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m-Iodosylbenzoic Acid: Recyclable Hypervalent Iodine Reagent for α-Tosyloxylation and α-Mesyloxylation of Ketones

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Abstract: *m*-Iodosylbenzoic acid–mediated reactions of various carbonyl compounds provided α-organosulfonyloxy carbonyl compounds in good yields. The final products could be easily isolated without any chromatographic purification by simple treatment of the crude mixture with an anionic exchange resin.

Keywords: Hypervalent iodine, α-organosulfonyloxy ketones, recycle, α-sulfonylation of ketones

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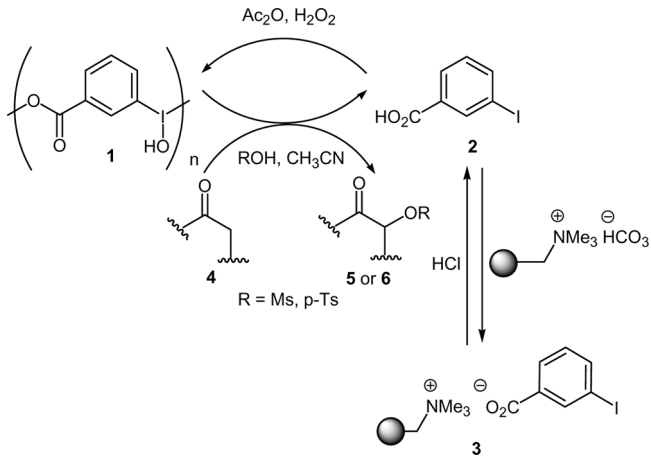
α-Organosulfonyloxy ketones are useful building blocks for the construction of heterocyclic compounds such as thiazoles, selenazoles, oxazoles, imidazoles, pyrazoles, benzofurans, and lactones.[1] Since the early 1980s, hypervalent iodine compounds have attracted significant interest as mild and selective oxidizing reagents in synthetic organic chemistry.[2] Among them, [hydroxy(mesyloxy)iodo]benzene (HMIB) and its tosyloxy analog (HTIB) are useful reagents for α-mesyloxylation and α-tosyloxylation of ketones.[1g,3] Common by-products in the reactions of HMIB and HTIB are their corresponding reduced products, namely aryliodides, which often have to be removed by a chromatographic treatment. A tedious chromatographic purification is also needed for the reaction with iodine(III) oxidant if the oxidant is employed in excess or not fully consumed.

Togo and coworkers have studied the α-tosyloxylation of ketones using five novel [hydroxy(tosyloxy)iodo]arenes that bear 2-thienyl, 3-thienyl, *N*-tosyl-4-pyrazolyl, 3-trifluoromethylphenyl, and 3,5-bis(trifluoromethy)phenyl as arenes.[4] Commonly, α-tosyloxylation of ketones was achieved by the in situ formation of the active reagent by mixing (diacetoxyiodo)arene (1.0–1.2 eq.) and *p*-toluenesulfonic acid monohydrate (2.0–2.4 eq.). Conventional workup of extraction and chromatographic purification was required in this synthetic method. Also, iodosylbenzene can serve as an iodine(III) reagent for α-tosyloxylations.[5] Additionally, *poly*[4-hydroxy(tosyloxy)iodo]styrene and *poly*{R-methyl[4-hydroxy (tosyloxy)iodo]styrene} can serve as iodine(III) reagents,[6] which lead to simplified workup, although the α-sulfonyloxy ketones were purified by flash chromatography.

Alternatively, homogeneously supported version of Koser's salt based on room-temperature ionic liquids were introduced by Handy and Okello.[7] Isolation of α-tosyloxy ketones is achieved by simple extraction with dichloromethane (DCM) and chromatographic purification on silica gel. Tohma and coworkers[8] found that the monomeric recyclable hypervalent iodine(III) reagents 1,3,5,7-tetrakis[4-(diacetoxyiodo)phenyl]-adamantine and tetrakis[4-(diacetoxyiodo)phenyl]methane can also be employed for the synthesis of α-sulfonyloxy ketones. However, both of these reagents require multistep procedures for their preparation.

In this report, we disclose a very simple method for the α-tosyloxylation and α-mesyloxylation of ketones with minimum purification that is based on the tagged iodine(III) reagent, *m*-iodosylbenzoic acid (**1**). Indeed, tagging strategies for reagents and catalysts have been widely investigated, as they allow easy purification by means of specific phase separation or scavenging.[9] *m*-Iodosylbenzoic acid (**1**) is an example of a tagged iodine(III) reagent.[10] If it is treated in excess, unreacted reagent can be conveniently removed at the end of the reaction by filtration after treatment with anion exchange resin Amberlite IRA-900 (carbonate



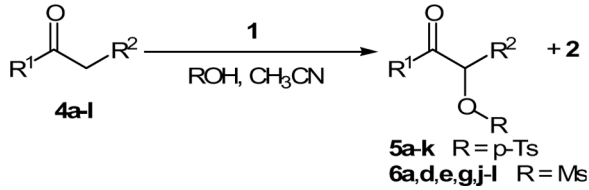
Scheme 1. α-Organosulfonyloxylation of ketones with *m*-iodosobenzoic acid (**1**).

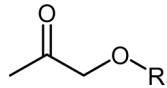
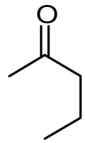
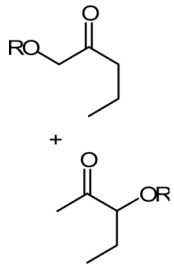
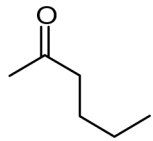
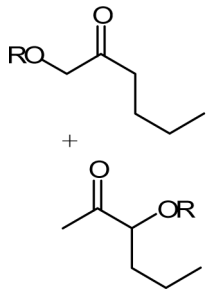
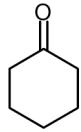
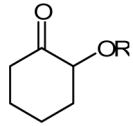
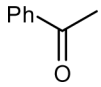
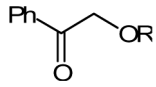
form) (Scheme 1). This concept can also be applied to scavenge a reduced product such as *m*-iodobenzoic acid (**2**). Importantly, by-product **2**, which also serves as the starting material for the preparation of **1**, can be easily regenerated (>95%) in a pure form from the polymeric salts **3** by treatment with aqueous HCl.

m-Iodosylbenzoic acid (**1**, 0.24 mmol) was added to a mixture of ketones **4a–l** (0.2 mmol) and *p*-toluenesulfonic acid monohydrate (or methanesulfonic acid) (0.3–0.4 mmol) in CH_3CN (1.0 mL). The reaction mixture was stirred under the reaction conditions indicated in Table 1, and the reactions were monitored by thin-layer chromatography (TLC). Then, DCM (1.0 mL) was added, and the resulting solution was cooled to 5°C. Amberlite IRA-900 (900–1200 mg; carbonate form) was added, and the mixture was stirred for 5 min. The polymer was removed by filtration, and the solution was concentrated at reduced pressure to afford pure α-organosulfonyloxy ketones **5** or **6** as judged by NMR spectroscopy in 51–93% yield. *m*-Iodobenzoic acid (**2**) can easily be regenerated from the produced salts **3** by treatment with aqueous HCl and oxidation with Ac_2O/H_2O_2 to yield **1** without additional purification as described previously.[10]

Various forms of Amberlite IRA-900 (azide, carbonate, and hydroxide forms) were tested for the removal of unreacted *m*-iodosobenzoic acid (**1**) and reduced *m*-iodobenzoic acid (**2**). The acids **1** and **2** were successfully removed only with the carbonate form of Amberlite IRA-900. When Amberlite IRA-900 in a hydroxide form was used, hydrolysis and elimination reactions were accompanied instead. In addition,

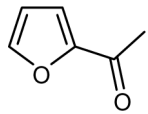
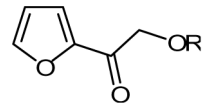
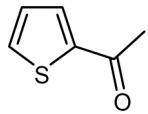
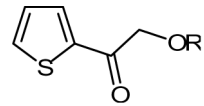
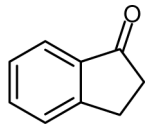
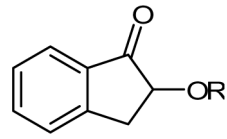
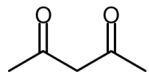
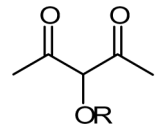
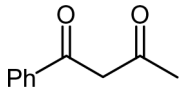
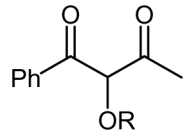
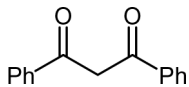
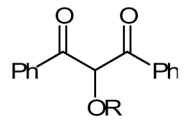
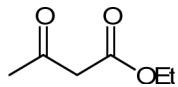
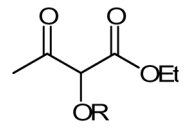
Table 1. α-Organosulfonyloxylation of ketones, diketones, and a β-ketoester



Entry	Ketone **4**	Products **5**, **6**		Temp. (°C)	Time (h)	Yield[a] (%)
1			**5a** **6a**	60 Reflux	1.0 1.0	67 53
2			**5b/5b′**	Reflux	2.0	70
3			**5c/5c′**	Reflux	2.0	75
4			**5d** **6d**	RT RT	8 1.5	51 54
5			**5e** **6e**	Reflux Reflux	3.0 2.0	96 84

(*Continued*)

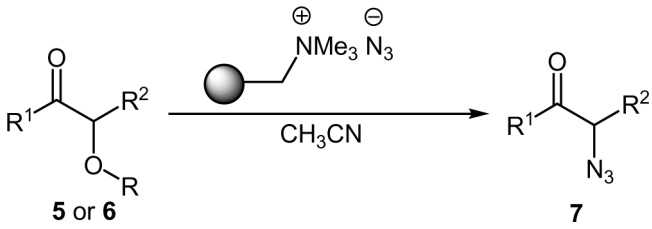
Table 1. Continued

Entry	Ketone **4**	Products **5**, **6**		Temp. (°C)	Time (h)	Yield[a] (%)
6			**5f**	60	6.0	81
7			**5g** **6g**	Reflux Reflux	5.0 13	88 84
8			**5h**	Reflux	2.0	77
9			**5i** **6i**	RT RT	1.0 1.0	87 79
10			**6j**	RT	1.0	88
11			**5k** **6k**	RT RT	1.0 1.0	93 92
12			**6l**	RT	4.0	87

[a]Isolated yields of pure products.

α-azidoketones **7** (Scheme 2) were obtained, especially at reflux temperature, when Amberlite IRA-900 in an azide anionic form was used.

α-Tosyloxylation of 3-acetylpyridine (**4 m**) was tried in vain. In the case of α-tetralone (**4n**), the reaction mixture darkened and the formation



Scheme 2. Synthesis of α-azidoketones.

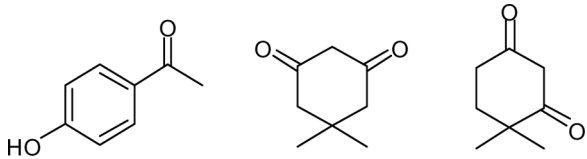
of complex by-products was observed. With ketones **4o–q**, the reaction proceeded successfully, but the products had a strong tendency to stick to the resin Amberlite IRA-900 (Figure 1).

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker DRX spectrometer (200 or 500 MHz); $CDCl_3$ was used as a solvent, and tetramethylsilane (TMS) was used as an internal standard. Infrared (IR) spectra were measured with a Perkin-Elmer Spectrum RX FTIR system. Thin-layer chromatography (TLC) was performed on precoated silica-gel 60 F_{254} plates (0.25 mm thick, Merck). Melting points were determined with a Kofler apparatus and are uncorrected. Commercially available solvents and reagents (Fluka, Aldrich, Merck) were used without further purification. *m*-Iodosylbenzoic acid (**2**) was prepared according to the published literature.[8] Amberlite IRA-900 (chloride form) was obtained from Supelco.

General Procedure for α-Organosulfonyloxylation of β-Diketones

m-Iodosylbenzoic acid (**1**, 0.24 mmol) was added to a mixture of β-diketones (0.2 mmol) and *p*-toluenesulfonic acid monohydrate (or methanesulfonic acid) (0.3–0.4 mmol) in CH_3CN (1.0 mL). The reaction



4o **4p** **4q**

Figure 1. Structures of ketones **4o–q**.

mixture was stirred at room temperature for 1.0–4.0 h, and the reaction was monitored by TLC. Then dichloromethane (1.0 mL) was added, and the resulting solution was cooled to 0°C. Amberlite IRA-900 (900–1200 mg, carbonate form) was added, and the mixture was stirred for 5 min. The polymeric solids were removed by filtration, and the filtrate was concentrated at reduced pressure to afford pure α-organosulfonyloxy ketones as judged by the ^{1}H NMR spectra.

Data

1-Tosyloxyacetone (Toluene-4-sulfonic acid 2-oxopropyl Ester) (**5a**)

Mp 34–35°C (lit.[3a] mp 35°C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 2.21 (s, 3H, CH_3–CO), 2.46 (s, 3H, CH_3), 4.48 (s, 2H, CH_2), 7.39 (d, J = 8.0 Hz, Hz, 2H$_{arom.}$), 7.79 (d, J = 8.0 Hz, 2H$_{arom.}$).

1-Mesyloxyacetone (Methanesulfonic Acid 2-Oxopropyl Ester) (**6a**)

Light yellow oil (lit.[3b] light yellow oil). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.22 (s, 3H, CH_3–CO), 3.19 (s, 3H, CH_3), 4.78 (s, 2H, CH_2).

1-Tosyloxypentan-2-one (**5b**) and 3-Tosyloxypentan-2-one (**5b′**) (1:2.5)

Oil. 1-Tosyloxypentan-2-one (**5b**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.81 (t, 3H, CH_3), 1.58 (m, 2H, CH_2), 2.46 (s, 3H, CH_3), 2.47 (t, 2H, CH_2), 4.48 (s, 2H, CH_2), 7.35 (d, J = 8.0 Hz, 2H$_{arom.}$), 7.79 (d, J = 8.0 Hz, 2H$_{arom.}$). 3-Tosyloxypentan-2-one (**5b′**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.81 (t, 3H, CH_3), 1.73 (m, 2H, CH_2), 2.19 (s, 3H, CH_3–CO), 2.46 (s, 3H, CH_3), 4.56 (dd, J = 7.5, 5.5 Hz, 1H, CH), 7.37 (d, J = 8.0 Hz, 2H$_{arom.}$), 7.81 (d, J = 8.0 Hz, 2H$_{arom.}$).

1-Tosyloxyhexan-2-one (**5c**) and 3-Tosyloxyhexan-2-one (**5c′**) (1:2)

Oil. 1-Tosyloxyhexan-2-one (**5c**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.72 (t, 3H, CH_3), 1.16 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.46 (t, 2H, CH_2), 4.56 (dd, J = 8.4, 4.8 Hz, 1H, CH), 7.35 (d, J = 8.0 Hz, 2H$_{arom.}$), 7.79 (d, J = 8.0 Hz, 2H$_{arom.}$). 3-Tosyloxyhexan-2-one (**5c′**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.90 (t, 3H, CH_3), 1.31 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 2.15 (s, 3H, CH_3-CO), 2.42 (s, 3H, CH_3), 4.56 (dd, J = 8.4, 4.8 Hz, 1H, CH), 7.37 (d, J = 8.0 Hz, 2H$_{arom.}$), 7.81 (d, J = 8.0 Hz, 2H$_{arom.}$).

2-Tosyloxycyclohexanone (Toluene-4-sulfonic Acid 2-Oxocyclohexyl Ester) (**5d**)

Mp 73–74°C (lit.[3a] mp 74–76°C). ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 1.69$–2.00 (m, 5H), 2.48 (s, 3H, CH_3), 2.28–2.58 (m, 3H), 4.90 (dd, $J = 9.8$, 5.9 Hz, 1H, CH), 7.35 (d, $J = 8.0$ Hz, $2H_{arom.}$), 7.86 (d, $J = 8.0$ Hz, $2H_{arom.}$).

2-Mesyloxycyclohexanone (Methanesulfonic Acid 2-Oxocyclohexyl Ester) (**6d**)

Mp 57°C (lit.[3b] mp 58–59°C). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 1.61$ (m, 1H), 1.76 (m, 1H), 1.90 (m, 1H), 2.00 (m, 1H), 2.03 (m, 1H), 2.15 (m, 1H), 2.41 (m, 1H), 2.57 (m, 1H), 3.21 (s, 3H, CH_3), 5.08 (dd, $J = 11.5$, 6.0 Hz, 1H, CH).

Tosyloxyacetophenone (Toluene-4-sulfonic Acid 2-Oxo-2-phenylethyl Ester) (**5e**)

Mp 92°C (lit.[3a] mp 91–92°C). ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 2.44$ (s, 3H, CH_3), 5.26 (s, 2H, CH_2), 7.35 (d, $J = 8.4$ Hz, $2H_{arom.}$), 7.46 (t, $J = 8.1$ Hz, $2H_{arom.}$), 7.57 (t, $J = 8.1$ Hz, $1H_{arom.}$), 7.83–7.86 (m, $4H_{arom.}$).

Mesyloxyacetophenone (Methanesulfonic Acid 2-Oxo-2-phenylethyl Ester) (**6e**)

Mp 75–77°C (lit.[3b] mp 76–77°C). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 3.29$ (s, 3H, CH_3), 5.52 (s, 2H, CH_2), 7.53 (t, $J = 8.5$ Hz, $2H_{arom.}$), 7.66 (t, $J = 8.5$ Hz, $1H_{arom.}$), 7.88 (d, $J = 8.5$ Hz, $2H_{arom.}$).

(Tosyloxy)methyl 2-Furanyl Ketone (Toluene-4-sulfonic Acid 2-Furan-2-yl-2-oxo-ethyl Ester) (**5f**)

Mp 64–66°C (lit.[1a] mp 63–64°C). ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 2.45$ (s, 3H, CH_3), 5.08 (s, 2H, CH_2), 6.58 (dd, $J = 3.7$, 1.7 Hz, $1H_{arom.}$), 7.34 (dd, $J = 3.7$, 0.7 Hz, $1H_{arom.}$), 7.37 (d, $J = 8.2$ Hz, $2H_{arom.}$), 7.60 (dd, $J = 1.7$, 0.7 Hz, $1H_{arom.}$), 7.86 (d, $J = 8.2$ Hz, $2H_{arom.}$).

(Tosyloxy)methyl 2-Thienyl Ketone (**5g**)

Mp 90–92°C (lit.[3a] mp 93–95°C). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 2.36$ (s, 3H, CH_3), 5.00 (s, 2H, CH_2), 7.07 (dd, $J = 5.0$, 3.6 Hz, $1H_{arom.}$), 7.26

(d, $J = 8.0$ Hz, $2H_{arom.}$), 7.65 (dd, $J = 5.0$, 1.0 Hz, $1H_{arom.}$), 7.73 (dd, $J = 3.6$, 1.0 Hz, $1H_{arom.}$), 7.77 (d, $J = 8.1$ Hz, $2H_{arom.}$).

(Mesyloxy)methyl 2-Thienyl Ketone (**6g**)

Mp 85–86°C (lit.[3b] mp 87–88°C). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 3.28$ (s, 3H, CH_3), 5.38 (s, 2H, CH_2), 7.20 (dd, $J = 5.0$, 3.6 Hz, $1H_{arom.}$), 7.26 (dd, $J = 5.0$, 1.0 Hz, $1H_{arom.}$), 7.76 (dd, $J = 3.6$, 1.0 Hz, $1H_{arom.}$).

2-Tosyloxyindan-1-one (**5h**)

Mp 110–112°C (lit.[11] mp 113–114°C). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 2.46$ (s, 3H, CH_3), 3.26 (dd, $J = 17.0$, 4.5 Hz, 1H), 3.65 (dd, $J = 17.5$, 8.0 Hz, 1H), 5.12 (dd, $J = 8.0$, 5.0 Hz, 1H), 7.41 (m, $4H_{arom.}$), 7.63 (t, $J = 7.5$ Hz, $1H_{arom.}$), 7.72 (d, $J = 7.5$ Hz, $1H_{arom.}$), 7.93 (d, $J = 8.0$ Hz, $2H_{arom.}$).

α-Tosyloxy-2,4-pentadione (**5i**)

Mainly enol tautomer; mp 81°C (lit.[3a] mp 82–83°C). ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.95$ (s, 6H, CH_3), 2.21 (s, 6H, CH_3, keto form), 2.46 (s, 3H, CH_3, keto form), 2.48 (s, 3H, CH_3), 5.20 (s, 1H, CH, keto form), 7.38 (d, $J = 8.19$ Hz, $2H_{arom.}$), 7.80 (d, $J = 8.19$ Hz, $2H_{arom.}$), 14.78 (s, 1H, OH).

α-Mesyloxy-2,4-pentadione (**6i**)

A mixture of keto-enol tautomers, colorless oil (lit.[3b] colorless oil). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 2.21$ (s, 6H, CH_3), 2.29 (s, 6H, CH_3), 3.15 (s, 3H, CH_3), 3.17 (s, 3H, CH_3), 5.46 (s, 1H, CH–OMs), 14.78 (s, 1H, OH).

α-Mesyloxy-1-phenyl-2,4-pentadione (**6j**)

Colorless oil (lit.[3c] oil). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 2.01$ (s, 3H, CH_3), 3.23 (s, 3H, CH_3), 6.23 (s, 1H, CH–OMs), 7.54 (t, $J = 7.5$ Hz, $2H_{arom.}$), 7.80 (t, $J = 7.5$ Hz, $1H_{arom.}$), 8.01 (d, $J = 7.5$ Hz, $2H_{arom.}$).

Dibenzoyl(tosyloxy)methane (**5k**)

Mp 88–89°C (lit.[3a] mp 88–90°C). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 2.39$ (s, 3H, CH_3), 6.66 (s, 1H, CH–OTs), 7.17 (d, $J = 8.1$ Hz, $2H_{arom.}$), 7.45 (t,

$J = 7.5$ Hz, $4H_{arom.}$), 7.56 (t, $J = 7.5$ Hz, $2H_{arom.}$), 7.71 (d, $J = 8.1$ Hz, $2H_{arom.}$), 7.96 (d, $J = 7.5$ Hz, $4H_{arom.}$).

Dibenzoyl(mesyloxy)methane (**6k**)

Mp 152–154°C (lit.[3b] mp 153–154°C). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 3.34$ (s, 3H, CH_3), 6.35 (s, 1H, CH–OMs), 7.53 (t, $J = 8.0$ Hz, $4H_{arom.}$), 7.66 (t, $J = 8.0$ Hz, $2H_{arom.}$), 7.90 (d, $J = 8.0$ Hz, $4H_{arom.}$).

Ethyl(mesyloxy)acetoacetate (**6l**)

A mixture of keto-enol tautomers (4.5:1), colorless oil (lit.[3b] nearly colorless oil). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 1.34$ (t, 3H, CH_3), 2.18 (s, 3H, CH_3, minor isomer), 2.37 (s, 3H, CH_3), 3.19 (s, 3H, CH_3, minor isomer), 3.24 (s, 3H, CH_3), 4.33 (q, 2H, CH_2), 5.43 (s, 1H, CH–OMs). 2.00 (s, 3H, CH_3). 3.23 (s, 3H, CH_3). 6.23 (s, 1H, CH–OMs).

2-Azido-1-phenylethanone (**7**)

m-Iodosylbenzoic acid (**1**, 0.24 mmol) was added to a mixture of acetophenone (**4e**, 0.2 mmol) and *p*-toluenesulfonic acid monohydrate (or methanesulfonic acid) (0.3–0.4 mmol) in CH_3CN (1.0 mL). The reaction mixture was stirred at reflux for 3.0 h, and the reaction was monitored by TLC. Then DCM (1.0 mL) was added, and the resulting solution was cooled to 0°C. Amberlite IRA-900 (800 mg, carbonate form) and Amberlite IRA-900 (300 mg, azide form) were added, and the mixture was stirred for 5 h at room temperature. The polymeric solids were removed by filtration, and the filtrate was concentrated at reduced pressure to afford pure 2-azido-1-phenylethanone (**7**) as a pale yellow oil (20 mg, 61%). ^{1}H NMR ($CDCl_3$, 500 MHz) $\delta = 4.44$ (s, 2H, CH_2), 7.53 (t, $J = 8.5$ Hz, $2H_{arom.}$), 7.66 (t, $J = 8.5$ Hz, $1H_{arom.}$), 7.88 (d, $J = 8.5$ Hz, $2H_{arom.}$).

CONCLUSION

In conclusion, we report here that the rarely employed *m*-iodosylbenzoic acid is an ideally tagged iodine(III) reagent that allows the easiest purification protocol for hypervalent aryliodine reagents known thus far. This tagging concept was utilized in the mild α-organosulfonyloxylation of ketones but should also be applicable for most other iodine(III)-mediated reactions.

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