Tetrahedron Vol. 26, pp. 575 to 581. Pergamon Press 1970. Printed in Great Britain

BROMOFORMATE FORMATION IN DIMETHYLFORMAMIDE[1]

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(*Received in USA* 3 *July* 1969; *Received in the UK for publication* 23 *September* 1969)

Abstract Dimethylformamide (DMF) is shown to react in a stereospecific, regioselective fashion with bromonium, or α-bromocarbonium ions, generated from a variety of olefins and N-bromosuccinimide (NBS) in the presence of water. The bromoformate is often accompanied by dibromide and bromohydrin; at least some of the latter arising from hydrolysis of the bromoformate. Although alkyl and aryl migration is not observed, rearrangement products derived from cationic intermediates through proton loss are found. The mechanism of formation of bromoformate is elucidated through the use of DMF-^{18}O.

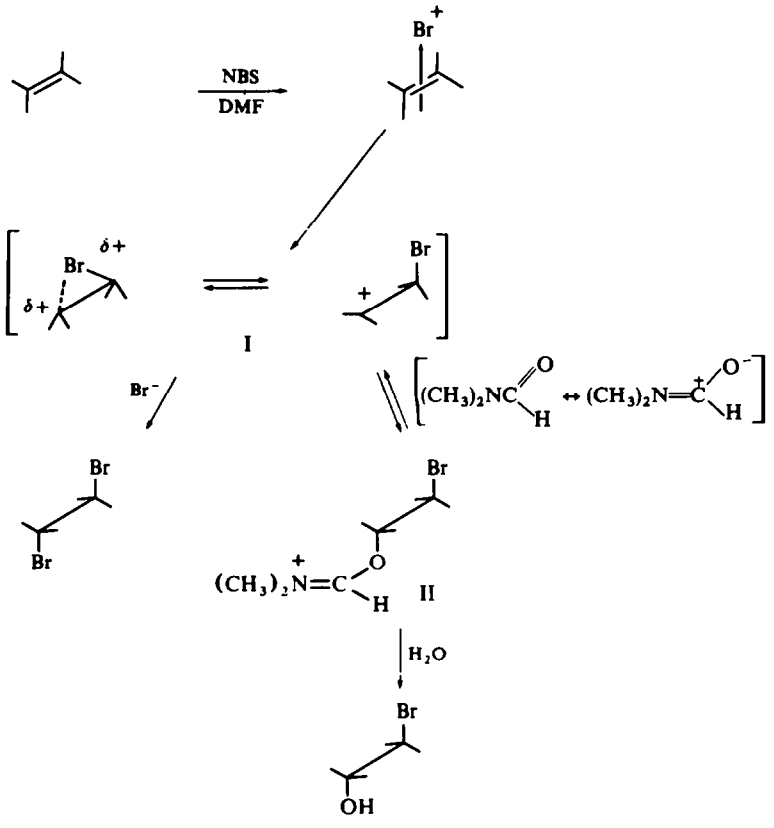
INTRODUCTION

PARTICIPATION by dipolar aprotic solvents,[2a,b] e.g. acetone, dioxan, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) in nucleophilic substitution reactions at saturated carbon has been well documented[3–5] and is one of the factors which tends to add confusion to the picture regarding the solvent properties of dipolar aprotic solvents.[2b]

The reactions in which these solvents participate generally involve either solvolytic displacement of halogen or solvolytic alkyl-oxygen cleavage of the esters of strong acids which is, however, only one facet of nucleophilic behaviour. That is, these dipolar aprotic solvents also demonstrate, as has been shown,[6–8] the ability to react with potent electrophiles, e.g. halonium or, as the case may be, α-halocarbonium, ions. Thus, it has been recently demonstrated that DMSO reacts with bromonium (or α-bromocarbonium) ions in a stereospecific, regioselective[9] fashion to yield, on hydrolysis, bromohydrins.[7] Similarly, acetonitrile,[10] acetone,[11] and DMF[1,11] have demonstrated their respective abilities to participate in this process.

In addition. although it has recently been demonstrated that bromination of olefins in polar protic[12] and nonpolar aprotic[13] solvents may, depending upon the structure of the olefin, proceed with lack of stereospecificity, the reactions with the dipolar aprotic solvents demonstrate no such propensity. Indeed, even though dibromide formed from *cis*- and *trans*-1-phenylpropene, on bromination in acetic acid, is a mixture of, in each case, *threo* and *erythro* dibromides, the bromoacetate formed in the same reaction is formed stereospecifically.[12] This information, when taken in conjunction with that concerning the stereospecificity of the reactions of dipolar aprotic solvents with the halonium ions has suggested[11–13] that formation of halogen-olefin complex[14] is followed by generation of a symmetrical or nonsymmetrical bromonium ion (with the exact extent of symmetry being a function of the olefin) which subsequently can, depending on the ability of the bromonium ion to delocalize the positive charge, lead to bromocarbonium ion and thence to product (Scheme).

SCHEME



It is within this context that we report the details of our examination of the behaviour of olefins (Table) toward NBS in DMF containing water.

RESULTS AND DISCUSSION

The products obtained from the addition of NBS to a solution, in moist DMF, of each of ten olefins investigated are presented (Table). It is to be noted that with the exception of *trans*- and *cis*-stilbene (Table, Compds **1** and **2**), bromohydrin accompanies bromoformate wherever the latter is observed.

Examination of the exclusive products* formed in the reactions of compounds **1** and **2**, i.e. "*erythro*"-2-bromo-1,2-diphenylethyl formate and "*threo*"-2-bromo-1,2-diphenylethyl formate, respectively, demonstrated the stereospecifity of the process. Stereospecificity, as well as regiospecificity[9] is also demonstrated for the reaction in

* In addition to the products specified, only starting material (i.e. olefin) could be recovered. The material balance, throughout, was 95–97% based on starting olefin.

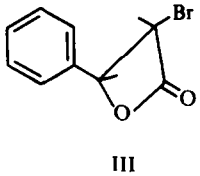
the case of *trans*- and *cis*-1-phenylpropene (Table, Compds 3 and 4). Here, the bromoformate, *viz.*, "*erythro*"-2-bromo-1-phenylpropyl formate and "*threo*"-2-bromo-1-phenylpropyl formate, respectively, is accompanied by the corresponding bromohydrin of known[7] stereochemistry as well as dibromide.[12, 13]*

Comparison of the dibromides formed in the reaction of 3 and 4 and examination of the crude reaction mixtures as well as known mixtures of dibromides, indicates that contrary to the results of bromination in polar protic[12] and nonpolar aprotic[13] solvents, the dibromide is, within experimental error,* formed stereospecifically.

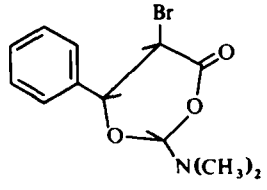
In addition, under the conditions of the reaction and/or work up, "*erythro*"-2-bromo-1-phenylpropyl formate is hydrolyzed to the extent of ca. 50% indicating that, at least in this case, and probably in others, where bromohydrin accompanies bromoformate, all bromohydrin could have been generated from bromoformate.

In the case of styrene (Table, Compd 5) the amount of bromoformate produced in the reaction appears to be a function of the amount of water present, i.e., dibromide increases as the amount of water added and bromoformate formed, decreases. Since we have shown[1] through the use of DMF-^{18}O that the reaction with *trans*-stilbene proceeds through the intermediacy of II (Scheme) which subsequently undergoes hydrolysis, we conclude that if styrene reacts by the same mechanism, the absence of water may preclude consummation of the reaction and II may suffer reversible conversion to I which then reacts with bromide.†

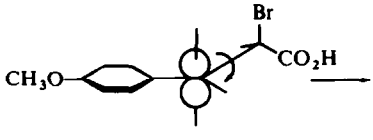
With *trans*-cinnamic acid (Table, Compd 7), and in contradistinction to the results obtained with moist dimethyl sulfoxide (DMSO) and NBS,[7] a reaction occurs to generate exclusively "*erythro*"-2-bromo-3-hydroxy-3-phenylpropanoic acid. We are aware that this process may involve the β-lactone (III)[16] or the anhydride (IV),



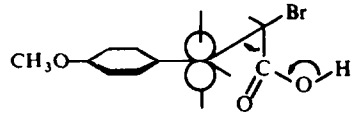
III



IV



V



VI

formed by reaction of the bromonium (or α-bromocarbonium) ion with DMF followed by partial hydrolysis or, simply, preferential reaction of a suitable cation with water.

Although the appropriate ^{18}O labelling experiment remains to be carried out,

* Although it proved impossible, under a variety of conditions, to separate the dibromides by TLC, comparison of the PMR spectra of the pure dibromides (as obtained from the reaction) and mixtures of known compositions would have permitted the detection of as little as 3% had it been present.

† Bromine, serving as the source of bromide ion, is apparently generated by a decomposition reaction of NBS in the presence of water and DMF.[15]

we currently favor a process involving IV or a suitable substitute since each of the other processes would also be acceptable in the DMSO–NBS reaction in which only starting material was recovered.[7]

Finally, both *trans*-*p*-methoxycinnamic acid (Table, Compd **8**) and *p*-methoxystyrene (Table, Compd **9**) yield, under the conditions of the reaction, only olefin [i.e. *trans*-1-bromo-2-(*p*-methoxyphenyl)ethene], the former with decarboxylation and the latter with proton loss.

We suggest that this implies that formation of a stabilized carbonium ion, capable of rotation into the antiperiplanar conformation necessary for elimination, i.e. V → VI, obtains here.

The last compound examined, *trans*-β-nitrostyrene (Table, Compd **10**), an olefin extremely deactivated toward electrophilic substitution[7] does not react with this reagent.

CONCLUSION

A number of olefins have been shown to react with NBS in moist DMF to generate, in a regio- and stereospecific process, bromoformates and, probably by hydrolysis *in situ*, bromohydrins.

Stereospecifically formed dibromide often accompanies the bromoformate and bromohydrin products, implying that the reaction proceeds *via* a bronium ion or

TABLE

Olefin	Product(s)	Yield (%)[a]			
trans-Stilbene (**1**)	"*erythro*"-2-Bromo-1,2-diphenylethyl formate	54			
cis-Stilbene (**2**)	"*threo*"-2-Bromo-1,2-diphenylethyl formate	65			
trans-1-Phenylpropene (**3**)	"*erythro*"-2-Bromo-1-phenylpropyl formate	40			
	"*erythro*"-2-Bromo-1-phenylpropanol	22			
	erythro-1,2-Dibromo-1-phenylpropane	28			
cis-1-Phenylpropene (**4**)	"*threo*"-2-Bromo-1-phenylpropyl formate	50			
	"*threo*"-2-Bromo-1-phenylpropanol	22			
	threo-1,2-Dibromo-1-phenylpropane	20			
Styrene (**5**)	2-Bromo-1-phenylethyl formate	35	26[b]	11[c]	0[d]
	2-Bromo-1-phenylethanol	23	32[b]	31[c]	0[d]
	1,2-Dibromo-1-phenylethane	37	36[b]	55[c]	55[d]
3,3-Dimethylbutene (**6**)	2-Bromo-3,3-dimethylbutyl formate	46			
	2-Bromo-3,3-dimethylbutanol	36			
	1,2-Dibromo-3,3-dimethylbutane	8			
trans-Cinnamic acid (**7**)	"*erythro*"-2-Bromo-3-hydroxy-3-phenylpropanoic acid	76			
trans-*p*-Methoxycinnamic acid (**8**)	*trans*-1-Bromo-2-(*p*-methoxyphenyl)ethene	65			
p-Methoxystyrene (**9**)	*trans*-1-Bromo-2-(*p*-methoxyphenyl)ethene	45			
trans-β-Nitrostyrene (**10**)	No reaction	—			

[a] Average isolated yield of two or more runs. Unreacted olefin was also invariably isolated. Material balance was 90–97% in each reaction. The mole ratio olefin:NBS:H_2O:DMF, throughout was 1:1:1:2.

[b] The mole ratio styrene:NBS:H_2O:DMF was 1:1:1:6.

[c] The mole ratio styrene:NBS:H_2O:DMF was 1:1:1:18.

[d] The mole ratio styrene:NBS:DMF:H_2O was 1:1:2:0.

α-bromocarbonium ion which retains its stereochemical integrity; we suggest, therefore, that in this solvent system, bromonium ion is intercepted by DMF or poorly solvated bromide more rapidly than in systems where solvent participation occurs to a lesser extent. Products of elimination, but not alkyl or aryl migration, are also detected.

EXPERIMENTAL

DMF (Baker Analyzed Reagent) was distilled and dried over molecular sieve (Linde type 4A) prior to use. Olefins were purchased from Chemical Samples Co., Columbus, Ohio, unless otherwise specified, and were used as received after routine GLPC examination. PMR spectra were obtained on a Varian A-60A spectrometer for all compounds and starting olefins reported and are in accord with assigned structures (values reported are in ppm (δ), TMS = 0·0). IR spectra were obtained on a Beckman IR5-A spectrophotometer* or a Perkin–Elmer Infracord and are in accord with assigned structures. Mass spectra were obtained as previously reported.[7] M.ps were obtained on a Fisher–Johns block or Thomas-Hoover Capillary M.P. Apparatus and are uncorrected. Analysis were performed by Micro-Analysis, Inc., Wilmington, Deleware or Schwartzkopf Microanalytical Laboratory, Woodside, N.Y. Alumina and silica gel plates of Woelm Activity Grade III supports were used throughout.

General experimental procedure. The olefin (1 equiv) in DMF (10 equivs) was treated with water (2 equivs) and, with stirring, NBS (Arapahoe Chemical Co., Boulder, Colorado, used as received) (2 equivs) was added as one portion. The reaction was permitted to stir overnight at room temp, quenched in water and extracted with ether. The ether was dried with $MgSO_4$ or Na_2SO_4, filtered and removed at reduced press to yield crude product(s).

^{18}-Dimethylformamide. Chloromethylenedimethylammonium chloride[17] (25·6 g, 0·2 mole) was dissolved in CH_2Cl_2 (400 ml) and pyridine (Karl Fisher Reagent; 31·6 g, 0·4 moles) added. The mixture was cooled to 0° and water (4·32 ml, 0·24 mole, 10·02% ^{18}O, 0·101% ^{17}O)† was added as one portion.

The reaction mixture was permitted to stir at 0° for 0·5 hr and then saturated with anhydrous HCl, dried over Na_2SO_4, and filtered. The CH_2Cl_2 was removed at reduced press and the residue distilled. The fraction (9·7 g) distilling at 45–60° (15 mm) was collected (67%). Redistillation through a Vigereaux column (3″) yielded ^{18}O-DMF (7·1 g) b.p. 52–54° (15 mm). Mass spectrometric‡ comparison of the parent ion peak ratios (73 and 75) to that of ^{16}O-DMF prepared in the same fashion from $H_2{}^{16}O$ indicated that an enrichment of 9·5 ± 0·5% of ^{18}O was present.

"erythro"-2-Bromo-1,2-diphenylethyl formate. R_f (silica gel), benzene, 0·6; CH_2Cl_2, 0·8; eluted from an 80 cm silica gel column, yields, from acetone, white crystals, m.p. 152° (dec). (Found: C, 59·55; H, 4·63; Br, 26·07. Calc. for $C_{15}H_{13}O_2Br$; C, 59·03; H, 4·29; Br, 26·19%). The PMR spectrum ($CDCl_3$) showed a doublet (1 H, J = 8 Hz) centered at δ 6·47 ppm, each half of which was further split (J = 1 Hz) by long-range coupling to the formyl hydrogen (1 H, J = 1 Hz) centered at δ 7·98 ppm. The ten aromatic protons appeared as a sharp singlet at δ 7·40 ppm.

^{18}O-DMF reaction. Crude bromoformate (ca. 600 mg) prepared from, respectively, ^{16}O-DMF and ^{18}O-DMF was heated (60°) for 1 hr in a soln of 5% potassium t-butoxide–t-butyl alcohol (18 ml) containing water (2 ml) and the reaction mixture quenched in a large excess of water. The crude product was extracted twice with half its volume of fresh ether and the ether extracts combined, washed with water and dried over $MgSO_4$. Filtration and evaporation of the ether yielded epoxide (ca. 300 mg).

The epoxide (30 mg), in $CHCl_3$ was deposited on a preparative TLC (Merck–Darmstadt, SiO_2, activity grade II) plate and eluted with benzene–cyclohexane (v/v 1:1). The band corresponding to epoxide[7] was removed and extracted with methanolic chloroform (v/v 10%) yielding ca. 20 mg of purified epoxide.

* The spectrophotometer was purchased from funds provided by The National Cancer Institute (Grant CA-08841) of the National Institutes of Health, to whom we are grateful.

† Obtained as normalized water from YEDA Research and Development Co., Ltd., Rehovoth, Israel.

‡ Mass spectra were determined on a CEC 21-103 Mass Spectrometer with an inlet temperature of 350° at 70 volts. We gratefully acknowledge the assistance of Mr. M. Henry, Mobil Oil Corporation Laboratories, Paulsboro, N.J.

The mass spectra of the material prepared from ^{16}O-DMF and ^{18}O-DMF were compared at *m/e* 105:107* and *m/e* 196:198. Agreement was ±5% in each case, and indicated that a 8·5 ± 0·5% enrichment in the epoxide derived from ^{18}O-DMF was present.

The normalized peak height for ^{16}O epoxide (*m/e* 198 vs. 196) was 6/370 while for ^{18}O epoxide, obtained as above from enriched ^{18}O-DMF was 33/328: at *m/e* 107 vs. 105, the normalized peak height ratio was 15/2471 for ^{16}O epoxide and 209/2213 for the ^{18}O-epoxide. Correction for isotopic peak heights in unlabelled material indicates, therefore, the minimum enrichment expressed.

The reaction sequence described above was repeated using ^{16}O-DMF and $H_2{}^{18}O$ to prepare the bromoformate. The epoxide generated as described above from this reaction product contained 0·0 ± 0·5% ^{18}O.

"threo"-2-Bromo-1,2-diphenylethyl formate. R_f (silica gel), benzene 0·7; eluted from a 90 cm silica gel column yields, from acetone, white crystals, m.p. 105–107°. (Found: C, 59·32; H, 4·72; Br, 26·56. Calc. for $C_{15}H_{13}O_2Br$: C, 59·03; H, 4·92; Br, 26·19%). The PMR spectrum ($CDCl_3$) showed a d (1 H, J = 9 Hz) centered at δ 5·18 ppm, a d (1 H, J = 9 Hz) centered at δ 6·35 ppm, each half of which was further split (J = 0·5 Hz) by long-range coupling to the formyl hydrogen (1 H, J = 0·5 Hz) centered at δ 8·19 ppm. The ten aromatic protons appeared as two overlapping singlets (δ 7·19 and δ 7·21 ppm).

trans-1-*Phenylpropene* (3). The crude reaction product obtained from the title olefin was transferred directly to a silica gel column and eluted with benzene. The first fraction (R_f ca. 0·9) crystallized spontaneously and was recrystallized from acetone, m.p. 67° (28%) and was identical (m.p., mixed m.p., IR and PMR) to an authentic sample† of *erythro*-1,2-dibromo-1-phenylpropane. No evidence could be found for the presence of the *threo* isomer.‡

Continued elution with benzene yielded a second fraction R_f ca. 0·7, which was identified as *"erythro"*-2-bromo-1-phenylpropyl formate, b.p. 217°, n_D^{25} 1·5422. The PMR spectrum exhibited a singlet (1 H) at δ 8·05 ppm. a s (5 H) at δ 7·3 ppm, a d, centered at 6·00 ppm (1 H, J = 7 Hz), a m, centered at δ 4·3 ppm (1 H) and a d (1 H, J = 7 Hz) centered at δ 1·63 ppm. (Found: C, 49·87; H, 4·88; Br, 33·08. Calc. for $C_{10}H_{11}BrO_2$: C, 49·45; H, 4·56; Br, 32·91%). This material was identified as the *"erythro"* isomer by hydrolysis of the formate to the corresponding bromohydrin.[7]

Further elution of the colum with benzene yielded a third fraction (R_f ca. 0·3) which was identified as the known *"erythro"*-2-bromo-1-phenylpropanol.[7]

cis-1-*Phenylpropene* (4). The crude product was treated as above, yielding (R_f ca. 0·9) *threo*-dibromide, b.p. 194°, n_D^{25} 1·5881. The PMR spectrum exhibited a multiplet, centered at δ 7·35 ppm (5 H), a doublet, centered at δ 5·2 ppm (1 H, J = 7 Hz) a multiplet centered at δ 4·5 pp, (1 H) and a doublet (3 H, J = 7 Hz), centered at δ 1·7 ppm.

Continued elution of the column with benzene yielded a second fraction (R_f ca. 0·7) which was identified as *"threo"*-2-bromo-1-phenylpropyl formate, b.p. 182°, n_D^{25} 1·5411. The PMR spectrum possessed a singlet (1 H) at δ 8·00 ppm, a s (5 H) at δ 7·3 ppm, a d, centered at δ 5·85 ppm (J = 7 Hz) (1 H), a m (1 H) centered at δ 4·25 ppm and a d (3 H) centered at δ 1·5 ppm (J = 7 Hz). (Found: C, 49·11; H, 4·60; Br, 32·31. Calc. for $C_{10}H_{11}BrO_2$: C, 49·45; H, 4·56; Br, 32·91%). In accord with its formulation as the *"threo"*-formate, it was successfully hydrolysed to the known *"threo"*-bromohydrin.[7]

Further elution of the column with benzene afforded a third fraction (R_f ca. 0·3) which was identified as the *"threo"*-bromohydrin, b.p. 143°, n_D^{25} 1·5533, by comparison with an authentic sample.[7]

Styrene (5). The crude product obtained from styrene (MC & B) was transferred directly to a silica gel column and eluted with benzene. The first fraction (R_f ca. 0·9) was identified as 1,2-dibromo-1-phenylethane, m.p. (light petroleum) 62° (lit.[19] 72°). The second fraction (R_f ca. 0·6) was identified as 2-bromo-1-phenylethyl formate, b.p. 185° n_D^{25} 1·5512. (Found: C, 47·09; H, 4·10. Calc. for $C_9H_9BrO_2$: C, 47·19; H, 3·96%). The PMR spectrum possessed a s (1 H)at δ 8·10 ppm, a s (1 H) at δ 7·35 ppm, a tr at δ 6·06 ppm (1 H) and a d (2 H) at δ 3·60 ppm. This material was successfully hydrolyzed to the known[7] 2-bromo-1-phenylethanol.

Continued elution of the column with benzene afforded the known[7] 2-bromo-1-phenylethanol, (R_f ca. 0·3).

3,3-*Dimethylbutene* (6). The crude product obtained from neohexene‖ was placed on a silica gel column

* The 105/107 ratio presumably corresponds to $C_6H_5CO^+$.[18]

† Prepared by the bromination of *trans*-1-phenylpropene. See, e.g. Ref. 13.

‡ See footnote * p. 577.

‖ Received as a gift from Sinclair Petrochemicals, Inc., to whom we are grateful.

and eluted with CCl_4. The first fraction (R_f ca. 0·8) was identified as 1,2-dibromo-3,3-dimethylbutane by comparison with an authentic sample (IR, PMR, TLC).[20]

Continued elution with the same solvent yielded 2-bromo-3,3-dimethylbutylformate, b.p. 153°, n_D^{25} 1·5772. (Found: C, 39·97; H, 6·26. Calc. for $C_7H_{13}BrO_2$: C, 40·21; H, 6·26%). The PMR spectrum possessed a singlet at 7·88 ppm (1 H), a broad, complex m centered about δ 4·0 ppm (3 H) and a sharp s at δ 1·09 ppm (9 H).

Finally, a third fraction (R_f ca. 0·1) was obtained and identified as 2-bromo-3,3-dimethylbutanol by comparison (TLC, IR and PMR) with an authentic sample.[7]

trans-*Cinnamic acid* (7). The crude product from cinnamic acid crystallized spontaneously and was recrystallized from $CHCl_3$, m.p. 125–6° (lit.[20] 125–126°). The "*erythro*"-2-bromo-3-hydroxy-3-phenylpropanoic acid was esterified with diazomethane and the ester treated with t-BuOK in t-BuOH to generate 3-phenyl-2,3-epoxypropionate, whose PMR spectrum exhibited a s at δ 7·25 ppm (5 H), a d at δ 3·96 ppm (1 H, J = 2 Hz) a s at δ 3·72 ppm and a d at δ 3·29 ppm (2 H, J = 2 Hz).

The acid could be titrated with NaOH aq (pK_a = 5·7) to a N.E. 238 (calc. 245).

trans-p-*Methoxycinnamic acid* (8). The crude product from *p*-methoxycinnamic acid (obtained from the Aldrich Chemical Co., Milwaukee, Wisc., used as received) was supported on a silica gel column and eluted with CH_2Cl_2. The only fraction (R_f ca. 0·9) was recrystallized from acetone, m.p. 52–53. (Found: C, 50·54; H, 4·05; Br, 37·09. Calc. for C_9H_9BrO: C, 50·76; H, 4·25; Br, 37·50%). The PMR spectrum possessed a s (3 H) at δ 3·76 ppm and a pair of d's (2 H, J = 14 Hz) one centered at δ 7·29 ppm and the other at δ 6·88 ppm. The aromatic protons appeared as the typical *p*-disubstituted pattern centered at δ 6·90 ppm.

p-*Methoxystyrene* (9). The crude product obtained from the title olefin crystallized directly on removal of the solvent. It was identical, in all respects, to the olefin obtained above.

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