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A convenient procedure for the efficient preparation of alkyl (Z)-3-iodo-2-alkenoates

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Reaction of alkyl 2-alkynoates with sodium iodide (1.6–5.5 equiv.) in acetic acid (6.2–13 equiv.) at 115°C provides good to excellent yields of the corresponding alkyl (Z)-3-iodo-2-alkenoates.

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La réaction des 2-alkynoates d'alkyles avec l'iodure de sodium (1,6–5,5 équiv.) dans l'acide acétique (6,2–13 équiv.) à 115°C conduit aux (Z)-3-iodo-2-alkénoates d'alkyles correspondants avec des rendements allant de bon à excellent.

[Traduit par la rédaction]

Introduction

Alkyl (Z)-3-iodo-2-alkenoates (general structure **1**), along with substances that have been or could readily be derived therefrom, are useful intermediates for organic synthesis (1–20). Recently, it has been reported (17–20) that **1** (R^1 = H) can be produced by reaction of alkyl propynoates **2** with lithium or sodium iodide in acetic acid at 70°C. However, this protocol requires reaction times that are quite lengthy (12–24 h) and has been applied to only two higher homologs of **2**, namely **3** (R^2 = Me) (19) and **4** (R^2 = Et) (17). In the latter case, the yield of **1**
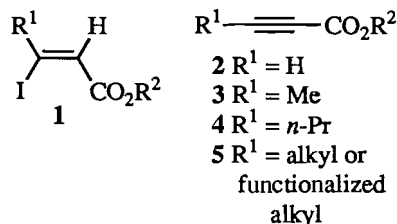
$(R^1 = n\text{-Pr}, R^2 = \text{Et})$ was very low (22%) (17). Indeed, we have found that this procedure (17–20) generally works poorly or not at all for substrates of general structure **5** in which R^1 is larger than methyl.

In connection with current research projects in our laboratory, we required a number of substances of general structure **1** in which the R^1 group is more bulky than methyl and, in some instances, is functionalized. We report herein a procedure, significantly modified from those reported earlier (17–20), that effects the efficient conversion of α,β-acetylenic esters **5** into the alkyl (Z)-3-iodo-2-alkenoates **1**. Essentially, the procedure that we have developed employs sodium iodide, a limited amount of acetic acid, and a reaction temperature (115°C) considerably higher than that employed previously (17–20). Under these conditions, substrates **5**, including those with functionalized or bulky (e.g., *tert*-butyl) R^1 groups, are transformed smoothly and efficiently into iodo esters of general structure **1**.

Results and discussion

(a) The α,β-unsaturated acetylenic substrates

The acetylenic ester starting materials **6–15** employed in this study are listed in Chart 1. Of these materials, a number (**6, 12–**
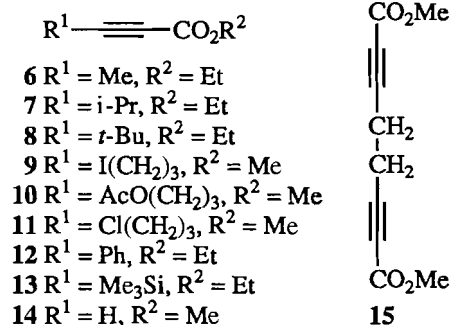

CHART 1

14) are commercially available, while others have been reported previously: **7** (21), **8** (22), **9** (22), **11** (23), **15** (24). Compound **10** was prepared by treatment of methyl 6-(tetrahydropyranyloxy)-2-hexynoate (22) with ethanoyl chloride (25) (see Experimental). Collectively, these ester substrates contain a variety of functional groups and have alkyl groups attached to C-3 of the alkyl propynoate unit that are sterically small, medium, and large (see compounds **6–8**).

(b) Preparation of alkyl (Z)-3-iodo-2-alkenoates and related substances

Initially, we carried out a series of experiments that involved treatment of ethyl 2-butynoate (**6**) with varying amounts of sodium iodide and acetic acid at a variety of temperatures. These studies quickly revealed that the rate of conversion of the substrate into ethyl (Z)-3-iodo-2-butenoate (**16**) (see Chart 2) increased significantly at temperatures above 100°C. Furthermore, it was found that the reaction product **16** was produced cleanly and efficiently (> 95% yield) when a stirred solution–suspension of **6** and sodium iodide (~1.6 equiv.) in a small amount of acetic acid (~6.7 equiv.) was heated at ~115°C for 90 min. Under these conditions, there was no indication of the formation of ethyl (E)-3-iodo-2-butenoate.

Subjection of the substrates **7–15** (Chart 1) to reaction conditions identical with or similar to those outlined above provided the results summarized in Table 1 (see Chart 2 for the structural formulas of the reaction products).

As shown by the data given in Table 1, the conversions investigated were generally efficient and complete in convenient reaction times. Of the reactions involving structurally "simple" substrates (Table 1, entries 1–3, 7, 9), the transformations of ethyl 4,4-dimethyl-2-pentynoate (**8**) and ethyl 3-phenylpropy-

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TABLE 1. Preparation of alkyl (Z)-3-iodo-2-alkenoates

Entry	Substrate[a] (amount: mg, mmol)	Equiv. of NaI	Equiv. of HOAc	Reaction time (h)	Product[a]	Distillation temperature (°C/Torr)	Yield[b] (g, %)
1	6 (655, 5.8)	1.6	6.4	1.5	16	35–50/0.3	1.37, 98
2	7 (674, 4.8)	1.6	6.4	1.5	17	60–80/0.3	1.14, 88
3	8 (541, 3.5)	3.2	13.0	7.0	18	60–72/0.3	0.84, 85
4	9 (929, 3.7)	1.6	6.2	1.5	19	90–100/0.3	1.08, 77[c]
5	10 (550, 3.0)	1.6	6.4	1.5	20	90–100/0.3	0.76, 81
6	11 (192, 1.2)	4.0	13.0	2.25	19	90–100/0.3	0.36, 80[d]
7	12 (932, 5.3)	3.2	12.8	4.0	21	95–100/0.03	1.54, 95
8	13 (178, 1.1)	5.5	9.5	3.25	22	40–45/0.08	0.11, 35[e]
9	14 (5170, 61.5)	1.6	6.4	1.0	24	30–40/0.03	10.79, 83
10	15 (194, 1.0)	3.2	12.8	1.75	25	—	0.34, 76

[a]See Charts 1 and 2 for the structural formulas of the substrates and products, respectively.
[b]Yield of purified, distilled (or crystallized) product.
[c]Also isolated, in 9% yield, was compound 20.
[d]Also isolated, in 3% yield, was compound 20.
[e]Also obtained were 19% of the starting material 13 and 28% of ethyl (Z)-3-iodopropenoate (23).

16 R^1 = Me, R^2 = Et
17 R^1 = i-Pr, R^2 = Et
18 R^1 = t-Bu, R^2 = Et
19 R^1 = I(CH$_2$)$_3$, R^2 = Me
20 R^1 = AcO(CH$_2$)$_3$, R^2 = Me
21 R^1 = Ph, R^2 = Et
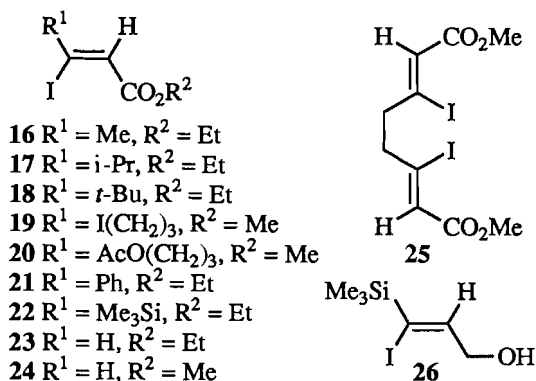22 R^1 = Me$_3$Si, R^2 = Et
23 R^1 = H, R^2 = Et
24 R^1 = H, R^2 = Me

CHART 2

noate (12) into the corresponding (Z)-3-iodoalkenoates 18 and 21 (entries 3, 7) are particularly noteworthy. Because of the presence of the sterically bulky tert-butyl and phenyl groups in 8 and 12, respectively, the reactions were, relatively speaking, quite slow and, in each case, the use of larger quantities of sodium iodide and acetic acid was found to be beneficial. Under these circumstances, the products 18 and 21 were produced cleanly and efficiently.

Functionalized substrates were also employed successfully (entries 4–6). Methyl (Z)-3,6-diiodo-2-hexenoate (19) could be derived from either the iodo ester 9 (entry 4) or the chloro ester 11 (entry 6). In each of these reactions, there was also produced a small amount of the acetoxy iodide 20. The latter substance was also derived in very good yield from the α,β-acetylenic ester 10 (entry 5), thus showing that an acetoxy function is stable under the reaction conditions.

The use of this method for the conversion of ethyl 3-(trimethylsilyl)propynoate (13) into the structurally novel substance ethyl (Z)-3-iodo-3-(trimethylsilyl)propenoate (22) turned out to be quite inefficient (entry 8). A significant side reaction in this (sluggish) process involved protonative loss of the Me$_3$Si function to produce the iodo ester 23.

More successful was the application of the developed procedure to a substrate possessing two α,β-acetylenic ester functions (entry 10). In this case, dimethyl 2,6-octadiyndioate (15) was converted in good yield into the structurally interesting diiodo ester 25, a crystalline solid with melting point 73–74°C.

In each of a number of representative cases (substances 16–18, 25), the expected (17–20) configuration of the product was confirmed by use of nuclear Overhauser enhancement (nOe) difference experiments (see Experimental). To confirm the structure of product 22, this material was reduced with diisobutylaluminum hydride to afford the known (26) alcohol 26 (Chart 2).

Finally, our procedure was employed to effect the conversion of propynoic acid (27) into (Z)-3-iodopropenoic acid (28)

[1]

NaI (1.6 equiv.)
HOAc (6.4 equiv.)
115 °C, 1.5 h
(75%)

27   28
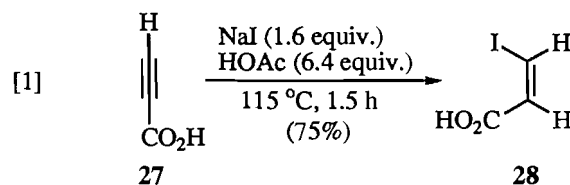
(eq.[1]). The required reaction time was quite short (1.5 h) and, following a simple workup procedure, crystalline 28 (2, 20, 27) was obtained in 75% yield.

Conclusion

This brief study resulted in the development of an effective general protocol for the conversion of alkyl 2-alkynoates into synthetically useful alkyl (Z)-3-iodo-2-alkenoates. The procedure is straightforward, the reaction times are conveniently short, and, importantly, the process works well for a structurally diverse set of substrates.

Experimental

General information

Distillation temperatures, which refer to short path (Kugelrohr) distillations, and melting points are uncorrected. Proton nuclear magnetic resonance (^{1}H nmr) spectra were recorded using CDCl$_3$ as the solvent. Signal positions (δ values) were measured relative to those of Me$_4$Si (δ = 0) or CHCl$_3$ (δ = 7.25). Carbon nuclear magnetic resonance (^{13}C nmr) spectra were recorded using CDCl$_3$ as the solvent and the signal positions are given relative to that of CDCl$_3$ (δ = 77.0). Infrared (ir) spectra were obtained on liquid films (NaCl plates), unless otherwise noted. Flash chromatography (28) was carried out with 230–400 mesh silica gel (E. Merck), while radial chromatography was performed with a Chromatotron model 7924, using plates coated with silica gel 60, PF$_{254}$, with CaSO$_4$ (E. Merck no. 7749).

Note: All reactions were carried out under an atmosphere of argon in flame- or oven-dried glassware.

Methyl 6-acetoxy-2-hexynoate (10)

Ethanoyl chloride (4.2 mL, 59 mmol) was added to a solution of methyl 6-(tetrahydropyranyloxy)-2-hexynoate (22) (2.68 g, 11.8 mmol) in dry THF (25 mL) and the resultant mixture was stirred at room temperature for 23 h. Saturated aqueous $NaHCO_3$ (50 mL) and diethyl ether (100 mL) were added and the phases were separated. The organic phase was washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography (150 g silica gel, 3:1 petroleum ether – Et_2O) of the crude product and distillation (90–110°C/0.3 Torr (1 Torr = 133.3 Pa)) of the acquired liquid afforded 1.51 g (70%) of the acetylenic ester **10**, a colorless oil that displayed ir (neat): 2239, 1737, 1719, 1255, 1046 cm^{-1}; ^{1}H nmr (400 MHz) δ: 1.88 (quintet, 2H, J = 7 Hz), 2.04 (s, 3H), 2.42 (t, 2H, J = 7 Hz), 3.73 (s, 3H), 4.13 (t, 2H, J = 7 Hz). Anal. calcd. for $C_9H_{12}O_4$: C 58.69, H 6.57; found: C 58.62, H 6.73. Exact Mass calcd. for $C_8H_9O_4$(M^+ – Me): 169.0501; found: 169.0492.

General procedure for the conversion of α,β-acetylenic esters 6–15 into alkyl (Z)-3-iodo-2-alkenoates

An oil bath was preheated at 115°C for 15 min. A flask (argon atmosphere) containing a mixture (suspension) of the α,β-acetylenic ester, sodium iodide, and glacial acetic acid was placed in the oil bath and the mixture was stirred at 115°C for the specified time. The bath was removed and the brown mixture was transferred while hot to a separatory funnel containing water (~8–10 mL per mmol of ester substrate). The reaction flask was washed with a mixture of water (~2–5 mL) and diethyl ether (~25–30 mL per mmol of ester substrate). The washings were added to the separatory funnel. The phases were separated and the aqueous phase was washed with diethyl ether. The combined organic phases were washed sequentially with saturated aqueous sodium bicarbonate, 1 M aqueous sodium thiosulfate, and brine (~8–10 mL of each solution per mmol of ester substrate), and then were dried ($MgSO_4$ or Na_2SO_4) and concentrated. Distillation of the remaining material from basic alumina (~30–50 mg per mmol of ester substrate) provided the alkyl (Z)-3-iodo-2-alkenoate. Details regarding quantities of reactants, reaction times, distillation temperatures, and yields are given in Table 1.

The following substances were prepared via the general procedure. Any deviations from this protocol are noted in each case.

Ethyl (Z)-3-iodo-2-butenoate (16) (16) (Table 1, Entry 1)

Colorless oil, ir (neat): 1728, 1629, 1309, 1180 cm^{-1}; ^{1}H nmr (400 MHz) δ: 1.28 (t, 3H, J = 7 Hz), 2.71 (d, 3H, J = 1.5 Hz), 4.20 (q, 2H, J = 7 Hz), 6.27 (q, 1H, J = 1.5 Hz). In nOe difference experiments, irradiation at each of δ 2.71 and 6.27 caused enhancement of the signals at 6.27 and 2.71, respectively; ^{13}C nmr (50.3 MHz) δ: 14.2, 36.5, 60.5, 113.1, 125.6, 164.2. Anal. calcd. for $C_6H_9IO_2$: C 30.02, H 3.78, I 52.87; found: C 29.84, H 3.71, I 52.60. Exact Mass calcd.: 239.9648; found: 239.9646.

Ethyl (Z)-3-iodo-4-methyl-2-pentenoate (17) (Table 1, Entry 2)

Colorless oil, ir (neat): 1730, 1619, 1192, 1033 cm^{-1}; ^{1}H nmr (400 MHz) δ: 1.11 (d, 6H, J = 7 Hz), 1.29 (t, 3H, J = 7 Hz), 2.46 (septet, 1H, J = 7 Hz), 4.20 (q, 2H, J = 7 Hz), 6.39 (s, 1H). In nOe difference experiments, irradiation at each of δ 2.46 and 6.39 resulted in enhancement of the signals of 6.39 and 2.46, respectively; ^{13}C nmr (50.3 MHz) δ: 14.2, 23.0, 43.8, 60.5, 122.8, 131.8, 164.9. Anal. calcd. for $C_8H_{13}IO_2$: C 35.84, H 4.89; found: C 35.69, H 4.93. Exact Mass calcd.: 267.9961; found: 267.9955.

Ethyl (Z)-3-iodo-4,4-dimethyl-2-pentenoate (18) (Table 1, Entry 3)

Colorless oil, ir (neat): 1733, 1611, 1301, 1179, 1040 cm^{-1}; ^{1}H nmr (400 MHz) δ: 1.22 (s, 9H), 1.29 (t, 3H, J = 7 Hz), 4.21 (q, 2H, J = 7 Hz), 6.38 (s, 1H). In nOe difference experiments, irradiation at each of δ 1.22 and 6.38 caused enhancement of the resonances at 6.38 and 1.22, respectively; ^{13}C nmr (50.3 MHz) δ: 14.2, 30.3, 42.1, 60.7, 123.0, 136.0, 165.5. Anal. calcd. for $C_9H_{15}IO_2$: C 38.32, H 5.36, I 44.98;

found: C 38.44, H 5.36, I 44.71. Exact Mass calcd.: 282.0118; found: 282.0111.

Methyl (Z)-3,6-diiodo-2-hexenoate (19)

(a) *From methyl 6-iodo-2-hexynoate (9) (Table 1, Entry 4)*

Radial chromatography (4 mm plate, 5:1 petroleum ether – diethyl ether) of the crude product, followed by distillation of the acquired oils, gave the diiodide **19** (77%) and the iodo acetate **20** (9%) (vide infra). Compound **19**, a colorless oil, displayed ir (neat): 1730, 1624, 1219, 1175 cm^{-1}; ^{1}H nmr (400 MHz) δ: 2.09 (quintet, 2H, J = 7 Hz), 2.80 (td, 2H, J = 7, 1 Hz), 3.13 (t, 3H, J = 7 Hz), 3.73 (s, 3H), 6.44 (t, 1H, J = 1 Hz); ^{13}C nmr (50.3 MHz) δ: 4.2, 32.0, 47.7, 51.7, 118.8, 126.0, 164.7. Anal. calcd. for $C_7H_{10}I_2O_2$: C 22.13, H 2.65, I 66.80; found: C 22.35, H 2.69, I 66.60. Exact Mass calcd. for $C_7H_{10}IO_2$ (M^+ – I): 252.9726; found: 252.9729.

(b) *From methyl 6-chloro-2-hexynoate (11) (Table 1, Entry 6)*

Radial chromatography (2 mm plate, 130 mL of 85:15 petroleum ether – diethyl ether and then 75:25 petroleum ether – diethyl ether) of the crude product gave compound **19** (80%) and the iodo acetate **20** (3%) (vide infra). The spectral data of **19** were found to be identical with those recorded above.

Methyl (Z)-6-acetoxy-3-iodo-2-hexenoate (20) (Table 1, Entry 5)

Colorless oil, ir (neat): 1734, 1624, 1243, 1174 cm^{-1}; ^{1}H nmr (400 MHz) δ: 1.92 (quintet, 2H, J = 7 Hz), 2.02 (s, 3H), 2.74 (t, 2H, J = 7 Hz), 3.70 (s, 3H), 4.03 (t, 2H, J = 7 Hz), 6.34 (s, 1H); ^{13}C nmr (50.3 MHz) δ: 20.9, 28.2, 44.4, 51.6, 62.5, 119.9, 125.3, 164.7, 170.9. Anal. calcd. for $C_9H_{13}IO_4$: C 34.64, H 4.20, I 40.66; found: C 35.00, H 4.22, I 40.37. Exact Mass calcd.: 311.9859; found: 311.9864.

Ethyl (Z)-3-iodo-3-phenylpropenoate (21) (Table 1, Entry 7)

Radial chromatography (4 mm plate, 9:1 petroleum ether – ethyl acetate) of the crude product, followed by distillation of the acquired liquid, produced the iodo ester **21**, a yellow oil that displayed ir (neat): 1724 cm^{-1}; ^{1}H nmr (400 MHz) δ: 1.31 (t, 3H, J = 7 Hz), 4.26 (q, 2H, J = 7 Hz), 6.61 (s, 1H), 7.32–7.33 (m, 3H), 7.49–7.52 (m, 2H); ^{13}C nmr (50.3 MHz) δ: 14.3, 60.8, 116.1, 126.9, 128.4, 128.8, 130.0, 143.3, 164.6. Anal. calcd. for $C_{11}H_{11}IO_2$: C 43.73, H 3.67, I 42.00; found: C 43.76, H 3.76, I 41.80. Exact Mass calcd.: 301.9804; found: 301.9803.

Ethyl (Z)-3-iodo-3-(trimethylsilyl)propenoate (22) (Table 1, Entry 8)

Radial chromatography (4 mm plate, 4:1 petroleum ether – dichloromethane) of the crude product, followed by distillation of the acquired liquids, gave 34 mg (19%) of the starting material **13**, along with the iodo silane **22** (35%) and ethyl (Z)-3-iodopropenoate (**23**) (20, 29) (65 mg, 28%). Compound **22**, a colorless oil, exhibited ir (neat): 1731, 1290, 1251, 1176, 844 cm^{-1}; ^{1}H nmr (400 MHz) δ: 0.23 (s, 9H), 1.31 (t, 3H, J = 7 Hz), 4.23 (q, 2H, J = 7 Hz), 6.89 (s, 1H); ^{13}C nmr (100.6 MHz) δ: –1.7, 14.2, 60.8, 125.6, 134.6, 164.1. Anal. calcd. for $C_8H_{15}IO_2Si$: C 32.22, H 5.07; found: C 32.27, H 5.00. Exact Mass calcd.: 297.9886; found 297.9890.

Ethyl (Z)-3-iodopropenoate (**23**) (20, 29), a colorless oil, displayed ir (neat): 1728, 1600, 1324, 1198, 1166, 1028, 807 cm^{-1}; ^{1}H nmr (400 MHz) δ: 1.30 (t, 3H, J = 7 Hz), 4.23 (q, 2H, J = 7.0 Hz), 6.86 (d, 1H, J = 9 Hz), 7.42 (d, 1H, J = 9 Hz); ^{13}C nmr (50.3 MHz) δ: 14.2, 60.8, 94.6, 129.9, 164.6.

Methyl (Z)-3-iodopropenoate (24) (19, 20) (Table 1, Entry 9)

The hot reaction mixture was poured into 200 mL of water (separatory funnel). The reaction flask was washed with a mixture of water (10 mL) and diethyl ether (60 mL) and the washings were added to the separatory funnel. The phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed (saturated aqueous sodium bicarbonate (20 mL), saturated aqueous sodium thiosulfate (20 mL), brine (20 mL)), dried ($MgSO_4$), and concentrated. Distillation of the derived oil gave methyl (Z)-3-iodopropenoate (**24**) (19, 20), a colorless oil that showed ^{1}H nmr (400

MHz) δ: 3.77 (s, 3H), 6.89 (d, 1H, *J* = 9 Hz), 7.45 (d, 1H, *J* = 9 Hz); ^{13}C nmr (50.3 MHz) δ: 51.6, 95.1, 129.4, 164.8.

Dimethyl (Z,Z)-3,6-diiodo-2,6-octadiendioate (25) (Table 1, Entry 10)

The crude product was passed through a short column of basic alumina (1 g, activity 1, elution with dichloromethane). Concentration (water aspirator, then vacuum pump) of the eluate afforded the diiodo diester **25**, a crystalline solid. This material exhibited mp 73–74°C (from petroleum ether – diethyl ether); ir (KBr): 1722, 1614, 1427, 1326, 1161, 1053, 875 cm^{-1}; ^{1}H nmr (400 MHz) δ: 2.95 (s, 4H), 3.71 (s, 6H), 6.38 (s, 2H). In nOe difference experiments, irradiation at each of δ 2.95 and 6.38 caused enhancement of the resonances at 6.38 and 2.95, respectively; ^{13}C nmr (50.3 MHz) δ: 46.5, 51.7, 117.2, 126.4, 164.5. Anal. calcd. for $C_{10}H_{12}I_2O_4$: C 26.69, H 2.69, I 56.40; found: C 26.87, H 2.75, I 56.46. Exact Mass calcd.: 449.8823; found: 449.8826.

(Z)-3-Iodo-3-trimethylsilyl-2-propen-1-ol (26)

To a cold (–78°C), stirred solution of ethyl (Z)-3-iodo-3-(trimethylsilyl)propenoate (**22**) (21 mg, 0.07 mmol) in 1.8 mL of dry diethyl ether was added a 1 M solution of diisobutylaluminum hydride in hexanes (0.21 mL, 0.21 mmol, 3 equiv.). The mixture was stirred at –78°C for 75 min and at 0°C for 95 min. Saturated aqueous ammonium chloride (1.5 mL) was added and the mixture was allowed to warm to room temperature. Water (15 mL) and diethyl ether (20 mL) were added and the phases were separated. The aqueous phase was extracted with diethyl ether (2 × 20 mL) and the combined organic phases were washed (brine), dried (Na_2SO_4), and concentrated. Radial chromatography (1 mm plate, 85:15 petroleum ether – diethyl ether) of the remaining liquid and subjection of the acquired oil to reduced pressure (0.3 Torr) afforded 13.5 mg (75%) of the alcohol **26** (26), a colorless oil that displayed ir (neat): 3331, 1250, 1031, 881, 842 cm^{-1}; ^{1}H nmr (400 MHz) δ: 0.18 (s, 3H), 1.6–1.7 (br s), 4.26 (d, 2H, *J* = 5 Hz), 6.49 (t, 1H, *J* = 5 Hz). In nOe difference experiments, irradiation at δ 6.49 caused enhancement of the signals at 0.18 and 4.26, while irradiation at δ 0.18 increased the intensity of the signal at 6.49; ^{13}C nmr (50.3 MHz) δ: –1.7, 69.5, 112.6, 146.4. Exact Mass calcd. for $C_6H_{13}IOSi$: 255.9780; found: 255.9787.

(Z)-3-iodopropenoic acid (28)

An oil bath was preheated to 115°C for 15 min. A flask (argon atmosphere) containing a solution–suspension of propynoic acid (**27**) (514 mg, 7.34 mmol), sodium iodide (1.76 g, 11.7 mmol), and glacial acetic acid (2.69 mL, 47.0 mmol) was placed in the oil bath and the mixture was stirred at 115°C for 90 min. The mixture was cooled to room temperature and the acetic acid was removed under reduced pressure (0.3 Torr, –78°C trap, ~10 min). The remaining dark oil was treated with dry diethyl ether (40 mL) and the resultant mixture was filtered. The collected material was washed with dry diethyl ether (~70 mL). The combined filtrate was washed with saturated aqueous sodium thiosulfate (20 mL) and the aqueous phase was extracted with diethyl ether (4 × 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated (water aspirator pressure, followed by vacuum pump, 0.3 Torr). Crystallization of the remaining viscous oil from hot diethyl ether – petroleum ether (cooled to 0°C) gave 1.09 g (75%) of the iodo acid **28**, which exhibited mp 62–64°C (lit. (27) mp 63–65°C); ^{1}H nmr

(400 MHz) δ: 6.96 (d, 1H, *J* = 9.5 Hz), 7.67 (d, 1H, *J* = 9.5 Hz), 11.95 (br s, 1H); ^{13}C nmr (100.6 MHz) δ: 98.0, 129.4, 169.7. Exact Mass calcd. for $C_3H_3IO_2$: 197.9177; found: 197.9181.

Acknowledgements

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