Addition of Iodine Electrophiles to Buta-1,3-diene: Effects of Charge Distribution and Ion-pair Stability on Product Ratios

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The addition of the following iodine electrophiles to buta-1,3-diene is described: *tert*-butyl hypoiodite (Bu^{t}OI) in the presence of BF_3, acetyl hypoiodite (AcOI), iodine monochloride (ICl) and iodine monobromide (IBr). Data from *tert*-butyl hypobromite (Bu^{t}OBr) and *tert*-butyl hypochlorite (Bu^{t}OCl) with buta-1,3-diene and BF_3 are reported for comparison. All of the electrophiles give mixtures of M 1,2- and 1,4-addition, but no AM 1,2-products. Radical reactions are reported for Bu^{t}OI, Bu^{t}OBr and Bu^{t}OCl. Greater 1,4-addition occurs for the electrophiles with anions of lower basicity (IBr and ICl), and the halonium ion with increased dispersal of charge (Bu^{t}OCl). The results are rationalized from the viewpoints of charge density and ion-pair stability.

In a recent investigation of the addition of *tert*-butyl hypoiodite (Bu^{t}OI) to olefins in the presence of BF_3,[1] we concluded that the bridging in the intermediate iodonium ion was more symmetrical than in the corresponding bromonium and chloronium ions from *tert*-butyl hypobromite (Bu^{t}OBr) and *tert*-butyl hypochlorite (Bu^{t}OCl) respectively. This conclusion was based primarily on the fact that Bu^{t}OI, but not Bu^{t}OBr and Bu^{t}OCl, added stereospecifically to the β-methylstyrenes. Furthermore, fluoro halides, which were major products in the addition of Bu^{t}OBr and Bu^{t}OCl, were not formed with *tert*-butyl hypoiodite. We interpreted this as implying that the fluoride ion from the hypoiodite–BF_3 complex conceivably was not sufficiently reactive to attack the symmetrically bridged iodonium ion with lower charge density on the carbon atoms.

With this study as a background, we proposed to investigate the additions of Bu^{t}OI and other iodine electrophiles to buta-1,3-diene. One goal was to observe whether the intermediate iodonium ion (Scheme 1), because of symmetry of bonding, would be opened by *tert*-butoxide-boron trifluoride anion $(Bu^tOBF_3)^-$ at the α-carbon of the iodonium ion (anti-Markovnikov, AM 1,2-product) as well as at the β-carbon (Markovnikov, M 1,2-product). An earlier study showed that AM 1,2-product was not formed in the additions of acetyl hypobromite and acetyl hypochlorite to buta-1,3-diene.[2] Another goal was to assess the extent of 1,4-addition with the more symmetrically-bridged iodonium ion and to observe how the 1,2- to 1,4-ratio changed as the basicities of the anions varied with the different iodine electrophiles. A final goal was to compare the product ratios from buta-1,3-diene with Bu^{t}OI–BF_3, Bu^{t}OBr–BF_3 and Bu^{t}OCl–BF_3, where the anion remained constant but the bonding in the intermediate halonium ion varied.

A practical aspect of the study was to determine whether the allylic iodide products, such as those anticipated in this study, could be analysed directly by capillary gas chromatography without decomposition and rearrangement.

Table 1 Addition of iodine electrophiles to buta-1,3-diene

		Product (%)			
Electrophile	Conditions[a]	M 1,2-	AM 1,2-	1,4-	Yield (%)
Bu^{t}OI	Ionic	92	0	8	82
Bu^{t}OI	Radical	Trace	6	94	88
AcOI	Ionic	90	0	10	75
ICl	Ionic	65	0	35	89
IBr	Ionic	56	0	44	73

[a] Reactions were conducted in CCl_4 at room temperature.

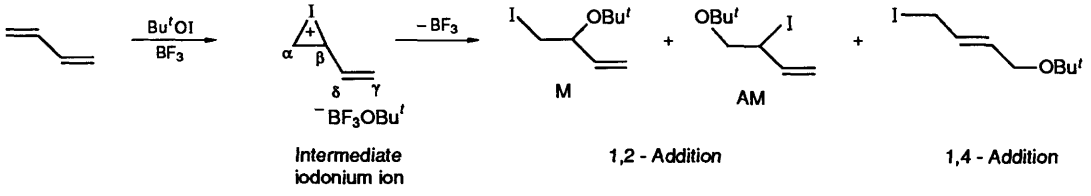
Table 2 Addition of *tert*-butyl hypobromite (Bu^{t}OBr) and *tert*-butyl hypochlorite (Bu^{t}OCl)

		Product			
Electrophile	Conditions[a]	M 1,2-	AM 1,2-	1,4-	Yield (%)
Bu^{t}OBr	Ionic	69	0	3	66
Bu^{t}OBr	Radical	0	17	83	89
Bu^{t}OCl	Ionic	54	0	46	75
Bu^{t}OCl	Radical	0	27	73	55

[a] Reactions were conducted in CCl_4 at room temperature.

Results

Addition of Iodine Electrophiles to Buta-1,3-diene.—The following iodine electrophiles were added to buta-1,3-diene in carbon tetrachloride (CCl_4): *tert*-butyl hypoiodite (Bu^{t}OI) in the presence of BF_3, acetyl hypoiodite (AcOI), iodine monochloride (ICl), and iodine monobromide (IBr). As shown in Table 1, a mixture of M 1,2- and 1,4-addition products was formed under ionic conditions. The mixtures represented kinetic products since rearrangement to thermodynamic products was



Scheme 1

accomplished under appropriate conditions. A previous study on the addition of ICl to buta-1,3-diene reported much higher amounts of 1,4-addition.[3] Apparently thermodynamic products were obtained. Under radical conditions (UV radiation), Bu^{t}OI gave a mixture of AM 1,2- and 1,4-addition products. The AM 1,2-product was shown to be stable under ionic reaction conditions.

Addition of tert-*Butyl Hypobromite and* tert-*Butyl Hypochlorite* (Bu^{t}OBr *and* (Bu^{t}OCl) *to Buta*-1,3-*diene.*—Bu^{t}OBr and Bu^{t}OCl were added to buta-1,3-diene in CCl_4 in the presence of BF_3 and under radical conditions to give data for comparison with Bu^{t}OI. The results are summarized in Table 2.

Attempt to Prepare Methyl Hypoiodite (MeOI).—The synthesis of MeOI and its addition to buta-1,3-diene under radical and ionic conditions were unsuccessful. MeOI could be synthesized only in low concentration, accompanied with impurities, and when this solution was added to buta-1,3-diene in CCl_4 with BF_3 and UV radiation, only trace amounts of 1,2- and 1,4-addition products were indicated by MS analysis.

Effect of the Concentration of ICl *on the Product Ratio.*—A slight increase in the amount of 1,4-addition product occurred as the concentration of ICl was reduced. The following percentages (%) of 1,2- and 1,4-products, respectively, were observed at the indicated ICl concentrations: 3.1 mol dm^{-3} (65 and 35); 0.70 mol dm^{-3} (55 and 45); 0.02 mol dm^{-3} (55 and 45).

Stability of the Products to Gas Chromatographic (*GLC*) *Analysis.*—The allylic iodides (M 1,2-, AM 1,2- and 1,4-) were found to be stable to analysis by capillary gas chromatography.

Discussion

The data in Table 1 show that the iodonium ion from buta-1,3-diene and Bu^{t}OI–BF_3 (Scheme 1) is opened overwhelmingly at the β-carbon (M 1,2-addition) by Bu^{t}OBF$_3^-$ with minor attack at the γ-carbon (1,4-addition) and no attack at the α-carbon (AM 1,2-addition). This result is surprising since the iodonium ion from hex-1-ene[1] underwent major attack (62%) at the α-carbon. We attributed that result to the bulkiness of the Bu^{t}OBF$_3$ ion and its preference for attack at the less restricted α-carbon. Since steric factors in the iodonium ions from hex-1-ene and buta-1,3-diene must be similar, we conclude that the absence of AM 1,2-attack is probably due to the greater reactivities of the allylic, β- and γ-carbons. This interpretation does not require extensive development of charge at the β-carbon since the rate of S_N2 reactions are known to be enhanced at allylic carbon.[4] Probably the charge is primarily centred on iodine. The γ-product would result from S_N2' attack.

Why is the reactivity so high at the β-carbon with Bu^{t}OI and AcOI but much less with ICl and IBr which show a major shift to the γ-carbon? If we assume that the charge distributions are the same in the iodonium ions, regardless of anion, then the differences in product distribution from Bu^{t}OI–AcOI and ICl–IBr must be due to the stabilities of the ion-pairs and the rate with which they collapse. Certainly the anions from Bu^{t}OI–BF_3 and AcOI(Bu^{t}OBF$_3^-$ and AcO$^-$) are much more basic than those from IBr and ICl (Br$^-$ and Cl$^-$).* Apparently the anions of lower basicity (Br$^-$ and Cl$^-$) have more time to migrate to the γ-carbon before collapse occurs. The greater γ-attack by Br$^-$ from IBr compared to Cl$^-$ from ICl also appears to correlate with the relationship of lower basicity and increased 1,4-addition. These data correlate well with our earlier study[2] on ClOAc–Cl_2 and BrOAc–Br_2, where the electrophiles in both pairs with anions of lower basicities gave the greater 1,4-addition. The similarity in amounts of 1,4-additions for Bu^{t}OI and AcOI support the involvement of the Bu^{t}OBF$_3^-$ ion, rather than Bu^{t}O$^-$, since the latter is approximately 10^9 times more basic than AcO$^-$ and should migrate considerably less.

Charge distributions must play a role in the differences in the 1,2- to 1,4-product ratios between Bu^{t}OI, Bu^{t}OBr and Bu^{t}OCl since the anion is the same for the three halonium ions. (See Table 2.) The bonding between halogen and the β-carbon should decrease from iodine to chlorine with increasing dispersal of charge into the allylic system. Apparently this shift of charge to the γ-carbon outweighs the influence of ion-pair stability and leads to greater 1,4-addition. It is interesting to note that less 1,4-addition was obtained from AcOBr (13%) and AcOCl (28%)[2] than from Bu^{t}OBr–BF_3 (31%) and Bu^{t}OCl–BF_3 (46%). This is in contrast with AcOI and Bu^{t}OI which gave nearly equal amounts of 1,4-addition. Apparently the extent of 1,2- *vs.* 1,4-addition is subject to subtle changes in charge distribution and ion-pair stability.

Experimental

Materials and Instrumentation.—Buta-1,3-diene was obtained as research grade from Matheson Company. Bu^{t}OCl was purchased from American Tokyo Kasei, Inc. Bu^{t}OBr[6] and Bu^{t}OI[1] were prepared as described earlier. AcOI was prepared by the same procedure[2] that was used previously for AcOBr. AcOI was identified by its λ_{max} at 280 nm in CCl_4; reported previously[7] in acetic acid, 290 nm. ICl and IBr were obtained commercially in high purity.

Mass spectral analyses were obtained at 70 eV on a Hewlett-Packard 5890 GC interfaced with an HP5970B mass selective detector. Results are expressed as *m/z* and as relative intensity (%). Products were analysed on a Hewlett-Packard 5890 GC with a 25-m, methyl silicone capillary column. Most of the NMR spectra were obtained on a Varian T60A spectrometer with $(CH_3)_4Si$ as the reference standard. *J* values are given in Hz.

Reaction Conditions.—A buta-1,3-diene–CCl_4 solution (*ca.* 0.02 mol fraction) was prepared by adding the appropriate amount, by weight, of the diene to CCl_4, followed by drying of the solution over molecular sieves. Reactions were carried out on a 5 cm^3 scale. Sufficient halogen electrophile in CCl_4 (0.1 mol dm^{-3}; except for AcOI which decomposed in concentrations exceeding 0.065 mol dm^{-3}) was added to a stirred diene solution at room temperature to react with approximately 50% of the diene. BF_3-etherate (called BF_3 here), as described earlier,[1] was added to catalyse the Bu^{t}OX reactions. Radical reactions were conducted by shining UV radiation from a sunlamp on a reaction solution until the colour changed into the faint purple colour of iodine. Precautions for sensitivities toward moisture as described previously[1] were taken for Bu^{t}OI and AcOI.

All reaction products were analysed directly by GLC. Solutions containing BF_3 were also washed with water, dried and analysed without change in product composition. Reaction products for NMR spectroscopic analysis were prepared by removing the solvent and excess diene under reduced pressure and then dissolving the residue in CCl_4 or $CDCl_3$ containing $(CH_3)_4Si$. Attempts to isolate products by column chromatography, preparative GLC or vacuum distillation failed because of immediate decomposition.

Yields were determined by NMR and/or GLC using internal standards.

* Based on the investigations of Schmid and co-workers[5] on the addition of ICl to alkenes, we assume that complex anions (ICl_2^- and IBr_2^-) are also involved. Variations in anion structure may account for the changes in product ratios when different concentrations of ICl are added to buta-1,3-diene.

Product identification. The structures of products were established by their mass spectra and the NMR spectra of crude reaction mixtures. Kinetic products were assured by appropriate rearrangement studies. Elemental analyses could not be obtained because of the instability of the products. GLC analysis conditions and retention times are reported for each compound.

Reaction of Bu^{t}OI *with Buta*-1,3-*diene.*—4-tert-*Butoxy*-3-*iodobut*-1-*ene* (*AM* 1,2-).—The NMR spectrum of this compound could not be obtained because of its low concentration in the radical reaction product; *m*/*z* 101 (M − C_4H_9O, 12%), 167 (M − CH_2OBu^t, 0.2), 127 (M − I, 2), 87 (CH_2OBu^t, 2), 57 (Bu^t, 100), 54 (C_4H_6, 15). The structure is confirmed by the CH_2OBu^t fragment (87) proving terminal Bu^{t}O, and by the ICHCH=CH_2 fragment (167) showing that I is on the β-carbon.

The stability of the AM 1,2-product to ionic reaction conditions was confirmed as follows: radical addition (UV) of Bu^{t}OI to buta-1,3-diene was carried to partial completion giving AM 1,2- and 1,4-products, but leaving some Bu^{t}OI and diene in solution. BF_3 was added to catalyse an ionic reaction of the remaining Bu^{t}OI and diene. The M 1,2-isomer was now formed, but the concentration of the AM 1,2-isomer was not reduced. This experiment eliminates the possibility that the AM 1,2-isomer is formed in an ionic reaction (BF_3) of buta-1,3-diene and Bu^{t}OI and subsequently decomposes or is converted into M 1,2- and 1,4-isomer by rearrangement.

3-tert-*Butoxy*-4-*iodobut*-1-*ene* (*M* 1,2-). δ_H 1.10 (s, 9 H), 2.93 (d, 2 H, *J* 6), 3.67–4.12 (m, 1 H) and 4.83–5.40 (m, 3 H); *m*/*z* 198 (M − C_4H_8, 4), 181 (M − C_4H_9O, 34), 141 (CH_2I, 3), 113 ($Bu^tOCHCH{=}CH_2$, 50), 57 (Bu^t, 100) and 54 (C_4H_6, 26).

The stability of the M 1,2-isomer to the reaction conditions, and the confirmation that the small amount of 1,4-isomer in an ionic reaction did not result from rearrangement of M 1,2-isomer, was established as follows: a typical ionic reaction of Bu^{t}OI–BF_3 was conducted by adding 2–3 drops of BF_3 (0.13 mmol) to Bu^{t}OI (0.30 mmol) and diene. The M 1,2- to 1,4-product ratio was not altered until more than 12 drops (0.52 mmol) of BF_3 was added. Furthermore, a reaction mixture stood for several hours in the presence of BF_3 without a change in product ratio occurring.

1-tert-*Butoxy*-4-*iodobut*-2-*ene*. δ_H 1.16 (s, 9 H), 3.64–4.07 (m, 4 H), 5.57–6.23 (m, 2 H); *m*/*z* 239 (M − CH_3, 0.2), 197 (M − C_4H_9, 0.2), 181 (M − C_4H_9O, 18), 141 (CH_2I, 0.2), 127 (M − I, 3), 87 (CH_2OBu^t, 0.1), 57 (Bu^t, 100) and 54 (C_4H_6, 20). The *E*-configuration is assumed for this compound and the other 1,4-addition products since only trace amounts of *Z*-1,4-isomers have been observed in the halogenation of 1,3-butadiene.[2,8]

The M 1,2-, AM 1,2- and 1,4-isomers were separated by programming from 80–150 °C at 15 °C min^{-1} with the following retention times/min, respectively: 4.6, 4.7 and 5.6.

Reaction of AcOI *with Buta*-1,3-*diene.*—3-*Acetoxy*-4-*iodobut*-1-*ene* (*M* 1,2-). δ_H 2.08 (s, 3 H), 3.26 (d, 2 H, *J* 6.0) and 5.00–6.14 (m, 4 H); *m*/*z* 181 (M − AcO_2, 2), 180 (M − AcOH, 4), 141 (CH_2I, 2), 113 (M − I, 16), 99 (M − I, 1), 53 (C_4H_5, 11) and 43 (CH_3CO, 100).

1-*Acetoxy*-4-*iodobut*-2-*ene*. δ_H 2.02 (s, 3 H), 3.82 (d, 2 H, *J* 7.5), 4.48 (d, 2 H, *J* 5.8) and 5.75–6.40 (m, 2 H); *m*/*z* 181 (M − AcO_2, 2), 113 (M − I, 22), 54 (C_4H_6, 13), 53 (C_4H_5, 8) and 43 (CH_3CO, 100).

The structure of the M 1,2-isomer, and the fact that it was the kinetic product, was established by its rearrangement to the 1,4-isomer in the presence of BF_3.

The M 1,2- and 1,4-isomers were separated by programming from 45–160 °C at 10 °C min^{-1} with the following retention times/min, respectively: 9.3 and 11.5.

Reaction of ICl *with Buta*-1,3-*diene.*—3-*Chloro*-4-*iodobut*-1-*ene* (*M* 1,2-).—(200 MHz) δ_H 3.35 (dd, 1 H, *J* 10, *J* 10, 3.57 (dd, 1 H, *J* 10, *J* 4.6), 4.24 (m, 1 H) and 5.12–5.65 (m, 3 H); *m*/*z* 218 and 216 (M, 2.4 and 7.8), 181 (M − Cl, 7), 91 and 89 (M − I, 26 and 83) and 53 (C_4H_5, 100).

1-*Chloro*-4-*iodobut*-2-*ene*. δ_H(200 MHz) 3.84 (d, 2 H, *J* 7.8), 4.00 (d, 2 H, *J* 6.8) and 5.79–6.38 (m, 2 H); *m*/*z* 218 and 216 (M, 2.3 and 8.4), 181 (M − Cl, 4), 91 and 89 (M − I, 28 and 89) and 53 (C_4H_5 100).

Heating the M 1,2-isomer with anhydrous zinc chloride produced the 1,4-isomer, confirming the structure of the 1,2-isomer and establishing that a kinetic product is formed in the addition of ICl.

The M 1,2- and 1,4-isomers were separated by programming from 45–110 °C at 5 °C min^{-1} with the following retention times/min, respectively: 9.8 and 14.0.

Reaction of IBr *with Buta*-1,3-*diene.*—3-*Bromo*-4-*iodobut*-1-*ene* (*M* 1,2-). δ_H(200 MHz) 3.50 (dd, 1 H, *J* 9.9 and *J* 11.3), 3.76 (dd, 1 H, *J* 9.9 and *J* 4.2), 4.22 (m, 1 H) and 5.05–5.40 (m, 3 H); *m*/*z* 135 and 133 (M − I, 100 and 95), 121 and 119 (M − CH_2I, 3 and 3) and 53 (C_4H_5, 89).

1-*Bromo*-4-*iodobut*-2-*ene*. δ_H(200 MHz) 3.83 (d, 2 H, *J* 7.0), 3.87 (d, 2 H, *J* 6.9) and 5.70–6.20 (m, 2 H); *m*/*z* 181 (M − Br, 82), 135 and 133 (M − I, 67 and 71), 121 and 119 (M − CH_2I, 0.6 and 0.7) and 53 (C_4H_5, 100).

Heating the M 1,2-isomer with anydrous zinc bromide produced the 1,4-isomer, confirming the structure of the 1,2-isomer and establishing that a kinetic product is formed in the halogenation (IBr) reaction.

The M 1,2- and 1,4-isomers were separated by programming from 45–110 °C at 5 °C min^{-1} with the following retention times/min, respectively: 10.9 and 15.3.

Reaction of Bu^{t}OBr *with But*-1,3-*diene.*—3-*Bromo*-4-tert-*butoxybut*-1-*ene* (*AM* 1,2-). The NMR spectrum of this compound could not be obtained because of its low concentration in the radical reaction product; *m*/*z* 193 and 191 (M − CH_3, 0.4 and 0.4), 135 and 133 (M − Bu^{t}O, 9 and 10), 127 (M − Br, 0.2), 87 (CH_2OBu^t, 25), 59 (C_3H_7O, 24), 57 (Bu^t, 100) and 53 (C_4H_5, 21).

4-*Bromo*-3-tert-*butoxybut*-1-*ene* (*M* 1,2-). δ_H 1.32 (s, 9 H), 3.28 (d, 1 H), *J* 7.0), 4.10–4.36 (m, 1 H) and 5.06–5.60 (m, 3 H); *m*/*z* 193 and 191 (M − CH_3, 1 and 1), 135 and 133 (M − Bu^{t}O, 11 and 11), 113 (M − CH_2Br, 23), 59 (C_3H_7O, 41), 57 (Bu^t, 100) and 53 (C_4H_5, 24).

1-*Bromo*-4-tert-*butoxybut*-2-*ene*. δ_H 1.32 (s, 9 H), 3.84–4.08 (m, 4 H) and 5.64–6.30 (m, 2 H); *m*/*z* 193 and 191 (M − CH_3, 7 and 7), 135 and 133 (M − Bu^{t}O, 14 and 14), 87 (CH_2OBu^t, 0.3), 59 (C_3H_7O, 24), 57 (Bu^t, 100) and 53 (C_4H_5, 19).

The stability of the ionic reaction product was established from the fact that it changed only slowly with time and that a considerable excess of BF_3 had no effect on the product ratio.

The M 1,2-, AM 1,2- and 1,4-isomers were separated by programming from 60–130 °C at 15 °C min^{-1} with the following retention times/min, respectively: 6.0, 6.07 and 8.3.

Reaction of Bu^{t}OCl *with Buta*-1,3-*diene.*—4-tert-*Butoxy*-3-*chlorobut*-1-*ene* (*AM* 1,2-). The NMR spectrum of this compound could not be obtained because of its low concentration in the radical reaction product; *m*/*z* 149 and 147 (M − CH_3, 0.3 and 0.9), 91 and 89 (M − Bu^{t}O, 3 and 8), 87 (CH_2OBu^t, 16), 59 (C_3H_7O, 40), 57 (Bu^t, 100) and 53 (C_4H_5, 21).

3-tert-*Butoxy*-4-*chlorobut*-1-*ene* (*M* 1,2-). δ_H 1.12 (s, 9 H), 3.43 (d, 2 H, *J* 7.0), 4.12–4.34 (m, 1 H) and 4.96–5.46 (m, 3 H); *m*/*z* 147 (M − CH_3, 3), 113 (M − CH_2Cl, 17), 91 and 89 (M − Bu^{t}O, 4 and 11), 59 (C_3H_7O, 56), 57 (Bu^t, 100) and 53 (C_4H_5, 7).

1-tert-*Butoxy*-4-*chlorobut*-2-*ene*. δ_H 1.16 (s, 9 H), 3.67–4.06 (m, 4 H) and 5.52–5.90 (m, 2 H); *m/z* 149 and 147 (M − CH_3, 0.4 and 0.1), 127 (M − Cl, 1), 91 and 89 (M − Bu^tO, 5 and 15), 59 (C_3H_7O, 68), 57 (Bu^t, 100) and 53 (C_4H_5, 26).

The M 1,2-, AM 1,2- and 1,4-isomers were separated by programming from 60–130 °C at 15 °C min^{-1} with the following retention times/min respectively: 4.95, 5.03 and 6.62.

Acknowledgements

Support for this work was provided by Research Corporation and the Research Associates of Point Loma Nazarene College. We thank Professor Leroy Lafferty, Department of Chemistry, California State University, San Diego, for the 200 MHz NMR data.

References

1 V. L. Heasley, B. R. Berry, S. L. Holmes, L. S. Holstein, III, K. A. Milhoan, A. M. Sauerbrey, B. R. Teegarden and D. F. Shellhamer, *J. Org. Chem.*, 1988, **53**, 198.
2 V. L. Heasley, G. E. Heasley, R. H. Loghry and M. R. McConnell, *J. Org. Chem.*, 1972, **37**, 2228.
3 C. K. Ingold and H. G. Smith, *J. Chem. Soc.*, 1931, 2752.
4 T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 1987, 3rd edn., p. 377.
5 G. H. Schmid and J. W. Gordon, *Can. J. Chem.*, 1984, **62**, 2526; 1986, **64**, 2171.
6 V. L. Heasley, R. K. Gipe, J. L. Martin, H. C. Wiese, M. L. Oakes, D. F. Shellhamer, G. E. Heasley and B. L. Robinson, *J. Org. Chem.*, 1983, **48**, 3195.
7 J. R. Barnett, L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, 1972, **94**, 6129.
8 V. L. Heasley and P. H. Chamberlain, *J. Org. Chem.*, 1970, **35**, 539.

Paper 1/00910I
Received 26*th February* 1991
Accepted 15*th April* 1991