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# ACID-CATALYZED HYDROLYSIS OF ALKYL VINYL AND PROPENYL SULFIDES

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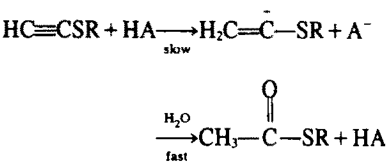
**Abstract**—The rates of acid-catalyzed hydrolysis of methyl, ethyl, isopropyl, and t-butyl vinyl sulfides have been measured in 10% aqueous acetonitrile. It was found that their reactivities decrease in this order. General acid catalysis was observed. The rate was smaller in a deuterium medium ($k_{D_2O}/k_{H_2O} = 0.34$). The deuterium exchange between sulfide and solvent was not detected during hydrolysis. Some propenyl sulfides have also been studied, their *cis* isomers being more reactive than the *trans* counterparts without geometrical isomerization involved. The reaction mechanism and the substituent effects on the reactivity have been discussed.

The acid-catalyzed hydrolysis of vinyl ethers has been extensively studied in the past decade and its reaction mechanism is well established.[1] The rate determining step is concluded to be the initial proton transfer from a general acid to the unsaturated $\beta$-carbon.

$$CH_2{=}CHOR + HA \longrightarrow CH_3\overset{+}{C}HOR + A^- \qquad (1)$$

Acetylenic sulfides[2,3] as well as ethers[4] undergo hydration via a similar reaction mechanism by acid catalysis.



$$HC{\equiv}CSR + HA \xrightarrow[\text{slow}]{} H_2C{=}\overset{-}{C}{-}SR + A^-$$

$$\xrightarrow[\text{fast}]{H_2O} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SR + HA \qquad (2)$$

In all these hydrations (hydrolyses) of unsaturated ethers and sulfides ($CH_2{=}CHOR$, $HC{\equiv}COR$ and $HC{\equiv}CSR$), the rate of reaction decreases in the order: R = t-$C_4C_9$ > i-$C_3H_7$ > $C_2H_5$ > $CH_3$. However, we have found that the rate of acid-catalyzed hydrolysis of alkyl vinyl sulfides ($CH_2{=}CHSR$) decreases in the reverse order: R = $CH_3$ > $C_2H_5$ > i-$C_3H_7$ > t-$C_4H_9$. Thus, we have undertaken detailed investigations on the mechanism of their hydrolysis in order to shed light on the origin of their unusual reactivity.

## EXPERIMENTAL

*Materials.* Alkyl vinyl sulfides were prepared by the dehydration[5] of alkyl 2-hydroxylethyl sulfides, which were obtained by the reaction of ethylene chlorohydrin with sodium mercaptides in ethanol.[6] B.ps of methyl, ethyl, isopropyl, and t-butyl vinyl sulfides were, respectively, 69–70° (lit.[7] 69–71°), 92–94° (lit.[7] 91–92°), 105–108° (lit.[8] 105.5°) and 115° (lit.[8] 115°). Their $^1$H and $^{13}$C NMR spectral data are summarized in Table 1.

Alkyl propenyl sulfides were obtained by the rearrangement[9] of the corresponding allyl sulfides, which were prepared from allyl bromide and alkyl mercaptides.[9] The *cis/trans* isomeric ratios of the sulfides obtained ranged 6/4 – 5/5. B.ps of ethyl, isopropyl, and t-butyl propenyl sulfides were, respectively, 119° (lit.[7] 120–122°), 132° and 138–140° (lit.[9] 139.1–140.8°). Isomeric mixtures obtained were separated by preparative VPLC. Isomeric structures were assigned by IR and PMR spectra.

Ethyl isopropenyl sulfide was prepared by the degradative distillation of acetone diethyl mercaptole from a small amount of silica gel. B.p. 113–115° (lit.[10] 113–114°). The mercaptole was obtained from acetone and ethyl mercaptan.[11] B.p. 73°/10 mmHg (lit.[11] 73°/11 mmHg).

*Kinetic measurements.* Hydrolysis was carried out in 10% aqueous acetonitrile soln. Ionic strength of the soln was adjusted to be 0.50 with the addition of KCl. The reaction was followed by the decrease in the absorption at ~220 nm in stoppered quartz cuvettes inserted in a water-jacketed cell holder, using a Shimadzu UV 200 spectrophotometer equipped with an automatic cell positioner assembly.

Acidic $D_2O$–$H_2O$ mixtures were prepared from $D_2O$ (deuterium purity >99%) and $H_2O$, each containing 0.1 M hydrochloric acid, without added KCl. The reaction was initiated by the addition of 0.3 ml of an acetonitrile soln containing an appropriate amount of methyl vinyl sulfide to a 2.7 ml portion of acidic $D_2O$–$H_2O$ mixture in a cuvette.

Deuterium exchange reaction was carried out in an NMR sample tube at 35°. The reaction mixture was made up by mixing 0.3 ml of dioxane-$d_8$ (Merck), 0.06 ml of 0.5 M DCl soln in $D_2O$, and 0.03 ml of methyl vinyl sulfide. The ratio of areas of signals at $\delta \sim 5$ and 6.3 ppm ($\beta$ and $\alpha$ protons) was examined during the course of reaction.

## RESULTS

Hydrolysis of vinyl sulfides was carried out in 10% aqueous acetonitrile at pH 1–3. The reaction was followed by the decrease in the absorption at ~220 nm.

The first order plots were linear over 90% conversion and the resulting first order rate constants were proportional to the acid concentration [HCl]. Namely, the rate is first order in both sulfide and acid (HCl). Furthermore, the reaction was catalyzed by general acid as was observed in buffer solutions (chloroacetic acids). That is,

$$\text{rate} = (k_{H_3O^+}[H_3O^+] + k_{HA}[HA])\,[\text{sulfide}]. \qquad (3)$$

Catalytic constants ($k_{HA}$) for methyl vinyl sulfide are given in Table 2. The Brønsted correlation was satisfactory within chloroacetic acids to give $\alpha \simeq 0.7$.

The hydrolysis rate of methyl vinyl sulfide was measured in $H_2O$–$D_2O$ mixture of varying compositions. The results are summarized in Table 3. The reaction was slower in a deuterium solvent than in a protium solvent. Furthermore, the PMR investigations on the hydrolysis in $D_2O$-dioxane-$d_8$ showed that any deuterium atom did not incorporate in the unreacted methyl vinyl sulfide during the course of reaction.

Table 1. The $^1H^a$ and $^{13}C^b$ NMR spectral data of alkyl vinyl sulfides

| Alkyl | $^1H$ chem. shift,$^c$ δ ppm | | | Coupl. const, Hz | | $^{13}C$ chem shift, δ ppm | |
|---|---|---|---|---|---|---|---|
| | $H_A$ | $H_B$ | $H_C$ | $J_{AB}$ | $J_{AC}$ | $C_\alpha$ | $C_\beta$ |
| $CH_3$ | 6.35 | 5.12 | 4 86 | 10.5 | 16.8 | 164.3 | 138.9 |
| $C_2H_5$ | 6.25 | 5 12 | 4 96 | 10.2 | 16.7 | 163.8 | 141.0 |
| $\underline{i}$-$C_3H_7$ | 6.27 | 5.14 | 5.10 | 10.2 | 16.8 | 163.2 | 143.1 |
| $\underline{t}$-$C_4H_9$ | 6.41 | 5.24 | 5.30 | 9.7 | 16.7 | 161.5 | 146.9 |

a Spectra of a 10% solution in $CCl_4$, recorded on a model JNM-MH-100 spectrometer.

b Spectra of a neat liquid, recorded on a model JNM-C-60HL spectrometer. Chemical shifts are given as those from TMS.

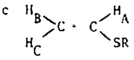
c 

Table 2. Catalytic constants of some acids in the hydrolysis of methyl vinyl sulfide at 25°$^a$

| HA | $pK_a^b$ | $10^4$ $k_{HA}$, $M^{-1}s^{-1}$ |
|---|---|---|
| $ClCH_2CO_2H$ | 2 86 | 2 86 |
| $Cl_2CHCO_2H$ | 1.29 | 27.8 |
| $Cl_3CCO_2H$ | 0.65 | 100 |
| $H_3O^+$ | -1.7 | 117 |

a 10% aqueous acetonitrile, μ = 0.50 (KCl).

b W. P. Jencks and J. Regenstein, CRC Handbook of Biochemistry, H A. Sober, ed., Chem. Rubber Co., Cleveland (1968), J-187.

Table 3. Solvent isotope effects in the hydrolysis of methyl vinyl sulfide at 25°

| $n^a$ | $10^4$ $k_1$,$^b$ $sec^{-1}$ | $k_n/k_0$ |
|---|---|---|
| 0 | 7.73 | 1.000 |
| 0.2 | 7.62 | 0.986 |
| 0.4 | 7.04 | 0.911 |
| 0.6 | 6.12 | 0.792 |
| 0.8 | 4.97 | 0.643 |
| 1.0 | 2.61 | 0.338 |

a Deuterium fraction of the solvent.

b First-order rate constant observed in 10 % $CH_3CN$ solution containing 0.09 M HCl (DCl).

Table 4. Kinetic data for the hydrolysis of alkyl vinyl sulfides, $CH_2$=CHSR, at 25°$^a$

| R | $10^3$ $k_{H_3O^+}$, $M^{-1}s^{-1}$ | $\Delta H^\ddagger$ kcal/mole | $\Delta S^\ddagger$ eu | Temp. range, °C | No. of measur |
|---|---|---|---|---|---|
| $CH_3$ | 11.7 | 17.5 | -13.5 | 15 - 42 | 15 |
| $C_2H_5$ | 10.4 | 17.0 | -15.3 | 15 - 42 | 11 |
| $\underline{i}$-$C_3H_7$ | 8.98 | 18.4 | -11.1 | 21 - 42 | 9 |
| $\underline{t}$-$C_4H_9$ | 4.17 | 21 0 | -4.1 | 21 - 42 | 12 |
| $EIS^b$ | 814 | 11.4 | -16.0 | 15 – 35 | 7 |

a 10% aqueous acetonitrile, μ = 0 50 (KCl).

b Ethyl isopropenyl sulfide.

Table 5. The rate constants of the hydrolysis of alkyl propenyl sulfides, $CH_3CH$=CHSR, at 25.3°$^a$

| R | $10^4$ $k_{H_3O^+}$, $M^{-1}s^{-1}$ | |
|---|---|---|
| | cis | trans |
| $C_2H_5$ | 4.88 | 2.81 |
| $\underline{i}$-$C_3H_7$ | 7.87 | 4.53 |
| $\underline{t}$-$C_4H_9$ | 5.42 | 3.39 |

a 10% aqueous acetonitrile, μ = 0.50 (KCl)

Kinetic data of various alkyl vinyl sulfides are summarized in Table 4. The reactivity decreases in the order: methyl > ethyl > isopropyl > t-butyl vinyl sulfide. Isopropenyl sulfide was highly reactive.

The hydrolysis of some *cis*- and *trans*-propenyl alkyl sulfides has also been studied for the sake of comparison. The sulfides subjected to kinetic measurements were isomerically pure in >98%. The first order plots were clearly linear over 90% conversion, indicating that the geometrical isomerization of neither isomer to the other takes place during the course of hydrolysis. The rate constants are given in Table 5. All the *cis* isomers are slightly more reactive than the corresponding *trans* sulfides.

## DISCUSSION

*Reaction mechanism.* It is known that acid-catalyzed hydrolysis of vinyl sulfide gives acetaldehyde and mercaptan.[9,12]

$$CH_2{=}CHSR + H_2O \xrightarrow{H_3O^+} CH_3CHO + RSH. \quad (3)$$

This reaction is formally very similar to the vinyl ether hydrolysis. The reaction mechanism may well be the one similar to that of the vinyl ether hydrolysis, which proceeds via rate-determining protonation of the unsaturated $\beta$-carbon.[1]

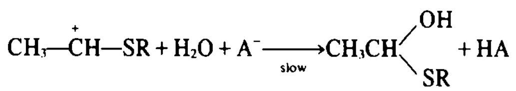
$$CH_2{=}CHSR + HA \xrightarrow[\text{slow}]{} CH_3{-}\overset{+}{C}H{-}SR + A^- \quad (4)$$

$$CH_3{-}\overset{+}{C}H{-}SR + H_2O \xrightarrow[\text{fast}]{} CH_3CHO + RSH. \quad (5)$$

A similar mechanism is also assigned to the acid-catalyzed hydration of acetylenic sulfides[3] and ethers.[4] The observed general acid catalysis and solvent isotope effects ($k_{D_2O}/k_{H_2O} = 0.34$) in the present reaction conform with the above mechanism (eqns 4 and 5).

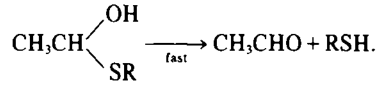
However, an alternative possible mechanism shown below, which involves proton transfer in the rate determining step, cannot be ruled out by the afore-mentioned observations alone.

$$CH_2{=}CHSR + H_3O^+ \rightleftharpoons CH_3{-}\overset{+}{C}H{-}SR + H_2O \quad (6)$$



$$CH_3{-}\overset{+}{C}H{-}SR + H_2O + A^- \xrightarrow[\text{slow}]{} CH_3CH\begin{smallmatrix}OH\\SR\end{smallmatrix} + HA$$

(7)



$$CH_3CH\begin{smallmatrix}OH\\SR\end{smallmatrix} \xrightarrow[\text{fast}]{} CH_3CHO + RSH. \quad (8)$$

A mechanism of this type was recently suggested, though not probable, for some unsaturated ethers.[13,14] Anomaly in the reactivity order of alkyl vinyl sulfides could be accommodated by this mechanism (nucleophilic attack by water in the rate determining step (eqn 7). However, the deuterium incorporation was not detected in the unreacted methyl vinyl sulfide during the hydrolysis in a deuterium solvent. Furthermore, geometrically isomeric propenyl sulfides did not show any sign of isomerization during the reaction. These two observations imply that the reaction (6) is irreversible; protonation of the substrate is rate determining. The second mechanism is thus excluded, the first one being supported for the hydrolysis of vinyl sulfides.

The results of solvent isotope effects can be treated according to eqn (9).[15]

$$\frac{k_n}{k_{H_2O}} = \frac{(1-n+nl^{1-\alpha})(1-n+nl^{1+2\alpha}k_{D_2O}/k_{H_2O})}{(1-n+nl)^3} \quad (9)$$

where n is the deuterium fraction of a reaction medium and l is isotopic fractionation factor of hydronium ion (l = 0.7).[15] As is shown in Fig. 1, the best fit with experimental points was obtained with $\alpha \simeq 0.8$. The Brønsted exponent $\alpha$ was estimated roughly to be 0.7. These rather high values of $\alpha$ are consistent with the $\alpha$ values (0.58–0.84) obtained for various vinyl ethers.[16] The ether of lower reactivity tends to have a higher value of $\alpha$, proton transfer being more complete in the transition state, as is the case for alkyl vinyl sulfides. Thus, the mechanism of the acid-catalyzed hydrolysis of vinyl sulfides is essentially the same as that of vinyl ethers (eqns 4 and 5).

*Reactivity.* The structural effects on the hydrolysis reactivity studied here are conveniently divided into two types. One is the effect of methyl substitution of a vinyl hydrogen and the other is the effect of a change in alkylthio groups.

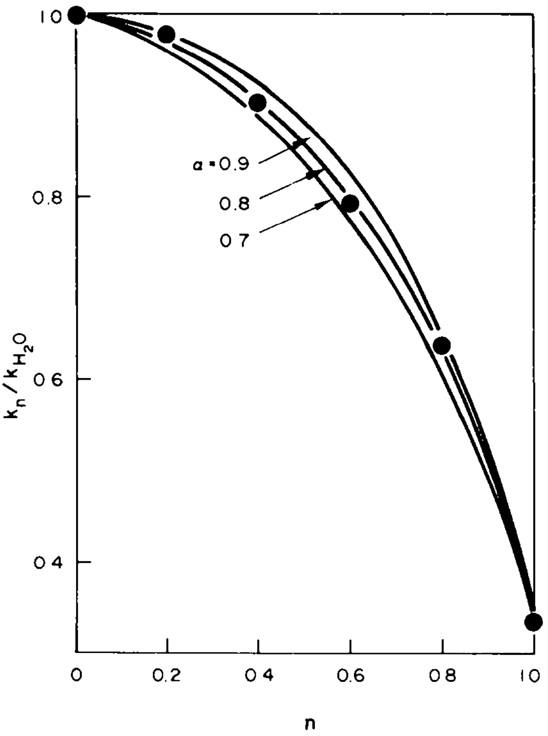


Fig. 1. Solvent isotope effects on the hydrolysis rate of methyl vinyl sulfide. Lines are calculated from eqn (9).

Comparison of rates among ethyl sulfides shows that an $\alpha$-methyl substitution increases the reactivity of vinyl sulfide by ~80 times (Table 4) while a $\beta$-methyl substitution decreases it by a factor of 20–40 (Table 5). These structural effects are similar to those observed for vinyl ethers[17] and conform with the reaction mechanism concluded above, which involves the rate-determining carbocation formation.

The *cis* isomers of propenyl sulfides were nearly 2 times more reactive than the *trans* counterparts (Table 5). The greater reactivity of the *cis* isomer falls in the general trend of reactivities found in the electrophilic additions to olefins, as discussed previously.[18]

The effect of alkylthio group is interesting. The reactivity order of alkyl vinyl sulfides is opposite to that of the related compounds. The rough correlation with Taft's $\sigma^*$ values[19] gives $\rho^*$ of about +1.8 in contrast to the negative values for other unsaturated sulfides and ethers (Table 6).[4,20–22] All the compounds included in Table 6 were

Table 6. Reactivities of various unsaturated sulfides and ethers

| Substrate | $\rho^{*a}$ | Ref. |
|---|---|---|
| $CH_2{=}CHSR$ | +1.8 | present work |
| $CH_2{=}CHOR^b$ | -4 | 20 |
| $CH{\equiv}CSR$ | -0.73 | 22 |
| $CH{\equiv}COR$ | -6.2 | 4 |

a Reaction constant in the correlation with Taft's $\sigma^*$ ($R = CH_3$, $C_2H_5$, i-$C_3H_7$, and t-$C_4H_9$).

b $\rho^* = -2.9$ including $R = C_6H_5CH_2$ and $ClCH_2CH_2$.[21]

hydrolyzed (hydrated) through essentially the same mechanism (rate-determining protonation). The electronic states of alkyl vinyl sulfides and ethers can be considered to be much the same as deduced from their NMR chemical shifts; chemical shifts in Table 1 parallel those of vinyl ethers[23,24] as is shown in Fig. 2.

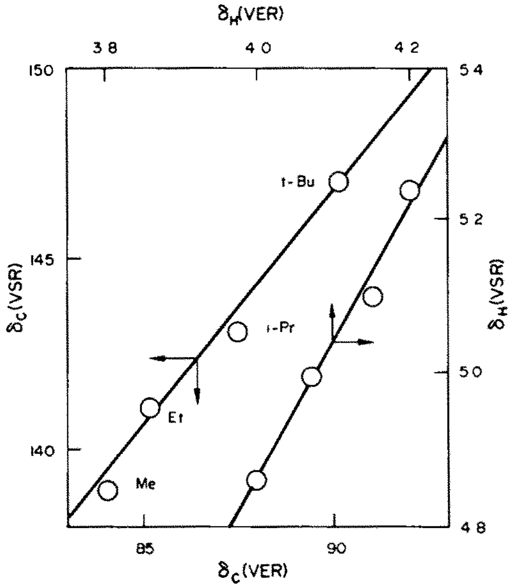
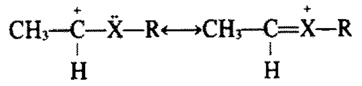


Fig. 2. Chemical shifts of the β-carbon and β-hydrogen of alkyl vinyl sulfides (ordinate) and ethers (abscissa). Data for the ethers are taken from Refs. 23 and 24.

Apparent from Table 6 is that both acetylenic sulfides and ethers have more negative $\rho^*$ values than the vinyl analogs. Furthermore, the $\rho^*$ values for sulfides are less negative than those for ethers. These substituent effects should be accounted for in terms of the stabilities of the transition states, which may resemble intermediate carbocations

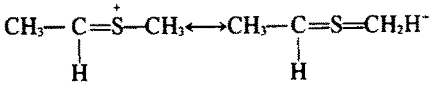


$$CH_3-\overset{+}{\underset{H}{C}}-\ddot{X}-R \longleftrightarrow CH_3-\underset{H}{C}=\overset{+}{X}-R$$

and

$$CH_2=\overset{+}{C}-\ddot{X}-R \longleftrightarrow CH_2=C=\overset{+}{X}-R \qquad (X=O \text{ or } S)$$

Alkyl groups R can donate electrons to the positive carbon only inductively through an O atom (X = O) but both inductively and (hyper-)conjugatively through an S atom (X = S). The hyperconjugation is effective through the intervening S atom by using its d-orbitals.



$$CH_3-\underset{H}{C}=\overset{+}{S}-CH_3 \longleftrightarrow CH_3-\underset{H}{C}=S=CH_2H^-$$

The inductive electron-donating effect of alkyl groups decreases in the order, $t\text{-}C_4H_9 > i\text{-}C_3H_7 > C_2H_5 > CH_3$, while the hyperconjugative effect decreases in the order just opposite to the above.† Thus, the balancing of these two opposing effects may result in varying values of $\rho^*$ in Table 6. Operation of conjugative effect may be a reason for the less negative $\rho^*$ values for sulfide hydrolyses.

Since an sp-hybridized carbon is more electronegative than an $sp^2$-carbon, the positive center of acetylenic compounds (vinylic cations) inductively demands more electron than that of vinyl analogs (trivalent cations) at the transition state. This may result in the more negative $\rho^*$ values for acetylenic compounds.

As a result of these circumstances, the $\rho^*$ value for hydrolysis of vinyl sulfides may happen to be positive; the conjugative effects determine the relative reactivities. A similar case was observed in the dissociation of *p*-alkylthiobenzoic acids,[25] Hammett's $\sigma_p$ values of $CH_3S$, $C_2H_5S$, and $i\text{-}C_3H_7S$ being 0.00, 0.03 and 0.07, respectively.[26] However, the cancellation of the two effects seems to make the apparent electronic effects quite delicate. The enthalpies of activation are much the same for both methyl and ethyl vinyl sulfides. The effects of alkylthio groups on the propenyl sulfide reactivity are not straight-forward although they are very small.

In conclusion, acid-catalyzed hydrolysis of vinyl sulfides takes place via the rate-determining protonation of the β carbon. The relative reactivities of alkyl vinyl sulfides are accounted for by the balancing of the inductive and hyperconjugative electron-donating effects of alkyl groups.

## REFERENCES

[1] A. J. Kresge and H. J. Chen, *J. Am. Chem. Soc.* **94**, 2818 (1972); and refs cited.
[2] W. F. Verhelst and W. Drenth, *J. Org. Chem.* **40**, 130 (1975).
[3] H. Hogeveen and W. Drenth, *Recl. Trav. Chim. Pays-Bas* **82**, 410 (1963); and refs cited.
[4] E. J. Stamhuis and W. Drenth, *Ibid.* **82**, 394 (1963); and refs cited.
[5] C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.* **75**, 4750 (1953).
[6] W. Windus and P. R. Shildneck, *Org. Synth.* Coll. Vol. II, 345 (1943).
[7] H. Böhme and H. Bentler, *Chem. Ber.* **89**, 1464 (1956).
[8] T. Otsu and H. Inoue, *J. Macromol. Sci.* **A4**, 35 (1970).
[9] D. S. Tarbell and W. E. Lovett, *J. Am. Chem. Soc.* **78**, 2259 (1956).
[10] W. H. Mueller and K. Griesbaum, *J. Org. Chem.* **32**, 856 (1967).
[11] A. Schönberg and K. Praefcke, *Chem. Ber.* **100**, 778 (1967).
[12] J. F. Arens, H. C. Volger, T. Doornbos, J. Bonnema, J. W. Greidanus and J. H. van den Hende, *Recl. Trav. Chim. Pays-Bas* **75**, 1459 (1956).
[13] J. D. Cooper, V. P. Vitullo and D. L. Whalen, *J. Am. Chem. Soc.* **93**, 6294 (1971).
[14] G. M. Loudon, C. K. Smith and S. E. Zimmerman, *Ibid.* **96**, 465 (1974); G. M. Loudon and C. Berke, *Ibid.* **96**, 4508 (1974).
[15] A. J. Kresge, *Pure Appl. Chem.* **8**, 243 (1964); V. Gold, *Adv. Phys. Org. Chem.* **7**, 259 (1969).
[16] A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne and D. S. Sagatys, *J. Am. Chem. Soc.* **93**, 413 (1971).
[17] T. Okuyama, T. Fueno, H. Nakatsuji and J. Furukawa, *Ibid.* **89**, 5826 (1967).
[18] T. Okuyama and T. Fueno, *J. Org. Chem.* **39**, 3156 (1974); K. Yamaguchi, T. Okuyama and T. Fueno, to be published.
[19] R. W. Taft, Jr., *Steric Effects in Organic Chemistry* (Edited by M. Newman), Chap. 13. Wiley, New York (1956).
[20] A. Ledwith and H. J. Woods, *J. Chem. Soc.* (B) 753 (1966).
[21] D. M. Jones and N. F. Wood, *Ibid.* 5400 (1964).
[22] H. Hogeveen and W. Drenth, *Recl. Trav. Chim. Pays-Bas* **82**, 375 (1963).
[23] H. Yuki, K. Hatada and M. Takeshita, *J. Polymer Sci.* A-1 **7**, 667 (1969).
[24] K. Hatada, K. Nagata and H. Yuki, *Bull. Chem. Soc. Japan.* **43**, 3195 (1970).
[25] V. Baliah, S. Shanmuganathan and R. Varadachari, *J. Phys. Chem.* **61**, 1013 (1957).
[26] D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958).

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†The magnitude of electronic effects can be deduced from Taft's $\sigma^*$ (inductive) and Brown's $\sigma^+$ values (conjugative).