The Application of the Hammett Equation to Nonaromatic Unsaturated Systems. V. *cis*-Vinylene Sets. Composition of Electrical Effects

MARVIN CHARTON

Department of Chemistry, School of Engineering and Science, Pratt Institute, Brooklyn 5, New York

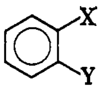
Received December 7, 1964

Ionization constants of five sets of *cis* 3-substituted acrylic acids and of four sets of *cis*-substituted enols have been correlated with the Hammett equation by means of the σ_p constants. Resonance effects in the *cis*-enols are smaller than those observed in 4-substituted phenols. Differences in the magnitude of substituent effects between the *cis* and *trans* sets are ascribed to the field effect. These results provide a direct method for the assignment of configuration to geometric isomers, provided that the *cis* substituent and the reaction site do not form a strong intramolecular hydrogen bond.

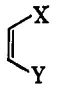
For some time we have been interested in the extension of the Hammett equation[1] to nonaromatic unsaturated systems.[2-4] We have also considered the application of the Hammett equation to *ortho*-substituted benzene sets I.[5,6] It therefore seemed of interest to consider the application of the Hammett equation to *cis*-substituted vinylene sets II. There is an obvious analogy between structural effects on reactivity in the *cis*-vinylene and *ortho*-benzene sets. The only structural difference between the sets is that the C-1–C-2 bond in I has an average value of about 1.39 Å., whereas that in II has an average value of 1.34 Å. In general, the "normal" electrical effects of an *ortho* substituent have been shown to be proportional to those of a *para* substituent[6] (eq. 1). It has also been shown that the

$$\sigma_o = m\sigma_p + c \qquad (1)$$

Hammett equation is applicable to *trans*-vinylene sets using the σ_p constants.[2,3,7,8] In order to study the applicability of the Hammett equation to *cis*-vinylene sets we have examined ionization constants taken from the literature for five sets of *cis*-3-acrylic acids and four sets of *cis*-enols. In the case of the enols we have also examined the correlation of the data with the σ_p^- constants which have been found to be necessary in the application of the Hammett equation to the ionization constants of phenols. The σ_p constants used are from the compilation of McDaniel and Brown[9] when possible. Values from other sources are given in Table I. The σ_p^- constants are all from Jaffé.[1] We have also correlated ionization constants of *cis* 3-substituted *trans*-3-phenylacrylic acids and have reexamined the *trans* 3-substituted acrylic acids and *trans* 3-substituted *cis*-3-methylacrylic acids for comparison. The data used in the correlations are given in Table II. Correlations were made by Jaffé's method.[1] The results are in Table III.



I



II

TABLE I

SUBSTITUENT CONSTANTS[a]

X	σ_p	X	σ_p
$PhCH_2$	−0.10[b]	2-furyl	0.004[c]
CH_2Cl	0.12[b]	4′-ClC_6H_4	0.071[d]
CO_2Me	0.436[e]	4′-$O_2NC_6H_4$	0.229[d]
trans-PhC_2H_2	−0.050[f]	4′-$MeOC_6H_4$	−0.088[d]
trans-MeC_2H_2	−0.07[g]		

[a] From sources other than ref. 9 or Jaffé.[1] [b] O. Exner and J. Jonaš, *Collection Czech. Chem. Commun.*, **27**, 2296 (1962). [c] Calculated from the pK_a of 2-furylacrylic acid (6.49) in 78.1% ethyl alcohol–water at 25° given by C. C. Price and E. A. Dudley [*J. Am. Chem. Soc.*, **78**, 68 (1956)] (set 13 in Tables II and III). [d] E. Berliner and L. H. Liu, *ibid.*, **75**, 2417 (1953). [e] Ref. 2. [f] J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3452 (1953). [g] Calculated from set 10 of Tables II and III using the average of the pK_a values for *trans,trans*-sorbic acid (4.48, 4.53) given by G. H. Mansfield and M. C. Whiting [*J. Chem. Soc.*, 4761 (1956)].

cis **3-Substituted Acrylic Acids.**—Five sets of this type were studied: *cis* 3-substituted acrylic acids (set 1), *cis* 3-substituted *trans*-3-phenylacrylic acids (set 2), *cis* 3-substituted *trans*-3-methylacrylic acids (set 3), *cis* 3-substituted *trans*-3-chloroacrylic acids (set 4), and *cis* 3-substituted 2-methylacrylic acids (set 5). The *cis*-acrylic acids have been correlated with the inclusion (set 1a) and omission (set 1b) of the pK_a for X = CO_2H. Exclusion of the pK_a values for the bulky phenyl and 2-furyl groups did not significantly change the results (set 1c). The results obtained are significantly better for set 1b. In view of the extensive evidence for the existence of a strong hydrogen bond in the hydrogen maleate ion, this result is not surprising. The increased likelihood of forming the ion will cause an increase in the extent of ionization of maleic acid. The results obtained in sets 2 and 3 are excellent (99% s.l.). Set 4 shows meaningful though poor correlation (90% confidence level). In set 5a the results of the correlation are not significant. Dropping the value for X = H (set 5b) gives significant results. This may be due to a difference in preferred conformation between the compound for which X = H (methylacrylic acid) and the other members of the set.

Substituted ***cis*****-Enols.**—Sets studied in this category are ionization constants of α-substituted tetronic acids (set 6), first and second ionization constants of 3,6-disubstituted 2,5-dihydroxybenzoquinones (set 7

---

[1] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956; V. Palm, *Russ. Chem. Rev.* (Eng. Transl.), **31**, 471 (1961); P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[2] M. Charton and H. Meislich, *J. Am. Chem. Soc.*, **80**, 5940 (1958); M. Charton, *J. Org. Chem.*, **30**, 552, 557 (1965).

[3] M. Charton, *ibid.*, **26**, 735 (1961).

[4] M. Charton, *ibid.*, **30**, 969 (1965).

[5] M. Charton, *Can. J. Chem.*, **38**, 2493 (1960).

[6] M. Charton, *J. Am. Chem. Soc.*, **86**, 2033 (1964).

[7] J. Hine and W. C. Bailey, Jr., *ibid.*, **81**, 2075 (1959); J. Hine and W. C. Bailey, Jr., *J. Org. Chem.*, **26**, 2098 (1961).

[8] P. B. D. de la Mare, *J. Chem. Soc.*, 3823 (1960).

[9] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

TABLE II

DATA USED IN CORRELATIONS (*See p. 976 for footnotes*)

cis 3-Substituted Acrylic Acids

1. Ionization Constants of *cis* 3-Substituted Acrylic Acids in Water at 25°

X	Me	Ph	H	2-Furyl	Cl	CO_2Et	CO_2H
pK_a	4.44	3.88	4.26	4.11	3.32	3.077	2.211
Ref.	*a*	*a*	*a*	*b*	*a, c*	*d*	*d, e*

2. Ionization Constants of *cis* 3-Substituted *trans*-3-Phenylacrylic Acids in Water at 25°

X	H	Ph	Cl	I
pK_a	4.44	4.5	3.56	3.39
Ref.	*a*	*f*	*g*	*g*

3. Ionization Constants of *cis* 3-Substituted *trans*-3-Methylacrylic Acids in Water at 25°

X	Me	Et	H	Cl	Br	I
pK_a	5.12	5.13	4.693	3.91	3.74	3.77
Ref.	*a*	*h*	*a*	*i*	*i*	*i*

4. Ionization Constants of *cis* 3-Substituted *trans*-3-Chloroacrylic Acids in Water at 25°

X	Me	Ph	H	CO_2Me
pK_a	4.07	3.57	3.32	2.8
Ref.	*i*	*i*	*a, c*	*j*

5. Ionization Constants of *cis* 3-Substituted 2-Methylacrylic Acids in Water at 25°

X	H	Me	Pr	Ph	Cl
pK_a	4.65	4.30	4.44	3.62	3.05
Ref.	*k*	*l*	*m*	*n*	*o*

cis-Substituted Enols

6. Ionization Constants of α-Substituted Tetronic Acids in Water at 25°

X	H	Cl	Br	I	Me	Et	CO_2Et	Ac	NO_2	$PhCH_2$	*i*-$PrCH_2CH_2$
pK_a	3.76	2.13	2.23	2.31	4.19	4.0	1.8	1.8	1.68	3.69	4.16
Ref.	*p*	*p*	*p*	*p*	*p*	*p*	*p*	*p*	*p*	*p*	*p*

7. First Ionization Constants of 3,6-Disubstituted 2,5-Dihydroxy-1,4-benzoquinones in Water at 25°

X	OH	H	F	Cl	Br	NO_2
pK_a	5.1	2.71	1.40	0.73	0.80	−3.0
Ref.	*e, q*	*r*	*r*	*r*	*r*	*r*

8. Second Ionization Constants of 3,6-Disubstituted 2,5-Dihydroxy-1,4-benzoquinones in Water at 25°

X	OH	H	F	Cl	Br	NO_2
pK_a	6.5	5.18	3.30	3.08	3.10	−0.5
Ref.	*q, s*	*r*	*r*	*r*	*r*	*r*

9. Ionization Constants of 3-Substituted 2-Hydroxy 1,4-Naphthoquinones in Water at 26–33°

X	H	Bz	Ph	$PhCH_2$	*i*-$PrCH_2CH_2$	*trans*-MeC_2H_4
pK_a	4.00	2.17	4.35	4.9	5.13	4.8
Ref.	*t*	*t*	*t*	*t*	*t*	*t*

Other Acids

10. Ionization Constants of *trans* 3-Substituted Acrylic Acids in Water at 25°

X	CO_2H	CO_2^-	CF_3	Cl	CO_2Et	CH_2Cl	H	Me	Et	Pr	*i*-Pr	Ac	*trans*-PhCH=CH—
pK_a	3.396	4.301	3.15	3.654	3.396	4.140	4.255	4.693	4.695	4.703	4.701	3.238	4.427
Ref.	*u*	*u*	*u*	*u*	*u*	*u*	*u*	*u*	*u*	*u*	*u*	*v*	*u*

11. Ionization Constants of *trans* 3-Substituted 2-Methylacrylic Acids in Water at 25°

X	Me	H	Ph	Cl	MeO_2C	EtO_2C
pK_a	4.96	4.65	4.82	4.03	3.452	3.468
Ref.	*c, w*	*k*	*n*	*o*	*x*	*x*

12. Ionization Constants of 2-Substituted *cis*-Cinnamic Acids in Water at 25°

X	H	MeO	EtO	AcO	Cl	Br
10^5K	1.32	5.40	4.54	11	12.3	9.5
Ref.	*y*	*z*	*z*	*z*	*aa*	*aa*

13. Ionization Constants of *trans* 3-Substituted Acrylic Acids (4-Substituted Cinnamic Acids) in 78.1% Ethyl Alcohol–Water at 25°

X	Ph	4-ClC_6H_4	4-$O_2NC_6H_4$	4-$MeOC_6H_4$
pK_a	6.46	6.32	5.87	6.73
Ref.	*bb*	*bb*	*bb*	*bb*

14. Ionization Constants of *trans* 3-Substituted *cis*-3-Methylacrylic Acids in Water at 25°

X	Cl	Br	I	H	Me	Et	CO_2Et
pK_a	4.07	3.98	3.90	4.44	5.12	5.15	3.26
Ref.	*i*	*i*	*i*	*a*	*h*	*h*	*x*

TABLE II (*Continued*)

[a] H. C. Brown, D. H. McDaniel, and O. Häfliger, "Determination of Organic Structure by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955, p. 567. [b] A. Liebermann, *Ber.*, **28**, 129 (1895). [c] At 18°. [d] G. F. Dahlgren and F. A. Long, *J. Am. Chem. Soc.*, **82**, 1303 (1960). [e] Statistical factor of $^1/_2$ included. [f] Calculated from the pK_a 6.36 in 80% methyl alcohol–water at 20° given by W. Voegtli and P. Lauger [*Helv. Chim. Acta*, **38**, 96 (1955)]. [g] T. C. James, *J. Chem. Soc.*, **103**, 1368 (1913). [h] D. J. G. Ives, R. P. Linstead, and H. L. Riley, *ibid.*, 561 (1933). [i] W. J. le Noble, *J. Am. Chem. Soc.*, **83**, 3897 (1961). [j] Estimated from the pK_a of 3.14 in 30% ethyl alcohol–water given by S. Veibel and C. Pedersen [*Acta Chem. Scand.*, **9**, 1674 (1955)]. [k] T. Alfrey and H. Morawetz, *J. Am. Chem. Soc.*, **74**, 436 (1952). [l] W. Ostwald, *Z. Phys. Chem.*, **3**, 369 (1889). [m] J. Cason and M. J. Kalm, *J. Org. Chem.*, **19**, 1947 (1954). [n] Estimated from the average pK_a values (4.98, 5.98) for the *cis* and *trans* acids, respectively, in 40% acetone–water at 25° given by R. D. Kleene, F. H. Westheimer, and G. W. Wheland [*J. Am. Chem. Soc.*, **63**, 791 (1941)]. [o] A. F. Ferris and I. G. Marks, *J. Org. Chem.*, **19**, 1975 (1954). [p] L. J. Haynes and J. R. Plimmer, *Quart. Rev.*, **14**, 292 (1960). [q] P. W. Preisler, L. Berger, and E. S. Hill, *J. Am. Chem. Soc.*, **69**, 326 (1947). [r] K. Wallenfels and K. Friedrich, *Chem. Ber.*, **93**, 3070 (1960). [s] Statistical factor of $^1/_3$ included. [t] M. G. Ettlinger, *J. Am. Chem. Soc.*, **72**, 3085 (1950). [u] Ref. 2. [v] M. Sanesi, *Ann. chim.* (Rome), **50**, 997 (1960). [w] W. Larson, *Z. physik. Chem.* (Leipizg), **A159**, 315 (1932). [x] R. Anschütz, F. Haas, and O. Sieplein, *Ann.*, **353**, 144 (1907). [y] J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939). [z] W. A. Roth and R. Stoermer, *Chem. Ber.*, **46**, 260 (1913). [aa] M. Betti and E. Lucchi, *Mem. accad. sci. ist. Bologna Classe sci. fis.*, **6**, 37 (1939). [bb] Data from reference in footnote *f* in Table I.

TABLE III

RESULTS OF CORRELATIONS

No.	ρ	r[a]	s[b]	t[c]	Q_H[d]	n[e]
1a	−3.03	0.933	0.311	5.812[f]	4.026	7
1b	−2.34	0.953	0.182	6.326[f]	4.044	6
1c	−2.42	0.968	0.208	5.441[i]	4.081	4
2	−3.87	0.9998	0.0115	68.85[g]	4.450	4
3	−3.29	0.994	0.0797	18.54[g]	4.617	6
4	−1.91	0.940	0.221	3.902[h]	3.562	4
5a	−3.33	0.777	0.481	2.139[i]	3.959	5
5b	−3.48	0.961	0.219	4.898[j]	3.784	4
6a	−3.05	0.939	0.383	8.177[g]	3.391	11
6b	−1.89	0.870	0.548	5.297[g]	3.386	11
6c	−3.75	0.972	0.256	11.72[g]	3.397	10
6d	−2.50	0.906	0.461	6.061[g]	3.418	10
6e	−4.36	0.973	0.226	10.43[g]	3.357	8
7a	−7.04	0.994	0.329	18.01[g]	2.380	6
7b	−2.83	0.813	1.25	2.789[j]	2.409	6
8a	−6.716	0.982	0.543	10.49[g]	4.625	6
8b	−4.46	0.950	0.904	6.089[f]	4.634	6
9	−4.55	0.985	0.210	11.39[g]	4.366	6
10	−2.20	0.993	0.0746	27.96[g]	4.335	13
11	−2.61	0.991	0.101	14.86[g]	4.637	6
12a	−0.622	0.807	0.129	2.729[h]	4.091	6
12b	−0.657	0.957	0.0645	5.734[f]	4.135	5
13	−2.62	0.993	0.514	12.04[f]	6.48	4
14	−2.90	0.989	0.110	15.12[g]	4.63	7

[a] Correlation coefficient. [b] Standard deviation. [c] Student *t* test. [d] Intercept. [e] Number of points in the set. [f] 99% significance level (s.l.). [g] 99.9% s.l. [h] 90% s.l. [i] Less than 90% s.l. [j] 95% s.l.

and 8, respectively), and ionization constants of 3-substituted 2-hydroxynaphthoquinones (set 9).

A comparison of the results obtained with σ_p (6a,c; 7a; 8a; 9a) and with σ_p^- (6b,c; 7b; 8b; 9b) shows that better correlation is obtained with the σ_p constants. This is in marked contrast to the behavior of phenols. Clearly there is very much less resonance interaction between the substituent and the hydroxyl group in the *cis*-enols than there is in 4-substituted phenols.

In set 6 the correlations have been made with both the inclusion (6a,b) and the exclusion (6c,d) of the value for the nitro substituent. The results were significantly improved when this value was omitted. The observation may possibly be explained in terms of an intramolecular hydrogen bond between the nitro and hydroxyl groups. When the correlation was repeated with the further exclusion of the values for the carbethoxy and acetyl groups (set 6e) no great change was found in the correlation, although these groups should also form intramolecular hydrogen bonds.

In correlating the values for the hydroxyl substituent in sets 7 and 8 the appropriate statistical factors of $^1/_2$ and $^1/_3$, respectively, have been used.

Discussion

Nature of the *cis* Electrical Effect.—The results obtained show clearly that the electrical effects of a *cis* substituent in a vinylene set are proportional to those of a *para* substituent in a phenylene set (eq. 2).

$$\sigma_{cis} = n\sigma_p + d \qquad (2)$$

This is in accord with the observations cited previously concerning the electrical effects of the *trans* vinylene[2] and of the *ortho* phenylene[5,6] substituents.

Composition of Electrical Substituent Effects.—The acrylic acid sets provide an opportunity to attempt to differentiate between the inductive effect and the field effect (direct effect). As the *cis* and *trans* sets have been studied under common conditions, and of course involve the same reaction and reaction site (*i.e.*, ionization of the carboxyl group), the ρ-value will depend solely on the nature of the substituent effects. Serious steric effects in the *cis* systems are precluded by the successful correlation of these sets with the Hammett equation. As the nature of the bonding is the same in both the *cis* and *trans* sets, resonance and inductive effects must also be the same. The *cis* and the *trans* sets differ only in their stereochemistry. Of the electrical effects considered, only the field effect must be dependent on molecular geometry. If only resonance and inductive effects are operative (or if the field effects for the *cis* and *trans* sets are significant but approximately equal), the ratio $\gamma_{c,t}$ will be about 1.

$$\gamma_{c,t} = \frac{\rho_{cis}}{\rho_{trans}} \qquad (3)$$

Significant deviation from a value of 1 for this ratio can be best rationalized in terms of an important field effect. Values of $\gamma_{c,t}$ are given in Table IV.

Of the five values of $\gamma_{c,t}$ available, three differ significantly in magnitude from 1.0. A significant difference is considered to be one of ≧20%. (This value was chosen in view of the statement by Jaffé[1] that the Hammett equation correlated data with an accuracy of ±15%.) Furthermore, all of the values of $\gamma_{c,t}$ are greater than 1, whereas in the absence of an unequal field effect they ought to be distributed about 1. On the basis of this evidence we may conclude that the field effect is a major constituent of the total electrical effect of substituents in these sets.

Table IV

Values of $\gamma_{c,t}$

Substituents						
2	3	ρ_{cis}	Ref.[a]	ρ_{trans}	Ref.[a]	$\gamma_{c,t}$
2	3					
H	H or X	−2.34	1b	−2.20	10	1.1
H	Me or X	−3.29	3	−2.90	14	1.1
Me	H or X	−3.48	5b	−2.61	11	1.3
H	H or 2-C_6H_4X	−0.657	12b	−0.389	*b*	1.7
H	H or 3- or 4-C_6H_4X	−0.643	*c*	−0.466	*d*	1.3

[a] Numbers refer to sets in Table II. [b] Ref. 5. [c] R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963). [d] Ref. 1.

Assignment of Configuration to Geometric Isomers.—It has previously been suggested[2] that assignments of configuration might be made by means of a comparison between the calculated value of some property for the *trans* compound and the observed value of the property. Thus, a comparison of the observed ionization constant for a substituted acrylic acid with the value of the ionization constant for the *trans* compound calculated from the Hammett equation would aid in the assignment of configuration. Assignment of configuration to a *cis* compound on this basis would rest on lack of agreement between the observed constant and the constant calculated for the *trans* compound. The correlations obtained above for *cis* olefinic sets make possible the calculation of a property for both *trans* and *cis* isomers (with the exception of those *cis* isomers in which a strong intramolecular hydrogen bond is likely to occur). This should greatly extend the utility of the Hammett equation as a method of assigning configuration.

The Reactions of Some 7-Chloronorbornenes with Sodium Cyanide[1,2]

Hiroshi Tanida and Yoshiteru Hata

Shionogi Research Laboratory, Shionogi and Company, Ltd., Osaka, Japan

Received October 21, 1964

The reactions of 7-chloronorbornadiene (1) and *anti*-7-chloronorbornene (2) with sodium cyanide in aqueous ethanol were studied. The former (1) produced β-cyclopentadienylacrylonitrile, whose formation was rationalized by the nucleophilic attack of a cyanide ion at the C-2 of 1 followed by ring cleavage. The latter (2) produced mainly *anti*-7-cyanonorbornene, along with 2-cyanotricyclo[4.1.0.0^{3,7}]heptane as a by-product. The kinetics and the stereochemical results are in accord with the SN1 mechanism.

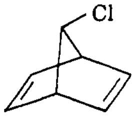
In view of providing a good model for the demonstration of anchimeric assistance for ionization, the solvolysis reactions of norbornyl systems have received much attention in recent years.[3] It seems to us that the position and stereochemistry of an entering nucleophile in the solvolysis of 7-norbornenyl derivatives, in which partial positive charges are developed at the 7-position, throw some light on the precise nature of participation and the precise structure of the carbonium ions produced in the ionization stages.[4]

Initially the purpose of this study was to devise a reaction which results in inversion of configuration of a 7-substituent without skeletal rearrangement. Although a highly nucleophilic reagent such as a sulfur or iodide anion might be more suitable for the purpose, we were afraid we would encounter some difficulties in the determination of stereochemistry of the products formed by these kinds of reagents. Accordingly, we undertook the reactions of 7-norbornenyl halides with sodium cyanide even though it may not be a sufficiently strong nucleophilic reagent.

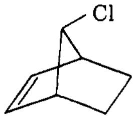
Brown[4a] recently reported the formation of tricyclo-[4.1.0.0^{3,7}]hept-4-ene and tricyclo[4.1.0.0^{3,7}]heptane in the solvolyses of 7-chloronorbornadiene and *anti*-7-norbornenyl tosylate in aqueous diglyme containing sodium borohydride, which was suggested by him as a convenient means for trapping carbonium ions formed in solvolysis.[5] Our results obtained here describe the formation of the above kind of product or intermediate and information on their stabilities, although the initial purpose concerning inversion of configuration was not accomplished.

Results

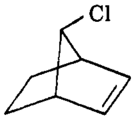
Reactions of the norbornyl chlorides 1–5 with sodium cyanide were carried out in 66% aqueous ethanol under a nitrogen atmosphere. All the reaction mixtures were colorless and homogeneous in the initial stages of the reactions. As expected from the solvolytic behaviors, *syn*-7-chloronorbornene (3), 7-chloronorbornane (4), and 3-chloronortricyclene (5) were so inert that reactions of 3 and 5 at refluxing temperature for 6 hr. and of 4 at 175° for 6 hr. did not show any product formation. However, the reactions of 7-chloronorbornadiene (1) and *anti*-7-chloronorbornene (2) with sodium cyanide proceeded smoothly, resulting in the precipitation of sodium chloride.



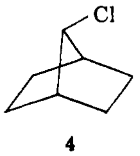
1



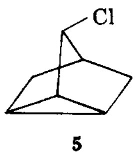
2



3



4



5

---

[1] Part VIII of a series on Bicyclic Systems. Part VII: H. Tanida and R. Muneyuki, *Tetrahedron Letters*, **No. 38**, 2787 (1964).

[2] Presented, in part, at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1964.

[3] For a recent review, see J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

[4] With respect to the discussion in this field, refer to (a) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); (b) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

[5] H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).