The products were characterized by spectral and analytical means as summarized in the table. This reaction represents a general, simple, mild, and superior procedure for the direct synthesis of a variety of isopropylidene diarylmalonates **3** and isopropylidene alkylarylmalonates **5**. Furthermore, since substituted isopropylidene malonates are readily hydrolyzed to carboxylic acids[12] or converted to esters,[13] this method represents an indirect, efficient preparation of α-aryl carboxylic acids or their esters.

Experimental Section

All melting points are uncorrected. NMR spectra were recorded at 60 MHz on a Varian EM-360 spectrometer with Me_4Si in $CDCl_3$ as the internal standard, and IR spectra were recorded on a PE-683 spectrometer.

Starting Materials. Meldrum's is commercially available or can be readily made by condensation of malonic acid with acetone. The necessary diaryliodonium salts **2** were prepared by standard procedures according to Beringer and co-workers.[14]

General Procedure for the Preparations of 3 and 5. Potassium metal (0.78 g, 20 mmol) was added to 20 mL of anhydrous *tert*-butyl alcohol. After reaction, 1.44 g (10 mmol) of Meldrum's acid (**1**) was added under nitrogen at 70 °C. To this solution was slowly added 20 mmol of the appropriate diaryliodonium salt **2**. (For reaction of **4** with **2** the molar ratio of K to **4** to **2** was 1:1:1.) The resulting solution was stirred at 70 °C for several hours (see Table I) until it turned clear. After cooling, the solvent was removed, and to the residue were added 30 mL of methylene chloride and 10 mL of water. The organic layer was separated, washed successively with 10 mL of water, 10 mL of 5% aqueous $NaHCO_3$, and 10 mL of water, and then dried over anhydrous $MgSO_4$. The methylene chloride was removed, to the residue was added 20 mL of petroleum ether, and the mixture was allowed to stand in a refrigerator overnight. The resulting crystals were collected by suction filtration and purified by recrystallization from benzene/hexane. All relevant data are summarized in the table.

Acknowledgment. This research was supported by the NCI of the NIH (Grant ROICA16903) at Utah and the NSFC in the PRC.

---

(12) Swoboda, G.; Swododa, J.; Wesseley, F. *Monatsh. Chem.* **1964**, *95*, 1283.

(13) Oikawa, Y.; Hirasawa, H.; Yonewitsu, O. *Tetrahedron Lett.* **1978**, *19*, 1759.

(14) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Massulo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* **1959**, *81*, 342.

Polyvalent Iodine in Synthesis. 2. A New Method for the Preparation of Aryl Esters of Dithiocarbamic Acids

Zhen-Chu Chen,*[1a,b] You-Yuan Jin,[1b] and Peter J. Stang[1c]

Departments of Chemistry, Hangzhou University,
Hangzhou, The People's Republic of China, and The
University of Utah, Salt Lake City, Utah 84112

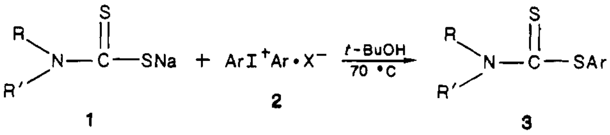
Received April 21, 1987

Esters of dithiocarbamic acids have received considerable interest because of their antimicrobial activity and application in organic synthesis.[2] Although a wide variety of methods have been reported for their synthesis, the most general and important one involves the alkylation of dithiocarbamic acid salts.[2,3] Since simple aryl halides cannot be used in alkylation reactions, this procedure only works for alkyl systems.

The current methods for the preparation of aryl esters of dithiocarbamic acids are essentially based upon the reactions of dithiochloroformates with amines,[4] or thioisocyanates with thiophenols,[5] and diazonium salts with salts of dithiocarbamic acid,[6] and certain organometallic reagents with tetramethylthiuran disulfide, $Me_2NC(S)SSC(S)NMe_2$.[7,8] These methods may be tedious and cumbersome, may employ some toxic and hazardous reagents, and generally give poor yields.

As indicated in the preceding paper,[9] the known[10] availability and reactivity of diaryliodonium salts **2** prompted us to examine their reaction with salts of dithiocarbamic acids for a general, efficient, new method of aryl ester synthesis.

Herein we report that salts of type **1** readily react with diaryliodonium salts **2** in either 2-methyl-2-propanol or acetonitrile at 70 °C to give aryl esters **3** (eq 1) in good isolated yields (Table I).



(1)

a: R=CH_3; R′=CH_3; Ar=C_6H_5
b: R=C_2H_5; R′=C_2H_5; Ar=C_6H_5
c: R, R′=-$(CH_2)_5$-; Ar=C_6H_5
d: R=$PhCH_2$; R′=CH_3; Ar=C_6H_5
e: R=Ph; R′=H; Ar=C_6H_5
f: R=CH_3; R′=CH_3; Ar=*p*-$CH_3C_6H_4$
g: R=C_2H_5; R′=C_2H_5; Ar=*p*-$CH_3C_6H_4$
h: R, R′=-$(CH_2)_5$-; Ar=*p*-$CH_3C_6H_4$
i: R=$PhCH_2$; R′=CH_3; Ar=*p*-$CH_3C_6H_4$
j: R=CH_3; R′=CH_3; Ar=*p*-$CH_3OC_6H_4$
k: R, R′=-$(CH_2)_5$-; Ar=*p*-$CH_3OC_6H_4$
l: R=CH_3; R′=CH_3; Ar=*p*-ClC_6H_4
m: R, R′=-$(CH_2)_5$-; Ar=*p*-ClC_6H_4
n: R=CH_3; R′=CH_3; Ar=*m*-$NO_2C_6H_4$
o: R=Ph; R′=H; Ar=*m*-$NO_2C_6H_4$

As in other arylations involving diaryliodonium salts **2** this reaction also exhibits a dependence[11,12] on the anion X^- associated with the iodonium salt **2** (Table I, entries 2–5). In particular, Cl^- and ^-OAc result in higher yields than Br^- and I^-. Moreover, isolated product yields are clearly superior to previous methods[6,7] (**3a–c,f–h**), and the procedure is applicable to a broad range of aryl systems.

Aryl esters of dithiocarbamic acid are easily hydrolyzed to the corresponding thiophenols.[8] For example, compound **31**, when heated under reflux in 20% aqueous KOH for 30 min, gave an 85% yield of pure *p*-chlorothiophenol. Hence, this procedure may also serve as an indirect method for the ready preparation of pure substituted thiophenols.

---

(1) (a) Formerly spelled as Cheng-Chu Chan. (b) Hangzhou University. (c) The University of Utah.

(2) Reid, E. E. *Organic Chemistry of Bivalent Sulfur*; Chemical Publishing: New York, 1982; Vol. IV.

(3) Kaplan, M. L.; Haddon, R. C.; Wudl, F.; Feit, E. D. *J. Org. Chem.* **1978**, *43*, 4642. Hori, I.; Hayashi, T.; Midorikawa, H. *Synthesis* **1974**, 705. Hiratani, K.; Nakai, T.; Okawara, M. *Chem. Lett.* **1974**, 1041. Matolcsy, G.; Bordas, B. *Chem. Ber.* **1973**, *106*, 1483.

(4) Teruhisa, N.; Yoshimoto, H.; Koshin, M.; Aritsune, K. *Yakugaku Zasshi* (*Japan*) **1968**, *88* (2), 227; *Chem. Abstr.* **1968**, *69*, 26887.

(5) Will, W. *Ber. Dtsh. Chem. Ges.* **1882**, *15*, 1303.

(6) Clifford, A. M.; Lichty, J. G. *J. Am. Chem. Soc.* **1932**, *54*, 1163.

(7) Grunwell, J. R. *J. Org. Chem.* **1970**, *35*, 1500.

(8) Jen, K.; Cava, M. P. *Tetrahedron Lett.* **1982**, *23*, 2001.

(9) Chen, Z.-C.; Jin, Y.-Y.; Stang, P. J. *J. Org. Chem.*, proceding paper in this issue.

(10) Varvoglis, A. *Synthesis* **1984**, 709.

(11) Beringer, F. M.; Galton, S. A.; Huang, J. *J. Am. Chem. Soc.* **1962**, *84*, 2918.

(12) Crivello, J. V.; Lam, J. H. W. *Synth. Commun.* **1979**, *9*(3), 151.

0022-3263/87/1952-4117$01.50/0

Table I. Aryl Esters of Dithiocarbamic Acids 3

entry	compd.	X^- in 2	solvent, 70 °C	reactn time, h	yield,[a,b] this work	yield,[a,b] lit.	mp, °C	lit. mp, °C	IR (KBr), cm^{-1}	^1H NMR ($CDCl_3$), ppm
1	**3a**	Cl^-	*t*-BuOH	5	86	32,[6] 26[7]	93–94	94–95[6]	1508, 1385, 1261, 754, 689	3.54 (s, 6 H), 7.52 (s, 2 H)
2	**3a**	OAc^-	*t*-BuOH	4	74					
3	**3a**	Cl^-	*t*-BuOH	4	72					
4	**3a**	Br^-	*t*-BuOH	4	46					
5	**3a**	I^-	*t*-BuOH	4	17					
6	**3b**	Cl^-	*t*-BuOH	10	56	17[6]	45–46	46[6]	1495, 1423, 1275, 750, 689	1.34 (m, 6 H), 3.95 (m, 4 H), 7.50 (s, 5 H)
7	**3c**	Cl^-	*t*-BuOH	5	81	16[6]	116–117	116–117[6]	1430, 1232, 749, 685	1.74 (s, 6 H), 3.80–4.40 (br, 4 H), 7.51 (s, 5 H)
8	**3d**	Cl^-	*t*-BuOH	5	84		68–69		1478, 1399, 1254, 750, 740, 696, 690	3.40 (s, 3 H), 5.22 (s, 2 H), 7.37 (s, 5 H), 7.52 (s, 5 H)
9	**3e**	Cl^-	*t*-BuOH	4	57		148–150	104–106[14]	3220, 1558, 1348, 765, 756, 698, 689	7.20–7.33 (m, 10 H), 8.18 (s, 1 H)
10	**3f**	I^-	*t*-BuOH	10	70	26[6]	111–112	111–112[6]	1511, 1380, 1255, 810	2.40 (s, 3 H), 3.53 (s, 6 H), 7.32 (m, 4 H)
11	**3g**	Br^-	*t*-BuOH	15	63	30[6]	75–76	77–78[6]	1492, 1275, 811	1.33 (m, 6 H), 2.43 (s, 3 H), 3.95 (m, 4 H), 7.34 (m, 4 H)
12	**3h**	I^-	*t*-BuOH	12	66	36[6]	118–119	118–119[6]	1485, 1248, 812	1.74 (s, 6 H), 2.42 (s, 3 H), 4.00–4.30 (br, 4 H), 7.32 (m, 4 H)
13	**3i**	Br^-	*t*-BuOH	18	71		65–66		1490, 1399, 1250, 806, 746, 701	2.38 (s, 3 H), 3.38 (s, 3 H), 5.22 (d, 2 H), 7.36 (m, 9 H)
14	**3j**	I^-	*t*-BuOH	18	76		92–93	105–108[15]	1504, 1385, 1258, 832	3.54 (s, 6 H), 3.87 (s, 3 H), 7.20 (q, 4 H)
15	**3k**	I^-	*t*-BuOH	18	68		102–103		1504, 1255, 832	1.73 (s, 6 H), 3.87 (s, 3 H), 3.90–4.30 (br, 4 H), 7.20 (q, 4 H)
16	**3l**	Cl^-	CH_3CN	13	58		101–103	102–103[4]	1511, 1380, 1242, 850	3.56 (s, 6 H), 7.30 (m, 4 H)
17	**3m**	Cl^-	CH_3CN	13	63		90–92	94–96[15]	1476, 1244, 1009, 820, 750	1.73 (s, 6 H), 4.00–4.30 (br, 4 H), 7.30 (m, 4 H)
18	**3n**	Cl^-	CH_3CN	3	63		139–141		1540, 1526, 1389, 1358, 1254, 809 732	3.50 (s, 6 H), 7.70–8.30 (m, 4 H)
19	**3o**	Cl^-	CH_3CN	4	56		150–152		3225, 1560, 1535, 1351, 1248, 810, 752, 730, 698	7.33 (m, 9 H), 8.13 (s, 1 H)

[a] Isolated yield of analytically pure product. [b] Satisfactory microanalyses obtained: C, ±0.29; H, ±0.13; N, ±0.03.

Experimental Section

All melting points are uncorrected. NMR spectra were recorded at 60 MHz on a Varian EM-360 spectrometer with Me_4Si in $CDCl_3$ as the internal standard. IR spectra were recorded on a PE-683 spectrometer.

General Procedure for the Preparation of 3. To a stirred solution of 1 (5 mmol) in 2-methyl-2-propanol or acetonitrile (15 mL) at 70 °C was slowly added 5 mmol of the appropriate iodonium salt 2.[11,13] Stirring was continued until the inorganic salts precipitated and the reaction mixture was clear (Table I). After removal of the solvent, 10 mL of water was added, and the resulting mixture was extracted with methylene chloride (3 × 10 mL). The combined organic layers were washed with water (10 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, hexane was added to the residue, and the product was allowed to crystallize in a refrigerator overnight. The crude product was collected and recrystallized from benzene/hexane. Products were identified by comparison of experimental values with literature values and by ^1H NMR and IR spectroscopy (Table I).

Acknowledgment. This research was supported at Utah by the NCI of the NIH (Grant RO1CA16903) and the NSFC in the PRC.

---

(13) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Massullo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* **1959**, *81*, 342.

(14) Rivier, H. *Bull. Soc. Chim. Belg.* **1907**, *4*, 733; *Chem. Abstr.* **1907**, *1*, 3004.

(15) Matsushima, K.; Kudamatsu, A.; Miyamoto, M. *Noyaku Seisan Gijutsu* **1966**, *14*, 31; *Chem. Abstr.* **1967**, *67*, 43534.

Activation of Platinum Catalysts with Oxygen To Enhance Hydrosilylation of Unactivated Alkyl-, Dialkyl-, and Trialkylsilanes with 1-Alkenes. Synthesis of Tetraalkylsilanes

Anatoli Onopchenko* and Edward T. Sabourin

Chevron Research Company, Richmond, California 94802

Received March 2, 1987

Introduction

We were interested in the one-step synthesis of tetraalkylsilanes in the C_{25}–C_{32} range via hydrosilylation of 1-alkenes with alkylsilanes. The reaction of methylsilane

0022-3263/87/1952-4118$01.50/0