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One-pot Synthesis of Alkyl Aryl Trithiocarbonates from Benzenethiols, Alkyl Halides, and Carbon Disulfide with a Phase-transfer Catalyst

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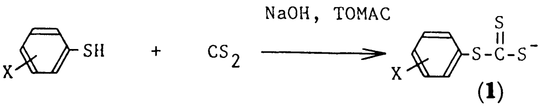
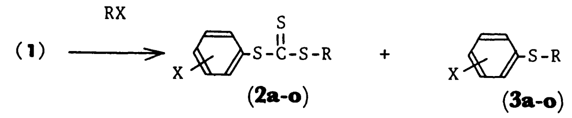
Synopsis. Various alkyl aryl trithiocarbonates may readily be synthesized in good yield at low temperatures such as 20 °C by allowing trioctylmethylammonium chloride (phase-transfer catalyst) to catalyze reaction of benzenethiols and alkyl halides with carbon disulfide.

Much attention has been focused on the synthesis of trithiocarbonates, which are very important intermediates for the preparation of insecticides and oil additives.[1] Some procedures for the synthesis of trithiocarbonates have been developed which employ reactions of sodium trithiocarbonates with alkyl halides,[2] thiophosgene with benzenethiols,[3] aryl chlorodithioformates with alkanethiols,[4] and lithio-2-alkyl thio-1,3-dithiolanes with alkyl halides.[5] Wepplo and Wright[6] synthesized alkyl cyanoalkyl trithiocarbonates *via* reaction of alkanethiols and haloalkanenitriles with carbon disulfide in the presence of tetrabutylammonium sulfate, but they were unable to obtain alkyl aryl trithiocarbonates.[6] These known procedures are not preferrable with respect to various points such as synthetic convenience, intractability of reagents and substrates, and availability of starting materials. In the course of our investigations on the chemistry of organosulfur compounds,[7] we have studied on the development of a new synthetic method for alkyl aryl trithiocarbonates. Here we wish to report of a convenient one-pot synthesis of trithiocarbonates from benzenethiols, carbon disulfide, and alkyl halides in the presence of a phase-transfer catalyst such as trioctylmethylammonium chlorid (TOMAC), the reaction sequence being summarized by Eqs. 1 and 2. Results obtained for the reaction of benzenethiol and carbon disulfide with methyl iodide are listed in Table 1. It should be noted that only a trace of trithiocarbonate is obtained in the absence of phase-transfer catalyst (run 5), whereas in the presence of 0.3 mmol TOMAC the desired trithiocarbonate **2a** is formed in a yield of 64% (run 6). Thus, a remarkable accelerating effect of TOMAC is found for this reaction. Moreover, a higher yield of trithiocarbonate **2a** is obtained with decreasing temperature (runs 3 and 4). This phenomenon is not unexpected since the intermediate, anion **1**, may be considered to be unstable at higher temperatures.



(1)



(2)

TABLE 1. REACTION OF BENZENETHIOL, CS_2, AND METHYL IODIDE IN THE PRESENCE OF TRIOCTYLMETHYLAMMONIUM CHLORIDE (TOMAC)

Run[a]	React. Temp/°C	React. Time/h	TOMAC /mmol	Yield of product/%[b] 2a	3a
1	r.t.	3	1.0	63	32
2	r.t.	3	1.0[c]	50	34
3	0	3	1.0	68	15
4	40	3	1.0	46	39
5	r.t.	3	0	trace	84
6	r.t.	3	0.3	64	26
7	r.t.	3	3.0	51	44

a) Benzenethiol, 10 mmol; methyl iodide, 10 mmol; NaOH, 10 mmol; CS_2, 20 mmol. b) Isolated yield based on benzenethiol. c) Tetrabutylammonium bromide was used as catalyst.

Many alkyl aryl trithiocarbonates **2a—o** were syn-

TABLE 2. SYNTHESIS OF ALKYL ARYL TRITHIOCARBONATES **2b—2o**

Run[a]	Thiol $X\text{-}C_6H_4\text{-}SH$/X	Alkyl halide	Yield of product/%[b] 2	3
1	H	$C_6H_5CH_2Br$	65 **2b**	25 **3b**
2	H	C_2H_5I	57 **2c**	32 **3c**
3	H	C_2H_5Br	40 **2c**	29 **3c**
4	H	$n\text{-}C_3H_7I$	56 **2d**	41 **3d**
5	H	$n\text{-}C_3H_7Br$	29 **2d**	18 **3d**
6	H	$(CH_3)_2CHI$[c]	39 **2e**	16 **3e**
7	H	$n\text{-}C_4H_9Br$[c]	41 **2f**	38 **3f**
8	H	$n\text{-}C_5H_{11}Br$	39 **2g**	51 **3g**
9	H	$i\text{-}C_5H_{11}Br$	38 **2h**	40 **3h**
10	H	$n\text{-}C_6H_{13}Br$	39 **2i**	48 **3i**
11	H	$n\text{-}C_8H_{17}Br$	40 **2j**	48 **3j**
12	4-CH_3	CH_3I	72 **2k**	22 **3k**
13	2-CH_3	CH_3I	61 **2l**	22 **3l**
14	3-CH_3	CH_3I	51 **2m**	37 **3m**
15	4-Cl	CH_3I	24 **2n**	44 **3n**
16	4-CH_3	$C_6H_5CH_2I$	85 **2o**	10 **3o**

a) Thiol, 10 mmol; alkyl halide, 10 mmol; CS_2, 20 mmol; NaOH, 10 mmol; TOMAC, 0.3 mmol; react. time, 3 h; react. temp., r.t. b) Isolated yield based on thiols. c) React. time, 24 h.

thesized *via* the reaction of benzenethiols with alkyl halides and carbon disulfide in the presence of TOMAC. As shown in Table 2, methyl 4-methylphenyl trithiocarbonate **2k** and benzyl 4-methylphenyl trithiocarbonate **2o** were obtained especially in high yields, 72 (run 12) and 85% (run 16), respectively. Trithiocarbonates bearing an electron-withdrawing group such as chlorine, however, were formed in low yield by this procedure (run 15). A plausible pathway for this reaction may comprise a nucleophilic attack of the thiolate anion moiety of intermediate **1** on the carbon atom of alkyl halides in the presence of TOMAC, as shown in Eqs. 1 and 2. The above results demonstrate that the catalytic approach utilized in this study may be of significant value for the preparation of alkyl aryl trithiocarbonates.

Experimental

IR spectra were obtained on a JASCO IR-G spectrophotometer. NMR spectra were measured with a Hitachi R-20B spectrophotometer (60 MHz) in $CDCl_3$ using TMS as internal standerd.

General Procedure. Carbon disulfide (20 mmol) and TOMAC (0.3 mmol) were added to a solution of benzenethiol (10 mmol) in aq NaOH (10 mmol) and after 2 h stirring at room temperature, alkyl halide (10 mmol) in benzene (10 ml) was added and stirring was continued for 3 h at room temperature. After completion of reaction the benzene layer was dried on sodium sulfate and then concentrated by evaporation of benzene under vacuum. Alkyl aryl trithiocarbonates **2a—o** and alkyl aryl sulfides **3a—o** were obtained by vacuum distillation and column chromatography on silica-gel (Wako Gel C-300) using hexane-chloroform (9:1) as eluent.

Physical Properties of ***2a—o****.* *Methyl Phenyl Trithiocarbonate* ***(2a)****:* Bp 142—6 °C (2 mmHg) (1 mmHg=133.322 Pa); IR 1048 and 1076 cm^{-1}; NMR ($CDCl_3$) δ=2.46 (S, 3H) and 7.39 (s, 5H). Found: C, 48.13; H,4.26. Calcd for $C_8H_8S_3$: C, 47.96; H, 4.03.

Benzyl Phenyl Trithiocarbonate ***(2b)****:* Bp 130—2 °C (2 mmHg); IR 1048 and 1062 cm^{-1}: NMR ($CDCl_3$) δ=4.46 (s, 2H) and 7.0—7.3 (m, 10H). Found: C, 60.52; H, 4.12. Calcd for $C_{14}H_{12}S_3$; C, 60.83; H, 4.38.

Ethyl Phenyl Trithiocarbonate ***(2c)****:* Bp 144—7 °C (2 mmHg); IR 1056 and 1072 cm^{-1}; NMR ($CDCl_3$) δ=1.12 (t, 3H), 3.12 (t, 2H), and 7.3—7.5 (m, 5H). Found: C, 51.14; H, 4.73. Calcd for $C_9H_{10}S_3$: C, 50.43; H, 4.70.

Phenyl Propyl Trithiocarbonate ***(2d)****:* Bp 145—9 °C (2 mmHg); IR 1037 and 1065 cm^{-1}; NMR ($CDCl_3$) δ=0.83 (t, 3H), 1.2—1.9 (m, 2H), 3.13 (t, 2H), and 7.0—7.5 (m, 5H). Found: C, 52.74; H, 5.52. Calcd for $C_{10}H_{12}S_3$: C, 52.59; H, 5.30.

Isopropyl Phenyl Trithiocarbonate ***(2e)****:* Bp 130—2 °C (2 mmHg); IR 1042 and 1062 cm^{-1}; NMR ($CDCl_3$) δ=1.22 (d, 6H), 4.00 (m, 1H), and 7.2—7.4 (m, 5H). Found: C, 52.73; H, 5.56. Calcd for $C_{10}H_{12}S_3$: C, 52.59; H, 5.30.

Butyl Phenyl Trithiocarbonate ***(2f)****:* Oil; IR 1060 and 1040 cm^{-1}, NMR ($CDCl_3$) δ=0.90 (t, 3H), 1.4—1.8 (m, 4H), 3.21 (t, 2H), and 7.45 (s, 5H). Found: C, 54.96; H, 5.96. Calcd for $C_{11}H_{14}S_3$: C, 54.55; H, 5.79.

Pentyl Phenyl Trithiocarbonate ***(2g)****:* Oil; IR 1060 and 1040 cm^{-1}; NMR ($CDCl_3$) δ=0.90 (t, 3H), 1.3—1.5 (m, 6H) and 7.48 (s, 5H). Found: C, 56.67; H, 6.20. Calcd for $C_{12}H_{16}S_3$: C, 56.25; H, 6.25.

Isopentyl Phenyl Trithiocarbonate ***(2h)****:* Oil; IR 1056 and 1045 cm^{-1}; NMR ($CDCl_3$) δ=0.92 (d, 6H), 1.4—1.7 (m, 3H), 3.22 (t, 2H), and 7.47 (s, 5H). Found; C, 56.61; H, 6.34. Calcd for $C_{12}H_{16}S_3$: C, 56.25; H, 6.25.

Hexyl Phenyl Trithiocarbonate ***(2i)****:* Oil; IR 1062 and 1040 cm^{-1}; NMR ($CDCl_3$) δ=0.88 (t, 3H), 1.25—1.6 (m, 8H), 3.21 (t, 2H), and 7.48 (s, 5H). Found: C, 58.04; H, 6.71. Calcd for $C_{15}H_{22}S_3$: C, 57.78; H, 6.67.

Octyl Phenyl Trithiocarbonate ***(2j)****:* Oil; IR 1063 and 1045 cm^{-1}; NMR ($CDCl_3$) δ=0.88 (t, 3H), 1.25—1.6 (m, 10H), 3.20 (t, 2H), and 7.45 (s, 5H). Found: C, 60.68; H, 7.36. Calcd for $C_{15}H_{22}S_3$: C, 60.40; H, 7.38.

Methyl 4-Methylphenyl Trithiocarbonate ***(2k)****:* Bp 152—157 °C (2 mmHg); IR 1048 and 1074 cm^{-1}; NMR ($CDCl_3$) δ=2.29 (s, 3H), 2.42 (s, 3H), and 7.2—7.4 (m, 4H). Found: C, 50.86; H, 4.65. Calcd for $C_9H_{10}S_3$: C, 50.43; H, 4.70.

Methyl 2-Methylphenyl Trithiocarbonate ***(2l)****:* Mp 49.2—49.5 °C; IR 1048 cm^{-1}; NMR ($CDCl_3$) δ=2.42 (s, 3H), 2.58 (s, 3H), and 7.4—7.3 (t, 4H). Found: C, 50.63; H, 4.73. Calcd for $C_9H_{10}S_3$: C, 50.43; H, 4.70.

Methyl 3-Methylphenyl Trithiocarbonate ***(2m)****:* Oil; IR 1072 and 1044 cm^{-1}; NMR ($CDCl_3$) δ=2.36 (s, 3H), 2.52 (s, 3H), and 7.3-7.2 (d, 4H). Found: C, 49.90; H, 4.83. Calcd for $C_9H_{10}S_3$: C, 50.43; H, 4.70.

4-Chlorophenyl Methyl Trithiocarbonate ***(2n)****:* Bp 152—159 °C (4 mmHg); IR 1050 and 1078 cm^{-1}; NMR ($CDCl_3$) δ=2.60 (s, 3H) and 7.43 (s, 4H). Found: C, 40.27; H, 3.15. Calcd for $C_8H_7S_3Cl$: C, 40.93; H, 3.01.

Benzyl 4-Methylphenyl Trithiocarbonate ***(2o)****:* Oil; IR 1040 and 1065 cm^{-1}; NMR ($CDCl_3$) δ=2.34 (s, 3H), 4.40 (s, 2H) and 7.17—7.46 (m, 9H). Found: C, 62.06; H, 4.84. Calcd for $C_{15}H_{14}S_3$: C, 62.02; H, 4.87.

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