyl sulfone 5b. Oil; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2885, 2850, 1450, 1310, 1155, 1100, 760, 740 and 700; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.03 (3 H, d, J 7.0, CH_3), 1.16–2.00 (16 H, m, Ad and $-\text{CH}_2-$), 2.71 (1 H, dd, J 14.2, 9.7, $-\text{CH}_2-$), 3.29 (1 H, d, J 14.2, $-\text{CH}_2-$), 7.50–7.68 (3 H, m, Ph) and 7.88–7.96 (2 H, m, Ph) (Found: C, 71.4; H, 7.9. Calc. for $\text{C}_{19}\text{H}_{26}\text{O}_2\text{S}$: C, 71.65; H, 8.23%).

X-Ray crystal structure determinations

Crystal data for compound 1b. $\text{C}_{29}\text{H}_{37}\text{IO}_4$, $M = 576.51$. Monoclinic, $a = 10.284(10)$, $b = 24.623(9)$, $c = 11.038(6)$ Å,

$\beta = 107.76(5)^\circ$, $V = 2.661(3) \text{ \AA}^3$. Cu-K α ($\lambda = 1.54178 \text{ \AA}$), space group $P2_1/n$ (#14), $Z = 4$, $D_x = 1.439 \text{ g cm}^{-3}$. Colourless, prismatic. Crystal dimensions $0.12 \times 0.11 \times 0.42 \text{ mm}$, $\mu(\text{Cu-K}\alpha) 96.99 \text{ cm}^{-1}$.

Crystal data for compound 1e. $\text{C}_{28}\text{H}_{34}\text{NiO}_6$, $M = 607.48$. Monoclinic, $a = 10.368(2)$, $b = 12.465(2)$, $c = 10.876(2) \text{ \AA}$, $\beta = 110.93(2)^\circ$, $V = 1312.8(5) \text{ \AA}^3$. Cu-K α ($\lambda = 1.54178 \text{ \AA}$), space group Pn (#7), $Z = 2$, $D_x = 1.537 \text{ g cm}^{-3}$. Colourless, prismatic. Crystal dimensions $0.11 \times 0.10 \times 0.41 \text{ mm}$, $\mu(\text{Cu-K}\alpha) 99.38 \text{ cm}^{-1}$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

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† For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

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