Stereoselectivity in the Synthesis of Enol Esters from Chloromercurio Aldehydes and Acyl Chlorides

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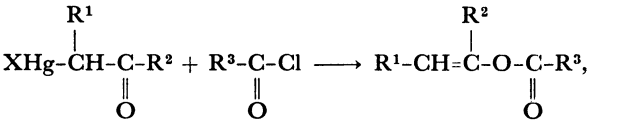
Reactions of chloromercurio aldehydes with acyl chlorides gave a variety of (*Z*)- and (*E*)-enol esters. The *Z*/*E* ratio of the enol esters is dependent on the structure of chloromercurio aldehydes but independent of that of acyl chlorides. *Z*-Rich enol esters were prepared by acylation of 2-chloromercurio aldehydes derived from propanal, butanal, and 2-phenylethanal, while *E*-rich 1-acyloxy-1,3-butadiene was obtained by acylation of (*E*)-4-chloromercurio-2-butenal. Reaction mechanisms for the stereoselective formation of these enol esters are discussed together with the isomer composition of starting enol acetates from which the chloromercurio aldehydes were prepared.

Various methods are available for synthesis of enol esters. The most practical technique involves treatment of aldehydes or ketones with appropriate acid anhydrides or acid chlorides under either acidic or basic conditions.[1-10] Other major methods for preparing enol esters involve addition of carboxylic acids to alkynes[11-16] and palladium-catalyzed acyloxylation of olefins.[17]

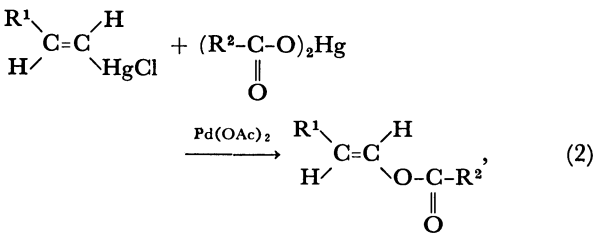
Although limited in scope, organomercurials are used for preparing enol esters.[18] Halomercurio aldehydes or ketones can be *O*-acylated with acyl chlorides:[19,20]



(1)

where R^1 and R^2 are each hydrogen, alkyl, or aryl, R^3 is alkyl or aryl, and X is halogen.

Reactions of vinylmercurials with mercury(II) carboxylates in the presence of a catalytic amount of palladium(II) acetate lead stereospecifically to formation of enol esters:[21]



(2)

where R^1 is hydrogen, alkyl, or aryl, and R^2 is alkyl or aryl.

An attempt was made to prepare enol acrylate from propanal and acrylic anhydride or acryloyl chloride in the presence of quinoline or potassium acetate, but it was unsuccessful since polymers were formed easily. Under mild conditions, enol acrylates and methacrylates were prepared by reaction of chloromercurio aldehydes with acryloyl chloride or methacryloyl chloride according to the procedure by Nesmeyanov et al.[20] It was found with this reaction that enol esters prepared were stereoselective depending on the structure of chloromercurio aldehydes.

In this article, the stereoselectivity in the synthesis of enol esters from chloromercurio aldehydes and acyl chlorides is described, together with the effect of the isomer composition (*Z*/*E*) of starting enol acetates from which chloromercurio aldehydes are prepared.

Results and Discussion

Compositions of Geometric Isomers of Starting Enol Acetates. Enol acetates can be prepared by reactions of aldehydes either with acetic anhydride in the presence of potassium acetate (method A) or with 2-acetoxy-1-propene in the presence of *p*-toluenesulfonic acid (method B). Their yields were in the range from 12 to 73% (1-acetoxy-1-propene (**1a**)<1-acetoxy-1-butene (**2a**)<1-acetoxy-1,3-butadiene (**4a**)<1-acetoxy-2-(phenyl)ethene (**3a**)). This order may be interpreted in terms of the stability of enol forms. The enol/keto ratio for ethanal was less than 10^{-7} under conditions where the enol content of acetone was measurable.[22] On the other hand, aryl-substituted ethanals gave stable enols.[23]

All of the enol esters prepared were mixtures of (*Z*)- and (*E*)-isomers. The 1-acetoxy-1-propene (**1a**) obtained by method A was a *Z*/*E* mixture with a ratio of 51/49, which is consistent with the literature.[5,6] The *Z*/*E* ratio of 1-acetoxy-1-butene (**2a**) was 47/53, while those of 2-phenyl-1-(acetoxy)ethene (**3a**) and 1-acetoxy-1,3-butadiene (**4a**) were 35/65 and 38/62, respectively.

Scheme 1 shows the reaction process for method A where an ambident enolate anion may be formed as an intermediate. The geometry of the enol esters will be determined in the addition step of acyl residue to the enolates. The results for **1a** and **2a** suggest that methyl and ethyl substituents (R^1=CH_3, C_2H_5)

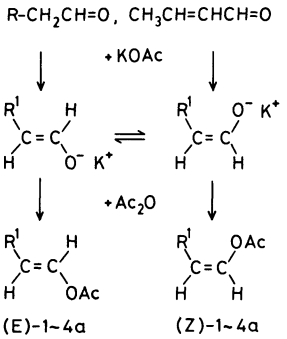
contribute little to the difference in stability and/or reactivity between (*Z*)- and (*E*)-enolates. Therefore, the *Z*/*E* ratios of **1a** and **2a** are almost 1/1.

When 2-substituent in the enolate is phenyl or vinyl, the *Z*/*E* ratios are less than 2/3. Heiszwolf and Kloosterziel[24] have reported an *O*-alkylation of ambident enolate anion obtained from 2-phenylethanal. The *Z*/*E* ratios of the enol ethers prepared in dimethyl sulfoxide and in liquid ammonia were 9/10 and 3/2, respectively, while those of the intermediate enolate anions were 3/2 in both solvents. Although the enolates prepared by method A are not so stable as those prepared in dimethyl sulfoxide and in liquid ammonia, the product determining step will be the reaction of the enolate with acetic anhydride. The result for **3a** suggests that the (*E*)-enolate of 2-phenylethanal reacts with acetic anhydride more rapidly than the (*Z*)-enolate. This may be interpreted in terms of steric and electronic effects of phenyl residue on the enolate anion. The reaction of 2-butenal with acetic anhydride may proceed along the same process as that of 2-phenylethanal. But the vinyl substituent will give little effect on both stability and reactivity of the enolates. Alternatively, the *Z*/*E* ratio of **4a** may rather be controlled by the concentrations of (*Z*)- and (*E*)-enolates since (*E*)-2-butenal is present mainly in *s-trans*-conformation[25,26] which leads to the formation of (*E*)-enolate.

The *Z*/*E* ratios of **2a** and **4a** prepared by method B were 65/35 and 17/83, respectively. Scheme 2 involves an intermediate cation in the reaction of butanal with 2-acetoxy-1-propene. The intermediate cation for (*E*)-isomer will be more stable than that for (*Z*)-isomer because of the steric interaction between acetoxy and ethyl residues. Both *anti*- and *syn*-elimination of proton from the intermediates will give *E*-rich enol ester. By contrast, the result suggests that the product determining step is not the elimination of proton but the addition of acetyl cation to butanal. It suggests a formation of the intermediate for (*Z*)-isomer in preference to that for (*E*)-isomer and no interconversion between the intermediates which was shown by Skell and Hall[27] for the E1 reaction of 3-deuteriobutyl-2-tosylate. The reason for the preferential formation of the intermediate for (*Z*)-isomer remains open.

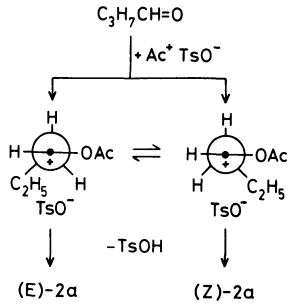
Scheme 3 shows the reaction process of 2-butenal and 2-acetoxy-1-propene. The *Z*/*E* ratio of **4a** will be determined by the addition of acetyl cation to the carbonyl oxygen of 2-butenal, since the elimination of terminal methyl proton in the intermediate is of no effect on the geometry of the products. As the *O*-acetylations of *s-cis*- and *s-trans*-2-butenal give the intermediate cations of (*Z*)- and (*E*)-enol acetates, respectively, the *Z*/*E* ratio of **4a** may be controlled by the s-cis/s-trans ratio of 2-butenal. The result, the *Z*/*E* ratio of 17/83, is in agreement with the s-cis/s-trans ratio of the literature.[25,26]

Stereoselectivity in the Reaction of Chloromercurio Aldehydes with Acyl Chlorides. Reactions of four chloromercurio aldehydes with acyl chlorides were conducted to give respective enol esters. Table 1 shows that the reactions of 2-(chloromercurio)butanal (**2x**) with three acyl chlorides give the correspond-

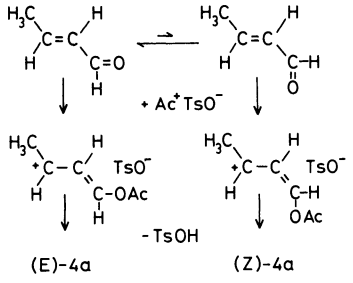


Scheme 1. Process of enol acetylation in the presence of potassium acetate.
R: CH_3, C_2H_5, C_6H_5.

Compound	**1a**	**2a**	**3a**	**4a**
R^1	CH_3	C_2H_5	C_6H_5	CH_2=CH



Scheme 2. Process for the acetylation of butanal with 2-aetoxy-1-propene in the presence of *p*-toluenesulfonic acid.



Scheme 3. Process for the acetylation of (*E*)-2-butenal with 2-acetoxy-1-propene in the presence of *p*-toluenesulfonic acid.

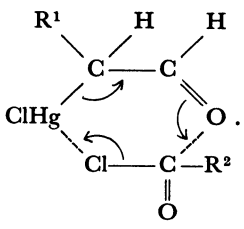
Table 1. Composition of Isomeric Enol Esters Prepared from Chloromercurio Aldehydes and Acyl Chlorides

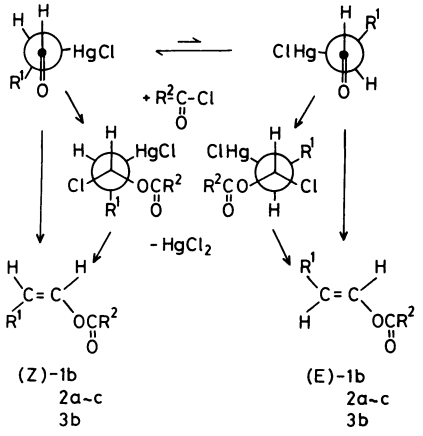
Starting enol acetate		Substrate		Reaction conditions		Resulting enol ester		
	Z/*E* ratio[a]	-R in ClHg-R	R^2- in R^2-COCl		time / h		Isolated yield / %	*Z*/*E* ratio[a]
1a	51/49	-CHCH=O | CH_3 **1x**	CH_2=CH-	b)	6	**1b**	58	84/16(88/12)
2a	47/53	-CHCH=O	CH_2=CH-	c)	6	**2b**	38	87/13(83/17)
	47/53	|	C_6H_5-	c)	4	**2c**	70	85/15(83/17)
	47/53	C_2H_5	CH_3-	b)	6	**2a**	91	82/18(80/20)
	82/18	**2x**	CH_3-	b)	6	**2a**	88	86/14(82/18)
	(65/35)		CH_3-	e)	2	**2a**	77	(84/16)
3a	35/65	-CHCH=O | C_6H_5 **3x**	CH_2=CH-	c)	6	**3b**	51	74/26(76/24)
4a	38/62	$-CH_2CH$	CH_2=CH-	d)	3	**4b**	39	32/68(30/70)
	38/62	||	CH_2=C(CH_3)-	c)	6	**4c**	63	34/66
	17/83	CH	CH_2=C(CH_3)-	c)	6	**4c**	42	13/87
	17/83	|	CH_3-	e)	0.5	**4a**	—	(5/95)
	17/83	CH=O **4x**	CH_3-	e)	24	**4a**	—	(15/85)

a) Determined by ^{1}H NMR and by GLC (shown in parentheses). b) At 40—60 °C in tetralin. c) At 40—60 °C in benzene. d) At 30—50 °C in benzene. e) At ambient temperature in benzene.

ing enol esters of which the *Z*/*E* ratios are about 85/15. These ratios for the enol esters (**2a—c**) are independent of the acyl chlorides. The reactions of 2-(chloromercurio)propanal (**1x**) and 2-phenyl-2-(chloromercurio)ethanal (**3x**) with acryloyl chloride give 1-acryloyloxy-1-propene (**1b**) and 2-phenyl-1-(acryloyloxy)ethene (**3b**) having the *Z*/*E* ratios of 84/16 and 76/24, respectively.

Scheme 4 shows the reaction pathways of 2-substituted 2-chloromercurio aldehydes with acyl chlorides. Two stable conformations of the 2-chloromercurio aldehydes are suggested on the basis of torsional angle (98°) of Hg-C-C=O which was given by Halfpenny and Small.[28] Of the two conformations suggested, *syn*-1,2-dihydrogen form may be more stable than *anti*-1,2-dihydrogen form because of the steric interaction of 1-hydrogen with 2-substituent (R^1). 2-Chloromercurio aldehydes in each conformation will give stereoselectively (*Z*)- and (*E*)-enol esters. There are two reaction routes to be considered in each case. One of them is a spontaneous 1,3-displacement reaction of acyl cation with chloromercurio residue. The stereoselectivity of this route can be interpreted in terms of the formation of a six-membered intermediate between acyl chloride and 2-chloromercurio aldehyde

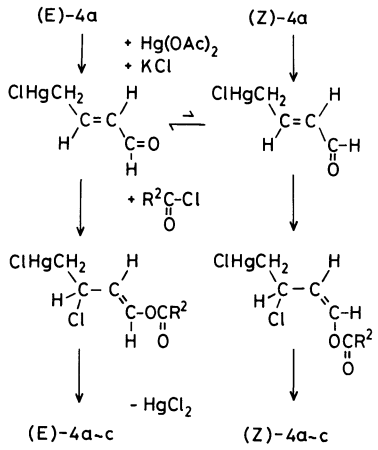




Scheme 4. Pathways for the formation of enol esters.

Compound	**1b**	**2a**	**2b**	**2c**	**3b**
R^1	CH_3	CH_3	C_2H_5	C_2H_5	C_6H_5
R^2	CH_2=CH	CH_3	CH_2=CH	C_6H_5	CH_2=CH

The other is an addition-elimination reaction between acyl chlorides and 2-chloromercurio aldehydes. The stereoselectivity will come from the *anti*-addition of chloride with respect to 2-chloromercurio residue and the *anti*-elimination of mercury(II) chloride from *threo*- and *erythro*-2-chloromercurio-1-acyloxy-1-chloro intermediates. Such compounds as 1-acyloxy-1-chloro derivatives were prepared by Kyburz et al.[29] through reaction of aldehydes or ketones with acyl chlorides in the presence of Lewis acid. The mechanism of *anti*-addition and *anti*-elimination was proposed by Larock and Bernhardt[30]



Scheme 5. Pathways for the formation of 1-acyloxy-1,3-butadienes.

Compound	4a	4b	4c
R^2	CH_3	CH_2=CH	CH_2=C(CH_3)

for the acylation of vinylmercurials.

In any cases the *syn*-1,2-dihydrogen conformation will lead to the formation of (*Z*)-enol ester. In conclusion, the stereoselectivity in the reactions of 2-chloromercurio aldehydes **1x—3x** with acyl chlorides may be controlled by the conformational structures of **1x—3x** when the reactions follow any one of the routes.

On the other hand, the reaction of 4-chloromercurio-2-butenal (**4x**) with acyl chlorides leads to the formation of *E*-rich 1-acyloxy-1,3-butadienes **4a—c** as shown in Table 1. Scheme 5 shows the reaction pathways for the stereoselective formations of *s-trans*- and *s-cis*-**4x** which react with acyl chlorides to give (*E*)- and (*Z*)-**4a—c**, respectively. The results suggest that conformational isomerization between *s-trans*- and *s-cis*-**4x** is difficult under reaction conditions where **4x** is slightly soluble and may associate together as verified on the basis of IR spectra. Another support for this suggestion is provided by the effect of reaction time on the *Z*/*E* ratio of product **4a** which was 5/95 at the beginning and 15/85 at the end for the reaction of **4x** with acetyl chloride. The *Z*/*E* ratio of the 1-acyloxy-1,3-butadiene prepared was almost equal to that of the starting enol acetate. The results also suggest that the product controlling step is the *O*-acylation of **4x**, since the elimination of a 4-chloromercurio residue from the *O*-acylated **4x** leads to the formation of a terminal vinylic double bond.

In conclusion, both the reaction of 1-acetoxy-1,3-butadiene with mercury(II) acetate and that with potassium chloride, as well as the reaction of the resultant (*E*)-4-chloromercurio-2-butenal with acyl chloride, can be carried out stereoselectively according to the structures of the substrates.

Experimental

General Method. Propanal, butanal, 2-phenylethanal, 2-butenal, 2-acetoxy-1-propene, acrylic acid, and methacrylic acid were commercial reagents and distilled before use. 2-Phenylethanal was supplied as a 50% solution in diethyl phthalate. Acryloyl chloride and methacryloyl chloride were prepared by the reaction of acrylic acid and methacrylic acid with benzoyl chloride, respectively. Solvents were purified in the usual way. The other reagents used were commercially available and used as they were.

Enol esters prepared were purified by distillation until their purities became higher than 99% as checked by GLC analyses on a 20% diethylene glycol succinate coated on Neopak 1A (Nishio Industry Co., Ltd.). They were identified by both IR and ^{1}H NMR spectra. GLC analyses were performed on a Shimadzu GC-4CPT gas chromatograph equipped with a thermal conductivity detector. ^{1}H NMR spectra were recorded on a JEOL-JNM C-60H spectrometer, and IR spectra were recorded on a Hitachi EPI-2 or a Shimadzu IR-400 spectrophotometer. The *Z*/*E* ratio of enol ester was determined by ^{1}H NMR spectrum and/or by GLC analysis. The peak of (*Z*)-olefinic proton in each ^{1}H NMR spectrum appeared at higher magnetic field than that of the (*E*)-olefinic proton. In the GLC analysis, the peak for the shorter retention time was assigned to the (*Z*)-isomer.

Preparation of Starting Enol Acetates. Method A: Enol acetylation with acetic anhydride in the presence of potassium acetate was conducted according to the procedure described in the literature.[2,3]

1-Acetoxy-1-propene (1a):[2] Propanal (1 mol), acetic anhydride (1.5 mol), and potassium acetate (0.125 mol) were refluxed for 8 h, the mixture was distilled, and the boiling fraction at 80—118 °C was washed with aqueous sodium carbonate and with distilled water and dried over sodium sulfate. Redistillation gave **1a**: Yield 12%; bp 103—106 °C; ^{1}H NMR δ=4.78 (0.51H, quintet, J=6.26 Hz, (*Z*)-2-H) and 5.30 (0.49H, quintet, J=6.24, 12.5 Hz, (*E*)-2-H); *Z*/*E* ratio 51/49 (lit,[5] 52.5/46.2; lit,[6] 48/52).

1-Acetoxy-1-butene (2a):[2] Similar treatment of butanal gave **2a**: Yield 37%; bp 122—124 °C; ^{1}H NMR δ=4.78 (0.47H, q, (*Z*)-2-H) and 5.36 (0.53H, sextet, (*E*)-2-H);[31,32] *Z*/*E* ratio 47/53.

1-Acetoxy-2-phenylethene (3a):[1] Similar treatment of 2-phenylethanal gave **3a**: Yield 73%; bp 73—74 °C/0.3 mmHg (1 mmHg=133.322 Pa); ^{1}H NMR δ=5.59 (0.35H, d, J=7.50 Hz, (*Z*)-2-H) and 6.32 (0.65H, d, J=13.05 Hz, (*E*)-2-H);[21,33] *Z*/*E* ratio 35/65.

1-Acetoxy-1,3-butadiene (4a):[3] 2-Butenal (1 mol) was added dropwise into a refluxing mixture of acetic anhydride (1.5 mol) and potassium acetate (1 mol). The mixture was refluxed further for half an hour. After cooling, it was washed successively with aqueous sodium carbonate, 20% sulfuric acid, and aqueous sodium carbonate and dried over sodium sulfate. Distillation under reduced pressure gave **4a**: Yield 57%; bp 56—58 °C/40 mmHg; ^{1}H NMR δ=7.05 (0.38H, d, (*Z*)-1-H) and 7.38 (0.62H, d, (*E*)-1-H); *Z*/*E* ratio 38/62.

Method B: Enol acetylation with 2-acetoxy-1-propene in the presence of *p*-toluenesulfonic acid and copper(II) acetate was carried out according to the literature.[4] Both **2a** and **4a** were prepared. **2a**: Yield 33%; bp 122—123 °C; *Z*/*E* ratio 65/35 by GLC. **4a**: Yield 70%; bp 51.0—52.5 °C/30 mmHg; *Z*/*E* ratio 17/83 by ^{1}H NMR.

Chloromercurio Aldehydes. 2-(Chloromercurio)propanal (1x): The preparative method for **1x** was a modification of that employed by Curtin and Hurwitz[2] as follows: Mercury(II) acetate (0.2 mole) was dissolved in 300 cm^3 of distilled water at ice-temperature. To this solution **1a** (0.2 mol) was added. When a homogeneous solution was obtained, 100 cm^3 of aqueous potassium chloride (0.2 mol) was added with vigorous stirring. It was agitated for several hours and allowed to stand overnight. The precipitate formed was separated on a suction funnel, washed with distilled water repeatedly, and dried in vacuo. **1x**: Yield 66%; mp 66—69 °C.

2-(Chloromercurio)butanal (2x):[2] Similarly, the reaction of **2a** with mercury(II) acetate and then with potassium chloride gave **2x**: Yield 83%; mp 90—94 °C; IR (benzene) 2700 (CO–H) and 1690 (C=O) and (Nujol mull) 2750 (CO–H) and 1630 cm^{-1} (C=O).

2-Chloromercurio-2-(phenyl)ethanal (3x): Similarly, the reaction of **3a** with mercury(II) acetate and then with potassium chloride gave **3x**: Yield 74%; mp 180 °C (decomp).

4-Chloromercurio-2-butenal (4x): The reaction of **4a** with mercury(II) acetate and then with potassium chloride gave **4x**: Yield 94%; mp 118—121 °C (decomp); IR (benzene) 1681 (C=O) and 1614 (C=C) and (Nujol mull) 1635 (C=O) and 1600 cm^{-1} (C=C). A comparison of the IR spectrum of **4x** with that of 2-butenal (1680 ((C=O) and 1640 cm^{-1} (C=C)) suggests that the chloromercurio group adds on 4-carbon rather than 2-carbon in **4x**. The lowering in wave number of the absorption band for the carbonyl stretching vibration has been observed by Susz[34] on a number of carbonyl compounds coordinated to Lewis acids; thus, coordination of mercury(II) chloride lowered 31 cm^{-1} the absorption band of the carbonyl in acetophenone.

The chloromercurio aldehydes (**1x—4x**) are slightly soluble in benzene, tetrahydrofuran, acetone, or tetrahydronaphthalene, and soluble in *N*,*N*-dimethylformamide.

Preparation of Enol Esters from Chloromercurio Aldehydes and Acyl Chlorides. The procedure employed was in general that employed by Nesmeyanov et al.[20]

1-Acryloyloxy-1-propene (1b): Acryloyl chloride (0.14 mol) was added to a tetrahydronaphthalene solution (150 cm^3) of **1x** (0.14 mol) and hydroquinone (0.5 g) at 40 °C under nitrogen stream. When the addition of acryloyl chloride was finished, the temperature was raised to 60 °C and the reaction was continued for 6 h. A few drops of quinoline were added to the reaction mixture. After the insoluble mercury(II) chloride was separated, the solution was distilled under reduced pressure. The low-boiling fraction was collected and redistillation gave **1b**: Yield 58%; bp 42.0—42.5/30 mmHg; n_D^{25} 1.4429; d_4^{25} 0.9409; IR (neat) 1730 (C=O), 1670 (enol C=C), and 1630 cm^{-1} (C=C); ^{1}H NMR δ=4.95 (0.84H, quintet, (*Z*)-2-H) and 5.33 (0.16H, sextet, (*E*)-2-H); *Z*/*E* ratio 84/16 and 88/12 by GLC.

1-Acryloyloxy-1-butene (2b): The reaction of **2x** with acryloyl chloride was carried out in benzene solution, the procedure employed being the same as that for **1b** except posttreatment: After removal of the insoluble mercury(II) salt, the benzene solution was evaporated off in a rotary evaporator. The residue was dissolved in diethyl ether, and the solution was washed with 10% aqueous sodium hydrogencarbonate and with distilled water, and then dried over sodium sulfate. Redistillation gave **2b**: Yield 38%; bp 47.5—48.0 °C/17 mmHg; n_D^{25} 1.4417; d_4^{25} 0.9260; IR (neat) 1730 (C=O), 1668 (enol C=C), and 1623 cm^{-1} (C=C); ^{1}H NMR δ=4.85 (0.87H, q, (*Z*)-2-H) and 5.45 (0.13H, sextet, (*E*)-2-H); *Z*/*E* ratio 87/13 and 83/17 by GLC.

1-Benzoyloxy-1-butene (2c): The reaction of **2x** with benzoyl chloride in a similar procedure with **2b** gave **2c**: Yield 70%; bp 66—70 °C/1.0 mmHg; IR (neat) 1724 (C=O) and 1663 cm^{-1} (enol C=C); ^{1}H NMR δ=4.91 (0.85H, q, (*Z*)-2-H) and 5.56 (0.15H, sextet, (*E*)-2-H); *Z*/*E* ratio 85/15 and 83/17 by GLC.

2-Phenyl-1-(acryloyloxy)ethene (3b): The reaction of **3x** with acryloyl chloride was carried out in a similar manner with **2b**. Redistillation gave **3b**: Yield 51%; bp 65—68 °C/0.15 mmHg; n_D^{25} 1.4480; d_4^{25} 1.0650; IR (neat) 1740 (C=O), 1660 (enol C=C), and 1630 cm^{-1} (C=C); ^{1}H NMR δ=7.96 (0.26H, d, (*E*)-1-H); *Z*/*E* ratio 74/26 and 76/24 by GLC.

1-Acryloyloxy-1,3-butadiene (4b): The reaction of **4x** with acryloyl chloride was carried out at 50 °C for 3 h because of a high polymerization tendency of **4b**. Redistillation gave **4b**: Yield 39%; bp 45.0—45.5 °C/5 mmHg; n_D^{25} 1.4956; d_4^{25} 0.9723; IR (neat) 1735 (C=O), 1660 (enol C=C), and 1631 cm^{-1} (C=C); ^{1}H NMR δ=7.10 (0.32H, d, (*Z*)-1-H) and 7.43 (0.68H, d, (*E*)-1-H); *Z*/*E* ratio 32/68 and 30/70 by GLC.

1-Methacryloyloxy-1,3-butadiene (4c): The reaction of **4x** with methacryloyl chloride was carried out in a similar manner to the preparation of **2b**. Redistillation gave **4c**: Yield 63%; bp 35.0—36.5 °C/1.5 mmHg; n_D^{25} 1.4897; d_4^{25} 0.9486; IR (neat) 1735 (C=O), 1660 (enol C=C), and 1637 cm^{-1} (C=C); ^{1}H NMR δ=7.14 (0.34H, d, (*Z*)-1-H) and 7.43 (0.66H, d, (*E*)-1-H); *Z*/*E* ratio 34/66.

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