

Stereochemistry of the Bromination of Acetylenes with Bromine and Copper(II) Bromide

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Reactions of acetylenes ($RC\equiv CR'$: R and/or R' = H, alkyl, or phenyl) (1) with molecular bromine in chloroform give a mixture of the corresponding *E*- and *Z*-dibromoalkenes in high yields, the *E*-isomer being predominant under kinetically controlled conditions except in the case of (1; R = Ph, R' = Bu^t) where the *Z*-isomer is the sole product. From the reaction with an excess of bromine or under u.v. irradiation a thermodynamic equilibrium mixture of both isomers was obtained, the same mixture being readily formed by u.v. irradiation of a solution of any mixture of isomers in chloroform. Reactions with copper(II) bromide in acetonitrile at 20–25 °C also give the same products, the rates of reaction being much less and the isomerization of the products much slower, and the stereospecificity being much higher than for bromination with molecular bromine. The kinetically controlled product ratios between *E*- and *Z*-dihalogenoalkenes are obtained from the reactions of four alkylphenylacetylenes (R = Ph, R' = H, Me, Prⁱ, or Bu^t) with iodine, iodine monochloride, bromine, and chlorine. The results are explained in terms of a cyclic iodonium ion intermediate for the former two reactions and an open vinyl cation intermediate for the last; for bromination, an open vinyl cation intermediate in which bromine may interact weakly with the benzylic carbon is postulated.

KINETIC and stereochemical studies of the bromination of acetylenes have so far been very limited.^{1,2} Since the bromine-catalysed isomerization of dihalogenoalkenes has been elucidated satisfactorily,³ it seemed to us important to investigate both kinetically and thermodynamically controlled product ratios, to clarify the reaction mechanism. To our knowledge there have been only a few studies performed from this view-

point.⁴⁻⁶ As part of our series of studies on halogenation of acetylenes with halogen and/or metal halide,^{7,8} we now report stereochemical data for the bromination

³ See for example, C. Walling, 'Free Radicals in Solution,' Chapman and Hall, New York, 1957, pp. 302–304.

⁴ I. N. Nazarov and L. D. Bergel'son, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 887, 896.

⁵ J. A. Pincock and K. Yates, *Canad. J. Chem.*, 1970, **48**, 3332.

⁶ J. König and V. Wolf, *Tetrahedron Letters*, 1970, 1629.

⁷ S. Uemura, A. Onoe, and M. Okano, *J.C.S. Chem. Comm.*, 1975, 925; 1976, 145.

⁸ S. Uemura, H. Okazaki, A. Onoe, and M. Okano, *J.C.S. Perkin I*, 1977, 676.

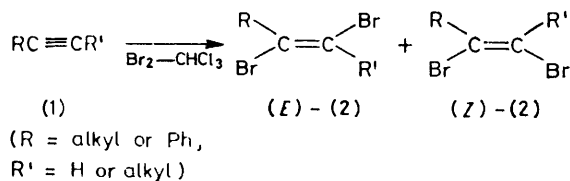
¹ R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 279.

² P. B. D. de la Mare, 'Electrophilic Halogenation,' Cambridge University Press, Cambridge, 1976, ch. 7.

of acetylenes with bromine and copper(II) bromide under conditions of kinetic and thermodynamic control, and compare the results with those of chlorination and chloriodination.⁸

RESULTS AND DISCUSSION

Treatment of an acetylene (1) with molecular bromine in chloroform gave a mixture of two isomeric dibromoalkenes (2) almost quantitatively when R = Ph and in good yield when R = alkyl (Scheme 1), the isomer ratio



SCHEME 1

depending very much on the reaction conditions. Typical results are shown in Table 1. Under conditions

TABLE 1
Bromination of acetylenes with molecular bromine in chloroform^a

(1)		Molar ratio of Br ₂ to (1)	Temp. (°C)	Time (h)	Products ^b (E)-(2) : (Z)-(2)	Yield ^c (%)
R	R'					
Ph	H	1	-50	0.5	92 : 8 ^d	
Ph	H	1	0	0.5	92 : 8	
Ph	H	1	20	0.5	85 : 15 ^e	
Ph	H	1	20	24	60 : 40	
Ph	H	1	20	1	91 : 9 ^f	
Ph	H	1	61	0.5	76 : 24	
Ph	H	1.5	20	24	20 : 80	
Ph	H	10	20	48	20 : 80	
Ph	Me	1	-50	0.5	93 : 7	
Ph	Me	1	20	0.5	89 : 11	
Ph	Me	10	20	48	77 : 23	
Ph	Et	1	20	0.5	86 : 14	
Ph	Et	10	20	48	69 : 31	
Ph	Pr ⁱ	1	-50	0.5	63 : 37	
Ph	Pr ⁱ	10	25	48	62 : 38	
Ph	Bu ^t	1	-50	0.5	0 : 100	
Ph	Bu ^t	1	20	0.5	19 : 81	
Ph	Bu ^t	10	20	48	28 : 72	
n-Hexyl	H	1	20	0.5	96 : 4	67 ^g
n-Hexyl	H	1.5	20	24	81 : 19	79
n-Hexyl	H	1	61	0.5	95 : 5	49
Pr ⁿ	Pr ⁿ	1	20	0.5	100 : 0	69 ^h
Pr ⁿ	Pr ⁿ	1	61	0.5	99 : 1	55
CH ₂ OH	H	1	20	0.5	72 : 28	45

^a Alkyne (1) (2.5 mmol) and CHCl₃ (25 ml) were used. ^b The isomer ratio was determined by g.l.c. analysis. ^c Yields (by g.l.c.) were almost quantitative except those stated. ^d When *m*-dinitrobenzene (0.3 mmol) was added here, the isomeric mixture (*E* : *Z* 91 : 9) was obtained quantitatively. ^e The reaction in the presence of *m*-dinitrobenzene (0.3 mmol) or oxygen also gave 100 or 70% yield of (2), respectively, the isomeric ratio being 85 : 15 in both cases. ^f Reaction in the dark. ^g Isolated yield 51%. ^h Isolated yield 48%.

of kinetic control, *i.e.* with a shorter reaction time, at lower temperature, and with equimolar amounts of bromine and (1), all reactions produced mainly the *E*-isomer, except in the case of *t*-butylphenylacetylene, where *cis*-addition, giving the *Z*-isomer, occurred

^g A. Debon, S. Masson, and A. Thuillier, *Bull. Soc. chim. France*, 1975, 2493.

selectively. The use of a prolonged reaction, higher temperature, and higher molar ratio of bromine to (1) generally resulted in *E* → *Z* isomerization without much affecting the yield of (2); the reverse effect was observed with *t*-butylphenylacetylene and no appreciable change in the case of isopropylphenylacetylene. Thus, after 48 h a thermodynamic equilibrium mixture was usually obtained in the presence of a ten-fold excess of bromine, only a slight excess of bromine being enough in some cases. These observations are consistent with the known fact³ that dihalogenoalkenes can be isomerized by bromine as catalyst. Although all reactions were carried out under daylight, no appreciable change in isomer ratio was observed even when the reaction was carried out in the dark, the *E* : *Z* ratio becoming only slightly higher if at all.

Since it had been reported that a thermodynamic equilibrium mixture of the dichloro-analogues of (*E*)- and (*Z*)-(2) is obtained by irradiation in the presence of a trace of bromine,⁹ we carried out this bromination under u.v. irradiation. As a result it was revealed that a thermodynamic equilibrium mixture of (*E*)- and (*Z*)-(2) can be obtained readily from an alkylphenylacetylene even when an equimolar amount of (1) and bromine is used, although the yields of (2) were sometimes slightly lower than those listed in Table 1. In the cases of alkylacetylenes and dialkylacetylenes the yields of product were generally low and it was difficult to find the thermodynamically controlled ratios from this experiment. We therefore tried irradiating a chloroform solution of the isolated (2) in order to obtain the thermodynamically controlled ratio in each case. Thus almost the same equilibrium mixture as that obtained in bromination under u.v. irradiation was formed in each case by irradiating a mixture of any composition of (*E*)- and (*Z*)-(2) in chloroform for 30 min at room temperature, with a recovered yield of the starting isomers of over 80%. Typical results are summarized in Table 2 together with the reported thermodynamic equilibrium ratio of the dichloro-analogues of (*E*)- and (*Z*)-(2).⁹

Castro *et al.*¹⁰ have studied the bromination of triple bonds with copper(II) bromide in methanol at reflux temperature and have found that tribromide and dibromide are obtained from terminal and internal acetylenes respectively. Since we had found previously⁸ that chlorination of (1) with copper(II) chloride in acetonitrile gives the chloro-analogues of (*E*)- and (*Z*)-(2) with high stereospecificity, we carried out bromination of the same acetylenes with copper(II) bromide in acetonitrile at room temperature, hoping that much higher *E*- or *Z*-selectivity would be obtained than in bromination with molecular bromine. It was found that although the reaction was slower and the yield generally lower than that with molecular bromine, a mixture of (*E*)- and (*Z*)-(2) was always formed except only in the case of (1; R = CH₂OH, R' = H) where the

¹⁰ C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, 1965, **30**, 587.

formation of tribromide was observed together with the expected dibromide. One of the most interesting characteristics found here was a very high stereospecificity; *i.e.* only the *E*-isomer was produced from

higher than that in bromination with molecular bromine when R = phenyl or alkyl and R' = H or primary and secondary alkyl. Since copper(II) bromide does not dissociate to give bromine under the conditions employed

TABLE 2
Bromination under u.v. irradiation in chloroform ^a

(1)		Time (min)	Products ^b (<i>E</i>)-(2) : (<i>Z</i>)-(2)	Yield ^b (%)	(E)-(2) : (Z)-(2) ^c	(E)-(2) _{Cl} : (Z)-(2) _{Cl} ^d
R	R'					
Ph	H	3	50 : 50	83		
Ph	H	30	27 : 73	56 ^e		
Ph	H	60	18 : 82	46 ^e	18 : 82	14 : 86
Ph	Me	3	77 : 23	87		
Ph	Me	60	70 : 30	99	69 : 31	54 : 46
Ph	Et	60	74 : 26	80	67 : 33	44 : 56
Ph	Bu ^t	3	24 : 76	100		
Ph	Bu ^t	60	25 : 75	94	25 : 75	
n-Hexyl	H	3	86 : 14	55		
n-Hexyl	H	60	60 : 40	34 ^f		53 : 47
n-Hexyl	H	180	58 : 42	35 ^f		

^a Alkyne (1) (2.5 mmol), bromine (2.5 mmol), and CHCl₃ (25 ml) were used; at 20–25 °C. ^b Determined by g.l.c. analysis. ^c A thermodynamic equilibrium mixture obtained by u.v. irradiation of the isolated mixture in CHCl₃ for 0.5 h at 20 °C. The recovered yields were over 80% in all cases. On prolonging the irradiation time no change in isomer ratio was observed. ^d A thermodynamic equilibrium mixture of the chloro-analogue of (2). ^e Other product, bromophenylacetylene (*ca.* 10%). ^f Appreciable amounts of high-boiling unidentified compounds were also obtained.

alkylacetylenes and (1; R = Ph, R' = Me). From *t*-butylphenylacetylene, the *Z*-isomer was obtained as the main product as in the case of bromination with molecular bromine. Typical results are shown in Table 3. The fact that the *E*-isomer was almost the sole product in the reaction of (1; R = Ph, R' = H) with 2–5 mol. equiv. of copper(II) bromide even for 48 h duration shows that copper(II) bromide does not dissociate to copper(I) and bromine under these conditions; if it did the *E*-isomer should be isomerized to the *Z*-isomer as in the foregoing reaction with molecular bromine. It should be noted here that bromination of (1; R = Ph, R' = H) with molecular bromine in acetonitrile at room temperature for 0.5 h afforded (2) quantitatively, the *E* : *Z* ratio being 77 : 23.

Both brominations seem to be ionic in nature, since no appreciable change in yield or isomer ratio was observed when the reaction of (1; R = Ph, R' = H) was carried out in the dark or in daylight, in the presence of bubbling oxygen or nitrogen, and in the presence of a radical scavenger such as *m*-dinitrobenzene, the stereospecificity for the *E*-isomer being always very high. The lack of formation of propargylic bromide also supports the ionic nature of these brominations. The ionic nature of the bromination of olefins and aromatic compounds with molecular bromine in chloroform, dichloromethane, or chlorobenzene is well known and has been attributed to the dipolar character of these solvents.¹¹ Under conditions of kinetic control the isomer ratio (*E* : *Z*) in the products from alkylphenylacetylene decreased markedly in both brominations on changing the alkyl group from primary to secondary and then to tertiary as has been observed in chlorinations with copper(II) chloride.⁸ In bromination with copper(II) bromide, the stereospecificity for the *E*-isomer was

here, this reaction seems to proceed through an intermediate similar to that proposed for chlorination with copper(II) chloride:⁸ an open vinyl cation intermediate

TABLE 3
Bromination of acetylenes with copper(II) bromide in acetonitrile ^a

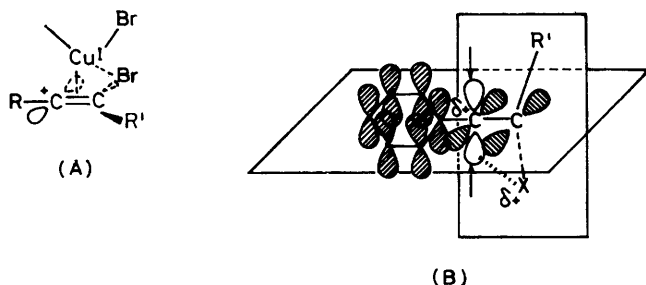
(1)		Molar ratio of CuBr ₂ to (1)	Time (h)	Products ^b (<i>E</i>)-(2) : (<i>Z</i>)-2	Yield ^b (%)
R	R'				
Ph	H	2	0.5	94 : 6	20
Ph	H	2	2	95 : 5	38 ^c
Ph	H	2	48	96 : 4	40
Ph	H	5	48	97 : 3	77
Ph	Me	5	48	100 : 0	51
Ph	Et	5	48	97 : 3	41
Ph	Pr ⁿ	5	48	91 : 9	60
Ph	Bu ^t	5	48	4 : 96	65
Ph	Bu ^t	10	48	9 : 91	100
n-Hexyl	H	2	48	100 : 0	23
n-Hexyl	H	5	48	100 : 0	73
Pr ⁿ	Pr ⁿ	5	48	100 : 0	65
CH ₂ OH	H	5	48	100 : 0	51 ^d

^a Alkyne (1) (2.5 mmol) and acetonitrile (25 ml) were used; at 20–25 °C. ^b Determined by g.l.c. analysis. ^c In the presence of *m*-dinitrobenzene (0.3 mmol), bubbling oxygen or bubbling nitrogen, the yields were 45, 24, or 25%, respectively, the isomer ratio being the same (*E* : *Z* 95 : 5) in all cases. ^d Other product Br₂C=C(Br)CH₂OH (48%); m.p. 64–66 °C (lit.,¹⁰ 69.2–69.5 °C).

(A) in which Cu^I co-ordinates weakly with both the π-orbital of the double bond and the lone pair of the bromine atom, the bromide anion co-ordinated to copper (like CuBr₃⁻) being the attacking species. When R' is sterically very large (*e.g.* *t*-butyl) it will hinder attack on its own side in (A) and lead to *Z*-bromination. Similarly, in the bromination with molecular bromine the reaction seems to proceed through an open vinyl cation intermediate (B; X = Br)⁵ in which the bromine may interact with the benzylic carbon much more

¹¹ Ref. 2, pp. 142–143.

weakly than in the case of iodine, because in the latter case the stereospecificity for the *E*-isomer is not very low even when $R = \text{Bu}^t$.



In order to examine more precisely the tendency of the halogen to interact with the benzylic carbon in the intermediate (B) we have investigated halogenations of four alkylphenylacetylenes (1; $R = \text{Ph}$, $R' = \text{H}$, Me, Pr^i , or Bu^t) with iodine, iodine chloride, and chlorine as far as possible under conditions of kinetic control and compared the results with those of bromination with bromine. Results are shown in Table 4. In

TABLE 4

Kinetically controlled *E*:*Z* ratio in halogenation of alkylphenylacetylene (1; $R = \text{Ph}$) in chloroform ^a

R'	I_2 ^b	ICl ^c	Br_2 ^d	Cl_2 ^e
H	100/0	100:0 ^f	92:8	55:45
Me	100/0 ^g	100:0 ^f	93:7	67:33
Pr^i	<i>h</i>	100:0	63:37	40:60
Bu^t	<i>h</i>	28:72 ⁱ	0:100	4:96

^a Equimolar amounts of (1) and halogen used except in chlorination, where a slight excess of chlorine gas to (1) was passed. The yields of the products were nearly quantitative (by g.l.c. analysis) except those stated. Characterization of the products in chloriodination and chlorination has been previously reported.⁸ ^b At 25 °C for 0.5 h. ^c At -50 °C for 0.2 h. ^d At -50 °C for 0.5 h. ^e At -60 °C for 0.2 h. ^f Also 100:0 at 20 °C for 0.5 h. ^g Yield 17% by n.m.r. analysis. ^h Too slow to give the product under the conditions employed. ⁱ 68:32 at 20 °C for 0.5 h.

iodination and chloriodination, only the *E*-isomer was obtained from (1; $R' = \text{H}$, Me, or Pr^i) and it was still obtained even from (1; $R' = \text{Bu}^t$), whereas in bromination the stereospecificity for the *E*-isomer was decreased in the cases of (1; $R' = \text{H}$ and Me) and only the *Z*-isomer was formed from (1; $R' = \text{Bu}^t$). In chlorination, it was further decreased to give isomeric products of *E*:*Z* ratios 2–0.7:1 in the cases of (1; $R' = \text{H}$, Me, or Pr^i). These observations may reflect the difference in degree of interaction of various halogens with the benzylic carbon in the intermediate (B); the increasing order of interaction should be $\text{Cl} < \text{Br} \ll \text{I}$. Thus a cyclic iodonium ion, an open vinyl cation in which bromine interacts weakly with the benzylic carbon,* and an almost completely open vinyl cation may be the respective intermediates in the cases of iodine, bromine, and chlorine. These trends are consistent

* In bromine addition to phenylacetylene and *p*-methylphenylacetylene in acetic acid, an open vinyl cation intermediate has been postulated on the basis of product isomer ratios.⁵ It is not clear, however, that these ratios are a result of kinetic control.

with the results of solvolysis of β -halogenovinyl sulphonic esters¹² and also in the addition of trinitrobenzenesulphonyl hypohalites¹³ and some other species¹⁴ to acetylenes. The reason for rather unusually high *Z*-stereospecificity in all halogenations of (1; $R = \text{Bu}^t$) may be ascribed to the fact that the attack of an anion must occur in a plane which contains a bulky *t*-butyl group.

EXPERIMENTAL

n-Alkyl-, isopropyl-, and *t*-butyl-phenylacetylenes were prepared as previously described.⁸ Chlorine was prepared by oxidation of conc. HCl with potassium permanganate. Other organic and inorganic materials were commercial products and used without further purification. ¹H N.m.r. spectra were taken with a Varian EM-360 instrument for solutions in CCl_4 with Me_4Si as internal standard (with internal lock). G.l.c. analyses were carried out with a Shimadzu 4BMPF apparatus [EGSS-X (15%)–Chromosorb W (1 or 3 m) column; N_2 as carrier gas]; the *E*-isomer has a shorter retention time than the *Z*-isomer in all cases. The internal standards for g.l.c. analyses were as follows: styrene dibromide for (2; $R = \text{Ph}$, $R' = \text{H}$ or alkyl), 1,2-dibromo-octane for (2; $R = \text{alkyl}$, $R' = \text{H}$ or alkyl), ethyl cinnamate for the di-iodo- and chloriodo-compounds from (2; $R = \text{Ph}$, $R' = \text{H}$ or alkyl), and ethyl benzoate for the dichloro-compounds from (2; $R = \text{Ph}$, $R' = \text{H}$ or alkyl). We have confirmed that the respective pure samples of the two isomers of the dibromide (isolated by preparative g.l.c.) have almost the same calibration factor relative to the same internal standard in the g.l.c. analysis in the cases of (2; $R = \text{Ph}$, $R' = \text{H}$ and Et) and (2; $R = n$ -hexyl, $R' = \text{H}$). U.v. irradiations were carried out with a high-pressure mercury lamp (Ushio UM-103).

Bromination with Molecular Bromine.—A typical procedure is as follows. A solution of bromine (0.40 g, 2.5 mmol) in chloroform (12.5 ml) was slowly added to chloroform (12.5 ml) containing (1; $R = \text{Ph}$, $R' = \text{H}$) (0.255 g, 2.5 mmol) at room temperature, and the mixture was stirred for 0.5 h. An aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ was then added and the organic layer was separated, washed with water, dried (MgSO_4), and concentrated to ca. 5 ml. G.l.c. analysis revealed the presence of (*E*)- and (*Z*)-(2; $R = \text{Ph}$, $R' = \text{H}$) and a trace of bromophenylacetylene. Distillation gave a mixture of (*E*)- and (*Z*)-(2; $R = \text{Ph}$, $R' = \text{H}$) (0.34 g, 1.3 mmol). Characterization of dibromoalkenes (2) is shown in Table 5.

Bromination with Copper(II) Bromide.—A typical procedure is as follows. A solution of (1; $R = \text{Ph}$, $R' = \text{H}$) (0.255 g, 2.5 mmol) in acetonitrile (5 ml) was added to acetonitrile (20 ml) containing copper(II) bromide (2.79 g, 12.5 mmol) at room temperature and the mixture was kept at that temperature for 48 h with stirring. It was then added to water (ca. 100 ml), the precipitated copper(I) salt was filtered off, and the filtrate was extracted with benzene. The extract was concentrated to ca. 5 ml, then analysed by g.l.c. as described above. It contained a mixture of (*E*)- and (*Z*)-(2; $R = \text{Ph}$, $R' = \text{H}$) (0.51 g, 1.93 mmol, 77%; *E*:*Z* = 97:3).

¹² P. Bassi and U. Tonellato, *J.C.S. Perkin II*, 1974, 1283.

¹³ P. Bassi and U. Tonellato, *J.C.S. Perkin I*, 1973, 669.

¹⁴ G. Modena and G. Scorrano, 'The Chemistry of Carbon-Halogen Bonds,' ed. S. Patai, Interscience, London, 1973, pp. 338–340.

Iodination of Alkylphenylacetylenes.—The reaction was carried out as for bromination with molecular bromine by (lit.,¹⁵ 76 °C). From (1; R = Ph, R' = Me) the di-iodo-analogue of (*E*)-(2; R = Ph, R' = Me) was obtained in

TABLE 5
Characterization of (*E*)- and (*Z*)-(2)

Compound			B.p. (°C) [Torr]	¹ H N.m.r. (δ)	Found (reqd.) (%)	
R	R'	(<i>E</i>):(<i>Z</i>)			C	H
Ph	H	59:41	134—135 [22]	7.63—7.06 (5 H, m, Ph), 7.00 (1 H, s, vinyl of <i>Z</i>), 6.75 (1 H, s, vinyl of <i>E</i>)	36.8 (36.7)	2.4 (2.3)
Ph	Me	79:21	118—120 [3]	7.30 (5 H, s, Ph), 2.60 (3 H, s, Me of <i>E</i>), 2.26 (3 H, s, Me of <i>Z</i>)	40.1 (39.2)	3.15 (2.9)
Ph	Et	75:25	109—111 [2]	7.25 (5 H, s, Ph), 2.83 (2 H, q, CH ₂ of <i>E</i>), 2.37 (2 H, q, CH ₂ of <i>Z</i>), 1.22 (3 H, t, Me of <i>E</i>), 1.10 (3 H, t, Me of <i>Z</i>)	41.0 (41.4)	3.4 ^a (3.5)
Ph	Pr ⁱ	66:34	93—95 [1] (m.p. 56—62 °C) ^b	7.26 (5 H, s, Ph), 3.43 (1 H, sept, CH of <i>E</i>), 2.63 (1 H, sept, CH of <i>Z</i>), 1.15 (6 H, d, Me of <i>E</i>), 0.92 (6 H, d, Me of <i>Z</i>)	43.4 (43.5)	4.3 (4.0)
Ph	Bu ^t	19:81	152—155 [3] (m.p. 50—52 °C) ^c	7.26 (5 H, s, Ph), 1.57 (9 H, s, Me of <i>E</i>), 1.10 (9 H, s, Me of <i>Z</i>)	45.4 (45.3)	4.6 (4.45)
n-Hexyl	H	89:11	89—92 [3]	6.49 (1 H, t, vinyl of <i>Z</i>), 6.36 (1 H, s, vinyl of <i>E</i>), 2.78—2.36 (2 H, m, =CCH ₂)	35.8 (35.6)	5.25 (5.2)
Pr ⁿ	Pr ⁿ	100:0	91—94 [5]	2.60 (2 H, t, =CCH ₂)	35.8 (35.6)	5.3 (5.2)
H	CH ₂ OH	88:12	89—91 [3]	6.93 (1 H, t, vinyl of <i>Z</i>), 6.51 (1 H, s, vinyl of <i>E</i>), 4.40 (2 H, s, CH ₂ of <i>E</i>), 4.22 (2 H, d, CH ₂ of <i>Z</i>)	16.9 (16.7)	1.85 (1.9)

^a *m/e* 288 (*M*), 290 (*M* + 2), 292 (*M* + 4); (*M* + 2)/*M* = 1.909, (*M* + 4)/*M* = 0.939. ^b M.p. of *E*:*Z* 93:7. ^c M.p. of *E*:*Z* 4:96.

use of iodine (2.5 mmol) and (1; R = Ph, R' = H or Me) (2.5 mmol) at 25 °C for 0.5 h. In the case of (1; R = Ph, R' = H) the di-iodo-analogue of (*E*)-(2; R = Ph, R' = H) was obtained almost quantitatively as a white solid after evaporation of chloroform; m.p. 73—76 °C (from MeOH)

17% yield (determined by n.m.r.) under the above conditions; δ 2.73 (3 H, s, Me). Almost no reaction occurred with (1; R = Ph, R' = Prⁱ or Bu^t) under these conditions.

[7/1486 Received, 16th August, 1977]

¹⁵ Beilstein, 5, 478.