salts were washed with acetone. Evaporation of the combined filtrate and washes under reduced pressure left a tan residue (11.30 g). Recrystallization from aqueous methanol gave small, off-white, needles (8.55 g, 77% yield), mp 117.5–120 °C. Another recrystallization did not change the melting point but gave an analytical sample.

Anal. Calcd for $C_{14}H_{13}O_3Cl$: C, 63.52; H, 4.95; Cl, 13.39. Found: C, 63.39; H, 5.12; Cl, 13.52.

4,5′,8-Trimethylpsoralen (5). Method A. A mixture of 4,8-dimethyl-7-[(β-bromoallyl)oxy]coumarin (200 mg, 0.65 mmol, mp 130–132 °C) and freshly distilled *N,N*-diethylaniline (5.0 mL) was stirred under a nitrogen atmosphere and heated under reflux for 24 h at an oil bath temperature of 225 ± 2 °C. An ether solution of the dark brown reaction mixture was filtered, and the filtrate was washed with several portions of 5% aqueous sodium hydroxide and one portion of 6 M hydrochloric acid. After drying ($MgSO_4$), the ether solution was concentrated under reduced pressure to a tan residue (131 mg, 88% yield, mp 222–228 °C). Recrystallization of 120 mg from 95% ethanol gave fine needles (82 mg, 60% yield), mp 232.5–233.5 °C (lit.[3] mp 234 °C). The melting point of a commercial sample[14] was 230–232 °C when determined simultaneously. The infrared spectra of the two samples were identical.

Method B. A mixture of 4,8-dimethyl-7-[(β-chloroallyl)-oxy]coumarin (500 mg, 1.89 mmol) and *N,N*-diethylaniline (5.0 mL) was protected by an Aquasorb tube while being heated under reflux for 24 h at an oil bath temperature of 220–225 °C. Treatment of the reaction mixture as described in method A gave some black, ether-insoluble material which was discarded. The desired product was obtained as a tan solid (154 mg, 41.6% yield), which was recrystallized from 95% ethanol to obtain light tan needles (53 mg, 14% yield), mp 233 °C (lit.[3] mp 234 °C). Its infrared spectrum was identical with that of a commercial sample.[14]

4,8-Dimethyl-6-(β-bromoallyl)-7-hydroxycoumarin (3a). A mixture of 4,8-dimethyl-7-[(β-bromoallyl)oxy]coumarin (1.00 g, 3.24 mmol) and freshly distilled *N,N*-diethylaniline (5.0 mL) was protected by an Aquasorb tube while being stirred and heated under reflux for 3 h at an oil bath temperature of 225 ± 3 °C. An ether solution of the dark brown reaction mixture was filtered to remove a black solid (ca. 10 mg), extracted with several portions of 5% aqueous sodium hydroxide, washed several times with 6 M hydrochloric acid, dried ($MgSO_4$), and concentrated to a tan solid (0.43 g, mp 114–125 °C) which was probably impure starting material. The alkaline extracts were acidified with concentrated hydrochloric acid to obtain an off-white solid (0.53 g, 53% yield, mp 154–161 °C) that was collected by ether extraction. Recrystallization from aqueous ethanol, followed by another recrystallization from benzene, gave an analytical sample, mp 175–176 °C.

Anal. Calcd for $C_{14}H_{13}O_3Br$: C, 54.39; H, 4.24; Br, 25.85. Found: C, 54.83; H, 4.39; Br, 25.87.

4,8-Dimethyl-6-(β-chloroallyl)-7-hydroxycoumarin (3b). A mixture of 4,8-dimethyl-7-[(β-chloroallyl)oxy]coumarin (500 mg, 1.89 mmol) and *N,N*-diethylaniline (5.0 mL) was protected by an Aquasorb tube while refluxing for 19 h at an oil bath temperature of 220–225 °C. The cooled mixture was treated as described above to obtain a tan solid (307 mg, 61% yield, mp 135–163 °C) from the acidified alkaline extracts. Recrystallization from benzene and Norit gave small yellow needles (183 mg, 37% yield, mp 172–175 °C).

Anal. Calcd for $C_{14}H_{13}O_3Cl$: C, 63.52; H, 4.95; Cl, 13.39. Found: C, 63.62; H, 4.75; Cl, 13.42.

4-Methyl-7-[(β-bromoallyl)oxy]coumarin (2c). 4-Methyl-7-hydroxycoumarin (2.00 g, 11.4 mmol) was refluxed with freshly distilled 2,3-dibromopropene (2.72 g, 13.6 mmol), anhydrous potassium carbonate (3.15 g, 22.8 mmol), and acetone (80 mL) for 4 h. The reaction mixture was treated as described for the preparation of **2a** to obtain an off-white solid (3.70 g) that contained some excess 2,3-dibromopropene. Recrystallization of a portion (500 mg) from ligroin (bp 100–120 °C) gave needles (394 mg, 89% yield), mp 109.5–110.5 °C. An analytical sample melting at 110–111 °C was obtained by recrystallization from methanol.

Anal. Calcd for $C_{13}H_{11}O_3Br$: C, 52.97; H, 3.75; Br, 27.08. Found: C, 52.98; H, 3.80; Br, 27.18.

4,5′-Dimethylisopsoralen (6). Rearrangement and cyclization of 4-methyl-7-[(β-bromoallyl)oxy]coumarin (500 mg, 1.69 mmol) was carried out as described in method A of the preparation of 4,5′,8-trimethylpsoralen except that *N,N*-dimethylaniline (12.5 mL) was used instead of the diethyl homologue. The same purification procedure gave a tan solid (289 mg, 80% yield), mp 173–179.5 °C. Recrystallization from methanol and Norit afforded light tan needles (161 mg, 45% yield), mp 182.5–184 °C (lit.[3] mp 182–183 °C). The infrared spectra of this sample and that of an authentic sample[3] were identical.

4-Methyl-8-(β-bromoallyl)-7-hydroxycoumarin (4). A mixture of 4-methyl-7-[(β-bromoallyl)oxy]coumarin (500 mg) and freshly distilled *N,N*-diethylaniline (12.5 mL) was stirred under a nitrogen atmosphere and heated under a reflux for 5 h at an oil bath temperature of ca. 225 °C. An ether solution of the reaction mixture was extracted with several portions of 5% aqueous sodium hydroxide, which were acidified and reextracted with ether to obtain an off-white solid (206 mg). Recrystallization from 95% ethanol gave fine, off-white needles (102 mg, 20% yield), mp 201–202 °C. Another recrystallization gave an analytical sample, mp 204.5–205 °C.

Anal. Calcd for $C_{13}H_{11}O_3Br$: C, 52.97; H, 3.75; Br, 27.08. Found: C, 52.97; H, 3.75; Br, 26.56.

2-[(β-Bromoallyl)oxy]naphthalene (7). A mixture of 2-naphthol (2.00 g, 13.9 mmol), anhydrous potassium carbonate (3.78 g, 27.8 mmol), freshly distilled 2,3-dibromopropene (3.24 g, 16.7 mmol), and acetone (90 mL) was stirred and heated under reflux for 4.5 h. Inorganic salts were filtered from the cooled solution and washed with acetone. Evaporation of the combined filtrate and washes left a yellow oil (3.81 g). Chromatography of a portion (300 mg) on a Florisil column, eluted with 5% acetone in hexane, gave a colorless solid (266 mg, 93% yield), mp 39–41.5 °C (Fisher-Johns apparatus).

Anal. Calcd for $C_{13}H_{11}OBr$: C, 59.37; H, 4.22; Br, 30.37. Found: C, 59.54; H, 4.48; Br, 29.93.

2-Methylnaphtho[2,1-*b*]furan (8). Rearrangement and cyclization of 2-[(β-bromoallyl)oxy]naphthalene (500 mg, 1.90 mmol) in freshly distilled *N,N*-diethylaniline (12.5 mL) was accomplished as described in method A of the preparation of 4,5′,8-trimethylpsoralen to obtain a dark oil that eventually solidified. Chromatography on a Florisil column (hexane eluant) gave a colorless solid (200 mg, 58% yield): mp 56.5–57.5 °C (Fisher-Johns apparatus); NMR ($CDCl_3$) δ 2.52 (3 H, s, CH_3), 6.85 (1 H, s, C_3-H), 7.2–7.6 (4 H, m, C_{4-7}-H), 7.83–8.14 (2 H, m, C_8-H and C_9-H).

Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.54; H, 5.97.

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Registry No. **1a**, 4115-76-8; **1b**, 90-33-5; **2a**, 72478-66-1; **2b**, 69897-63-8; **2c**, 72478-67-2; **3a**, 72478-68-3; **3b**, 72478-69-4; **4**, 72478-70-7; **5**, 3902-71-4; **6**, 4063-41-6; **7**, 72478-71-8; **8**, 18747-04-1; 2,3-dibromopropene, 513-31-5; 2,3-dichloropropene, 78-88-6; 2-naphthol, 135-19-3.

(14) Supplied by the Paul B. Elder Co.

A Novel Synthesis of Aryl Orthoesters: Trimethyl *m*-Iodoorthobenzoate

Ronald Breslow* and P. S. Pandey

Department of Chemistry, Columbia University, New York, New York 10027

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For some applications of our procedure of remote template-directed halogenation[1] to specific steroid problems, we required an orthoester of *m*-iodobenzoic acid. Unfortunately, the standard method for preparation of

(1) R. Breslow, R. J. Corcoran, B. B. Snider, R. J. Doll, P. L. Khanna, and R. Kaleya, *J. Am. Chem. Soc.*, **99**, 905 (1977).

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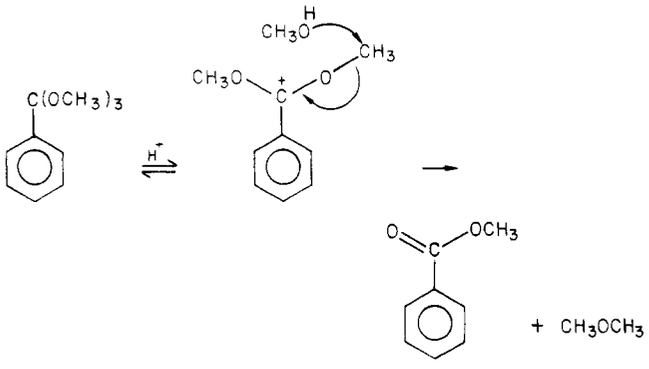
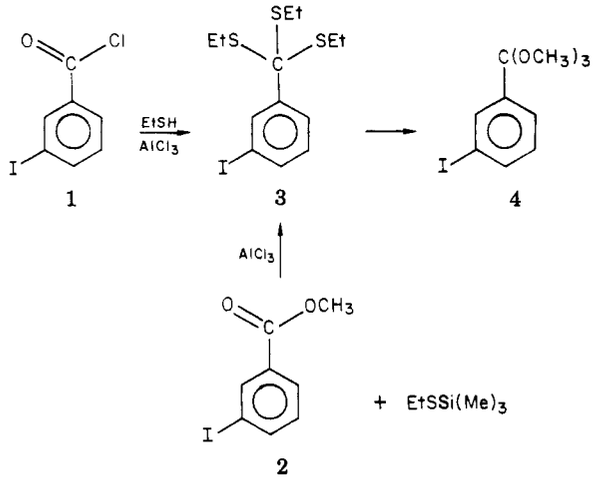
orthoesters,[2,3] the Pinner reaction of a nitrile, works very poorly for arylcarbonitriles.[4] As we have confirmed for *m*-iodobenzonitrile, it affords a difficultly separable mixture of the orthoester with (predominantly) the simple ester, from alkyl oxygen fission of the intermediate reversibly formed dimethoxybenzyl cation. Orthobenzoates



can also be prepared from benzotrichlorides, but chlorination of *m*-iodotoluene led to loss of iodine. Accordingly, we were forced to devise a new method for the synthesis of the desired orthoester, which produces the product in very good yield and excellent purity.

Our procedure is related to the report[3] that formate esters can be converted to orthothioformates with thiols and HCl and that the orthothioformates can then be converted to ethyl orthoformate with ethanol and $ZnCl_2$. We find that triethyl *m*-iodoorthothiobenzoate (3) can be



prepared in 90% yield[5] from *m*-iodobenzoyl chloride (1) with ethanethiol and $AlCl_3$ or directly in 70% yield from methyl *m*-iodobenzoate (2) with trimethylsilyl ethyl sulfide and $AlCl_3$. However, methanolysis of 3 with $AlCl_3$ catalyst led to a mixture of ester and orthoester, presumably again because of alkyl oxygen fission in a reversibly formed dimethoxyaryl carbocation. Thus, we needed reaction conditions for this methanolysis which would not affect the product orthoester, so we turned to silver-assisted solvolysis in a mildly basic medium. Treatment of the orthothioester 3 with $AgNO_3$ and collidine in methanol leads to rapid precipitation of silver mercaptide and the essentially quantitative formation of trimethyl *m*-iodoorthobenzoate (4). No other product can be detected by NMR, and the distilled crystalline product (4) is isolated in 85% yield.

In preliminary work we established that triethyl orthobenzoate could also be prepared from benzoyl chloride by our method. Thus it seems likely that this clean, high-yielding procedure will prove generally useful for the synthesis of aryl orthoesters.

Experimental Section

Triethyl *m*-Iodoorthothiobenzoate (3). Ethanethiol (25 mL) was added slowly to an anhydrous mixture of 8.0 g (30 mmol) of *m*-iodobenzoyl chloride (1) and 16.0 g of anhydrous $AlCl_3$. The homogeneous mixture was stirred and heated under reflux at 60 °C for 48 h, then cooled, and poured slowly with stirring into 150 mL of ice-cooled 4 N aqueous NaOH. Extraction with ether, washing, drying (Na_2SO_4, Na_2CO_3), and solvent evaporation afforded 12.0 g (100% of theoretical weight) of crude 3 which by NMR consisted of 90–95% of 3 contaminated with ethyl *m*-iodothiobenzoate. Chromatography[5] of 4.0 g of this oil on 200 g of basic alumina with ether–petroleum ether (20:80) afforded 3.6 g (90%) of pure 3 as the first fraction: bp 140 °C (0.3 mm); NMR (CCl_4) δ 1.15 (t, 9 H), 2.52 (q, 6 H), 7.00 (t, 1 H), 7.50 (d, 1 H), 7.75 (d, 1 H), 8.10 (s, 1 H).

Anal. Calcd for $C_{13}H_{19}S_3I$: C, 39.19; H, 4.81; S, 24.14; I, 31.86. Found: C, 38.95; H, 5.05; S, 23.88; I, 31.98.

This compound could also be prepared (in lower yield) by heating 3.5 g of (ethylthio)trimethylsilane[6] with 1.31 g of methyl *m*-iodobenzoate and 2.0 g of $AlCl_3$ at 110 °C for 24 h. Quenching and isolation as above yielded 1.8 g of crude 3, which afforded 1.40 g (70%) of pure 3 after chromatography.

Trimethyl *m*-Iodoorthobenzoate (4). To a solution of 2.0 g (5 mmol) of the orthothioester 3 and 2.50 g of collidine in 200 mL of anhydrous methanol was added 2.55 g (15 mmol) of $AgNO_3$ in 20 mL of acetonitrile. After 4 h of stirring at room temperature, the solid silver mercaptide was filtered away, the filtrate was taken to dryness, and the product was collected in ether (100 mL), which was filtered and evaporated. The crude product, 1.5 g (97%), was pure 4 by NMR. It was distilled to afford 1.30 g (85%) of pure crystalline 4: bp 110–115 °C (0.2 mm); mp 58–60 °C; NMR (CCl_4) δ 3.10 (s, 9 H), 7.05 (t, 1 H), 7.50 (d, 1 H), 7.65 (d, 1 H), 7.90 (s, 1 H).

Anal. Calcd for $C_{10}H_{13}O_3I$: C, 38.98; H, 4.25; I, 41.18. Found: C, 39.07; H, 4.42; I, 40.57.

Registry No. 1, 1711-10-0; 2, 618-91-7; 3, 72525-28-1; 4, 72525-29-2; ethanethiol, 75-08-1; (ethylthio)trimethylsilane, 5573-62-6.

(2) R. H. DeWolfe, "Carboxylic Ortho Acid Derivatives", Academic Press, New York, 1970.
(3) R. H. DeWolfe, *Synthesis*, 153 (1974).
(4) E.g., ref 2, p 4, reports an overall 27% yield from benzonitrile.
(5) The remainder is the thioester. On a moderate scale, as in the described procedure, this can be removed by simple chromatography. On a larger scale it would be more convenient to cleave the thioester with KOH hydrolysis. We find that in a few hours the thioester is completely hydrolyzed, while the orthothioester is inert and can be isolated by simple extraction. The thioester boils too close to the orthoesters 3 and 4 for easy removal by distillation.
(6) D. Evans, L. K. Truesdale, K. G. Grinn, and S. L. Nesbitt, *J. Am. Chem. Soc.*, **99**, 5009 (1977).

C(15) Configuration of Isopimaren-15,16-diols[1]

Ernest Wenkert* and Muppala S. Raju

Department of Chemistry, Rice University, Houston, Texas 77001

Paolo Ceccherelli,* Massimo Curini, and Marco Tingoli

Istituto di Chimica Organica della Facoltà di Farmacia, Università degli Studi, Perugia, Italy

Roberto Pellicciari*

Istituto di Chimica Farmaceutica e Tossicologica, Università degli Studi, Perugia, Italy

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The tricarbocyclic, pimaric diterpenes appear in nature mainly as dienes of the pimaradiene (1), sandaraco-

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