Photochemical Bromination of Methyl (*E*)-2-Methylbut-2-enoate with *N*-Bromosuccinimide: Formation of 4-Bromo-2-methylbut-2-en-4-olide[1]†

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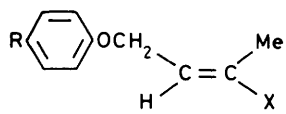
Bromination of methyl (*E*)-2-methylbut-2-enoate (**4**) with *N*-bromosuccinimide under irradiation with light was described. The formation of 4-bromo-2-methylbut-2-en-4-olide (**8**) in fairly good yield together with the desired methyl (*E*)-4-bromo-2-methylbut-2-enoate (**5**), methyl (*E*)-2-(bromomethyl)but-2-enoate (**6**), and methyl 2,3-dibromo-2-methylbutanoate (**7**) was clarified.

Methyl (*E*)-4-(*p*-formylphenoxy)-2-methylbut-2-enoate (**16**) was smoothly subject to catalytic hydrogenation using Wilkinson complex, while the rate of the hydrogenation of its geometrical isomer (**17**) was extremely retarded.

In a previous paper,[2] we reported the structures and syntheses of the phenylpropanoids cuspidiol[2,3] (**1**), boninenal[2,4] (**2**), and methyl boninenalate[2,4] (**3**). In this work, methyl (*E*)-2-methylbut-2-enoate (**4**) was allowed to react with *N*-bromosuccinimide (NBS) both with and without irradiation by light to give two mixtures, I and II, respectively. We believed that these mixtures contained the desired methyl (*E*)-4-bromo-2-methylbut-2-enoate[5] (**5**) as the sole reactive component until we detected a by-product 4-bromo-2-methylbut-2-en-4-olide (**8**), in mixture II, but not mixture I. Here we discuss this result further.



(1) R = $CH_2CH_2CH_2OH$, X = CH_2OH

(2) R = CH=CHCHO, X = CH_2OH

(3) R = CH=CHCHO, X = CO_2Me

In 1953, Inhoffen *et al.*[5a] reported the NBS bromination of the (*E*)-butenoate (**4**) with irradiation with light. The brominated product, believed to be pure (*E*)-4-bromobutenoate (**5**), was used in the synthesis of naturally occurring crocetin dimethyl ester (**11**),[5a] zeatin (**12**),[5b] and other compounds.[5c] Later, Löffler *et al.*[5d] reported that the brominated product was, in fact, an inseparable mixture of the (*E*)-4-bromobutenoate (**5**) and the (*E*)-2-(bromomethyl)butenoate (**6**) and that photochemical bromination was the best method of preparing mixtures consisting predominantly of (**5**). The mixture prepared according to Löffler's procedure[5d] has been widely used in syntheses of methyl 4-substituted (*E*)-2-methylbut-2-enoates because the (*E*)-4-bromo derivative (**5**) is a more effective alkylating agent than the (*E*)-2-bromo compound (**6**).

As reported in a previous paper,[2] mixture I gave methyl boninenalate (**3**) as the sole product in 75.7% yield on treatment with *p*-hydroxycinnamaldehyde (**13**), mixture II providing (**3**) only in 53.6% yield along with the unexpected aryloxy lactone (**14**) (26.2% yield) which showed a carbonyl absorption band at 1 780 cm^{-1} in its i.r. spectrum. This suggests the existence of a fairly large amount of the bromo lactone (**8**) in mixture II. The elemental analysis of the aryloxy lactone (**14**) coincides with the empirical formula, $C_{14}H_{12}O_4$, but no useful information on the structure could be obtained from its ^1H n.m.r. spectrum.

In order to obtain confirmatory evidence for the presence of the bromo lactone (**8**) in mixture II and to establish a synthetic procedure, *via* a Wittig reaction, for the preparation of methyl boninenalate (**3**), both mixtures I and II were treated with *p*-hydroxybenzaldehyde (**15**). The former gave the (*E*)-4-aryloxy product (**16**), m.p. 83—84 °C, and a trace of the (*Z*)-compound (**17**), m.p. 91—92 °C. These products gave elemental analyses in agreement with the same formula, $C_{13}H_{14}O_4$, corresponding to that of the expected methyl (*E*)-4-(*p*-formylphenoxy)-2-methylbut-2-enoate (**16**). Catalytic hydrogenation of both products (**16**) and (**17**) using Wilkinson complex[7] as a catalyst gave the dihydro derivative (**18**) as an oil.

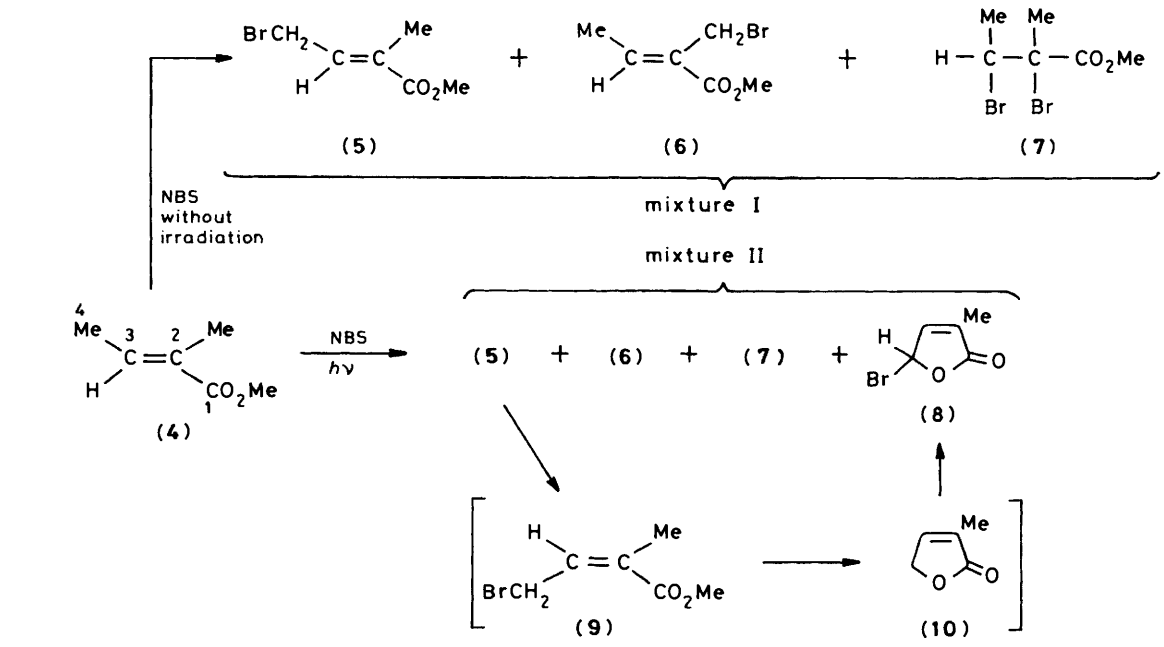
In the measurement of nuclear Overhauser effects, the minor product (**17**) shows a 10.0% increase in the intensity of the olefinic proton signal at δ 6.22 on irradiation at δ 1.98 (the vinyl methyl group). In the ^{13}C n.m.r. spectrum, the major product (**16**) shows the signal of the *C*-methyl group at δ 13.1 p.p.m., indicating that the *C*-methyl group was subject to steric compression, compared with that of the minor product (**17**) (δ 19.7 p.p.m.). In addition, general inspection of other spectral data (see Experimental section) also supported the view that these compounds were methyl (*E*)-4-(*p*-formylphenoxy)-2-methylbut-2-enoate (**16**) and its geometrical isomer (**17**).

On the catalytic hydrogenation of disubstituted olefins using Wilkinson complexes, previous researchers[7b] have claimed that the (*Z*)-isomer is more easily hydrogenated than the (*E*)-isomer. In our hands, (*E*)-isomer (**16**) easily provided the dihydro derivative (**18**), while the (*Z*)-isomer (**17**) needed 7 days for complete reduction. In other words, the *cis* orientation of the most bulky and the second most bulky functions affects the rate of hydrogenation of trisubstituted olefins.

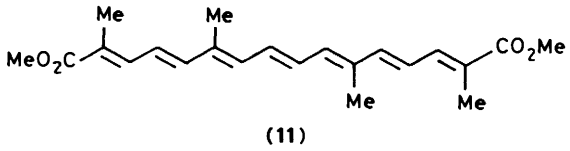
Similar treatment of mixture II with *p*-hydroxybenzaldehyde (**15**) gave the aryloxy lactone (**19**), showing a carbonyl band at 1 785 cm^{-1} in its i.r. spectrum, along with the butenoates (**16**) and (**17**). Elemental analysis of the new lactone (**19**) coincided with the empirical formula $C_{12}H_{10}O_4$, demonstrating that the new lactone (**19**) and the aryloxy lactone (**14**) were formed from the same bromo lactone (**8**) in mixture II.

It is of interest that the (*Z*)-isomer (**17**) was commonly formed from both mixtures. Gedye *et al.*[8] reported that the treatment of pure methyl (*E*)- (**20**) and (*Z*)- (**21**) but-2-enoate with NBS gave the same equilibrium mixture of the (*E*)- and (*Z*)-isomers (**20**) and (**21**) and only the (*E*)-4-bromobutenoate (**22**) was isolated as a final brominated product. The 3-phenyl derivatives (**23**) and (**24**) displayed the same behaviour. The possibility existed therefore that the (*Z*)-4-bromobutenoate (**9**) might be contained

† This paper forms part 61 of the series 'Studies on the Chemical Constituents of Rutaceous Plants' by H. Ishii.



Scheme 1.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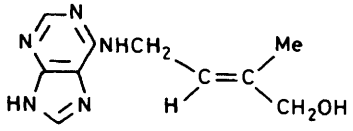
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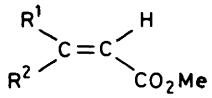
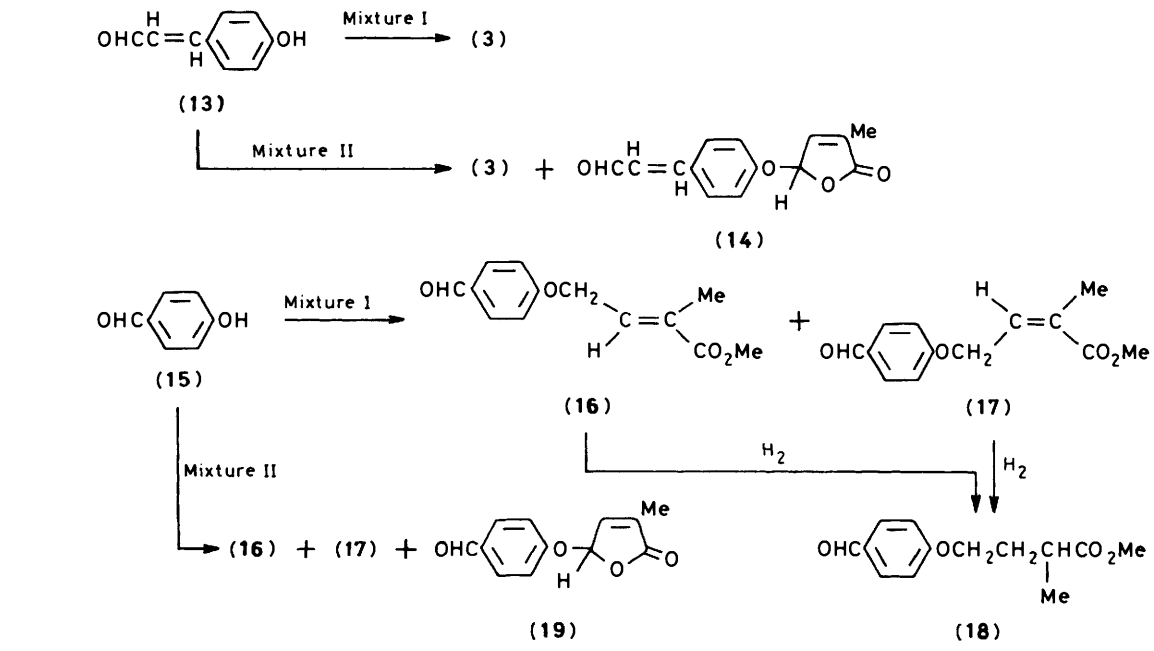

(20) R^1 = Me, R^2 = H
(21) R^1 = H, R^2 = Me
(22) R^1 = CH_2Br, R^2 = H
(23) R^1 = Me, R^2 = Ph
(24) R^1 = Ph, R^2 = Me



Scheme 2.

Table 1. Assignment of the signals of the ^1H n.m.r. spectra (CCl_4) of the mixtures I and II in the presence of [Eu(dpm)$_3$]

		Mixture I[a]			Mixture II[b]		
Compd.	Assignment	δ	Relative intensity	Splitting pattern	δ	Relative intensity	Splitting pattern
(5)	2-Me	2.81	27/14	s	4.28[d]	24/17	s
	4-H_2	4.27	18/14	d, *J* 8.0 Hz	4.78	16/17	d, *J* 8.0 Hz
	OMe	5.00[c]	27/14	s	7.07[e]	24/17	s
	3-H	8.06	9/14	t, *J* 8.0 Hz	10.07	8/17	t, *J* 8.0 Hz
(6)	4-H_3	2.22	12/14	d, *J* 7.0 Hz	2.71	12/17	d, *J* 7.0 Hz
	2-CH_2	5.00[c]	8/14	s	6.38	8/17	s
	OMe	5.00[c]	12/14	s	7.04	12/17	s
	3-H	8.36	4/14	q, *J* 7.0 Hz	10.69	4/17	q, *J* 7.0 Hz
(7)	4-H_3	1.95	3/14	d, *J* 6.5 Hz	2.05	9/17	d, *J* 7.0 Hz
	2-Me	2.08	3/14	s	2.35	9/17	s
	OMe	3.96	3/14	s	4.28[d]	9/17	s
	3-H	5.00[c]	1/14	s	5.23	3/17	q, *J* 7.0 Hz
(8)	2-Me				2.26	6/17	br s
	4-H				7.07[e]	2/17	s
	3-H				7.30	2/17	s

[a] Mixture I–[Eu(dpm)$_3$] = 1:0.8 (w/w). [b] Mixture II–[Eu(dpm)$_3$] = 1:0.7 (w/w).[c,d,e] These signals overlap.

Table 2. ^1H N.m.r. and i.r. data for 2-methylbut-2-en-4-olide derivatives

		(10)[5d]	(8)[9]	(8)[a]	Strigol[10] (25)	(14)	(19)
δ_H ($CDCl_3$)	2-Me	1.87[b] (dt, *J* 2.0, 1.6 Hz)	2.00 (dd, *J* 1.7, 1.7 Hz)	2.00[b] (dd, *J* 1.5, 1.5 Hz)	1.99 (t, *J* 1.5 Hz)	2.00 (dd, *J* 1.5, 1.5 Hz)	2.00 (dd, *J* 1.5, 1.5 Hz)
	3-H	7.24[b] (tq, *J* 1.6, 1.6 Hz)	7.20 (dq, *J* 1.7, 1.0 Hz)	7.16[b] (dq, *J* 1.5, 1.5 Hz)	6.89 (dq, *J* 1.5, 1.5 Hz)	7.00 (dq, *J* 1.5, 1.5 Hz)	7.00 (m)
	4-H	4.73[b] (dq, *J* 2.0, 1.6 Hz)	6.82 (dq, *J* 1.7, 1.0 Hz)	6.79[b] (dq, *J* 1.5, 1.5 Hz)	6.11 (dq, *J* 1.5, <1.5 Hz)	6.34 (dq, *J* 1.5, 1.5 Hz)	6.38 (m)
ν_{CO} (cm^{-1})		1 764 (CCl_4)	1 770 (neat)	1 780 (neat)	1 787 (CH_2Cl_2)	1 780 (Nujol)	1 785 (Nujol)

[a] Our data. [b] Measured in CCl_4.

in our crude reaction mixtures I and II. If this were so, the (*Z*)-4-bromobutenoate (**9**) would be cyclized to the corresponding butenolide (**10**), and could not give the (*Z*)-4-aryloxy derivative (**17**) on treatment with a phenol derivative during the purification by distillation. Since, the presence of (**17**) had, in fact, been observed by other groups[5d,8] and since detailed examination of the ^1H n.m.r. spectrum in the presence of the shift reagent provided no evidence for the presence of the (*Z*)-4-bromobutenoate (**9**) in either of the mixtures, we excluded the possibility that compound (**9**) was present in mixtures I and II.

That (*E*)-but-2-enoic acid derivatives sometimes isomerize to give the (*Z*)-product, and *vice versa*, because a small change in the bulkiness of the substituent causes the thermodynamically stable form of the product to vary in this system is well known.* We therefore supposed that the (*Z*)-isomer (**17**) was produced from the (*E*)-isomer (**16**) during alkylation. On the basis of this conclusion, we examined the differences in the components of mixtures I and II by the detailed examination of various spectral data.

In their i.r. spectrum, both mixtures showed carbonyl absorptions at 1 720s cm^{-1} and 1 750w cm^{-1} attributable to the ester groups of the brominated butenoates (**5**) and (**6**), and the dibromide (**7**), respectively. In the case of mixture II, an additional carbonyl band, assignable to the bromo lactone (**8**), was observed at 1 780 cm^{-1}.

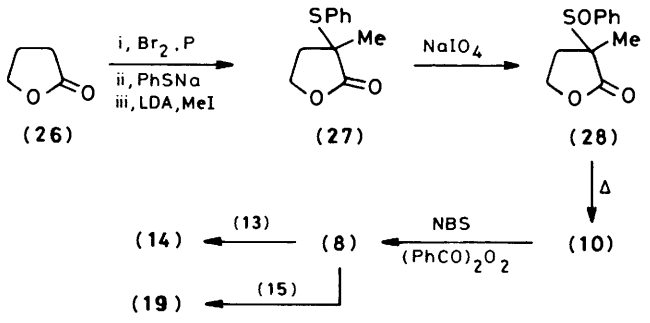
Evidence for the presence of the dibromide (**7**) came from the fact that, in the chemical ionization (c.i.) mass spectrum of mixture II, the protonated molecular ion ($C_6H_{11}Br_2O_2^+$) and its isotope peaks at *m/z* 273, 275, and 277 appeared in a ratio of 1:2:1. Since Löffler *et al.*[5d] described the formation of the 2,3-dibromide (**7**) showing a carbonyl band at 5.73 nm (1 745 cm^{-1}) in the i.r. spectrum by treatment of the starting (*E*)-butenoate (**4**) with NBS in *N*,*N*-dimethylformamide, *N*-bromoacetamide in carbon tetrachloride, or trimethylanilinium perbromide in tetrahydrofuran, we believe our dibromide to be the same compound.

In the ^1H n.m.r. spectrum in the presence of the shift reagent tris(dipivaloylmethanato)europium(III), [Eu(dpm)$_3$], the mixtures I and II showed three sets of signals which were allocated to the (*E*)-4-bromobutenoate (**5**), the (*E*)-2-(bromomethyl)-butenoate (**6**), and the dibromide (**7**). However, mixture II showed an additional fourth set attributable to the bromo lactone (**8**). Comparison of the intensities of the methyl signals of mixtures I and II disclosed that they contain the bromobutenoate (**5**), the (bromomethyl)butenoate (**6**), the dibromide (**7**), and the bromo lactone (**8**) in ratios of 9:4:1:0, and 8:4:3:2, respectively (Table 1).

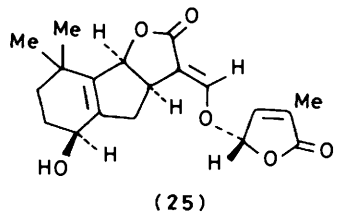
There are two papers on the preparation[5d] of the lactone (**10**) from the (*E*)-butenoate (**4**) by treatment with NBS in the presence of benzoyl peroxide or under photochemical conditions, and on the formation[9] of the bromo lactone (**8**) by

* For example, Kubo and Kitahara *et al.* reported that treatment of 1-hydroxymethylisoquinoline-5,8-quinone derivative with (*Z*)-2-methylbut-2-enoyl chloride and its geometrical isomer gave the (*E*)-2-methylbutenoate derivative in the same yield (A. Kubo, Y. Kitahara, S. Nakahara, N. Saito, and R. Iwata, Abstracts of Papers, 14th Congress of Heterocyclic Chemistry, Tokyo, Japan, 1981, p. 61).

photochemical treatment of the lactone (**10**) in carbon tetrachloride with NBS. Although the carbonyl band position (1 770 cm^{-1}) of the reported bromo lactone (**8**) was different from that of the bromo lactone (**8**) in our mixture II (1 780 cm^{-1}), taking into account the observation that the carbonyl bands of both the aryloxy lactones (**14**) and (**19**) appeared in the higher region assignable to α,β-unsaturated γ-lactone involving the naturally occurring strigol[10] (**25**) (Table 2), we undertook to synthesize them from the pure bromo lactone (**8**) *via* an alternative route for direct comparison.



Scheme 3.



(25)

Since the lactone[11] (**10**) and the bromo lactone[12] (**8**) are also useful starting materials in terpenoid synthesis, there are many reports on their synthesis.[11] The desired bromo lactone (**8**) was synthesized by bromination of the lactone (**10**) prepared from γ-butyrolactone (**26**) essentially according to Iwai's method[11a] involving thermal *syn*-elimination of a sulphoxide. Sodium metaperiodate was used as oxidising agent for the sulphide (**27**) in our work after preliminary tests on all of the reagents described in the report.[11a] The resulting lactone (**10**) was brominated by the reported procedure[12a] using NBS and benzoyl peroxide to give the bromo lactone (**8**) showing a carbonyl band at 1 780 cm^{-1} in its i.r. spectrum. Treatment of the bromo lactone (**8**) with the phenols (**13**) and (**15**) gave the aryloxy lactones (**14**) and (**19**) in yields of 43.5 and 26.1% based on the bromo lactone (**8**), respectively.

Our results clearly show that bromination of the butenoate (**4**) without irradiation is a better method for the preparation of the 4-bromobutenoate (**5**) and that photochemical conditions may provide a commercial route from the butenoate (4) to the bromo lactone (**8**). Since we could find no evidence for the presence of the bromo lactone (**8**) in mixture I, we may deduce that it was mainly formed from (*E*)-4-bromobutenoate (**5**) by the following steps: (i) photochemical isomerization of the (*E*)-bromobutenoate (**5**); (ii) lactonization of the (*Z*)-bromobutenoate (**9**); and (iii) photochemical allylic bromination of the lactone (**10**) with NBS to the bromo lactone (**8**) (Scheme 1).

That the above observations had previously gone unrecorded may be due to the fact that earlier experiments had been conducted either with insufficient irradiation or with lengthy work-up procedures under basic conditions.

(29) (30)

Finally, treatment of the aldehyde (**16**) with formylmethylenetriphenylphosphorane[13] (**29**) for 24 h gave methyl boninenalate (**3**) in only 15.8% yield, the starting aldehyde (**16**) being recovered in 36.1% yield. When 1,3-dioxolan-2-ylmethylenetriphenylphosphorane[14] (**30**), a more reactive ylide, was used, the desired ester (**3**) was obtained in only 17.6%.

Experimental

All m.p.s were measured on a micro melting-point hot stage (Yanagimoto) and are uncorrected. I. r. spectra were recorded for Nujol mulls on a Hitachi 215 spectrophotometer. ^1H and ^{13}C N.m.r. spectra were recorded on JEOL JNM-MH-100 and JEOL FX-270 spectrometers, respectively, in deuteriochloroform, with tetramethylsilane as internal reference. Mass spectra were measured with a Hitachi M-60 spectrometer using a direct inlet system at 70 eV chamber voltage for e.i. mass spectra and using isobutane as reactant gas at 100 eV chamber voltage for c.i. mass spectra. For chromatography, silica gel 60 (70—230 mesh ASTM; Merck) was used, while for t.l.c. and preparative t.l.c., silica gel GF_{254} (Merck) was used. Products were identified by i.r., mixed m.p., and t.l.c. Couplings among the methyl, the olefinic, and the allylic protons were confirmed by decoupling experiments on the aryloxy lactone (**14**), the (*Z*)-aryloxybutenoate (**17**), the lactone (**10**), and the 4-bromolactone (**8**). NBS was freshly recrystallized from water before use.

Bromination of Methyl (E)-2-*Methylbut*-2-*enoate* (**4**) *with NBS under Photochemical Conditions* (*Mixture II*).—A solution of methyl (*E*)-2-methylbut-2-enoate (**4**) (5.01 g) and NBS (8.68 g) in carbon tetrachloride (6.5 ml) was refluxed and irradiated (60 W incandescent illumination) for 4 h. After cooling with ice, the reaction mixture was filtered, and the filtrate evaporated under reduced pressure. Distillation of the residue at 93—95 °C (14 mmHg) gave a mixture of brominated products as a pale yellow oil (5.18 g); $\nu_{max.}$(neat) 1 780, 1 750, and 1 720 cm^{-1}; δ_H (see Table 1); *m/z** 277 (1.6), 275 (3.4), 273 (1.9), 195 (100), and 193 (91%).

Treatment of Mixture II with p-*Hydroxycinnamaldehyde* (**13**).—A suspension of mixture II (0.194 g), *p*-hydroxycinnamaldehyde (**13**) (0.051 g), and potassium carbonate (0.070 g) in acetone (2.4 ml) was refluxed for 2 h. The precipitate was filtered off and the mixture was evaporated under reduced pressure. Preparative t.l.c. of the oily residue [benzene–ethyl acetate (20:1 v/v)] gave two fractions.

(a) *Methyl boninenalate* (**3**). The less polar fraction provided colourless prisms (0.048 g), m.p. 174 °C (softened at 100—101 °C) [lit.,[4] 180 °C (softened at 107—108 °C)], which were recrystallized from benzene–hexane. This material was identical with a sample of methyl boninenalate[2,4] (**3**) obtained from a natural source.

(b) 4-[p-(*Formylvinyl*)*phenoxy*]-2-*methylbut*-2-*en*-4-*olide* (**14**). The more polar fraction gave 4-[*p*-(formylvinyl)phenoxy]-2-methylbut-2-en-4-olide (**14**) as colourless fine *prisms* (0.022 g), m.p. 130—132 °C, which were recrystallized from benzene–hexane (Found: C, 69.0; H, 4.9. $C_{14}H_{12}O_4$ requires C, 68.8; H, 4.95%); $\nu_{max.}$ 1 780 and 1 680 cm^{-1}; δ_H 2.00 (3 H, dd, *J* 1.5 and 1.5 Hz, 2-Me), 6.34 (1 H, dq, *J* 1.5 and 1.5 Hz, 4-H), 6.62 (1 H, dd, *J* 16.0 and 8.0 Hz, OHCC*H*=CH), 7.00 (1 H, dq, *J* 1.5 and 1.5 Hz,

* Data obtained by c.i. mass spectral analysis.

3-H), 7.15 (2 H, d, *J* 9.0 Hz, 2'- and 6'-H), 7.43 (1 H, d, *J* 16.0 Hz, CH=C*H*Ar), 7.55 (2 H, d, *J* 9.0 Hz, 3'- and 5'-H), and 9.67 (1 H, d, *J* 8.0 Hz, CHC*H*O). This material was identical with a sample obtained by condensation of *p*-hydroxycinnamaldehyde (**13**) with the pure 4-bromo lactone (**8**).

Bromination of Methyl (E)-2-*Methylbut*-2-*enoate* (**4**) *with NBS without Irradiation* (*Mixture I*).—A solution of methyl (*E*)-2-methylbut-2-enoate (**4**) (10.0 g) and NBS (17.3 g) in carbon tetrachloride (60 ml) was refluxed for 4 h and then set aside in a refrigerator. The precipitate was filtered off and the filtrate was evaporated under reduced pressure. Distillation of the oily residue at 60—64 °C (3 mmHg) gave a mixture of brominated products as a pale yellow oil (11.6 g); $\nu_{max.}$(neat) 1 750 and 1 720 cm^{-1}; δ_H (see Table 1).

Treatment of Mixture I with p-*Hydroxybenzaldehyde* (**15**).—A suspension of mixture I (0.511 g), *p*-hydroxybenzaldehyde (**15**) (0.633 g), and potassium carbonate (1.06 g) in dry acetone (30 ml) was stirred at room temperature for 1.5 h. The potassium carbonate was filtered off and the filtrate was evaporated under reduced pressure. The residue was suspended in diethyl ether and the insoluble material was filtered off and washed with diethyl ether, and the filtrate and washings were combined, washed with 5% aqueous sodium hydroxide, dried ($MgSO_4$), and evaporated to dryness under reduced pressure.

(a) *Methyl* (E)-4-(p-*formylphenoxy*)-2-*methylbut*-2-*enoate* (**16**). Recrystallization of the residue from benzene–hexane gave methyl (*E*)-4-(*p*-formylphenoxy)-2-methylbut-2-enoate (**16**) as colourless fine *needles* (0.264 g), m.p. 83—84 °C (Found: C, 66.7; H, 6.0. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.0%); $\nu_{max.}$ 1 705 and 1 680 cm^{-1}; δ_H 1.95 (3 H, diffuse s, 2-Me), 3.77 (3 H, s, OMe), 4.80 (2 H, br d, *J* 5.5 Hz, 4-H_2), 6.93 (1 H, diffuse t, *J* 5.5 Hz, 3-H), 7.00 (2 H, d, *J* 9.0 Hz, 2'- and 6'-H), 7.85 (2 H, d, *J* 9.0 Hz, 3'- and 5'-H), and 9.89 (1 H, s, CHO); δ_C 13.1 (q, C-*Me*), 52.1 (q, OMe), 65.1 (t, C-4), 114.9 (d, C-2' and -6'), 130.4 and 130.5 (each s, C-2 and -4'), 132.0 (d, C-3' and -5'), 135.5 (d, C-3), 163.2 and 167.5 (each s, C-1 and -1'), and 190.7 p.p.m. (d, CHO).

(b) *Methyl* (Z)-4-(p-*formylphenoxy*)-2-*methylbut*-2-*enoate* (**17**). The mother liquor from the recrystallization of the (*E*)-4-aryloxybutenoate (**16**) was evaporated under reduced pressure and preparative t.l.c. of the residue [hexane–diethyl ether (1:1 v/v)] gave methyl (*Z*)-4-(*p*-formylphenoxy)-2-methylbut-2-enoate (**17**) as colourless fine *needles* (0.007 g), m.p. 91—92 °C, which were recrystallized from diethyl ether–hexane (Found: C, 66.5; H, 6.0. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.0%); $\nu_{max.}$ 1 710 and 1 690 cm^{-1}; δ_H 1.98 (3 H, dt, *J* 1.7 and 1.7 Hz, 2-Me), 3.80 (3 H, s, OMe), 5.00—5.18 (2 H, m, 4-H_2), 6.14—6.30 (1 H, m, 3-H), 6.99 (2 H, d, *J* 9.0 Hz, 2'- and 6'-H), 7.82 (2 H, d, *J* 9.0 Hz, 3'- and 5'-H), and 9.86 (1 H, s, CHO); δ_C 19.7 (q, C-*Me*), 51.8 (q, OMe), 67.0 (t, C-4), 115.0 (d, C-2' and -6'), 128.6 and 130.1 (each s, C-2 and -4'), 132.0 (d, C-3' and -5'), 139.7 (d, C-3), 163.4 and 167.4 (each s, C-1 and -1'), and 190.8 p.p.m. (d, CHO).

Catalytic Hydrogenation of the (*E*)-4-*Aryloxybutenoate* (**16**) *using Wilkinson Complex* [*Methyl* 4-(p-*Formylphenoxy*)-2-*methylbutanoate* (**18**)].—Wilkinson complex[7] [$RhCl(PPh_3)_3$] (0.493 g) was added to a solution of the (*E*)-4-aryloxybutenoate (**16**) (1.01 g) in dry benzene–dry ethanol (5:2 v/v) (170 ml) and the mixture was hydrogenated at room temperature under atmospheric pressure for 9 h. The reaction mixture was evaporated under reduced pressure and the residue chromatographed with benzene. After elution with benzene, benzene–ethyl acetate (30:1 v/v) as eluant gave methyl 4-(*p*-formylphenoxy)-2-methylbutanoate (**18**) as a pale yellow *oil* (0.775 g), b.p. 158 °C (2.5 mmHg) (Found: C, 65.8; H, 6.8. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8%); $\nu_{max.}$ 1 735 and 1 690 cm^{-1}; δ_H 1.25 (3 H, d, *J* 7.0 Hz, 2-Me), 1.67—2.47 (2 H, m, 3-H_2), 2.47—3.00 (1 H, m, 2-H), 3.68 (3 H, s, OMe), 4.09 (2 H, t, *J* 6.5 Hz, 4-H_2), 6.96 (2 H, d, *J* 9.0 Hz, 2'- and 6'-H), 7.82 (2 H, d, *J* 9.0 Hz, 3'- and 5'-H), and 9.87 (1 H, s, CHO).

Catalytic Hydrogenation of the (Z)-4-*Aryloxybutenoate* (**17**) *using Wilkinson Complex* [*Methyl* 4-(p-*Formylphenoxy*)-2-*methylbutanoate* (**18**)].—Wilkinson complex[7] [$RhCl(PPh_3)_3$] (0.035 g) was added to a solution of the (*Z*)-4-aryloxybutenoate (**17**) (0.066 g) in dry benzene–dry ethanol (5:2 v/v) (12 ml) and the mixture was continuously hydrogenated at room temperature under atmospheric pressure for one week. The reaction mixture was then evaporated under reduced pressure and the residue chromatographed with benzene. After elution with benzene, benzene–ethyl acetate (30:1 v/v) as eluant gave a pale yellow oil (0.032 g), b.p. 158 °C (2.5 mmHg). This material was identical with a sample of methyl 4-(*p*-formylphenoxy)-2-methylbutanoate (**18**) obtained from the (*E*)-4-aryloxybutenoate (**16**).

Treatment of Mixture II with p-*Hydroxybenzaldehyde* (**15**).—A suspension of mixture II (2.92 g), *p*-hydroxybenzaldehyde (**15**) (0.630 g), and potassium carbonate (1.06 g) in acetone (36 ml) was stirred at room temperature for 4 h. The precipitate was filtered off and the mixture was evaporated under reduced pressure. Column chromatography of the oily residue [hexane–ethyl acetate (1:1 v/v)] gave three fractions.

(a) *Methyl* (Z)-4-(p-*formylphenoxy*)-2-*methylbut*-2-*enoate* (**17**). The less polar fraction gave the ester (**17**) as colourless fine needles (0.067 g), m.p. 91—92 °C, which were recrystallized from diethyl ether. This material was identical with a sample of the 4-aryloxybutenoate (**17**) obtained from mixture I.

(b) *Methyl* (E)-4-(p-*formylphenoxy*)-2-*methylbut*-2-*enoate* (**16**). The second fraction gave the ester (**16**) as colourless needles (0.527 g), m.p. 83.5—85.5 °C, which were recrystallized from benzene–hexane. This material was identical with a sample of (*E*)-4-aryloxybutenoate (**16**) obtained from mixture I.

(c) 4-(p-*Formylphenoxy*)-2-*methylbut*-2-*en*-4-*olide* (**19**). The more polar fraction gave 4-(*p*-formylphenoxy)-2-methylbut-2-en-4-olide (**19**) as colourless *needles* (0.039 g), m.p. 96—98 °C, which were recrystallized from benzene–hexane (Found: C, 65.8; H, 4.5. $C_{12}H_{10}O_4$ requires C, 66.05; H, 4.6%); $\nu_{max.}$ 1 785 and 1 695 cm^{-1}; δ_H 2.00 (3 H, dd, *J* 1.5 and 1.5 Hz, 2-Me), 6.33—6.43 (1 H, m, 4-H), 6.94—7.07 (1 H, m, 3-H), 7.22 (2 H, d, *J* 9.0 Hz, 2'- and 6'-H), 7.87 (2 H, d, *J* 9.0 Hz, 3'- and 5'-H), and 9.93 (1 H, s, CHO). This material was identical with a sample which was obtained by condensation of *p*-hydroxybenzaldehyde (**15**) with the pure 4-bromo lactone (**8**).

2-*Methyl*-2-*phenylsulphinylbutan*-4-*olide* (**28**).—Sodium metaperiodate (2.10 g) was added to a suspension of 2-methyl-2-phenylthiobutan-4-olide (**27**) (1.54 g), m.p. 60—63 °C, prepared from γ-butyrolactone (**26**), in 50% aqueous methanol (30 ml). After being stirred at room temperature for 24 h, the mixture was poured into water (200 ml) and extracted with methylene dichloride. The organic layer was dried (K_2CO_3) and evaporated under reduced pressure. Recrystallization of the residue from diethyl ether gave 2-methyl-2-phenylsulphinylbutan-4-olide (**28**) as colourless prisms* (0.977 g), m.p. 97—104 °C (softened at 78—80 °C) (Found: C, 58.6; H, 5.4. Calc. for $C_{11}H_{12}O_3S$: C, 58.9; H, 5.4%); $\nu_{max.}$ 1 760 cm^{-1}.

Direct Preparation of 2-*Methylbut*-2-*en*-4-*olide* (**10**) *from* 2-*Methyl*-2-*phenylthiobutan*-4-*olide* (**27**).—Sodium metaperio-

* The spot of this material was observed as an overlapped one with another component on t.l.c. We supposed this to be caused by the presence of diastereomeric mixture of 2-methyl-2-phenylsulphinylbutan-4-olide (**28**).

date (2.58 g) was added to a suspension of the phenylthiobutanolide (**27**) (2.00 g) in 50% aqueous methanol (40 ml). The mixture was stirred at room temperature until the starting material became undetectable by t.l.c. (*ca.* 6 h*). The reaction mixture was then poured into water (250 ml) and extracted with methylene dichloride. The organic layer was dried (K_2CO_3) and then evaporated to dryness under reduced pressure.

Immediately, the residue† was dissolved in toluene (30 ml) and refluxed for 0.5 h. The cooled solution was carefully evaporated under reduced pressure below 40 °C. After elution with hexane and hexane–ethyl acetate (10:1 v/v), elution with hexane–ethyl acetate (5:1 v/v) gave 2-methylbut-2-en-4-olide as a pale yellow oil (0.465 g), b.p. 90 °C (19 mmHg) [lit.,[11b] 82 °C (7 mmHg); 97—98.6 °C (20 mmHg)[11c]]; $\nu_{max.}$(neat) 1 755 cm^{-1}; δ_H 1.88—1.99 (3 H, m, 2-Me), 4.67—4.80 (2 H, m, 4-H_2), and 7.05—7.20 (1 H, m, 3-H); *m/z* 98 (M^+, 29), 41 (46), and 18 (100%).

4-*Bromo*-2-*methylbut*-2-*en*-4-*olide* (**8**).—A mixture of the lactone (**10**) (0.200 g), NBS (0.400 g), and benzoyl peroxide (0.003 g) in carbon tetrachloride (5 ml) was refluxed for 8 h and then set aside in a refrigerator. The resulting precipitate was filtered off and the filtrate evaporated under reduced pressure to give 4-bromo-2-methylbut-2-en-4-olide (**8**) as a yellow oil‡[12] (0.330 g); $\nu_{max.}$ and δ_H (see Table 2).

4-[p-(*Formylvinyl*)*phenoxy*]-2-*methylbut*-2-*en*-4-*olide* (**14**).—A suspension of the 4-bromo lactone (**8**) (0.310 g), *p*-hydroxycinnamaldehyde (**13**) (0.255 g), and potassium carbonate (0.443 g) in dry acetone (15 ml) was stirred at room temperature for 2.5 h. The resulting precipitate was filtered off, the filtrate evaporated under reduced pressure, and the residue added to a two-phase mixture of benzene (200 ml) and water (100 ml). The benzene layer was separated, washed with 5% aqueous sodium hydroxide, dried (K_2CO_3), and then evaporated under reduced pressure. Recrystallization of the residue from benzene–hexane gave 4-[*p*-(formylvinyl)phenoxy]-2-methylbut-2-en-4-olide (**14**) as colourless needles (0.186 g), m.p. 135—137 °C. This material was identical with a sample of the aryloxy lactone (**14**) obtained from mixture II.

4-(p-*Formylphenoxy*)-2-*methylbut*-2-*en*-4-*olide* (**19**).—A suspension of the 4-bromo lactone (**8**) (0.330 g), *p*-hydroxybenzaldehyde (**15**) (0.343 g), and potassium carbonate (0.577 g) in dry acetone (16 ml) was stirred at room temperature for 2 h. The resulting precipitate was filtered off, the filtrate evaporated under reduced pressure, and the residue dissolved in a large quantity of diethyl ether. The ethereal solution was washed with 5% aqueous sodium hydroxide, dried (K_2CO_3), and then evaporated under reduced pressure. Recrystallization of the residue from benzene–hexane gave 4-(*p*-formylphenoxy)-2-methylbut-2-en-4-olide (**19**) as colourless needles (0.106 g), m.p. 93—96 °C. This material was identical with a sample of the aryloxy lactone (**19**), obtained by condensation of mixture II with *p*-hydroxybenzaldehyde (**15**).

Condensation of Methyl (E)-4-(p-*Formylphenoxy*)-2-*methylbut*-2-*enoate* (**16**) *with Formylmethylenetriphenylphosphorane* (**29**) [*Methyl Boninenalate* (**3**)].—A solution of the (*E*)-4-aryloxybutenoate (**16**) (0.108 g) and formylmethylenetriphenylphosphorane[13] (**29**) (0.268 g), m.p. 195—198 °C [lit.,[13] 186—187 °C (decomp.)], in dry benzene (20 ml) was refluxed for 24 h under argon. The reaction mixture was then evaporated under reduced pressure and the residue suspended in diethyl ether and filtered. The filtrate was evaporated to dryness under reduced pressure. Column chromatography of the residue [hexane–ethyl acetate (20:1 v/v)] gave two fractions. The first fraction contained starting material (**16**) as colourless fine needles (0.039 g), m.p. 83—84 °C. The second fraction contained methyl boninenalate (**3**), as colourless prisms (0.019 g), m.p. 172 °C (softened at 103—107 °C), which were recrystallized from benzene–hexane. This material was identical with a sample of methyl boninenalate[2,4] (**3**) obtained from a natural source.

Condensation of Methyl (E)-4-(p-*Formylphenoxy*)-2-*methylbut*-2-*enoate* (**16**) *with* 1,3-*Dioxolan*-2-*ylmethylenetriphenylphosphorane* (**30**) [*Methyl Boninenalate* (**3**)].—A portion (2 ml) of a solution prepared by addition of lithium metal (0.010 g) in dry methanol (2.5 ml) was added dropwise to a stirred solution of the (*E*)-4-aryloxybutenoate (**16**) (0.102 g) and the 1,3-dioxolanylphosphorane§[14] (**30**) (0.473 g), m.p. 176—183 °C {lit.,[14] 172—174 °C [191.5—193 °C after drying at 56 °C (0.5 mmHg)]}, in *N*,*N*-dimethylformamide (20 ml) at 80—90 °C under argon. The mixture was heated at 80—90 °C for 6.5 h, poured into water, and then extracted with diethyl ether. The ethereal solution was washed with saturated brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue (crude acetal) was dissolved in tetrahydrofuran (2 ml). After addition of 10% hydrochloric acid (2 ml), the mixture was kept at room temperature for 5.5 h after which it was diluted with water (20 ml) and extracted with diethyl ether. The extracts were washed with 5% aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and then evaporated under reduced pressure. Column chromatography of the residue [hexane–ethyl acetate (20:1 v/v)] gave methyl boninenalate as colourless prisms (0.020 g), m.p. 162 °C (softened at 93—112 °C), which were recrystallized from benzene. This material was identical with a sample of methyl boninenalate[2,4] (**3**) obtained from a natural source.

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* Prolonged stirring should be avoided.

† Since we recognized that the sulphoxide (**28**) was apt to undergo over-oxidation by air to give the sulphone derivative, the crude product (**28**) was used in the subsequent thermal *syn*-elimination, without any purification.

‡ This material was purified by distillation according to MacAlpine *et al.*[12a] but was claimed to be labile by Ingham *et al.*[12b] We recognized that the material could not be purified by distillation without decomposition even under reduced pressure.

§ This material melts at 201—205 °C after drying at 50 °C overnight *in vacuo*. The dried material was used in this experiment.

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