3.04 (d, 1, J = 3 Hz, H-3), 4.22 (q, 2, J = 7 Hz, OCH_2), 5.3–5.5 (m, 1, H-8), 5.78 (s, 1, H-1); ^{13}C NMR δ 14.0 (ethyl Me), 23.1 (7-Me), 28.3 (C-9), 32.1 (C-4), 33.1 (C-5), 38.0 (C-6), 39.2 (C-5a), 41.3 (C-9a), 46.3 (C-3a), 59.1 (C-3), 61.3 (OCH_2), 119.2 (C-8), 123.3 (C-1), 133.1 (C-7), 169.0 (ester C=O), 186.3 (C-9b), 200.9 (C-2).

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.43; H, 8.08. Found: C, 74.52; H, 8.01.

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Registry No. **1a**, 541-47-9; **1c**, 29166-18-5; **2a**, 123992-56-3; **2c**, 123992-74-5; **2d**, 123992-70-1; **3a**, 123992-57-4; **3c**, 123992-75-6; **3d**, 123992-71-2; **4a**, 123992-58-5; **4c**, 123992-76-7; **4d**, 123992-72-3; **5a**, 13733-51-2; **5c**, 123992-77-8; **5d**, 13733-50-1; **6a**, 123992-59-6; **6b**, 123992-79-0; **6c**, 123992-78-9; **6d**, 123992-73-4; **7a**, 123992-60-9; **7b**, 123992-69-8; **8**, 40790-56-5; **9**, 123992-61-0; **10**, 123992-62-1; **11**, 83586-09-8; **12**, 123992-63-2; **13**, 123992-64-3; **14**, 2758-18-1; **15a**, 123992-65-4; **15b**, 76803-50-4; **16**, 123992-66-5; **17**, 123992-67-6; **18a**, 123992-68-7; **18b**, 123992-80-3; i, 41441-74-1; ii, 83-33-0; ethyl bromoacetate, 105-36-2; ethyl diazoacetate, 623-73-4; dirhodium tetraacetate, 15956-28-2; 4-*tert*-butylcyclohexanone, 98-53-3; 2,6-dimethylcyclohexanone, 2816-57-1; *cis*-2,6-dimethylcyclohexanone, 766-42-7; *trans*-2,6-dimethylcyclohexanone, 766-43-8; 2-bromo-2,6-dimethylcyclohexanone, 55234-03-2; 2,6-dimethyl-1-[(trimethylsilyl)oxy]cyclohexene, 63547-53-5.

Preparation of [Hydroxy(((+)-10-camphorsulfonyl)oxy)iodo]benzene and Its Reactivity toward Carbonyl Compounds†

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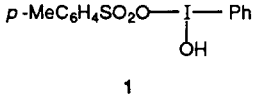
The title compound is prepared and used for the direct α-((10-camphorsulfonyl)oxylation) of various ketones and carbonyl compounds with an active methylene group. Its reaction with 2-butanone and 4-methyl-2-pentanone yields predominantly the corresponding 1-sulfonyloxy derivatives. The stereoselectivity of the reaction is studied by using benzoylacetone, ethyl benzoylacetate, and propiophenone. In some reactions 10-camphorsulfonyl peroxide is formed as a byproduct.

Organic hypervalent iodine reagents are useful in effecting direct α-functionalization of ketones and active methylene compounds. Groups attached through oxygen include hydroxy, methoxy or ethoxy,[1] acetoxy,[2] phosphoryloxy,[3] and sulfonyloxy;[4,5] also, azido[5] and saccharinyl[6] groups as well as fluorine[7] and chlorine[8] have been successfully introduced to ketones, β-diketones, and esters of β-keto acids.

Presently there is considerable interest in various α-sulfonyloxy ketones because of their potential in organic synthesis[4] and their photochemical reactivity.[9] Approaches toward their preparation not requiring the availability of α-hydroxy ketones and involving enolic ketone derivatives have been summarized.[4] The direct introduction of a tosyloxy or a mesyloxy group to carbonyl compounds has been effected by using [hydroxy(tosyloxy)iodo]benzene[10] (1) or [hydroxy(mesyloxy)iodo]-



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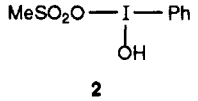

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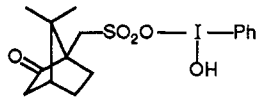

3

benzene[4,11] (2), respectively; the latter reagent can also be used as formed in situ from iodosylbenzene, $(PhIO)_n$, and methanesulfonic acid.[5] Both reagents 1 and 2 have been shown to react not only with carbonyl compounds but also with their trimethylsilyl enol ethers affording again α-sulfonyloxylated carbonyl compounds.[12] The synthetic utility of reagents 1 and 2 and also of some analogues of 1 in which the phenyl group has been changed to pentafluorophenyl or perfluoropropyl has been demonstrated further in their reactions with alkenes,[13–15] alkynes,[16–18] trimethylsilyl aromatics,[19,20] thiophenes,[21] alkenoic

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† Dedicated to the memory of Professor E. B. Merkushev.
‡ In part.

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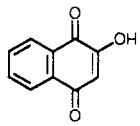
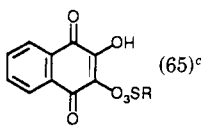
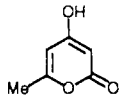
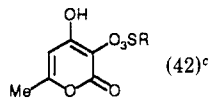
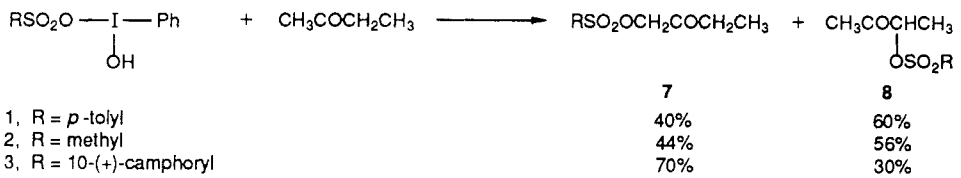
Table I. Reaction Conditions and Yields for the α-(10-Camphorsulfonyl)oxylation of Carbonyl Compounds with 3

carbonyl compd (equiv)	reaction conditions: solv	time, h	temp, °C	product(s)[a] (% yield)
$CH_3COCH_2CH_3$ (5)	MeCN	0.75	80	$RSO_3CH_2COCH_2CH_3$ (66.6)[b] + $CH_3COCH(O_3SR)CH_3$ (28.5)
$(CH_3)_2CHCH_2COCH_3$ (5)	MeCN	0.25	80	$(CH_3)_2CHCH_2COCH_2O_3SR$ (60)[c] + **10** (19)[c]
CH_3COCH_3 (5)	MeCN	0.75	80	$CH_3COCH_2O_3SR$ (87)[c]
 (1.15)	CH_2Cl_2	3	20	 (38)[c] + **10** (19)[c]
$PhCOCH_3$ (2.1)	MeCN	0.25	80	$PhCOCH_2O_3SR$ (95)[c]
$(CH_3CO)_2CH_2$ (1.5)	MeCN	0.25	80	$(CH_3CO)_2CHO_3SR$ (70)[c]
$PhCOCH_2COCH_3$ (1.5)	CH_2Cl_2	24	20	$PhCOCH(O_3SR)COCH_3$ (95)[b]
$PhCOCH_2COOEt$ (1.1)	CH_2Cl_2	8	20	$PhCOCH(O_3SR)COOEt$ (95)[b]
$PhCOCH_2CH_3$ (1.1)	MeCN	0.75	80	$PhCOCH(O_3SR)CH_3$ (90)[c]
 (1.1)	CH_2Cl_2	24	20	 (65)[c]
 (1.1)	CH_2Cl_2	72	20	 (42)[c]
$CH_2(COOEt)_2$ (1.1)	MeCN	3	80	$RSO_3CH(COOEt)_2$ (40)[c] + **10** (12)[c]

[a] R is 10-camphoryl. [b] Determined by ^1H NMR. [c] Isolated purified product.

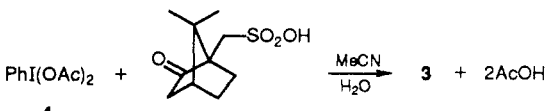
Scheme I



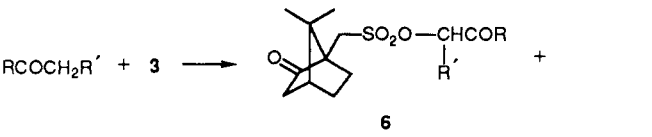
acids,[22,23] amides,[24-26] flavonols,[27] and thiouridine.[28]

This intense activity over the last few years has led us to examine the utility of a new stable hypervalent iodine reagent incorporating a chiral ligand, i.e., [hydroxy-(((+)-10-camphorsulfonyl)oxy)iodo]benzene (**3**). It is noted that various (bis(acyloxy)iodo)arenes in which the acyloxy ligands are derived from L-amino acids have been synthesized.[29] Also, certain chiral hypervalent iodine compounds have been generated in situ by reaction of iodosylbenzene with derivatives of L-tartaric acid. These oxidize prochiral sulfides to optically active sulfoxides in high optical yield.[30]

Compound **3** is readily prepared in good yield from the reaction of (diacetoxyiodo)benzene (**4**) and (+)-10-camphorsulfonic acid (**5**) in aqueous acetonitrile.



It is a stable compound, storable at room temperature with light protection for long periods of time. Treatment of carbonyl compounds with **3** leads to the formation of esters of the general formula **6**, according to the following general equation:



Ketones of various kinds, β-diketones, and some other carbonyl compounds with an active methylene group react readily with **3** either at room temperature in dichloromethane or in refluxing acetonitrile to afford in satisfactory yields the corresponding (10-camphorsulfonyl)oxy esters **6**, which have been summarized in Table I. It is noted that some carbonyl compounds did not react with **3**. Thus, whereas cyclohexanone reacts at room temperature, 3-methylcyclopentanone is unreactive. Similarly unreactive were Meldrum's acid, diethyl phenylmalonate, and 3-methyl-1-phenyl-2-pyrazolin-5-one; also, a compound with an active methylene group but without a carbonyl, i.e., phenylsulfonylacetonitrile, did not react with **3**.

The reactivity of **3** is broadly similar to that of **1** and **2**. However, the bulkiness of the (camphorsulfonyl)oxy group may differentiate **3** from **1** and **2** in certain cases. The regiochemistry of sulfonyloxylation has been tested by using 2-butanone and 4-methyl-2-pentanone. Both reagents (**1**)[10] and (**2**)[3] in their reaction with 2-butanone gave mixtures of the isomeric 1- and 3-sulfonyloxy esters, of the general formula **7** and **8**, with a slight preference for **8**. By contrast, **3** gives predominantly the ester **7**. Isomer distribution for all three reactions is shown in Scheme I.

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Since the minor product **8**, from the reaction with **3**, has incorporated the chiral camphoryl group at C-3, two diastereoisomers were expected to result; however, in its ^1H NMR spectrum different signals attributable to two diastereoisomers could not be detected.

The reaction of **3** with 4-methyl-2-pentanone was highly selective, since only one ester was detected, the one with the (camphorsulfonyl)oxy group attached to C-1.

The two β-diketones tested, acetylacetone and benzoylacetone, gave exclusively sulfonyloxylation products at the methylene position. In the case of the reaction of **3** with benzoylacetone, some evidence of stereoselectivity was obtained by examination of the ^1H NMR spectrum of the crude reaction mixture. The ester formed (**9**) has a new chiral carbon whose proton is not split into two signals, as with the ester **8** of 2-butanone. However, in contrast to **8**, the protons of both methyl groups of the camphoryl moiety as well as the protons of the acetyl group are well differentiated, so that two sets of three signals are observed, assignable to two diastereoisomers ($\mathbf{9}_1$ and $\mathbf{9}_2$) as follows: the methyl protons of the camphoryl group appear at δ values 0.85 and 0.57 for $\mathbf{9}_2$ and at 1.00 and 0.85 for $\mathbf{9}_1$, while the methyl protons of the acetyl group appear at 2.30 ($\mathbf{9}_1$) and 2.42 ($\mathbf{9}_2$). A $\mathbf{9}_1$:$\mathbf{9}_2$ ratio of 3:1 was determined by integration:

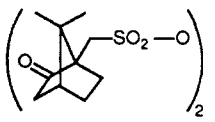
$$PhCOCH_2COCH_3 + \mathbf{3} \rightarrow \underset{\mathbf{9}}{PhCOC^*H(OSO_2R)COCH_3}$$

R = 10-(+)-camphoryl

When an attempt was made to purify the reaction products, by passing them through a silica gel column, an oily product was obtained shown to be pure ester **9** in which the ratio of different methyl signals had become approximately 1:1. Therefore, it appears that under these conditions an isomerization of $\mathbf{9}_1$ to $\mathbf{9}_2$ occurred.

The stereoselectivity of the (camphorsulfonyl)oxylation reaction was also examined by using ethyl benzoylacetate and propiophenone, but in both cases approximately equal amounts of diastereoisomers were obtained, as shown by NMR spectroscopy.

In several reactions the formation of a byproduct, besides iodobenzene, was noted. This was isolated in substantial amounts from the reaction of **3** with cyclohexanone, 4-methyl-2-pentanone, and diethyl malonate. On the basis of elemental analysis, spectroscopic data, and an iodometric estimation of "active oxygen", the peroxide structure **10** is proposed for this compound. An inde-

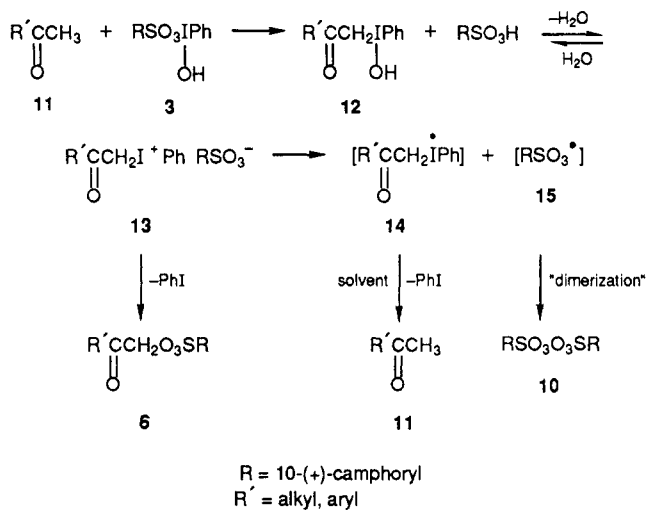


10

pendent preparation of **10** was effected by electrolysis of 10-camphorsulfonic acid under conditions similar to those previously described for methanesulfonyl peroxide.[31]

The formation of peroxide **10** from the reaction between **3** and 4-methyl-2-pentanone occurs either in refluxing acetonitrile or in dichloromethane at 20 °C. In refluxing acetonitrile the reaction is over in 10 min and all of **3** is consumed. However, when the reaction was run in the presence of tetrachloro-*p*-benzoquinone (10% by weight relative to **3**, with which it does not react), no **10** was formed after 30 min of reflux, while the yield of the ester was increased slightly. This experiment indicates that a free-radical mechanism is responsible for the formation of the peroxide but not for the ester. The peroxide does not come from the ester, since heating of 1-((10-camphorsulfonyl)oxy)-4-methyl-2-pentanone in acetonitrile for 90 min did not produce any peroxide. A plausible mechanism accounting for the formation of both kinds of products, i.e., esters **6** and the peroxide **10** is suggested in Scheme II. The interaction of an enolizable ketone such as **11** with **3** leads to the formation of the hypervalent iodine intermediate **12**, as previously suggested.[10] This can be transformed after protonation and expulsion of water into the iodonium salt **13**, which by a formal nucleophilic substitution will afford the ester **6**. A single electron transfer between the ions of **13** should lead to the free radicals **14** and **15**; the former may then react with the solvent, giving back the initial ketone **11**, whereas the latter dimerizes to form the peroxide **10**. An iodonium salt such as **13** has recently been described. It is $PhCOCH_2{}^+IPh$ BF_4^-, resulting from the reaction of the trimethylsilyl enol ether of acetophenone with iodosylbenzene and HBF_4–Me_2O at −50 °C, and it has been found to be stable up to 0 °C.[32] The inertness toward **3** of some compounds previously mentioned can be attributed to their reluctance to enolize.

Scheme II



Sulfonyl peroxides constitute a class of not well studied compounds, no doubt because of their lability. Few aliphatic[31,33] and aromatic[34] members have been described, and all are of low thermal stability, often decomposing explosively at room temperature. The stability of aromatic compounds increases when they bear electron-withdrawing substituents. The thermal stability of **10**, which survives heating at 80 °C and melts at 192–197 °C, is remarkable and may be attributed to a combination of electronic and steric effects. The steric protection offered by the bicyclic skeleton is likely to play a major role also in stabilizing the free camphorsulfonyl radical (**15**), thus permitting its dimerization. The corresponding free radicals $RSO_3^•$, where R is *p*-tolyl or methyl, must be very unstable since no sulfonyl peroxides were formed in the reactions of **1** and **2** with carbonyl compounds. The easy access to a chiral sulfonyl peroxide such as **10** may open a new route to chiral α-hydroxy ketones, as electron-rich ketone derivatives are known to react with *p*-nitrobenzenesulfonyl peroxide affording regiospecifically α-sulfonyloxy ketones.[35]

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Experimental Section

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer, and ^1H NMR spectra on a Brucker AW 80 spectrometer. Routine mass spectra were obtained by using a Hitachi Perkin-Elmer RMU-6L single-focusing spectrometer at 70 eV. Combustion analyses were performed with a Perkin-Elmer 240 B apparatus.

[Hydroxy(((+)-10-camphorsulfonyl)oxy)iodo]benzene (3). To a stirred suspension of (diacetoxyiodo)benzene (6.4 g, 20 mmol) in MeCN (40 mL) a solution of (+)-10-camphorsulfonic acid[36] (6.96 g, 30 mmol) and water (0.6 mL) in MeCN (70 mL) is added. The mixture is stirred for 30 min, until a clear solution results. The solution is concentrated to about half its volume in vacuo and allowed to crystallize, providing 7.23 g (80% yield) of **3** as colorless crystals, mp 118–120 °C (from MeOH/Et_2O); $[\alpha]^{20}_D$ = +24.5° (MeOH); IR (Nujol) 2950, 1735, 1300, 1250, 1150 cm^{-1}; ^1H NMR ($CDCl_3/CD_3SOCD_3$) δ 0.78 (3 H, s), 0.98 (3 H, s), 1.28–2.45 (7 H, m), 2.62–3.45 (2 H, m), 5.0 (1 H, br s), 7.42–8.33 (5 H, m); MS, *m/e* 384 (3), 216 (3), 204 (90), 151 (7), 77 (100). Anal. Calcd for $C_{16}H_{21}IO_5S$: C, 42.47; H, 4.65. Found: C, 42.27; H, 4.72.

General Procedure for the Reaction between 3 and Carbonyl Compounds. A mixture of **3** (1.8 g, 4 mmol) in MeCN or CH_2Cl_2 (7 mL) and the carbonyl compound (1.1–5 equiv) was maintained at the conditions described in Table I. Then the resulting clear solution was concentrated in vacuo to an oil from which the (10-camphorsulfonyl)oxylated carbonyl compounds (**6**) were isolated either by crystallization or by column chromatography on silica gel (Merk 40–60 μm) using a 1:1 mixture of Et_2O–petroleum ether (bp 40–60 °C) as eluent.

Reaction with 2-Butanone. The crude reaction mixture was analyzed by ^1H NMR spectroscopy and shown to contain, besides iodobenzene, a mixture of 1-((10-camphorsulfonyl)oxy)-2-butanone (**7**) and 3-((10-camphorsulfonyl)oxy)-2-butanone (**8**). Integration of the protons in the α-position to the sulfonyloxy group at 4.87 ppm (2 H, s) for **7** and 5.13 ppm (1 H, q) for **8** gave a 7:3 ratio of these compounds. The isomer **7** crystallized from the reaction mixture on standing, as colorless crystals, mp 78–80 °C (from MeOH–Et_2O); IR (Nujol) 2950, 1735, 1300, 1220, 1195, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3 H, s), 1.1 (3 H, s), 1.13 (3 H, t), 1.45–3.0 (7 H, m), 2.48 (2 H, q), 3.1–3.7 (2 H, m), 4.87 (2 H, s). Anal. Calcd for $C_{14}H_{22}O_5S$: C, 55.63; H, 7.28. Found: C, 55.55; H, 7.28. The isomer **8** was not isolated pure. Its ^1H NMR spectrum, as obtained from the reaction mixture, gave ($CDCl_3$) δ 0.9 (3 H, s), 1.1 (3 H, s), 1.53 (3 H, d), 1.45–3.0 (7 H, m), 2.28 (3 H, s), 3.1–3.87 (2 H, m), 5.13 (1 H, q).

Reaction with 4-Methyl-2-pentanone. The reaction mixture was treated with Et_2O and the bis–sulfonyl peroxide **10** separated and filtered out. 1-((10-Camphorsulfonyl)oxy)-4-methyl-2-pentanone was isolated by column chromatography as an oil; IR (neat) 2960, 1740, 1580, 1460, 1370, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (9 H, s), 1.1 (3 H, s), 1.2–2.8 (9 H, m), 3.1–3.8 (2 H, m), 4.7 (2 H, s).

Bis(10-camphorsulfonyl) peroxide (10) was obtained as a dihydrate; colorless crystals, mp 192–197 °C (dec) (from CH_2Cl_2/Et_2O); $[\alpha]^{20}_D$ = +35.9° (MeOH); IR (KBr) 3150–2700, 1730, 1595, 1550, 1310, 1270 cm^{-1}; ^1H NMR ($CD_3SOCD_3/CDCl_3$) δ 0.9 (3 H, s), 1.1 (3 H, s), 1.33–2.66 (7 H, m), 2.83–3.7 (2 H, m), 7.83 (4 H, br s, H_2O); MS *m/e* 232 (7), 168 (10), 151 (100), 123 (90), 109 (95). Anal. Calcd for $C_{20}H_{30}O_8S\cdot 2H_2O$: C, 48.18; H, 6.87. Found: C, 48.35; H, 7.20.

An iodometric peroxide determination in CCl_4 with aqueous potassium iodide[30] showed the presence of "active oxygen" in 95% of the theoretical amount.

Electrolysis of (+)-10-Camphorsulfonic Acid. Electrolysis of the acid (2.5 g) in water (10 mL) at 0 °C was carried out with platinum electrodes and a current of 0.5 A at 6 V during 3.5 h. After concentration to dryness, **10** was obtained by trituration with a little CH_3CN, which did not dissolve it; yield 11% (0.3 g).

1-((10-Camphorsulfonyl)oxy)acetone. This ester was isolated by column chromatography as an oil; IR (neat) 2950, 1725, 1340, 1175, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3 H, s), 1.1 (3 H, s), 1.3–3.1 (7 H, m), 3.1–3.8 (2 H, m), 4.9 (2 H, s).

1-((10-Camphorsulfonyl)oxy)-2-cyclohexanone. The reaction mixture was treated with Et_2O and filtered to remove some peroxide formed. The ester precipitated from the filtrate by adding hexane as a white solid, mp 48–50 °C (from Et_2O–hexane); IR (Nujol) 2950, 1740, 1285, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3 H, s), 1.12 (3 H, s), 1.32–2.7 (7 H, m), 3.22–3.92 (3 H, m). Anal. Calcd for $C_{16}H_{24}OS$: C, 58.56; H, 7.31. Found: C, 58.6; H, 7.60.

1-((10-Camphorsulfonyl)oxy)acetophenone was obtained by column chromatography as colorless crystals, mp 60–61 °C (from Et_2O/CH_2Cl_2 9:1); IR (neat) 2940, 1735, 1705, 1590, 1450, 1380, 1220, 1170, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (3 H, s), 1.1 (3 H, s), 1.17–2.67 (7 H, m), 2.68–3.95 (2 H, m), 5.58 (2 H, s), 7.45–8.07 (5 H, m). Anal. Calcd for $C_{18}H_{22}O_5S$: C, 61.59; H, 6.27. Found: C, 61.71; H, 6.28.

3-((10-Camphorsulfonyl)oxy)pentane-2,4-dione crystallized upon addition of Et_2O to the reaction mixture residue as colorless crystals, mp 70–71 °C (from $CHCl_3/Et_2O$); IR (Nujol) 2950, 1740, 1725, 1295, 1195, 1170; ^1H NMR ($CDCl_3$) δ 0.9 (3 H, s), 1.1 (3 H, s), 1.3–2.9 (7 H, m), 2.3 (3 H, s), 3.2–3.9 (2 H, m). Anal. Calcd for $C_{15}H_{22}O_6S$: C, 54.56; H, 6.67. Found: C, 54.92; H, 6.62.

3-((10-Camphorsulfonyl)oxy)-4-phenylbutane-2,4-dione (9). The reaction mixture was analyzed by ^1H NMR spectroscopy and shown to contain a mixture of two diastereoisomers, $\mathbf{9}_1$ and $\mathbf{9}_2$, in a ratio of 3:1, as determined by integration of the methyl protons (see text). Column chromatography provided a colorless oil consisting of a 1:1 mixture of the two diastereoisomers; IR (neat) 2940, 1730, 1680, 1590, 1440, 1350, 1270, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.57 ($\mathbf{9}_2$) and 0.85 ($\mathbf{9}_1$) (3 H, s), 0.85 ($\mathbf{9}_1$) and 1.05 ($\mathbf{9}_2$) (3 H, s), 1.2–2.53 (7 H, m), 2.33 ($\mathbf{9}_1$) and 2.42 ($\mathbf{9}_2$) (3 H, s), 3.03–3.88 (2 H, m), 6.3 (1 H, s), 7.43–8.15 (5 H, m).

Ethyl 2-((10-Camphorsulfonyl)oxy)-2-benzoylacetate. The reaction product is a 1:1 mixture of two idastereoisomers (not separable by column chromatography) as shown by NMR integration of the protons in the α-position to the sulfonyloxy group; IR (neat) 2950, 1735, 1670, 1595, 1455, 1380, 1240, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (3 H, s), 1.1 (3 H, s), 1.23 (3 H, t), 1.63–2.62 (7 H, m), 3.29–3.9 (2 H, m), 4.28 (2 H, q), 6.14 and 6.18 (1 H, s), 7.41–8.0 (5 H, m).

2-((10-Camphorsulfonyl)oxy)-1-phenyl-1-propanone. The reaction product is a 1:1 mixture of two diastereoisomers, inseparable by column chromatography; IR (neat) 2960, 1750, 1705, 1600, 1455, 1360, 1230, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (3 H, s), 1.07 and 1.11 (3 H, s), 1.65 (3 H, d), 1.39–2.46 (7 H, m), 3.11–3.8 (2 H, m), 6.0 (1 H, q), 7.43–8.0 (5 H, m).

2-((10-Camphorsulfonyl)oxy)-3-hydroxy-1,4-naphthoquinone. Crystallized out from a methanolic solution of the reaction mixture as yellow crystals; mp 186–188 °C (from MeOH); IR (Nujol) 3320, 2950, 1745, 1670, 1650, 1590, 1290, 1195, 1170 cm^{-1}; ^1H NMR ($CDCl_3/CD_3SOCD_3$) δ 1.0 (3 H, s), 1.2 (3 H, s), 1.2–2.7 (7 H, m), 3.65–4.3 (2 H, m), 5.7 (1 H, br s), 7.8–8.3 (4 H, m). Anal. Calcd for $C_{20}H_{20}O_7S$: C, 59.40; H, 4.99. Found: C, 59.62; H, 5.09.

3-((10-Camphorsulfonyl)oxy)-4-hydroxy-6-methyl-α-pyrone. Crystallized from a solution of the crude reaction product in $CHCl_3$ as colorless crystals, mp 201–203 °C (from MeOH); IR (Nujol) 3400, 2950, 1745, 1630, 1580, 1540, 1190, 1140 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$) δ 0.9 (3 H, s), 1.1 (3 H, s), 1.4–3 (7 H, m), 2.25 (3 H, s), 3.85 (1 H, br s), 3.85–4.1 (2 H, m), 6.1 (1 H, s). Anal. Calcd for $C_{16}H_{20}O_7S$: C, 53.92; H, 5.66. Found: C, 53.83; H, 5.45.

Diethyl 2-((10-Camphorsulfonyl)oxy)malonate. The reaction mixture was treated with Et_2O to precipitate the peroxide **10**. The ester was obtained as an oil by column chromatography; IR (neat) 2900, 1730, 1370, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (3 H, s), 1.2 (3 H, s), 1.2 (3 H, t), 1.3–2.7 (7 H, m), 3.4–3.9 (2 H, m), 4.3–4.7 (2 H, q), 4.4 (1 H, s).

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