intensity) 301 (M^+, 0.6), 246 (1.5), 214 (4.6), 91 (100).

Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.70; H, 6.34; N, 4.70.

S-Methyl-S-phenyl-N-(ethoxycarbonyl)sulfilimine (2c): mp 77-78 °C (from isopropyl ether); IR ($CHCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.4-7.9 (5, m), 4.09 (2, q, J = 7 Hz), 2.82 (3, s), 1.27 (3, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 211 (M^+, 7.9), 168 (40.9), 138 (9.9), 124 (100).

Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.84; H, 6.20; N, 6.63. Found: C, 56.90; H, 6.19; N, 6.61.

S-n-Butyl-S-phenyl-N-(ethoxycarbonyl)sulfilimine (2d): an oil; IR ($CHCl_3$) 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.4-7.9 (5, m), 4.10 (2, q, J = 7 Hz), 3.3-2.6 (2, m), 1.28 (3, t, J = 7 Hz), 1.9-0.7 (7, m); mass spectrum, m/e (relative intensity) 254 (M^+ + 1, 0.8), 253 (M^+, 0.1), 208 (15.9), 197 (100).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{13}H_{20}NO_2S$ (M^+ + 1 ion) m/e 254.1213, found m/e 254.1208.

S-[3-(Ethoxycarbonyl)propyl]-S-phenyl-N-(ethoxycarbonyl)sulfilimine (2e): an oil; IR ($CHCl_3$) 1720, 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.4-8.0 (5, m), 4.11 (4, q, J = 7 Hz), 3.2-3.0 (2, m), 2.65-1.85 (4, m), 1.27 (3, t, J = 7 Hz), 1.23 (3, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 312 (M^+ + 1, 0.1), 311 (M^+, 0.1), 266 (9.9), 224 (8.6), 197 (80.3), 115 (100).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{15}H_{21}NO_4S$, m/e 311.1190; found, m/e 311.1190.

Thiochroman-N-(ethoxycarbonyl)sulfilimine (2f): an oil; IR ($CHCl_3$) 1620 cm^{-1}; NMR ($CDCl_3$) δ 7.1-8.0 (4, m), 4.09 (2, q, J = 7 Hz), 3.6-1.9 (6, m), 1.26 (3, t, J = 7 Hz); mass spectrum, m/e (relative intensity) 237 (M^+, 4.8), 192 (10.6), 149 (100).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{12}H_{15}NO_2S$, m/e 237.0821; found, m/e 237.0818.

S,S-Diphenyl-N-(ethoxycarbonyl)sulfilimine (2g): mp 88.5-89 °C (from isopropyl ether) (lit.[14] mp 88.5-89 °C).

Thioxanthene-N-(ethoxycarbonyl)sulfilimine (2h): thermally unstable crystals; IR ($CHCl_3$) 1640 cm^{-1}; NMR ($CDCl_3$) δ 7.1-8.0 (8, m), 4.47, 3.92 (1 each, AB q, J = 17 Hz), 4.18 (2, q, J = 7 Hz), 1.30 (3, t, J = 7 Hz).

Ethyl N-Allyl-N-phenylthiocarbamate (3). By use of a procedure similar to that described for **2**, **3** was obtained from allyl phenyl sulfide (50 mg) and **1** (100 mg) in a 77% yield as an oil: IR ($CHCl_3$) 1690 cm^{-1}; NMR ($CDCl_3$) δ 7.22 (5, s), 6.4-4.9 (3, m), 4.23 (2, q, J = 7 Hz), 4.19 (2, dd, J = 6, 1 Hz), 1.28 (3, t, J = 7 Hz).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{12}H_{15}NO_2S$, m/e 237.0822; found, m/e 237.0817.

Ethyl N-Allenyl-N-phenylthiocarbamate (4). By use of a procedure similar to that described for **2**, **4** was obtained from phenyl propargyl sulfide (100 mg) and **1** (192 mg) in 86% as an oil: IR ($CHCl_3$) 1970, 1700 cm^{-1}; NMR ($CDCl_3$) δ 7.4-7.0 (6, m), 5.31 (2, d, J = 6 Hz), 4.24 (2, q, J = 7 Hz), 1.29 (3, t, J = 7 Hz).

Analysis was carried out by high-resolution mass spectrometry: calcd for $C_{12}H_{13}NO_2S$, m/e 235.0664; found, m/e 235.0665.

9-[(Ethoxycarbonyl)amino]thioxanthene (5). A solution of **2h** (100 mg) in ethyl acetate (4 mL) was refluxed for 3 min and concentrated to give **5**: 100 mg; mp 175-176 °C (from AcOEt); IR ($CHCl_3$) 3420, 1700 cm^{-1}; NMR ($CDCl_3$) δ 7.7-7.0 (8, m), 5.88 (1, d, J = 10 Hz), 5.5-5.1 (1, br), 4.09 (2, q, J = 7 Hz), 1.20 (3, t, J = 7 Hz).

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.10; H, 5.40; N, 4.86. Found: C, 67.34; H, 5.30; N, 4.91.

N-(Ethoxycarbonyl)triphenylphosphinimine. To a solution of triphenylphosphine (100 mg, 0.38 mmol) in methylene chloride (5 mL) was added **1** (130 mg, 0.55 mmol), and the mixture was stirred at room temperature for 30 min. The reaction mixture was washed with $NaHCO_3$, dried ($MgSO_4$), and concentrated to give crystals of N-(ethoxycarbonyl)triphenylphosphinimine: 92 mg (61%); mp 135-136.5 °C (from ether) (lit.[2] mp 135-136 °C).

Attempted Preparation of N-[(Trifluoromethanesulfonyl)oxy]benzamide (6). To a suspension of sodium benzohydroxamate (318 mg, 2 mmol) in methylene chloride (10 mL) was added with stirring a solution of trifluoromethanesulfonic anhydride (584 mg, 2 mmol) in methylene chloride (5 mL) at -40 °C. The mixture was stirred at room temperature for 3 h. The precipitate was filtered off, and the filtrate was concentrated. The residue was diluted with ether, filtered, and concentrated to give phenyl isocyanate (124 mg, 52%), which was identified by IR spectral comparison with an authentic sample and by its conversion to N,N'-diphenylurea [mp 233-235 °C (lit.[15] mp 235 °C)] by treatment with aniline.

Attempted Preparation of N-[(Trifluoromethanesulfonyl)oxy]acetamide (7). To a solution of acetohydroxamic acid (300 mg, 4 mmol) in acetone (15 mL) was added dropwise thallium ethoxide (998 mg, 4 mmol), and the mixture was stirred at room temperature for 3 h. The precipitated white thallium salt was collected, washed with acetone, and dried. The thallium salt (1.08 g, 3.88 mmol) was suspended in methylene chloride (15 mL), and solution of trifluoromethanesulfonic anhydride (1.09 g, 3.88 mmol) in methylene chloride (10 mL) was added dropwise at -40 to -50 °C. The mixture was stirred at room temperature for 3 h. The precipitate was filtered off. The filtrate was concentrated under reduced pressure below 25 °C. The residue was an intractable mixture. The distillate was collected in a trap cooled at -78 °C and treated with aniline to give diphenylurea (18 mg, 2%) and N-methyl-N'-phenylurea: 21 mg (3.5%); mp 148-150 °C (lit.[16] mp 151-152 °C).

Registry No. 1, 76447-86-4; **2a**, 37939-75-6; **2b**, 76447-87-5; **2c**, 59742-66-4; **2d**, 76447-88-6; **2e**, 76447-89-7; **2f**, 76447-90-0; **2g**, 39149-62-7; **2h**, 76447-91-1; **3**, 76447-92-2; **4**, 76447-93-3; **5**, 35707-41-6; ethyl N-hydroxycarbamate, 589-41-3; ethyl N-hydroxycarbamate thallium salt, 76447-94-4; ethyl N-hydroxycarbamate sodium salt, 54149-38-1; allyl phenyl sulfide, 5296-64-0; phenyl propargyl sulfide, 5651-88-7; N-(ethoxycarbonyl)triphenylphosphinimine, 17437-51-3; triphenylphosphine, 603-35-0; sodium benzohydroxamate, 22513-32-2; acetohydroxamic acid, 546-88-3; acetohydroxamic acid thallium salt, 76447-95-5; diphenylurea, 102-07-8; N-methyl-N'-phenylurea, 1007-36-9; ethyl sulfide, 352-93-2; benzyl sulfide, 538-74-9; methyl phenyl sulfide, 100-68-5; butyl phenyl sulfide, 1126-80-3; ethyl 4-(phenylthio)butanoate, 29193-72-4; thiochroman, 2054-35-5; phenyl sulfide, 139-66-2; thioxanthene, 261-31-4.

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(15) Sonn, A. *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 2437.

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Preparation of Vinylene Diacetate

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Recently, (Z)-vinylene diacetate (**1a**) has been shown to be useful as a 1,2-ethylenediol species for the photochemical cycloaddition with 1,3-diacetoxy-2-propanone; the adduct was converted to a branched-chain sugar, DL-apiose.[1] However, **1** was obtained in only 14% yield[2] by pyrolysis of 1,1,2-triacetoxyethane (**2**),[3] which was prepared in 38% yield from vinyl acetate through addition of bromine followed by acetoxylation.[3] In order to make **1** a more promising material for photochemical reactions, we examined some preparative routes to **1**.

First we attempted enolacetylation of acetoxyacetaldehyde (**3**); **3**[4] was prepared from (E)-1,4-diacetoxy-2-

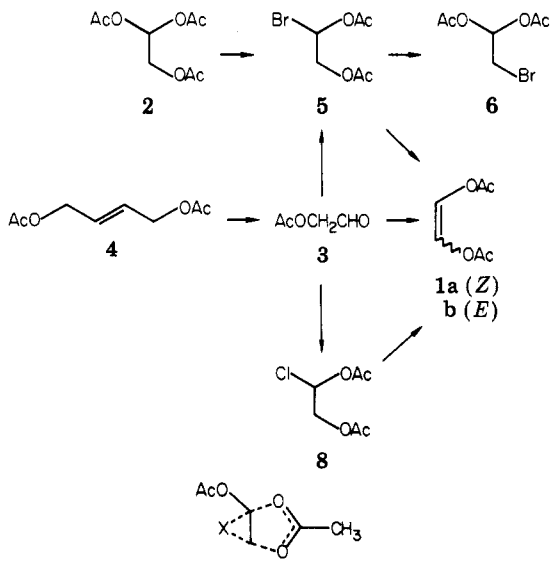
(1) Y. Araki, J. Nagasawa, and Y. Ishido, *J. Chem. Soc., Perkin Trans. 1*, 12-23 (1981).

(2) Several attempts at the pyrolysis of **2** carried out in our laboratory resulted in formation of **1** in yields of less than 5%.

(3) M. F. Shostakovskii, N. V. Kuznetsov, and C.-M. Yang, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 710-716 (1962).

0022-3263/81/1946-1734$01.25/0

Scheme I



butene (**4**)[5] by its oxidation with osmium(VIII) oxide–sodium metaperiodate. Treatment of **3** with acetic anhydride–triethylamine in the presence of 4-(dimethylamino)pyridine[6] afforded **1** (93:7 mixture of *Z* isomer **1a** and *E* isomer **1b**)[7] in 30% overall yield from **4**[8] (Scheme I).

Subsequently, dehydrobromination of 1,2-diacetoxy-1-bromoethane (**5**) was examined. Crude **5**[9] was prepared from **2** by brominating it with a solution of hydrogen bromide in acetic acid and treatment with triethylamine[10] to give **1** (90:10 mixture of **1a** and **1b**) in 31% overall yield from **2**. In a similar dehydrobromination of pure **5**,[11] which was prepared by bromoacetylation of **3** with acetyl bromide in the presence of zinc chloride,[12] **1** was obtained in only 10% yield. Several investigations listed in Table I suggest that chloride or bromide ion facilitated the dehydrobromination reaction.

Then, as an alternative pathway to **1**, utilization of 1,2-diacetoxy-1-chloroethane (**8**) for **5** was examined since a similar treatment of **3** with acetyl chloride in the presence of zinc chloride gave **8** which is more stable[13] than **5**. The results of NMR spectroscopic investigation of dehydrochlorination of **8** are summarized in Table II. In this case, the utility of chloride ion was also confirmed, as seen from Table II, although bromide ion was ineffective. The reaction was shown to be facilitated by increasing the amount of the ammonium salt and by using a lesser amount of the solvent. On the basis of the results, we subsequently attempted the reactions on a preparative scale by proceeding from **4** to **1** via **5** or **8**; the results thus obtained are summarized in Table III. Compound **1** was obtained in 30–50% overall yield from **4**.

In conclusion, the route **4** → **3** → **8** → **1** was found to be the best among the routes examined in the present study.

Table I. Dehydrobromination of 1,2-Diacetoxy-1-bromoethane (5) with Triethylamine[a]

entry	ammonium salts (molar equiv)	rel ratio[b] of 5	1a	3
1		43	39	18
2		68	14	18
3	n-Bu_4NCl (0.05)		89	11
4	n-Bu_4NBr (0.05[c])	45	35	20
5	n-Bu_4NI (0.05[c])	73	12	15
6	n-Bu_4NHSO_4 (0.05)	62	14	24

[a] All the reactions were performed at room temperature for 46 h with 1.0 g of **5**, which contained 5% of **3**, and 0.55 g (1.2 equiv with respect to **5**) of Et_3N. The reaction of entry 1 contained no solvent, and each of the reactions of entries 2–6 contained 1 mL of tetrahydrofuran (THF). The other solvents examined were as follows: 1,2-dimethoxyethane (similar result to that for THF; 1,4-dioxane, Et_2O, and benzene (less effective than THF); hexamethylphosphoric triamide, *t*-BuOH, dimethyl sulfoxide, and dimethylformamide (increment of side reaction). [b] Calculated from the intensities of the methylene and methine signals in the ^1H NMR spectra of each product. [c] The salts were not completely dissolved due to their poor solubility.

Experimental Section

IR spectra were determined on a Hitachi 285 spectrometer. ^1H NMR spectra were taken with a Varian T-60 spectrometer using tetramethylsilane as the internal standard. The melting point of **1a** was determined with a Yanagimoto micro melting point apparatus and is uncorrected.

Acetoxyacetaldehyde (3). A mixture of (*E*)-1,4-acetoxy-2-butene (**4**;[5] 17.2 g, 0.10 mol), pulverized sodium metaperiodate (47.0 g, 0.22 mol), osmium(VIII) oxide (500 mg), and water (150 mL) was mechanically stirred at 10–20 °C for 2 h; the color of the mixture (reddish brown) changed into pale yellow after 1.5 h. The resulting mixture was cooled with ice–water, and the precipitated salts were filtered off. The filtrate was washed with CCl_4 (4 × 20 mL) to remove osmium(VIII) oxide. Cold acetone (200 mL) was added to the aqueous layer, and the precipitated salts were filtered off. The filtrate was evaporated at 30–40 °C, and the residue was then diluted with CH_2Cl_2 (150 mL). Evaporation of the solvent after the mixture was dried over anhydrous magnesium sulfate afforded crude aldehyde (**3**), which was used in the following reaction without any purification.

1,2-Diacetoxy-1-chloroethane (8). The crude **3** obtained from 17.2 g (0.10 mol) of **4** as described above was dissolved in CH_2Cl_2 (30 mL), and the solution was added dropwise to a mixture of acetyl chloride (18.8 g, 0.24 mol), zinc chloride (ca. 30 mg), and CH_2Cl_2 (30 mL) in an ice bath over a period of 1 h with stirring.

(4) Another method, hydrolysis of 1,2-diacetoxy-1-ethoxyethane, is known: N. A. Keiko, T. N. Musorina, I. A. Tkacheva, D. Kalikhman, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1630–1631 (1976).
(5) R. A. Raphael, *J. Chem. Soc.*, 401–405 (1952).
(6) T. J. Cousineau, S. L. Cook, and J. A. Secrist III, *Synth. Commun.*, **9**, 157–163 (1979).
(7) Sample of *E* isomer (**1b**) was isolated from the photochemical isomerization of *Z* isomer (**1a**).[1]
(8) Attempts at enolacetylation of **3** using Ac_2O–NaOAc, isopropenyl acetate–TsOH, Ac_2O–C_5H_5N, AcCl–C_5H_5N, and Ac_2O–K_2CO_3 resulted in little or no formation of the enol acetate **1**.
(9) This sample contains **2**, 1,1-diacetoxy-2-bromoethane (**6**), and 1-acetoxy-1,2-dibromoethane (**7**) in a **5**/**2**/**6**/**7** ratio of 67:9:5:19 (from the ^1H NMR spectrum). Compounds **6** and **7** were identical with the corresponding authentic samples by ^1H NMR spectroscopy. For **6**: N. V. Kuznetsov, I. I. Krasavtsev, and M. M. Aleksankin, *Ukr. Khim. Zh.* (*Russ. Ed.*), **42**, 175–178 (1976). For **7**: S. M. McElvain and B. Fajardo-Pinzón, *J. Am. Chem. Soc.*, **67**, 650–653 (1945). Purification of crude **5** by distillation was unsuccessful due to its facile isomerization to **6** at an elevated temperature; heating **5** (neat), which was prepared from **4** as described below and contained no **6**, gave a mixture of **5** and **6**. The relative ratios of **5** to **6** (from ^1H NMR spectrum were as follows: >95:trace (40 °C, 1 h), 92:8 (40 °C, 2 h), 88:12 (40 °C, 4 h), 75:25 (40 °C, 8 h), 60:40 (40 °C, 16 h), 65:35 (80 °C, 0.5 h), 44:56 (80 °C, 1 h), 30:70 (80 °C, 2 h), trace:>95 (80 °C, 4 h).
(10) C_5H_5N, $PhMe_2N$, and *i*-Pr_2MeN gave no **1**, and DBU and Dabco undesirably induced a side reaction.
(11) This sample is ^1H NMR spectroscopically pure.
(12) P. Bigler, H. Mühle, and M. Neuenschwander, *Synthesis*, 593–594 (1978).
(13) Isomerization of **8** was barely induced at 80 °C to give 1,1-diacetoxy-2-chloroethane (**9**) in 10% yield after 54 h, and no isomerization was observed at all at 40 °C. The difference in thermal stabilities between **5** and **8** may be due to the difference of their abilities to form halogeno-bridging intermediate **10**. Compound **9** was identical with an authentic sample by ^1H NMR spectroscopy: E. Kopp and J. Smidt, *Justus Liebigs Ann. Chem.*, **693**, 117–127 (1966).

Table II. Dehydrochlorination of 1,2-Diacetoxy-1-chloroethane (8) with Triethylamine[a]

entry	vol of THF, mL	X of n-Bu_4NX	(molar equiv)	reaction time, h	rel ratio[b] of 8	rel ratio[b] of 1a
1				46	88	12
2	1			46	94	6
3	1	Cl	(0.1)	46		100
4	1	Br	(0.1)	46	>95	trace
5		Cl	(0.01)	15	86	14
6		Cl	(0.02)	15	29	71
7		Cl	(0.04)	15		100
8	1	Cl	(0.1)	15	trace	>95
9	2	Cl	(0.1)	15	34	66
10	4	Cl	(0.1)	15	100	

[a] All the reactions were performed at room temperature by using 8 (800 mg) and Et_3N (540 mg, 1.2 equiv with respect to 8). [b] Calculated from the intensities of methine signals in the ^1H NMR spectra of each product.

Table III. Synthesis of Vinylene Diacetate (1) from (E)-1,4-Diacetoxy-2-butene (4) via 5 or 8[a]

entry	% yield of 5 or 8 from 4[b]	conditions for dehydrohalogenation[c] solvent[d]	molar equiv of n-Bu_4NCl	reaction time, day	isolated % yield of 1 from 4	E/Z isomer ratio[e]
1	58[g]		0.04	1	44	90:10
2	(75)[g]		0.04	1	39	91:9
3	(62)[h]		0.04	3	27	93:7
4	54[g]	DME[f]	0.1	1	39	91:9
5	(80)[g]	DME	0.1	1	49	91:9
6	(72)[g]	THF	0.1	2	43	95:5
7	(72)[h]	DME	0.1	4	29	91:9

[a] Reactions in entries 3 and 7 were performed by using 0.083 mol of 4 and the others by using 0.1 mol of 4. [b] Yields in parentheses are of crude products, which were directly used for the dehydrohalogenation reaction. [c] Dehydrohalogenations were performed by using 1.2 equiv of Et_3N with respect to 5 or 8. [d] Twenty milliliters of solvent was used per 0.1 molar equiv of 5 or 8. [e] Calculated from the intensities of vinyl signals in the ^1H NMR spectra of 1 obtained. [f] 1,2-Dimethoxyethane. [g] For 8. [h] For 5.

After 30 min, the bath was removed and the stirring was continued at room temperature for 3 h. The reaction mixture was poured into a cold solution of sodium hydrogen carbonate (20 g) in water (300 mL), the mixture was stirred for 30 min, and CH_2Cl_2 (200 mL) was added. The organic layer was separated, washed with cold water (100 mL), and dried over anhydrous magnesium sulfate. After evaporation of the solvent, distillation of the residue gave 8: 20.9 g (58% yield); bp 95.5–97 °C (16 mm); IR $\nu_{C=O}$ 1765 and 1755 cm^{-1}; NMR ($CDCl_3$) δ 6.49 (1 H, dd, J_{CH-CH_2} = 5.0, 6.0 Hz, CH), 4.36 (2 H, d, CH_2), 2.14 (3 H, s, CH_3CO), 2.10 (3 H, s, CH_3CO).

Anal. Calcd for $C_6H_9O_4Cl$: C, 39.91; H, 5.02. Found: C, 39.98; H, 4.93.

1,2-Diacetoxy-1-bromoethane (5). (a) From 1,1,2-Triacetoxyethane (2). A solution of hydrogen bromide in acetic acid (33%, 244 g) was added to a solution of 2 (51.0 g, 0.25 mol) in CH_2Cl_2 (30 mL). The reaction vessel was sealed and left at room temperature for 3 h. A usual workup of the mixture followed by evaporation afforded a mixture (54 g)[9] containing 5.

(b) From (E)-1,4-Diacetoxy-2-butene (4). The crude sample of 3 obtained from 14.3 g (0.083 mol) of 4 as described above was dissolved in CH_2Cl_2 (30 mL), and the resulting solution was added to a mixture of acetyl bromide (25.0 g, 0.20 mol), zinc chloride (ca. 30 mg), and CH_2Cl_2 (30 mL) at −15 to −5 °C over a period of 30 min with stirring. After being stirred for 2 h, the mixture was treated in the same manner as described above in the synthesis of 8. Compound 5[11] (23 g) was thus obtained: IR (NaCl) $\nu_{C=O}$ 1760 and 1750 cm^{-1}; NMR ($CDCl_3$) δ 6.72 (1 H, dd, J_{CH-CH_2} = 5.0, 6.0 Hz, CH), 4.50 (2 H, d, CH_2), 2.17 (3 H, s, CH_3CO), 2.12 (3 H, s, CH_3CO).

Vinylene Diacetate (1). (a) From 1,2-Diacetoxy-1-chloroethane (8). Entry 1 in Table III is a representative example. To a solution of tetrabutyl ammonium chloride (1.28 g, 4.6 mmol) in 8 (20.9 g, 0.116 mol) was added triethylamine (13.8 g, 0.14 mol), and the resulting mixture was left at room temperature for 1 day. Diethyl ether (100 mL) was added to the resulting mixture, and the ammonium salt that precipitated out was filtered off. The filtrate was diluted to a volume of 200 mL with diethyl ether, and the solution was washed with water (2 × 100 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent after the removal of the desiccant by filtration and subsequent distillation gave 1 [12.8 g, 77% yield; Z/E ratio of 90:10; bp 107–108 °C (43 mm)], which solidified in the receiver. Recrystallization from diethyl ether–hexane gave Z isomer 1a: 9.5 g; mp 43–43.5 °C (lit.[14] mp 42.6–43.8 °C); IR (KBr) 3130, 3020, 1770, 1760, 1695, 1640, 1435, 1380, 1345 cm^{-1}; NMR ($CDCl_3$) δ 6.82 (2 H, s, 2 CH), 2.22 (6 H, s, CH_3CO); NMR (CCl_4) δ 6.76, 2.18 (lit.[14] δ 6.7, 2.15).

Anal. Calcd for $C_6H_8O_4$: C, 50.00; H, 5.60. Found: C, 49.86; H, 5.52.

(b) Through Enolacetylation of Acetoxyacetaldehyde (3). Crude aldehyde 3 obtained from 17.2 g (0.10 mol) of 4 as described above was dissolved in tetrahydrofuran (30 mL), and the solution was added dropwise to a mixture of triethylamine (40.5 g, 0.40 mol), 4-(dimethylamino)pyridine (2.44 g, 20 mmol), and acetic anhydride (61.3 g, 0.60 mol) below room temperature over a period of 30 min with stirring. A usual workup of the mixture after it was stirred for 4 h at room temperature followed by distillation gave 1 [8.75 g, 30% yield; Z/E ratio of 93:7; bp 106–108 °C (40 mm)], which solidified in the distillation receiver.

(c) From 1,2-Diacetoxy-1-bromoethane (5). To the mixture (54 g)[9] containing 5 obtained from 2 (51.0 g, 0.25 mol) was added triethylamine (30 g, 0.30 mol), and the resulting mixture was allowed to stand at room temperature for 5 days. Similar treatment of the mixture to that of method a gave crude 1 [20 g; bp 80–110 °C (25 mm)]; redistillation gave 1 [11.2 g, 31% yield; Z/E ratio of 90:10; bp 88.5–92 °C (17 mm)] which solidified in the receiver.

Acknowledgment. The authors thank Miss Mikiko Aoki, Laboratory of Organic Analysis, Department of Chemistry, Tokyo Institute of Technology, for the elementary analyses.

Registry No. (E)-1, 19191-10-7; (Z)-1, 19191-11-8; 2, 2983-35-9; 3, 5371-49-3; 4, 1576-98-3; 5, 76403-53-7; 8, 76403-54-8.

(14) R. A. Caldwell, J. Org. Chem., 34, 1886–1889 (1969).