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Oxidatively sonochemical dealkylation of various *N*-alkylsulfonamides to free sulfonamides and aldehydes

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Abstract—Various *N*-alkylsulfonamides were easily dealkylated to give the corresponding free sulfonamides in moderate to good yields in the presence of (diacetoxyiodo)benzene and iodine under ultrasonic irradiation. Application of this methodology to various *N*-protected alkylamines with sulfonyl, phosphonyl, and acyl groups was carried out, and the oxidative conversion occurred only in *N*-sulfonyl-protected phenylalkylamines to give the corresponding aldehydes together with free sulfonamides in moderate to good yields.

1. Introduction

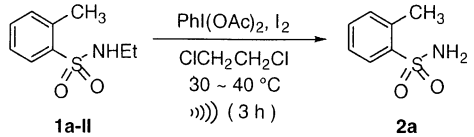
Recently, synthetic application of ultrasonic irradiation has been a focus of interest in organic synthesis.[1] Sometimes this technique leads not only to the simple rate enhancement of chemical reactions, especially in organometallic chemistry, but also to the induction of radical pathways, giving products which are normally not accessible via ionic reactions.[2] Thus, ultrasonic irradiation for organic reactions has become popular to improve yields, to reduce reaction time, and to develop new reactions. On the other hand, extensive study on hypervalent iodine compounds has been carried out and their utilization for organic synthesis has been popularized.[3] Especially, (diacetoxyiodo)benzene has been widely used in organic synthesis in view of its potential utility for oxidation and radical reactions. In spite of these advantages, sonochemical reactions of a (diacetoxyiodo)benzene/iodine system are extremely limited.[4] A part of our study on the synthetic use of sulfonamidyl radicals with (diacetoxyiodo)benzene as a radical precursor,[5] we would like to report on the oxidative dealkylation of various *N*-alkylsulfonamides[6] to give the corresponding aldehydes together with free sulfonamides in moderate to good yields by ultrasonic irradiation in the presence of (diacetoxyiodo)benzene and iodine. Nowadays, the removal of the sulfonyl group (deprotection) in sulfonamides has been well investigated.[7] However, most of these approaches were focused on cleavage of the S–N bond in sulfonamides; meanwhile, study on the C–N bond cleavage of *N*-alkylsulfonamides is scarcely known,[8] though the direct oxidation of amines to carbonyl groups is known,[9] and *N*-dealkylation of trialkylamines to dialkylamines was studied.[10]

2. Results and discussion

2.1. Sonochemical dealkylation of various *N*-alkylsulfonamides

At first, sonication of *N*-ethyl(*o*-methyl)benzenesulfonamide (**1a**-**II**) was studied. The reaction was carried out under various reaction conditions as shown in Table 1. Deethylation of *N*-ethyl(*o*-methyl)benzenesulfonamide proceeds smoothly in 1,2-dichloroethane to give *o*-methylbenzenesulfonamide (**2a**) in 69% yield under ultrasonic irradiation (200 W; 28 kHz) in the presence of

Table 1. Sonochemical deethylation of *N*-ethyl(*o*-methyl)benzenesulfonamide **1a**–**II**



1a-II **2a**

Entry	Equiv.		Yield (%)	Recovery (%)
	$PhI(OAc)_2$	I_2		
1	3.0	1.0	69	0
2	3.0	–	0	98
3	–	1.0	0	96
4	3.0	1.0[a]	0	94
5	3.0	1.0[b]	0	83

[a] THF was used as a solvent.
[b] Br_2 was used instead of I_2.

Keywords: (diacetoxyiodo)arene; *N*-alkylsulfonamide; oxidative dealkylation; ultrasonic irradiation.
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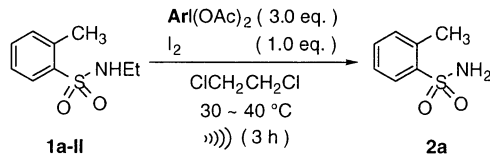
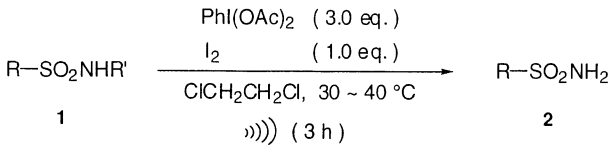
Table 2. Substituent effect of (diacetoxyiodo)arenes

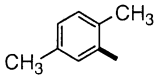
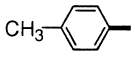
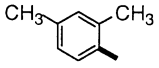
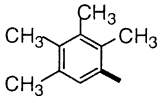
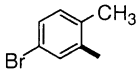
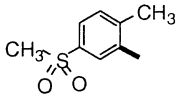
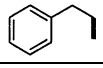


Entry	Ar	Yield (%)
1	CH_3O–	42
2	CH_3–	68
3	H–	69
4	Cl–	60

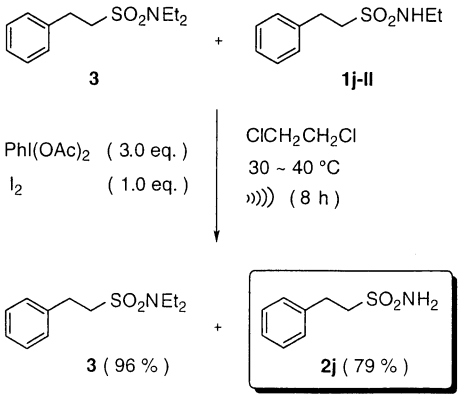
(diacetoxyiodo)benzene (3.0 equiv.) and iodine (1.0 equiv.). *N*-Iodo-*N*-ethyl(*o*-methyl)-benzenesulfonamide was quantitatively obtained by the reaction of *N*-ethyl(*o*-methyl)-benzenesulfonamide, (diacetoxyiodo)benzene and iodine without ultrasonic irradiation. The reaction does not proceed at all with (diacetoxyiodo)benzene or iodine alone, and with (diacetoxyiodo)benzene and bromine instead of iodine, under ultrasonic irradiation. Moreover, a tetrahydrofuran or ethanol solvent inhibits the present deethylation completely, due to the hydrogen-atom abstraction from the solvent by the formed sulfonamidyl radical. Use of [bis(trifluoroacetoxy)iodo]benzene instead of (diacetoxyiodo)-benzene under the same conditions does not induce the deethylation, and a wet 1,2-dichloroethane solvent (including 1% v/v H_2O) instead of dry 1,2-dichloroethane also does not give rise to deethylation. In these systems, the starting amide **1a-II** was recovered.

Table 3. Sonochemical dealkylation of various *N*-alkysulfonamide **1**



Entry	R-	R′	**1**	**2**/Yield (%)	
1		$-CH_3$	**1a-I**	0	**2a**
2		$-CH_2CH_3$	**1a-II**	69	
3		$-CH_2CH_3$	**1b-II**	63	**2b**
4		$-CH_2CH_2CH_3$	**1b-III**	54	
5		$-CH_2(CH_2)_2CH_3$	**1b-IV**	43	
6		$-CH_3$	**1c-I**	0	**2c**
7		$-CH_2CH_3$	**1c-II**	50[a]	
8		$-CH_2CH_3$	**1d-II**	66	**2d**
9		$-CH_2CH_3$	**1e-II**	40	**2e**
10		$-CH_2CH_3$	**1f-II**	51[a]	**2f**
11		$-CH_2CH_3$	**1g-II**	0	
12		$-CH_2CH_3$	**1h-II**	71	**2h**
13		$-CH_2CH_3$	**1i-II**	69	**2i**
14		$-CH_2CH_3$	**1j-II**	81	**2j**

[a] Irradiated for 6 h.



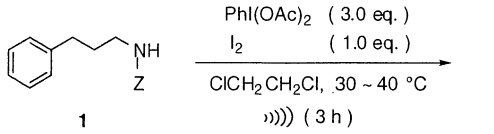
Scheme 1. Selective removal of the *N*-ethyl group.

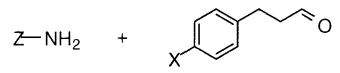
The substituent effect of (diacetoxyiodo)arenes for the present deethylation was examined as shown in Table 2. (Diacetoxyiodo)benzene showed the best reactivity and gave the compound **2a** in 69% yield, though there is no big difference among (diacetoxyiodo)benzene, (diacetoxyiodo)-*p*-toluene, and (diacetoxyiodo)-*p*-chlorobenzene, and (diacetoxyiodo)-*p*-methoxybenzene was less effective. Probably, this difference comes from the fact that iodine is consumed through the iodination of the formed *p*-iodoanisole by an acetylhypoiodite species derived from the (diacetoxyiodo)-*p*-methoxybenzene/iodine system.[11]

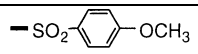
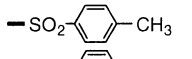
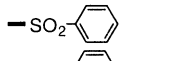
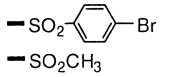
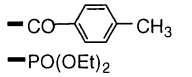
Various *N*-alkylarenesulfonamides and *N*-alkylalkanesulfonamides were used as substrates as shown in Table 3. Here, *N*-ethyl, *N*-propyl and *N*-butylsulfonamides were dealkylated in moderate to good yields (entries 1–7); especially, the *N*-ethyl group shows the best reactivity. Demethylation of *N*-methylsulfonamide does not proceed at all, and the starting material was recovered in 93% yield (entry 1). In addition, dealkylation of *N*,*N*-dimethyl-, *N*,*N*-diethyl-, *N*-isopropyl-, *N*-*tert*-butylsulfonamides and *N*-ethylbenzamide did not occur. Moreover, deethylation of *N*-ethylarenesulfonamides bearing an electron-withdrawing group such as a methanesulfonyl (entry 11), nitro, and *N*,*N*-diethylaminocarbonyl groups on the aromatic ring, did not proceed. In these reactions, the starting amides were recovered. So the present dealkylation reaction is significantly affected by both steric effects and electronic effects.

The selective removal of the *N*-ethyl group was studied as shown in Scheme 1. When a mixture of *N*,*N*-diethyl-2-phenylethanesulfonamide **3** and *N*-ethyl-2-phenylethanesulfonamide **1j-II** was treated with (diacetoxyiodo)benzene and iodine under irradiation with an ultrasonic cleaning bath, only sulfonamide **1j-II** was dealkylated to give the corresponding dealkylated sulfonamide **2j** in 79% yield,

Table 4. Oxidative deamination of various *N*-protected 3-phenyl-1-propylamines **1** (Z=protecting group)





Entry	–Z	1	Yields (%)	
			2	4-V (A/B)
1		1k-V	76	64 (50/14)
2		1c-V	70	72 (61/11)
3		1h-V	74	91 (76/15)
4		1l-V	74	90 (65/25)
5	$-SO_2CH_3$	1m-V	66	63 (24/39)
6		5	0[a]	0
7	$-PO(OEt)_2$	6	0[a]	0

[a] Starting material was recovered in 94% yield.

together with the complete recovery of sulfonamide **3** (96%).

2.2. Oxidative deamination of various *N*-protected phenylalkylamines

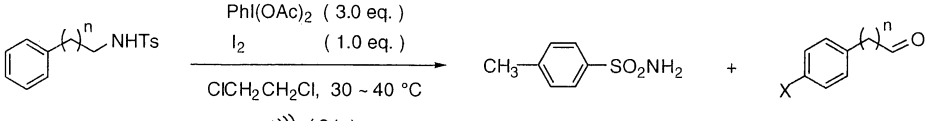
Now, what is the side product in the sonochemical dealkylation of *N*-alkylsulfonamides? As an extension of the present *N*-deethylation methodology, reactivity of various *N*-protected 3-phenyl-1-propylamines **1** was studied as shown in Table 4. Here, the reaction proceeds effectively to give 3-phenylpropionaldehyde **4-V-A** and its *p*-iodinated aldehyde **4-V-B** together with dealkylated sulfonamide **2**. *p*-Iodinated aldehyde was formed by the iodination of the starting sulfonamide **1** or the aldehyde **4-V-A** through the ionic pathway with an acetylhypoiodite species generated from (diacetoxyiodo)benzene and iodine.[11] Thus, aldehydes are the side product in the present sonochemical dealkylation of sulfonamides. When the amides were protected by a diethyl phosphate or *p*-methylbenzoyl group, the corresponding aldehydes were not formed and both starting amides were recovered in 94% yields, respectively (entries 6 and 7). The addition of potassium carbonate (1.0 equiv.), did not accelerate the reactions.

Next, we worked on changing the number of methylene units of the starting alkylamines. Various *N*-tosylamines bearing an aromatic ring at the α-, β-, γ-, and δ-positions, respectively, were treated under similar sonochemical conditions. The results are summarized in Table 5. Here, in entries 3 and 4, oxidative deamination occurred efficiently to give *p*-toluenesulfonamide **2c** and aldehydes **4** in good yields. In addition, in entry 4, the Hofmann–Löffler–Freytag type reaction partly occurred to form *N*-tosyl-2-phenylpyrrolidine as a by-product in 19% yield, through cyclization of the formed sulfonamidyl radical. *N*-Tosybenzylamine did not react efficiently (entry 1), and the starting sulfonamide was recovered in 18% yield in spite of increasing the irradiation time. In entry 2, the reaction proceeded efficiently; however, the phenethyl group may react further to give a complicated reaction mixture via the formation of phenylacetaldehyde, together with toluenesulfonamide in 72% yield (Table 5).

To optimize the reaction conditions, the effects of output and frequency in the ultrasonic device were also studied (Table 6). Here, as the frequency was elevated, the yield of sulfonamide **2c** decreased and the recovery yield of the starting material was increased. Thus, as general reaction conditions, high output and low frequency of the ultrasonic device were effective for this reaction (entry 4).

Based on these results, a reasonable reaction pathway of the present reaction is shown in Scheme 2. Here, the formation of the *N*-iodinated compound under dark conditions and the formation of an unstable imino compound after ultrasonic irradiation were observed by ^1H NMR measurements. Moreover, the addition of a galvinoxyl free radical (1.0 equiv.) inhibited this reaction completely. Thus, the present reaction proceeds through the oxidative β-hydrogen elimination of the formed sulfonamidyl radical to give an

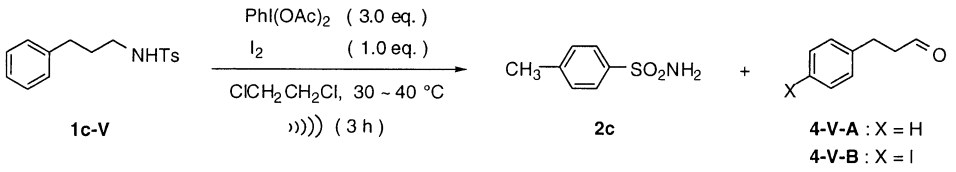
Table 5. Oxidative deamination of various *N*-tosylphenylalkylamines



Entry	*n*	1	Yields (%)		Recovery (%)
			2c	4 (A/B)	
1	0	1c-VI	45[a]	Trace	18
2	1	1c-VII	72	Trace	0
3	2	1c-V	70	73 (61/11)	0
4	3	1c-VIII	71[b]	56 (33/23)	0

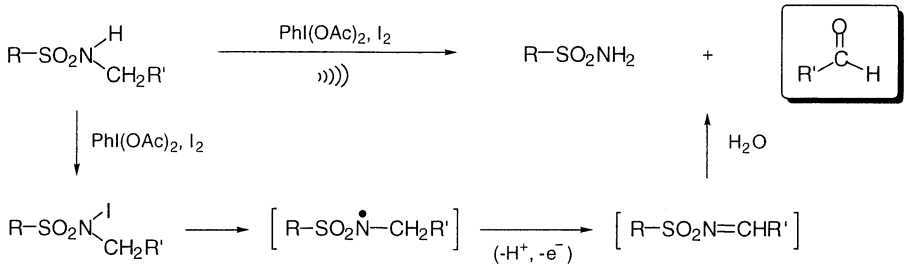
[a] Irradiated for 6 h.
[b] *N*-Tosyl-2-phenylpyrrolidine was obtained in 19%.

Table 6. Effects of output and frequency of ultrasonic device



1c-V 2c 4-V-A : X = H 4-V-B : X = I

Entry	Output (W)	Frequency (kHz)	Yields (%)		Recovery (%)
			2c	**4-V (A/B)**	
1	100	28	64	63 (52/11)	0
2	100	45	53	42 (38/4)	32
3	100	100	33	24 (21/3)	65
4	200	28	70	72 (61/11)	0



Scheme 2. Plausible reaction mechanism.

imino derivative. The dealkylated sulfonamide and aldehyde come from the hydrolysis of the corresponding imino compound. Hence, *N*-demethylation probably did not occur at all due to the slightly stronger C–H bond in the *N*-methyl group than that in the *N*-ethyl group.

In conclusion, novel and efficient sonochemical dealkylation of various *N*-alkylsulfonamides and oxidative deamination of various *N*-protected alkylamines were studied. Ultrasound promises to be a new and powerful technique in hypervalent iodine chemistry. To the best of our knowledge, this type of dealkylation of sulfonamides to form free sulfonamides and aldehyde has not hitherto been reported. A similar conversion from an amino group to aldehyde is known in vitamin B_6 using pyridoxal. Thus, the establishment and application of this methodology in the bioorganic field is also interesting.

3. Experimental

3.1. General methods

^{1}H NMR Spectra were recorded on 400 MHz spectrometer. Chemical shifts are reported as ppm downfield from tetramethylsilane (TMS) in δ units. J values are given in Hz. Mass spectra were measured with QMS (EI), and high-resolution mass spectra (HRMS) were measured with a 110A mass spectrometer. Silica gel C-200 was used for column chromatography, Kieselgel 60 F 254 (Merck) was used for TLC, and Wakogel B-5F was used for preparative thin-layer chromatography (p-TLC). Sonication was performed with Tokyo Rika Kikai AC-70 CO (200 W; 28 kHz) or HONDA W-113 (100 W; 28, 45 and 100 kHz) ultrasonic cleaning device.

3.2. Materials

(Diacetoxyiodo)benzene and [bis(trifluoroacetoxy)iodo]-benzene are commercially available. The other (diacetoxyiodo)arenes were prepared by the oxidation of the corresponding iodoarenes based on the literature method.[12] Most *N*-alkylsulfonamides were easily prepared by the reaction of sulfonyl chlorides and alkylamines.[13] *o*-Toluenesulfonamide, *p*-toluenesulfonamide, benzenesulfonamide, methanesulfonamide and 3-phenylpropionaldehyde were identified with commercially available compounds.

3.3. General procedure—oxidative deamination of various *N*-alkylsulfonamides

(Diacetoxyiodo)benzene (1.5 mmol) and iodine (0.5 mmol) were added to a solution of *N*-alkylsulfonamide (0.5 mmol) in 1,2-dichloroethane (7 ml). The mixture was stirred preliminarily for 10 min. under dark conditions, and then irradiated with an ultrasonic cleaning bath (200 W; 28 kHz or 100 W; 28, 45, and 100 kHz) for an appropriate time under an argon atmosphere in the range of 30–40°C. After the reaction, the mixture was poured into ethyl acetate and washed with aq. sodium sulfite (Na_2SO_3) solution and subsequently with water. The organic layer was dried over sodium sulfate (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel by preparative thin-layer chromatography using a mixture of hexane and ethyl acetate (3:1–5:1) as an eluent.

3.3.1. 2,5-Dimethylbenzenesulfonamide (2b). Mp 142.5–143.5°C (lit.[14] 145.5–146.5°C); IR (KBr) 3350, 3255, 1290, 1140 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.64 (s, 3H), 4.75 (bs, 2H), 7.20 (d, J=7.7 Hz, 2H), 7.27 (d, J=8.6 Hz, 1H), 7.84 (s, 1H); MS (EI) found M^+=185.

3.3.2. 2,4-Dimethylbenzenesulfonamide (2d). Mp 135.5–136.5°C (lit.[14] 136.5–137.0°C); IR (KBr) 3365, 3260, 1320, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.64 (s, 3H), 4.89 (bs, 2H), 7.10 (d, J=8.0 Hz, 2H), 7.13 (s, 1H), 7.87 (d, J=8.0 Hz, 1H); MS (EI) found M^+=185.

3.3.3. 2,3,4,5-Tetramethylbenzenesulfonamide (2e). Mp 180.0–181.5°C (lit.[14] 183.5–184.0°C); IR (KBr) 3300, 3240, 1295, 1155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.26 (s, 3H), 2.31 (s, 3H), 2.59 (s, 3H), 4.77 (bs, 2H), 7.72 (s, 1H); MS (EI) found M^+=213.

3.3.4. 5-Bromo-2-methylbenzenesulfonamide (2f). Mp 163.0–164.5°C (lit.[15] 164.0–165.0°C); IR (KBr) 3400, 3295, 1295, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 4.92 (bs, 2H), 7.21 (d, J=8.0 Hz, 1H), 7.58 (dd, J=8.2, 2.2 Hz, 1H), 8.15 (d, J=2.2 Hz, 1H); MS (EI) found M^+=249, 251.

3.3.5. Benzylsulfonamide (2i). Mp 98.5–100.0°C (lit.[16] 101.0–102.0°C); IR (KBr) 3380, 3320, 1325, 1125 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.30 (s, 2H), 4.72 (bs, 2H), 7.37–7.44 (m, 5H); MS (EI) found M^+=171.

3.3.6. Phenylethanesulfonamide (2j). Mp 114.0–115.5°C; IR (KBr) 3360, 3250, 1310, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.14–3.18 (m, 2H), 3.39–3.43 (m, 2H), 4.85 (bs, 2H), 7.21–7.27 (m, 3H), 7.30–7.35 (m, 2H); MS (EI) found M^+=185.

3.3.7. 4-Methoxybenzenesulfonamide (2k). Mp 107.5–109.0°C (lit.[17] 109.0°C); IR (KBr) 3350, 3260, 1330, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 4.96 (bs, 2H), 6.98 (d, J=9.2 Hz, 2H), 7.86 (d, J=8.9 Hz, 2H); MS (EI) found M^+=187.

3.3.8. 4-Bromobenzenesulfonamide (2l). Mp 158.5–159.5°C (lit.[17] 162.0°C); IR (KBr) 3330, 3240, 1330, 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.93 (bs, 2H), 7.67 (d, J=8.7 Hz, 2H), 7.80 (d, J=8.7 Hz, 2H); MS (EI) found M^+=235, 237.

3.3.9. 3-(4-Iodophenyl)propionaldehyde (4-V-B). Oil; IR (neat) 2925, 2855, 1720, 1590, 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.75 (td, J_1=7.3, J_2=1.2 Hz, 3H), 2.89 (t, J=7.3 Hz, 2H), 6.94 (d, J=8.5 Hz, 2H), 7.60 (d, J=8.5 Hz, 2H), 9.79 (t, J=1.2 Hz, 1H); HRMS (EI) found M^+=259.9687, calcd for C_9H_9OI M=259.9698.

3.3.10. 4-Phenylbutyraldehyde (4-VIII-A). Oil; IR (neat) 2930, 2860, 1720, 1605, 1495 cm^{-1}; ^1H NMR[18] (400 MHz, $CDCl_3$) δ 1.97 (quint., J=7.3 Hz, 2H), 2.46 (td, J_1=7.3, J_2=1.5 Hz, 2H), 2.66 (t, J=7.6 Hz, 2H), 7.17–7.31 (m, 5H), 9.76 (t, J=1.6 Hz, 1H); HRMS (EI) found M^+= 148.0891, calcd for $C_{10}H_{12}O$ M=148.0888.

3.3.11. 4-(4-Iodophenyl)butyraldehyde (4-VIII-B). Oil; IR (neat) 2925, 2855, 1720, 1595, 1485 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.93 (quint., J=7.5 Hz, 2H), 2.45 (td, J_1=7.3 Hz, J_2=1.5 Hz, 2H), 2.60 (td, J_1=8.0, J_2= 1.5 Hz, 2H), 6.93 (d, J=8.5 Hz, 2H), 7.61 (d, J=8.2 Hz, 2H), 9.76 (t, J=1.6 Hz, 1H); HRMS (EI) found M^+= 273.9866, calcd for $C_{10}H_{11}OI$ M=273.9855.

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