mL) was added dropwise to a solution of aluminum chloride (36.8 g, 0.28 mol) and acryloyl chloride (25 g, 0.28 mol) in dichloromethane (100 mL) with stirring at 0 °C over 30 min. After the reaction mixture was stirred for 2 h at the same temperature, it was poured into 500 mL of ice/water, extracted with dichloromethane, and washed with water. After evaporation of the solvent, the resulting residue was distilled under reduced pressure to obtain 2,3,4,5,6-pentamethyl-1-acryloylbenzene (**1a**) (26.4 g, 70%, bp 145–147 °C/3 mmHg). Recrystallization of the product from methanol gave the purified **1a** of mp 76–77 °C (40% yield).

In a similar manner, compounds **1b–m** were prepared from Friedel–Crafts reactions of corresponding polymethylbenzenes with alkenoyl chlorides.

Preparation of KF/Basic Alumina. The KF/alumina was prepared by the procedure described in the literature.[12e] The mixture of potassium fluoride (1.00 g), water (8 mL), and basic alumina (5.00 g, from ICN Biochemical GmbH) was placed on a rotary evaporator, and the water was removed under reduced pressure. The resulting powder was dried at 145 °C at 1 mmHg for 7 h before use.

General Procedure for the Nitration of 1. The Nitration of 2,3,4,5,6-Pentamethyl-1-acryloylbenzene (1a). A solution of 99% nitric acid (0.623 g, 9.9 mmol) in acetic anhydride (8 mL) was added to a solution of **1a** (1.00 g, 4.9 mmol) in acetic anhydride (8 mL) with stirring at 0 °C over 15 min. After the reaction mixture was stirred for 2 h at the same temperature, it was poured into 300 mL of ice/water and then stirred overnight. The resulting solid was extracted with ether, washed with water (3 × 100 mL), and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crude product (1.28 g). After measurement of the HPLC, the product was chromatographed on silica gel with benzene to isolate **2a** (0.63 g, 51%, mp 93–98 °C), **8** (0.019 g, 2%, mp 143–145 °C), **5** (0.013 g, 1.1%, mp 116–118 °C), and oily products (0.15 g). The above obtained oily products were again chromatographed by HPLC using a Finepack SIL column (JASCO silica gel) as the column and *n*-hexane/ethyl acetate (8/2 v/v) as the eluent to give **6** (0.028 g, 2.2%, mp 62–63 °C) and **7** (0.006 g, 0.5%, mp 128–131 °C). Recrystallization of the individual compounds from methanol gave the purified compounds **2a** (mp 105–106 °C), **5** (mp 117–118 °C), **6** (mp 63–64 °C), **7** (mp 129–131 °C), and **8** (mp 155–156 °C, lit.[14] mp 158–159 °C). The nitration of **1b–m** was also carried out under the same conditions described above.

General Procedure for the Intramolecular Michael Reaction. The Reaction of 2e with DBU. To a solution of **2e** (1.00 g, 3.83 mmol) in dichloromethane (20 mL) was added a solution of DBU (0.062 g, 0.38 mmol) in dichloromethane (5 mL) at room temperature, and the mixture was stirred for 24 h at the same temperature. The reaction was quenched by addition of 1 M hydrochloric acid (ca. 30 mL), and the reaction mixture was extracted with dichloromethane (50 mL), washed with water, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave a brown-colored residue. After measurement of the HPLC, the residue was passed on a short column of silica gel with *n*-hexane/ethyl acetate (8/2 v/v) to afford the adduct (0.70 g, 70%). The crude adduct was subjected to preparative column chromatography on silica gel. Elution with *n*-hexane/ethyl acetate (8/2 v/v) afforded the cis adduct (*cis*-**3e**) (0.15 g, 15% yield, mp 82–85 °C) and the trans adduct (*trans*-**3e**) (0.42 g, 42% yield, mp 142–144 °C). Recrystallization of the adducts from 80% MeOH and EtOH gave the compounds of mp 84–85 °C and 143–144 °C, respectively. In a similar manner, the Michael reactions of nitromethyl compounds **2b–m** were carried out to give the corresponding **3b–m**.

The Reaction of 2e with KF/Basic Alumina. The typical procedure for the Michael reactions is illustrated by the following procedure for **2e**. The KF/basic alumina (0.5 g) was added to a solution of **2e** (0.100 g, 0.38 mmol) in dry THF (7 mL), and the resulting suspension was stirred at room temperature for 2 h. After that, the reaction mixture was filtered, and the alumina was washed with ether (20 mL). The solvent of the combined filtrate was removed under reduced pressure to give the crude adduct of 0.095 g (95% yield). The product was subjected to HPLC measurement to determine the product distribution.

The Oxidation of 3f. The reaction was carried out according to the procedure described in the literature,[5] to give 5,6,7,8-tetramethyltetralin-1,4-dione (**77**): 99% yield; mp 125–126 °C (MeOH); ^{1}H NMR δ 2.33 (s, 6 H), 2.50 (s, 6 H), 3.00 (s, 4 H); IR ν 1685, 1671 cm^{-1}; MS *m/e* 216 (M$^+$, 95), 201 (17), 187 (23), 173 (100). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.83; H, 7.66.

MNDO Calculations. The MNDO calculations of 2,3,4,6-tetramethyl-1-acryloylbenzene (**1f**) and its protonated benzenonium ions were made by using the MOPAC-MNDO program of Dewar and collaborators.[7] All geometric parameters (bond length, bond angles, and dihedral angles) were optimized without any specific assumptions.

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Supplementary Material Available: Physical and spectroscopic data of **1a–m**, **2a–m**, **3a–m**, **5–7**, and **9–16** (15 pages). Ordering information is given on any current masthead page.

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Conjugate Addition of Acyloxy Groups to Alkynylphenyliodonium Tetrafluoroborates under Both Basic and Acidic Conditions. Synthesis of α-Acyloxy Ketones

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Reaction of alkynylphenyliodonium tetrafluoroborates **1** with sodium salts of carboxylic acids in the presence of water affords α-acyloxy ketones. The reaction also proceeds under acidic conditions. The fact that the reaction of (4-hydroxy-1-butynyl)phenyliodonium tetrafluoroborate (**11**) with 2 equiv of sodium acetate in THF–water (3:1) gives 1,4-diacetoxy-2-butanone (**12**) suggests a reaction mechanism involving an intervention of [2-(acyloxy)-1-alkenyl]phenyliodonium tetrafluoroborates, produced by Michael-type addition of acyloxy groups to **1**.

Alkynylphenyliodonium salts are highly electron-deficient species and react with a variety of nucleophiles. They are formally tetraphilic (α-, α′-, and β-carbons and iodine) toward the attack of nucleophiles.[1] Conjugate addition

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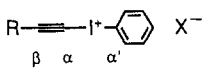


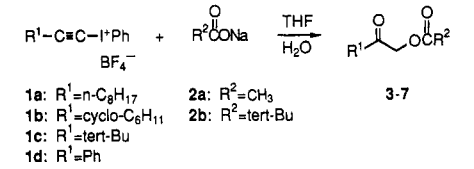
of nucleophiles to the β-carbon of alkynyliodonium salts constitutes a key step for the synthesis of cyclopentenes, polysubstituted furans, β-heteroatom-substituted alkenyliodonium salts, and esters.[2-5] A ligand exchange reaction of the *tert*-butylethynyl group at trivalent iodine with 2-lithiofuran yielding aryl(2-furyl)iodonium tosylates has been reported.[6,7] It has been well documented that alkenylphenyliodonium tetrafluoroborates behave similarly to the highly activated species of vinyl iodides, namely, vinyl cation equivalents, because of the high leaving ability of the phenyliodonium group.[8] Alkynylphenyliodonium salts similarly serve as reactive alkynyl cation equivalents and afford substitution products with concomitant reductive elimination of iodobenzene. Thus, alkynyltriphenylphosphonium tetrafluoroborates,[9] alkynyl sulfonates, carboxylates, and phosphates,[10] and conjugated enynes[11] were synthesized in good yield from alkynylphenyliodonium salts.

In 1979, Merkushev and co-workers reported that oxidation of phenylacetylene with [bis(trifluoroacetoxy)iodo]benzene in refluxing chloroform containing a small amount of water led to 2-hydroxyacetophenone via the formation of phenyl(phenylethynyl)iodonium trifluoroacetate.[12,13] Tamura and Kita successfully applied the reaction to the synthesis of dihydroxyacetone moieties of adriamycin antitumor antibiotics.[14] We report herein a synthesis of α-acyloxy ketones through Michael-type addition of acyloxy groups to alkynylphenyliodonium tetrafluoroborates 1 under both basic and acidic conditions.

Results and Discussion

Synthesis of α-Acyloxy Ketones under Basic Conditions. Alkynyliodonium tetrafluoroborates 1 were prepared from 1-alkynes and/or alkynyltrimethylsilanes (Scheme I) according to the method developed by us.[9,15]

Scheme I



Scheme II

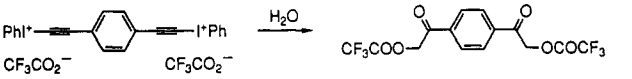


Table I. Reaction of Alkynyliodonium Tetrafluoroborates 1 with Sodium Carboxylates[a]

run	1	2 (equiv)	time, h	prod. (%)[b]
1	**1a**	**2a** (1.1)	0.5	**3** (72)
2	**1a**	**2a** (2.0)	0.5	**3** (78)
3	**1a**	**2b** (1.1)	0.5	**4** (75)
4	**1b**	**2a** (1.1)	0.5	**5** (48)
5	**1b**	**2a** (2.5)	0.5	**5** (58)
6	**1c**	**2a** (1.1)	4.5	**6** (30)
7	**1c**	**2a** (2.5)	4.5	**6** (47)
8	**1d**	**2a** (1.1)	1.0	**7** (24)
9	**1d**	**2a** (2.5)	1.0	**7** (29)

[a] Reactions were carried out at room temperature. [b] All yields are for isolated pure materials.

Table II. Reaction of Alkynyliodonium Tetrafluoroborates 1 with Acetic Acid[a]

run	1	time, h	prod. (%)[b]
10	**1a**	15	**3** (86)
11	**1b**	24	**5** (55)
12	**1c**	24	**6** (36)
13	**1d**	24	**7** (11)

[a] Reactions were carried out at 80 °C. [b] All yields are for isolated pure materials.

Treatment of (1-decynyl)phenyliodonium tetrafluoroborate (**1a**) with 1.1 equiv of sodium acetate in THF–water (2:1) at room temperature under nitrogen afforded 1-acetoxy-2-decanone (**3**)[16] in 72% yield (Table I, run 1). With 2 equiv of sodium acetate, the yield of **3** was improved to some extent (run 2). As shown in Table I, yields of α-acyloxy ketones decrease as the size of alkyl groups attached to the β-carbon of ethynyl groups of **1** increase. For example, **1c** bearing a sterically demanding *tert*-butyl group gave 1-acetoxy-3,3-dimethyl-2-butanone (**6**)[17] in low to moderate yields (runs 6 and 7). This is in marked contrast with the results obtained by altering the size of attacking nucleophiles, where the size of acyloxy groups showed negligible effect on product yields. This is exemplified by the reaction of **1a** with sodium pivalate (**2b**) to give a good yield of 1-(pivaloyloxy)-2-decanone (**4**) (run 3). Reaction of (arylethynyl)iodonium salts gave poor results; 2-acetoxyacetophenone (**7**)[18] was obtained in 29% yield (run 9).

The use of water is crucial to the success of this reaction. When the reaction was carried out in THF without adding water, the reaction course was dramatically altered and the desired α-acyloxy ketones were not obtained. In the absence of water, reaction of **1a** with sodium acetate in THF under solid–liquid heterogeneous conditions resulted in

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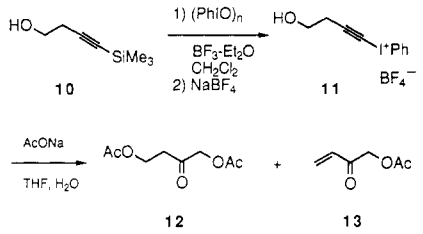
Scheme III



cleavage of the carbon–iodine bond, yielding 1-iododecyne (58% yield).

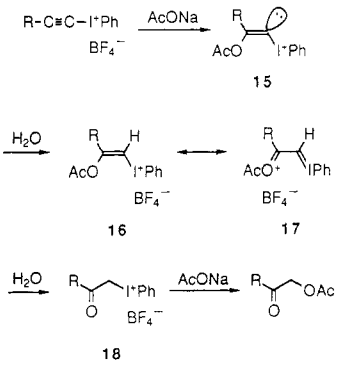
Synthesis of α-Acyloxy Ketones under Acidic Conditions. α-Acetoxy ketones may be synthesized from **1** under acidic conditions. Reaction of **1a** with a large excess of acetic acid in dichloromethane in the presence or in the absence of boron trifluoride–diethyl ether at room temperature gave the starting material. However, refluxing a solution of **1a** in acetic acid for 15 h gave **3** in 86% yield. α-Acetoxy ketones **5–7** were obtained in low to reasonable yields (Table II).

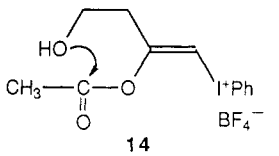
Reaction Mechanism. The synthesis of α-acyloxy ketones under basic conditions proceeds through a Michael-type addition of a nucleophile to the electron-deficient β-carbons of alkynyliodonium tetrafluoroborates **1**. Both an acetate anion and water should be considered as possible nucleophiles in this reaction. Merkushev and co-workers reported that hydrolysis of the alkynyliodonium trifluoroacetate **8** occurs readily even in the presence of traces of moisture in chloroform and leads to the bis(trifluoroacetate) **9** (Scheme II).[12a] As a first step of the hydrolysis, conjugate addition of either a trifluoroacetate anion[12b] or water[14] toward the alkynyliodonium salts was proposed, without any evidence. In contrast to the unstable nature of **8** toward moisture, the iodonium tetrafluoroborate **1a** was found to resist hydrolysis by water, for example, 65% of **1a** was recovered unchanged even by prolonged treatment with a large excess of water in THF at room temperature.[19] The results may suggest that water itself does not serve as a good nucleophile for the conjugate addition to **1a** at room temperature.

Why is water required in the synthesis of α-acyloxy ketones from **1**? (4-Hydroxy-1-butynyl)phenyliodonium tetrafluoroborate (**11**) was prepared from 4-hydroxy-1-(trimethylsilyl)-1-butyne (**10**) by the reaction with iodosylbenzene in the presence of boron trifluoride–diethyl ether in dichloromethane in 68% yield in order to answer the question and to gain evidence against the conjugate addition of water to **1**. Reaction of **11** with sodium acetate (2 equiv) in THF–water (3:1) at room temperature for 30 min did afford the expected diacetate **12**,[20] albeit in low yield (39%). The diacetate **12** contains a small amount of the conjugated enone **13**, which was probably produced by the β-elimination of acetic acid from **12** during isolation with preparative thin-layer chromatography using silica gel (Scheme III).[21] More importantly, in the absence of water the reaction of **11** with sodium acetate gave **12** in 36% yield. The results show that the hydroxy group of **11** can play the role of water in the reaction.

It is generally accepted that acetylation of hydroxy groups does not take place by the reaction with sodium acetate in the presence of water. To explain the transformation of the hydroxy group of **11** to an acetoxy group under these conditions, we should consider a reaction process involving a reactive intermediate that can undergo the acetylation of the hydroxy group. We propose an intervention of the (β-acetoxyvinyl)iodonium tetrafluoroborate **14** produced by Michael-type addition of an acetate anion. The acetate **14** may undergo an intramolecular 1,5-shift of the acetyl group via a six-membered transition state, shown by the arrow.

Scheme IV





The results obtained suggest that the synthesis of α-acetoxy ketones under basic conditions involves an initial conjugate addition of acetate anion to **1**, yielding iodonium ylide **15** (Scheme IV). In the presence of an appropriate proton source such as water, the ylide **15** affords (β-acetoxyalkenyl)phenyliodonium tetrafluoroborates **16**. The *Z* stereochemistry of **16** was deduced tentatively, based on the results of the synthesis of ((*Z*)-β-azidoalkenyl)phenyliodonium tetrafluoroborates by the addition of hydrazoic acid to **1**.[1,3] It is reasonable to assume that **16** may be highly susceptible toward hydrolysis. In fact, all efforts to isolate **16** were unsuccessful. Hydrolysis by water yielding alkyliodonium salts **18**, followed by substitution of the phenyliodonium group with acetate anion, gives α-acetoxy ketones.[12b,22]

The reaction process of Scheme IV addresses the role of water in the reaction, namely, protonation of **15** and hydrolysis of **16**. In addition, it is noted that the use of water makes the reaction mixture liquid–liquid heterogeneous. The reaction process may be valid in the case of the synthesis of α-acetoxy ketones under acidic conditions.

Conclusions. Alkynylphenyliodonium tetrafluoroborates **1** serve as a useful precursor for the synthesis of α-acyloxy ketones under both basic and acidic conditions. The reaction proceeds via the facile Michael-type addition of an acyloxy group to **1**, due to the highly electron-deficient nature. In conjunction with the versatility of α-acyloxy ketones in organic synthesis,[23] the reaction offers many advantages including high efficiency and mildness of the reaction conditions.

Experimental Section

Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO A-202 spectrophotometer. NMR spectra were recorded on either a JEOL JNM-FX 100, Varian VXR 200, or JEOL

(19) Exposure of **1a** to sodium hydroxide in THF–water (2:1) at 0 °C for 20 min undergoes the extensive sp-carbon–iodine bond cleavage yielding 1-decyne (33%) and iodobenzene (97%).

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JNM-GX 400 spectrometer. Chemical shifts (^1H, ^{13}C) were reported in parts per million (ppm) downfield from internal tetramethylsilane. Mass spectra (MS) were taken on a JEOL JMS-DX 300 spectrometer. Preparative thin layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254).

Materials. Alkynyliodonium tetrafluoroborates **1** were prepared from 1-alkynes and/or alkynyltrimethylsilanes.[9,15] Sodium pivalate (**2b**) was prepared from pivalic acid and sodium carbonate.[24]

General Procedure for Synthesis of α-Acyloxy Ketones under Basic Conditions. A solution of alkynylphenyliodonium tetrafluoroborate **1** (0.1 mmol) in freshly distilled THF (1 mL) was added dropwise to a stirred solution of sodium carboxylate **2** (1.1–2.5 mmol) in water (0.5 mL) at 0 °C under nitrogen. The mixture was stirred under the conditions described in Table I. The reaction mixture was poured into water and extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by preparative TLC to give α-acyloxy ketones **3–7**.

1-Acetoxy-2-decanone (3): colorless needles (recrystallized from diethyl ether–hexane); mp 56 °C (lit.[16] mp 54 °C); IR ($CHCl_3$) 1750, 1730, 1235 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.65 (s, 2 H), 2.41 (t, J = 7.3 Hz, 2 H), 2.17 (s, 3 H), 1.61 (quint, J = 7.3 Hz, 2 H), 1.35–1.20 (10 H), 0.88 (t, J = 7.3 Hz, 3 H); MS m/z (relative intensity) 214 (3, M^+), 141 (100).

1-(Pivaloyloxy)-2-decanone (4): colorless oil; IR ($CHCl_3$) 2975, 2940, 2870, 1730, 1480, 1460, 1365, 1280, 1160, 1135 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.62 (s, 2 H), 2.40 (t, J = 7.5 Hz, 2 H), 1.60 (quint, J = 7.5 Hz, 2 H), 1.35–1.20 (19 H), 0.88 (t, J = 7 Hz, 3 H); MS m/z (relative intensity) 256 (2, M^+), 158 (22), 141 (29), 85 (40), 57 (100); HRMS calcd for $C_{15}H_{28}O_3$ (M^+) 256.2039, found 256.2057. Anal. Calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01. Found: C, 70.36; H, 11.23.

Acetoxymethyl cyclohexyl ketone (5): colorless prisms (recrystallized from diethyl ether–hexane); mp 40 °C (lit.[25] mp 38–39.5 °C); IR ($CHCl_3$) 1750, 1725, 1230 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.73 (s, 2 H), 2.42 (tt, J = 11.3, 3.5 Hz, 1 H), 2.17 (s, 3 H), 1.89–1.76 (m, 4 H), 1.71–1.64 (m, 1 H), 1.46–1.16 (m, 5 H); MS m/z (relative intensity) 184 (4, M^+), 124 (9), 111 (40), 83 (100).

1-Acetoxy-3,3-dimethyl-2-butanone (6): colorless oil;[17] IR ($CHCl_3$) 1750, 1725, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.88 (s, 2 H), 2.17 (s, 3 H), 1.21 (s, 9 H); MS m/z (relative intensity) 158 (8, M^+), 101 (9), 85 (17), 71 (10), 57 (100).

2-Acetoxyacetophenone (7): colorless plates (recrystallized from diethyl ether–hexane);[18] mp 48.5–49 °C; IR (KBr) 1735, 1690, 1225 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.96–7.88 (m, 2 H), 7.67–7.56 (m, 1 H), 7.56–7.43 (m, 2 H), 5.34 (s, 2 H), 2.23 (s, 3 H).

Reaction of 1a with Sodium Acetate in the Absence of Water. To a suspension of sodium acetate (32 mg, 0.39 mmol) in THF (1.5 ml) was added a solution of **1a** (150 mg, 0.35 mmol) in THF (2.5 ml) at room temperature under nitrogen, and the mixture was stirred for 30 min. The reaction mixture was quenched with water and extracted with diethyl ether. Preparative TLC (8:2 hexane–ethyl acetate) afforded 1-iododecyne (55 mg, 58%): ^1H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, J = 7.2 Hz, 2 H), 1.51 (quint, J = 7.2 Hz, 2 H), 1.42–1.20 (10 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 94.7, 31.9, 29.3, 29.1, 28.8, 28.6, 22.8, 20.9, 14.2, –7.3; MS m/z (relative intensity) 264 (5, M^+), 208 (8), 180 (7), 95 (36), 81 (100); HRMS calcd for $C_{10}H_{17}I$ (M^+) 264.0377, found 264.0386.

General Procedure for Synthesis of α-Acyloxy Ketone under Acidic Conditions. A solution of alkynylphenyliodonium tetrafluoroborate **1** (0.17 mmol) in acetic acid (2 mL) was heated at 80 °C under nitrogen for 15–24 h. The solvent was removed under reduced pressure to give a crude oil. Purification by preparative TLC gave α-acyloxy ketones (Table II).

Synthesis of (4-Hydroxy-1-butynyl)phenyliodonium Tetrafluoroborate (11). Boron trifluoride–diethyl ether (1.28 g, 9.0 mmol) was added dropwise to a stirred suspension of iodosylbenzene (0.99 g, 4.5 mmol) and 4-hydroxy-1-(trimethylsilyl)-1-butyne (**10**) (0.54 g, 3.8 mmol), prepared from commercially available 4-hydroxy-1-butyne through bissilylation and then selective hydrolysis, in dichloromethane (16 mL) at 0 °C. A yellow color developed. The mixture was stirred at 0 °C for 10 min. Sodium tetrafluoroborate (8.3 g, 76 mmol) was added and the mixture was stirred vigorously at 0 °C for 10 min. The insoluble precipitate was filtered off and washed with dichloromethane (3 × 30 mL). The combined organic solution was concentrated under aspirator vacuum to give an oil. Decantation with hexane and diethyl ether several times afforded 0.921 g (68%) of **11** as an oil: IR (film) 3590, 3400, 2180, 1565, 1475, 1450, 1100–1000, 740, 670 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 8.23–8.18 (m, 2 H), 7.79–7.73 (m, 1 H), 7.64–7.58 (m, 2 H), 3.68 (t, J = 6.4 Hz, 2 H), 2.78 (t, J = 6.4 Hz, 2 H); ^{13}C NMR (50 MHz, CD_3OD) δ 135.3, 133.6, 133.1, 116.7, 108.0, 60.2, 24.6, 23.7; MS (FAB) m/z [$(M - BF_4)^+$].

Reaction of 11 with Sodium Acetate in the Presence of Water. A solution of sodium acetate (22 mg, 0.26 mmol) in water (0.5 mL) was added to a stirred solution of **11** (48 mg, 0.13 mmol) in THF (1.5 mL) at 0 °C under nitrogen. The reaction mixture was stirred for 30 min at room temperature. Usual workup left an oil. Preparative TLC (1:1 hexane–ethyl acetate) gave 9.6 mg (39%) of the diacetate **12**[20] as a colorless oil, which was contaminated with a small amount of **13**. **12**: IR ($CHCl_3$) 3040, 2950, 1740, 1415, 1370, 1230, 1050, 605 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 4.68 (s, 2 H), 4.36 (t, J = 6.3 Hz, 2 H), 2.77 (t, J = 6.3 Hz, 2 H), 2.18 (s, 3 H), 2.04 (s, 3 H); MS m/z (relative intensity) 188 (0.4, M^+), 149 (3), 128 (2), 115 (100), 73 (15); HRMS calcd for $C_8H_{12}O_5$ (M^+) 188.0685, found 188.0685.

Reaction of 11 with Sodium Acetate in the Absence of Water. To a stirred suspension of sodium acetate (26 mg, 0.32 mmol) in THF (0.4 mL) was added a solution of **11** (58 mg, 0.16 mmol) in THF (0.8 mL) dropwise at 0 °C under nitrogen, and the mixture was stirred for 30 min at room temperature. Usual workup left an oil. The yield of **12** (36%) was determined by ^1H NMR.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of **11** (1 page). Ordering information is given on any current masthead page.

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