New Route to Esters from 2-Substituted 1,3-Benzoxathiolium Tetrafluoroborates. An Effective Protection of Esters against Nucleophilic Attack[1]

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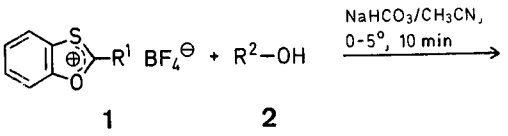
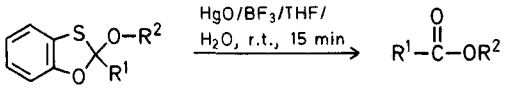
In previous works we have shown the synthetic effectiveness of 1,3-benzoxathiolium salts as masked acylating agents[2-6].

Hitherto, these salts – readily obtainable from carboxylic acids[3,4,7], acyl halides[5], anhydrides[8], esters[8], ortho esters[8], tri-[8] and di-halomethyl derivatives[7], and aldehydes[7] – have been utilized in the synthesis of aldehydes[2,3,6], aldehydes-1-d[3], and ketones[2,4].

We now wish to report an additional synthetic application of 2-substituted 1,3-benzoxathiolium tetrafluoroborates **1** to prepare esters **4**.



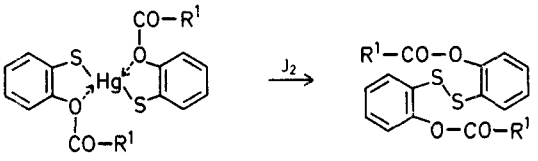
1 **2**



3 **4**

The reactions of tetrafluoroborates **1** with 2 equivalents of alcohols **2** generally furnished good yields of 2-alkoxy-2-alkyl(or aryl)-benzoxathioles **3** (Table 1). However, with *sec*-alcohols the yields were improved by using a larger excess of **2**. Under similar conditions, the reactions with *t*-butyl alcohol failed, but the corresponding adducts **3** could be otherwise achieved by addition of **1** to potassium *t*-butoxide in diglyme.

The following hydrolysis of **3** readily gave esters **4** in excellent yields (Table 2). Only hindered 2-*t*-butoxy-1,3-benzoxathioles reacted in a different way to give the organomercury compounds **5a, b**, which in accord with the assigned structures afforded disulfides **6a, b** on oxidation with iodine.



5a $R^1 = C_6H_5$
b $R^1 = t\text{-}C_4H_9$

6a, b

The stability of benzoxathioles **3** to nucleophilic attack was tested on the compounds **3a** and **3h**. The former was stable to potassium hydroxide (1.5 eq.) in aqueous methanol at room temperature for 12 h. The latter, however, on reaction with lithium aluminium hydride or methylmagnesium iodide, respectively, gave benzoxathioles **3s** or **3t**, which could be converted to corresponding esters **4s** and **4t** by hydrolysis under the general conditions.

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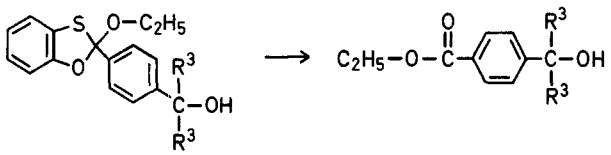

3 s R^3 = H
t R^3 = CH_3

4 s, t

Therefore, benzoxathioles **3** – which constitute a particular class of thioortho esters – are masked esters from which the protecting group can be easily removed without loss of the alkoxy group. While in the past the problem of ester protection has been resolved only in the case of cyclic esters (lactones)[9], the above procedure, besides representing a new route to esters, offers the first example of an effective protection of open esters against nucleophilic attack.

Table 1. Preparation of 2-Alkoxy-2-alkyl(or aryl)-1,3-benzoxathioles **3a–r**

Entry	Product	Starting Materials R^1 in **1**	R^2 in **2**	Yield [%]	b.p./torr or m.p. (solvent)	n_D^{20}	Molecular formula[a]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
1	**3a**	C_6H_5	C_2H_5	97	127–128°/0.01[b]	1.6030		1.22 (t, CH_3, J = 7 Hz); 3.32–4.1 (m, CH 6.7–7.85 (m, 9 H_{arom})
2	**3b**	C_6H_5	n-C_8H_{17}	88[c]	179–180°/0.01	1.5597	$C_{21}H_{26}O_2S$ (342.5)	0.65–1.9 (m, CH_2—C_7H_{15}); 3.35–4.0 (CH_2—C_7H_{15}); 6.7–7.9 (m, 9 H_{arom})
3	**3c**	C_6H_5	i-C_3H_7	78	123°/0.01	1.5895	$C_{16}H_{16}O_2S$ (272.4)	1.25 and 1.3 (2 d, t-C_4H_9, J = 6 Hz); 3.88– (hept., CH); 6.7–7.88 (m, 9 H_{arom})
4				92[d]				
5	**3d**	C_6H_5	t-C_4H_9[e]	70	87–88° (CH_3OH)	—	$C_{17}H_{18}O_2S$ (286.4)	1.28 (s, t-C_4H_9); 6.8–7.9 (m, 9 H_{arom})
6	**3e**	4-H_3C—C_6H_4	C_2H_5	97	61–62° (C_2H_5OH)	—	$C_{16}H_{16}O_2S$ (272.4)	1.22 (t, CH_2—CH_3, J = 7 Hz); 2.3 (s, CH 3.32–4.1 (m, CH_2); 6.65–7.35 (m, 4 H_{ben} 7.18 and 7.6 (2 pd, 4 H_{phenyl}, J = 8 Hz)
7	**3f**	4-H_3CO—C_6H_4	C_2H_5	89	64–65° (C_2H_5OH)	—	$C_{16}H_{16}O_3S$ (288.4)	1.25 (t, CH_3, J = 7 Hz); 3.45–4.12 (m, CH 3.77 (s, OCH_3); 6.75–7.35 (m, 4 H_{benzo}); 6 and 7.62 (2 pd, 4 H_{phenyl}, J = 8.5 Hz)
8	**3g**	4-Cl—C_6H_4	C_2H_5	92	140–142°/0.02	1.6076	$C_{15}H_{13}ClO_2S$ (292.8)	1.21 (t, CH_3, J = 7 Hz); 3.32–4.1 (m, CH 6.75–7.25 (m, 4 H_{benzo}); 7.3 and 7.6 (2 4 H_{phenyl}, J = 8 Hz)
9	**3h**	4-H_5C_2COO—C_6H_4	C_2H_5	95	183°/0.05	1.5848	$C_{18}H_{18}O_4S$ (330.4)	1.27 and 1.38 (2 t, 2 CH_3, J = 7 Hz); 3.3 4.15 (m, CH_2—CH_3); 4.2–4.57 $COOCH_2$—CH_3, J = 7 Hz); 6.95–7.32 (4 H_{benzo}); 7.73 and 8.12 (2 pd, 4 H_{phe} J = 8.5 Hz)
10	**3i**	n-C_5H_{11}	C_2H_5	90	104°/0.005	1.5288	$C_{14}H_{20}O_2S$ (252.4)	0.65–1.95 (m, CH_2—CH_3 and CH_2 C_4H_9); 2.0–2.45 (m, CH_2—C_4H_9); 3.2–3 (m, CH_2—CH_3); 6.65–7.25 (m, 4 H_{arom})
11	**3j**	n-C_5H_{11}	i-C_3H_7	66	100°/0.01	1.5212	$C_{15}H_{22}O_2S$ (266.4)	0.7–1.9 (m, CH_2—C_4H_9); 1.13 and 1.18 (
12				89[d]				i-C_3H_7, J = 6 Hz); 1.9–2.4 (m, CH_2 C_4H_9); 3.78–4.4 (hept., CH); 6.7–7.3 4 H_{arom})
13	**3k**	n-C_5H_{11}	C_6H_{13}—$CH(CH_3)$	64[c]	124–125°/0.01	1.5085	$C_{20}H_{32}O_2S$ (336.5)	0.6–1.9 (m, CH_3—CH—C_6H_{13} and CH_2 C_4H_9); 1.9–2.4 (m, CH_2—C_4H_9); 3.7–4 (m, CH); 6.68–7.23 (m, 4 H_{arom})
14				90[c, d]				
15	**3l**	i-C_3H_7	n-C_4H_9	93	90°/0.01	1.5263	$C_{14}H_{20}O_2S$ (252.4)	0.75–1.85 (m, CH_2—C_3H_7); 1.07 and 1 [2 d, $CH(CH_3)_2$, J = 6.5 Hz]; 2.1–2.8 (he CH); 3.25–3.88 (m, CH_2—C_3H_7); 6.7– (m, 4 H_{arom})
16	**3m**	t-C_4H_9	n-C_4H_9	93	97°/0.01	1.5222	$C_{15}H_{22}O_2S$ (266.4)	0.7–1.8 (m, CH_2—C_3H_7); 1.13 (s, t-C_4H 3.2–3.88 (m, CH_2—C_3H_7); 6.65–7.25 4 H_{arom})
17	**3n**	t-C_4H_9	i-C_3H_7	84	67.5–69°	—	$C_{14}H_{20}O_2S$ (252.4)	1.05–1.2 (m, i-C_3H_7); 1.1 (s, t-C_4H_9); 3.6
18				98[d]	(C_2H_5OH)			4.3 (hept., CH); 6.65–7.25 (m, 4 H_{arom})
19	**3o**	t-C_4H_9	C_2H_5—$CH(CH_3)$	83	38–39°	—	$C_{15}H_{22}O_2S$ (266.4)	0.68–1.80 (m, CH_3—CH—C_2H_5); 1.12
20				97[d]	(CH_3OH)			t-C_4H_9); 3.58–4.03 (m, CH); 6.65–7.35 4 H_{arom})
21	**3p**	t-C_4H_9	t-C_4H_9[e]	70	63–64° (CH_3OH)	—	$C_{15}H_{22}O_2S$ (266.4)	1.07 and 1.32 (2 s, 2 t-C_4H_9); 6.72–7 (m, 4 H_{arom})
22	**3q**	C_6H_5—CH_2	C_2H_5	84	133–134°/0.01	1.5922	$C_{16}H_{16}O_2S$ (272.4)	1.13 (t, CH_3, J = 7 Hz); 3.22–3.88 (m, CH_2 CH_3), 3.48 (s, CH_2); 6.58–7.5 (m, 9 H_{ar}
23	**3r**	C_6H_5—CH=CH	C_2H_5	88	138°/0.02	1.6186	$C_{17}H_{16}O_2S$ (284.4)	1.22 (t, CH_3, J = 7 Hz); 3.35–4.0 (m, CH 6.52 and 7.0 (AB System, CH=C J = 16 Hz); 6.78–7.50 (m, 9 H_{arom})

[a] The microanalyses are in good accord with the calculated values.
[b] Lit.[2] b.p. 151–152°/0.8 torr.
[c] The excess of reactive **2** is eliminated by filtration through a short column of silica gel, using petroleum ether as eluent; in entry 14, before the filtration, the major amount of alcohol is distilled under vacuo.
[d] An excess of alcohol is used (20 ml for 20 mmol of tetrafluoroborate
[e] Potassium t-butoxide is used instead of t-butyl alcohol.

Table 2. Overall Yields of **4** from **1** and Physical Properties of **4**

Entry	Compound	Yield[a] [%]	b.p./torr or m.p. (solvent)	Lit. b.p./torr or Lit. m.p.	n_D^{20}	Lit. n_D^{20}	Reference
1	**4a**	90	211°/760	213.5°/775	1.5050	1.50519	10
2	**4b**	82	189°/32	163°/9	1.4902	1.4896	11
3	**4c**	60	108°/20	85°/9	1.4940	1.4941	11
4	**4c**	81	108°/20		1.4940		
5	**4d**	—					
6	**4e**	95	124°/25	122°/22	1.5085	1.50888 at 18.2°	12
7	**4f**	80	150°/23	104.2°/2	1.5254	1.5254	13
8	**4g**	89	127°/23	235–236°/760	1.5246	1.5240	14
9	**4h**	95	44° (CH_3OH)	44°			15
10	**4i**	80	166°/760	165.5°/785	1.4076	1.40785 at 19.5°	16
11	**4j**	56	168°/760	161°/754	1.4072	1.4073	17
12	**4j**	80	168°/760		1.4072		
13	**4k**	60	170–171°/60	133°/10	1.4275	1.4272	18
14	**4k**	80	170–171°/60		1.4275		
15	**4l**	91[b]	155°/760	154–155°/760	1.4032	1.4032	19
16	**4m**	81	161°/760	163°/760	1.4047	1.4040	20
17	**4n**	60	126–127°/760	126°/760	1.3902	1.3902	21
18	**4n**	77	126–127°/760		1.3902		
19	**4o**[c,d]	60	147–149°/760		1.3978		22
20	**4o**[c,d]	75	147–149°/760		1.3978		
21	**4p**	—					
22	**4q**	75	118°/25	228°/760	1.4973	1.49734	10
23	**4r**	72	146°/22	127°/6	1.5600	1.55983	23
	4s[e]	58[f]	148°/0.7	161–163°/5	1.5294		24
	4t[c,g]	89[h]	113°/0.02		1.5200		

[a] The reported overall yields of **4** (based on **1**) are of pure distilled product.
[b] The pure ester is obtained by distillation through a Spaltrohr Column (Fisher).
[c] Satisfactory microanalyses (C, ±0.18; H ±0.17).
[d] ^{1}H-N.M.R. ($CDCl_3$): $\delta = 0.7$–1.95 (m, CH_2—CH_3); 1.15 (d, CH—CH_3, $J = 6$ Hz); 1.18 (s, t-C_4H_9); 4.55–5.15 ppm (m, CH).
[e] ^{1}H-N.M.R. ($CDCl_3$): $\delta = 1.37$ (t, CH_3, $J = 7$ Hz); 4.0 (s, OH; disappeared on addition of D_2O); 4.35 (q, CH_2—CH_3, $J = 7$ Hz) 4.67 (s, CH_2—OH); 7.38 and 7.98 ppm (2 pd, $4H_{phenyl}$, $J = 8$ Hz).
[f] Starting from **3s**.
[g] ^{1}H-N.M.R. ($CDCl_3$): $\delta = 1.33$ (t, CH_2—CH_3, $J = 7$ Hz); 1.57 (s, t-C_4H_9); 3.38 (s, OH; disappeared on addition of D_2O); 4.35 (q CH_2—CH_2, $J = 7$ Hz); 7.57 and 8.02 ppm (2 pd, $4H_{phenyl}$, $J = 8$ Hz).
[h] Starting from **3t**.

All esters **4a–t** were identified by N.M.R. and I.R. spectra and, in some cases, by comparison of b.p. or m.p., N.M.R., I.R., n_D data and G.L.C. retention times with those of authentic samples of analytical purity.

As previously reported[5], 2-aryl- and 2-t-butyl-1,3-benzoxathiolium tetrafluoroborates were prepared starting from o-mercaptophenol[25] (1.26 g, 10 mmol) and the appropriate acyl chloride (10 mmol) in tetrafluoroboric acid (54% in ether; 5 ml). Also 2-pentyl-, 2-isopropyl-, 2-benzyl-, and 2-styryl-1,3-benzoxathiolium tetrafluoroborates were prepared in the same way (Table 3). All the salts were directly used in the following step, without purification.

2-Alkoxy-2-alkyl(or aryl)-1,3-benzoxathioles (3a–c, e–o, q, r); General Procedure:

The alcohol **2** (40 mmol) and then sodium hydrogen carbonate (5.04 g, 60 mmol) are added under stirring to a cooled (ice-bath) solution of 2-substituted 1,3-benzoxathiolium tetrafluoroborate **1** (20 mmol) in acetonitrile (dried on phosphorus pentoxide; 50–80 ml). The reaction is immediate and the solution changes from yellow to colourless. The mixture is stirred for 5–10 min, poured into water, and extracted with ether, which is washed with sodium hydroxide solution (5%) and several times with water. After drying, the ether is removed to yield 2-alkoxy-1,3-benzoxathioles **3** (Table 1). Unless otherwise noted, **3** are pure (T.L.C. and ^{1}H-N.M.R.) and are directly used in the following step.

2-t-Butoxy-2-phenyl(or t-butyl)-1,3-benzoxathioles (3d, p); General Procedure:

2-Substituted 1,3-benzoxathiolium tetrafluoroborate **1** (20 mmol) is added in one portion to a suspension of potassium t-butoxide (11.22 g, 100 mmol) in diglyme (100 ml) under vigorous stirring and cooling with an ice-bath. The mixture is stirred for 15 min and then poured into water and extracted with ether, which is washed several times with water, then with sodium hydroxide solution (5%) and again with water. The residue obtained after evaporation of the solvent is purified by washing with cold methanol (3 ml) (Table 1).

Hydrolysis of 2-Alkoxy-2-alkyl(or aryl)-1,3-benzoxathioles 3 to Esters 4; General Procedure:

Boron trifluoride etherate (45% in ether; 4 ml) is added at room temperature to a suspension of red mercury(II) oxide (4.33 g, 20 mmol) in 15% aqueous tetrahydrofuran (60 ml). 2-Alkoxy-1,3-benzoxathiole **3** (20 mmol) is dissolved in the minimum of tetrahydrofuran (3–5 ml) and then is added, in one portion, to the reaction mixture, under stirring. The reaction is weakly exothermic and the mercury(II) oxide gradually dissolves in the course of 5 min. Stirring is maintained for 10 min, until the solution changes from yellow to orange and then ruby. The solution is diluted with petroleum ether (entries 1–14, 21–23; 100 ml) or pentane (entries 15–20; 100 ml), the organic layer is decanted, and the precipitated material is extracted, under vigorous stirring, with three 50 ml

Table 3. 2-Pentyl-, 2-Isopropyl-, 2-Benzyl- and 2-Styryl-1,3-benzoxathiolium Tetrafluoroborates **1**

Compound **1** R^1	Yield [%]	m.p.[a]	Molecular formula[b]	^{1}H-N.M.R. (CF_3COOD) δ [ppm]
n-C_5H_{11}[c]	88	82–84°	$C_{12}H_{15}BF_4OS$ (294.1)	0.75–1.25, 1.25–1.95 and 1.95–2.55 (3m, 3:4:2, CH_2—C_4H_9); 3.82 (t, CH_2—C_4H_9, J = 7 Hz); 7.88–8.55 (m, $4H_{arom}$)
i-C_3H_7[c]	88	73–75°	$C_{10}H_{11}BF_4OS$ (266.1)	1.82 [d, $CH(CH_3)_2$, J = 7.5 Hz]; 3.70–4.35 (hept., CH); 7.9–8.55 (m, $4H_{arom}$)
C_6H_5—CH_2[c]	87	92–94°	$C_{14}H_{11}BF_4OS$ (314.1)	7.58 (s, C_6H_5); 7.82–8.45 (m, CH_2 and $4H_{arom}$)
C_6H_5—CH=CH	83	135–137°	$C_{15}H_{11}BF_4OS$ (326.1)	7.3–8.4 (m, CH=CH—C_6H_5 and $4H_{benzo}$); 8.74 (d, CH=CH, J = 16 Hz)[d]

[a] Analytical samples recrystallized from acetonitrile/ether and a few drops of tetrafluoroboric acid; the melting points depend on the speed of heating and are always preceeded by decomposition.
[b] All compounds gave satisfactory microanalyses (C, ±0.22; H, ±0.18; S, ±0.21).
[c] These remain stable only if protected from the atmospheric moisture.
[d] Identical to that of the corresponding perchlorate[3].

portions of the same solvent. The combined extracts are washed successively with 10% potassium iodide, 5% sodium hydroxide and water, dried, and evaporated under vacuo by heating up to 70° (entries 1–14, 21–23) or 40–45° (entries 15–20), to afford esters **4**. The crude esters are generally pure (T.L.C. and N.M.R.); the reported overall yields are of distilled product (Table 2).

Hydrolysis of 2-*t*-Butoxy-2-phenyl(or *t*-butyl)-1,3-benzoxathioles (3d, p) to Organomercury(II) Compounds 5a, b and Oxidation of these to Disulfides 6a, b:

When R^2 in **3** is a *t*-butyl group, in the conditions reported above, a brown suspension is obtained after 2 h stirring at room temperature. After this time the reaction mixture is worked up as indicated above to afford **5a, b** in 71 or 75% yield, respectively (benzene is used for extraction of **5a**).

5a (R^1 = C_6H_5); m.p. 132–133° from acetone/ethanol.

$C_{26}H_{18}HgO_4S_2$	calc.	C 47.38	H 2.75	Hg 30.43
(659.2)	found	47.30	2.80	30.51[27]

^{1}H-N.M.R. ($CDCl_3$): δ = 6.95–7.8, 8.0–8.25 ppm (2m, 7:2, H_{arom}).

I.R. (CCl_4): ν_{max} = 688, 700, 880, 940, 1020, 1060, 1080, 1122, 1158, 1177, 1195, 1245, 1265, 1315, 1450, 1465, 1490, 1582, 1602, 1720, 1748, 3045 cm^{-1}.

A solution of iodine (0.25 g, 0.001 mol) in chloroform (100 ml) is added, under stirring, to a solution of **5a** (0.66 g, 1 mmol) in the same solvent (10 ml). The reaction is immediate and mercury(II) iodide separates from the colourless solution. After filtration and evaporation of the solvent, 2,2'-dibenzoyloxydiphenyl disulfide (**6a**) is obtained in quantitative yield; m.p. 88–89° from petroleum ether; m.p., N.M.R., and I.R. spectra are identical with those previously reported for the authentic sample[2].

5b (R^1 = *t*-C_4H_9); m.p. 87–88° from methanol.

$C_{22}H_{26}HgO_4S_2$	calc.	C 42.68	H 4.23	Hg 32.40
(619.2)	found	42.53	4.23	32.54

M.S.: m/e = 621 (M^+).

^{1}H-N.M.R. ($CDCl_3$): δ = 1.33 (s, 2 *t*-C_4H_9); 6.85–7.4, 7.5–7.75 ppm (2m, 3:1, $8H_{arom}$).

I.R. (CCl_4): ν_{max} = 680, 900, 948, 1030, 1062, 1120, 1132, 1198, 1255, 1280, 1372, 1400, 1448, 1468, 1480, 1728, 1758, 2940, 2955, 2970, 2990, 3038 cm^{-1}.

The reaction with iodine affords 2,2'-dipivaloyloxydiphenyl disulfide (**6b**) in quantitative yield; m.p. 77–78°, from ethanol; m.p., N.M.R., and I.R. spectra are identical with those of a sample prepared independently by oxidation of 2-*t*-butyl-1,3-benzoxathiolium tetrafluoroborate with manganese dioxide, according to the procedure previously reported for the oxidation of 2-phenyl-1,3-benzoxathiolium perchlorate[2].

$C_{22}H_{26}O_4S_2$	calc.	C 63.13	H 6.26	S 15.32
(418.6)	found	63.00	6.12	15.47

^{1}H-N.M.R. ($CDCl_3$): δ = 1.39 (s, 2 *t*-C_4H_9); 6.85–7.45, 7.5–7.75 ppm (2m, 3:1, $8H_{arom}$).

I.R. (CCl_4): $\nu_{C=O}$ = 1755 cm^{-1}.

2-Ethoxy-2-(4-hydroxymethylphenyl)-1,3-benzoxathiole (3s):

Lithium aluminium hydride (0.38 g, 10 mmol) is gradually added under stirring, to a solution of **3h** (3.3 g, 10 mmol) in dry ether (100 ml). After the complete disappearance of **3h** (T.L.C.; 5 min), the mixture is poured into a 10% ammonium chloride solution and worked up by ether extraction to give, in almost quantitative yield, pure **3s** for conversion to **4s**; b.p. 170°/0.01 torr; n_D^{20} = 1.6047.

$C_{16}H_{16}O_3S$	calc.	C 66.64	H 5.59	S 11.12
(288.4)	found	66.81	5.70	11.25

^{1}H-N.M.R. ($CDCl_3$): δ = 1.23 (t, CH_3, J = 7 Hz); 2.9 (s, OH; disappeared on addition of D_2O); 3.3–4.1 (m, CH_2—CH_3); 4.53 (s, CH_2—OH); 6.90–7.2 (m, $4H_{benzo}$); 7.28, 7.62 ppm (2 pd, $4H_{phenyl}$, J = 8 Hz).

2-Ethoxy-2-[4-(1-hydroxy-1-methylethyl)-phenyl]-1,3-benzoxathiole (3t):

To the Grignard reagent from methyl iodide (4.26 g, 30 mmol) and magnesium turnings (0.73 g, 30 mmol) in dry ether (15 ml), a solution of **3h** (3.3 g, 10 mmol) in dry ether (20 ml) is slowly added in a period of 15–20 min so as to maintain a gently reflux. Stirring is continued until the complete disappearance of **3h** (about 15 min; T.L.C.). Usual work up gives, in almost quantitative yield, pure **3t** for conversion to **4t**; m.p. 114–115° from ligroin.

$C_{18}H_{20}O_3S$	calc.	C 68.33	H 6.37	S 10.13
(316.4)	found	68.24	6.30	10.27

^{1}H-N.M.R. ($CDCl_3$): δ = 1.27 (t, CH_2—CH_3, J = 7 Hz); 1.55 (s, $2CH_3$); 1.88 (s, OH; disappeared on addition of D_2O); 3.45–4.05 (m, CH_2—CH_3); 6.9–7.35 (m, $4H_{benzo}$); 7.48, 7.65 ppm (2 pd, $4H_{phenyl}$, J = 8 Hz).

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