chloroform. The chloroform solution was extracted with water (100 ml.). Analysis of the aqueous solution indicated 0.001 mole of base, 0.018 mole of bromide and 0.007 mole of chloride. After drying the chloroform layer and removing the solvent *in vacuo* the remaining brown oil (3.8 g.) contained only benzophenone and triphenylphosphine oxide identified by infrared analysis. The first filtrate above was concentrated *in vacuo* to a red oil, 1.5 g., which also by infrared analysis contained only benzophenone and triphenylphosphine.

Reaction of Dibromomethyltriphenylphosphonium Bromide with Potassium *t*-Butoxide.—Dibromomethyltriphenylphosphonium bromide was prepared by the procedure of Ramirez and McKelvie[10]; m.p. 235–238°. The above phosphonium salt (26.0 g., 0.05 mole) was added to potassium *t*-butoxide (0.05 mole) in *n*-heptane (200 ml.) at 0–5° with vigorous stirring. Benzophenone (9.1 g., 0.05 mole) was added and the mixture stirred until room temperature was attained. A yellow color developed slowly. The mixture was heated to 70–80° for 3 hr., cooled, and filtered to yield a brown residue which by infrared analysis contained both starting material and triphenylphosphine oxide. The filtrate was concentrated to an oil *in vacuo* and extracted with hexane (50 ml.). The hexane extract was evaporated and the resulting oil was crystallized to give benzophenone.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY, PITTSBURGH 19, PA.]

Conjugation in the Naphthalene Series. II.[1] Solvolysis of x-Methoxy-y-bromomethylnaphthalenes

BY KURT C. SCHREIBER AND RONALD G. BYERS

RECEIVED JULY 19, 1961

The solvolyses in acetic acid and 80% aqueous acetone of 4-, 5-, 6- and 7-methoxy-1-bromomethylnaphthalene, and 6- and 8-methoxy-2-bromomethylnaphthalenes are reported at various temperatures. The data indicate that there is little resonance stabilization of the carbonium ion by the methoxy group in the intermediates from 5-methoxy-1-bromomethyl or the 8-methoxy-2-bromomethyl compounds. A small effect is observed in the case of the 7-methoxy-1-bromomethyl- and 6-methoxy-2-bromomethylnaphthalenes.

Introduction

The first paper in this series[1] and other papers[2,3] have been concerned with the resonance stabilization of an unshared pair of electrons in the naphthalene ring system. These studies show similarity with the benzene system when the groups are in the 1,2- or 1,4-positions, but show little resonance interaction when one group is attached to one ring and the other group to the second ring of the naphthalene system. This paper reports an extension of the investigation to systems in which a positive charge is being distributed over the naphthalene ring system. The reaction chosen is the solvolysis[4] of the appropriate naphthyl halide.

Experimental[5]

Synthetic. Preparation of x-Methoxy-y-naphthoic Acids (x = 5,6,7,8; y = 1,2).—*y*-Naphthylamine-*x*-sulfonic acid was diazotized and converted to the corresponding cyano-sulfonic acid by the method of Royle and Schedler,[6] with the following modification: Instead of slowly adding the sodium nitrite solution to the hydrochloric acid solution of the naphthylaminesulfonic acid, the mixture of sodium nitrite and naphthylaminesulfonic acid was added rapidly to a cooled hydrochloric acid solution. This modification reduced the amount of decomposition of the diazonium salt and a more easily filtrable precipitate was formed.

The cyano-sulfonic acid was hydrolyzed, fused, and then methylated, according to the method of Anderson and Thomas,[7] to give the desired *x*-methoxy-*y*-naphthoic acid.

Reduction of naphthoic acids is illustrated by the reduction of 2-naphthoic acid. A solution of 2-naphthoic acid (25 g., 0.14 mole) and tetrahydrofuran (200 ml.) was added dropwise to a cooled solution of lithium aluminum hydride (5.2 g., 0.14 mole) and tetrahydrofuran (150 ml.). After the addition, the solution was allowed to come to room temperature and then stirred for 2 hours. The solution was cooled in an ice-bath and 50 ml. of ethyl acetate was added dropwise to destroy any unreacted lithium aluminum hydride. The reaction mixture was then poured into 1 l. of 6 *N* hydrochloric acid and 500 g. of crushed ice. The precipitate was filtered, washed with a 5% solution of sodium bicarbonate, and recrystallized from a 50% solution of ethanol and water. The yield of 2-hydroxymethylnaphthalene was 17 g. (80%), m.p. 80–81° (reported[8] 80.5°). The yields for the various acids varied between 66 and 80%. The m.p.'s, derivatives and analyses of the compounds prepared are given in Table I.

Preparation of x-Methoxy-y-bromomethylnaphthalenes.—The hydroxymethyl-methoxynaphthalenes were converted to the corresponding bromo compounds by the method of Shoesmith and Rubli[9]; melting points and bromine analyses are listed in Table I.

Acetolysis of 6-Methoxy-2-bromomethylnaphthalene (I).—Compound I (10.091 g., 0.0402 mole) was dissolved in 1,000 ml. of 0.0573 *M* sodium acetic acid, and was allowed to react for a period of 10 half-lives at 74.1°. The volume of the solution was concentrated under reduced pressure to approximately 100 ml. After addition of 500 ml. of water, the mixture was extracted with five 100-ml. portions of ether, the ether layers dried and ether distilled yielding a residue which, after recrystallization from ethanol, melted at 73–74° and did not depress the melting point of 6-methoxy-2-naphthyl acetate. The amount of acetate recovered was 8.3 g. (90.2%). Saponification yielded only 6-methoxy-2-hydroxymethylnaphthalene, m.p. and mixed m.p. 116–17°.

Kinetics.—The solvents and standard solutions were prepared as reported in the literature: anhydrous acetic acid,[10] 80% aq. acetone by volume,[4] standard sodium acetate solution[10] and standard *p*-toluenesulfonic acid solution.[11]

The rate measurements of the bromomethyl compounds in acetic acid were carried out as described by Winstein and co-workers.[10] The infinity titers were obtained from samples allowed to react for at least 10 half-lives. In all cases, the experimental value at infinite time agreed within experimental limits with the calculated value.

Procedure for Rate Measurements of the Chloromethyl Compounds in Acetic Acid.[11]—Since *p*-methoxybenzyl

(1) Paper I, K. C. Schreiber and Sr. M. C. Kennedy, *J. Am. Chem. Soc.*, **78**, 153 (1956). This work was supported by a grant from the National Science Foundation, for which the authors express their gratitude.

(2) A. Bryson, *Trans. Faraday Soc.*, **45**, 257 (1949).

(3) P. van Berk, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **76**, 286 (1957).

(4) J. B. Conant and W. Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924).

(5) All melting points and boiling points are uncorrected. Analyses were performed by A. Bernhardt and Galbraith Microanalytical Labs. or Elek Microanalytical Labs.

(6) F. Royle and J. Schedler, *J. Chem. Soc.*, 1643 (1923).

(7) L. Anderson and D. Thomas, *ibid.*, **65**, 237 (1943).

(8) E. Bamberger and O. Bockmann, *Ber.*, **20**, 1115 (1887).

(9) J. Shoesmith and H. Rubli, *J. Chem. Soc.*, 3098 (1927).

(10) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **70**, 812 (1948).

(11) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957).

TABLE I

MELTING POINTS AND ANALYSES OF *x*-METHOXY-*y*-HYDROXYMETHYLNAPHTHALENES AND DERIVATIVES

		Found, %				Found, %				
x	*y*	M.p., °C.	Carbon[a]	Hydrogen	M.p., °C.	Bromine[b]	Carbon	Hydrogen	Nitrogen	M.p., °C.
5	1	97–98	76.32	6.28	63–64		59.50	3.89	7.28	224–225[c]
6	1	93–94	76.33	6.52	83–84	31.98	59.55	3.69	7.22	158[c]
7	1	72–73	76.35	6.52	71–72	31.77	59.87	3.80	7.15	182–183[c]
6	2	116–117[e]	76.65	6.65	79–80	31.72	74.01	5.66	4.85	129–130[d]
8	2	64–65	76.30	6.54	44–46	31.72	74.40	5.72	4.69	124–125[d]
4	1	76–77								

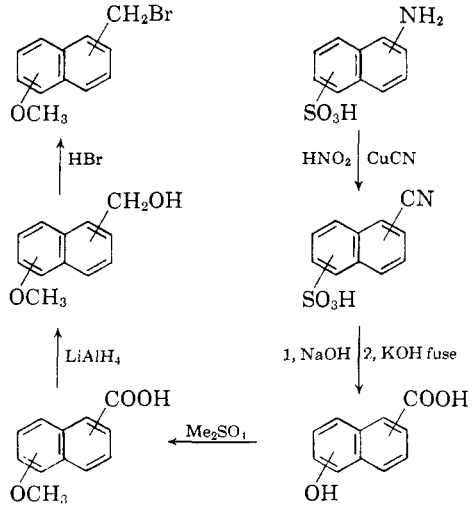
[a] *Anal.* Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.42. [b] *Anal.* Calcd. for $C_{12}H_{11}BrO$: Br, 31.82. [c] 3,5-Dinitrobenzoate, *Anal.* Calcd. for $C_{19}H_{14}N_2O_7$: C, 59.54; H, 3.69; N, 7.33. [d] Phenylurethan, *Anal.* Calcd. for $C_{19}H_{17}NO_3$; C, 74.24; H, 5.57; N, 4.55. [e] Acetate, m.p. 74–75°; *Anal.* Calcd. for $C_{14}H_{14}O_3$; C, 73.02; H, 6.13. Found: C, 73.04; H, 6.11.

chloride and 4-methoxy-1-chloromethylnaphthalene were unstable in a moist atmosphere, the compounds were not isolated. After the solvent was removed *in vacuo* at 0° the reaction vessel was immediately placed in a constant temperature bath, solvent added and 5-ml. aliquots removed and titrated as previously described. Time was counted at the start of the titration. The infinity titer was obtained from samples which were allowed to react for 1–2 hours at 80–90°. Because of the swiftness of the reaction of 4-methoxy-1-chloromethylnaphthalene, the experimental error in the rate measurements may be as high as 10%.

Procedure for Rate Measurements in 80% Aqueous Acetone.—The same procedure employed for the rate measurements in acetic acid was used. The 5-ml. aliquots were titrated with standard sodium hydroxide to the methyl red end-point.[11] Values at infinite time were not determined.

Results

The synthetic route to the compounds desired for kinetic investigation started with the commercially available naphthylaminesulfonic acids, using the reaction sequence described in detail in the Experimental section, and illustrated in the flow sheet. The yields of the methoxynaphthoic acids were always lower than those reported in the literature.



The reduction of the naphthoic acids was attempted using anhydrous ether as the solvent. However, the acids were only slightly soluble in ether. The acids dissolved readily in tetrahydrofuran, and the reductions proceeded smoothly with good yields.

The bromomethyl compounds were prepared from the corresponding carbinols by hydrobromic acid treatment in benzene solution. Since the bromomethylnaphthalenes decomposed slowly, they were prepared immediately before their use in the kinetic experiments.

The rate constants for the above prepared halides are summarized in Tables II and III. The energies and entropies of activation for some of the halides, also shown in Tables II and III, were calculated from the rate data at only two temperatures, and therefore are not as precise as might be desired. The first order rate constants have been calculated from the equation

$$K = \frac{2.303}{t_1 - t_0} \log \frac{A}{A - X}$$

where A = the amount of bromomethylnaphthalene at zero time, and $A-X$ = the amount of compound remaining at a given reaction time, as determined by the amount of acid liberated.

TABLE II

SUMMARY OF KINETIC DATA FOR HYDROLYSIS REACTIONS IN 80% AQUEOUS ACETONE

Methylnaphthalene	k_1, sec.$^{-1}$ × 10^6 (29.4 ± 0.05°)	k_1, sec.$^{-1}$ × 10^5 (49.25 ± 0.05°)	$E^{\ddagger}$, kcal. (29.4°)	$\Delta S^{\ddagger}$, e.u. (29.4°)
1-Bromo-	1.33 ± 0.04	0.986 ± 0.003	20.2	−18.8
2-Bromo-	0.937 ± .01	0.711 ± .01	20.4	−20.2
5-Methoxy-1-bromo-	1.91 ± .03	1.41 ± .03	20.1	−20.3
7-Methoxy-1-bromo-	12.5 ± .3	.....	..	....
6-Methoxy-2-bromo-	26.4 ± .3	21.0 ± .4	20.2	−12.6
8-Methoxy-2-bromo-	1.55 ± .04	.....	..	....

TABLE III

SUMMARY OF KINETIC DATA FOR ACETOLYSIS REACTIONS

Methylnaphthalene	k_1, sec.$^{-1}$ × 10^7 (23.4 ± 0.05°)	k_1, sec.$^{-1}$ × 10^6 (74.1 ± 0.05°)	k_1, sec.$^{-1}$ × 10^5 (99.1 ± 0.05°)
1-Bromo-[a]	0.037[c]	2.82 ± 0.06	3.83 ± 0.06
2-Bromo-[b]	0.015[c]	1.14 ± .06	1.39 ± 0.07
5-Methoxy-1-bromo-	.....	8.21 ± .08	.....
6-Methoxy-1-bromo-	.....	3.44 ± .07	.....
7-Methoxy-1-bromo-	.....	51.5 ± .20	.....
6-Methoxy-2-bromo-	.....	74.6 ± 1.30	.....
8-Methoxy-2-bromo-	.....	4.99 ± 0.11	.....
1-Chloro-	.....	.....	1.11 ± .03[d]
4-Methoxy-1-chloro-	3820.0 ± 490.0	.....	.....
p-Methoxybenzyl chloride	16.6 ± 0.4	.....	.....

[a] $E^{\ddagger}$, (74.1°) 27.5 kcal., $\Delta S^{\ddagger}$ (74.1°) −7.1 e.u. [b] $E^{\ddagger}$ (74.1°) 26.1 kcal., $\Delta S^{\ddagger}$ (74.1°) 12.5 e.u. [c] Calculated from higher temperatures. [d] 100.0 ± 0.05°.

The rate constant for benzyl chloride in acetic acid at 100°[12] is 1.19×10^{-6} sec.$^{-1}$. The rate constant for 1-chloromethylnaphthalene is 10 times faster at this temperature. This increased reactivity of the naphthyl compound is in accord with the data in the literature. 1-Naphthol is a stronger

(12) L. Riccobini, *et al.*, *Ricerca Sci.*, **23**, 415 (1953).

acid than phenol. Hall[13] has also shown that 1-naphthylamine is a weaker base than aniline.

The above effects are attributed to the increased capacity of the naphthalene system to stabilize a positive or negative charge.

Discussion

The rate constant of 1-chloromethylnaphthalene in acetic acid at 25° was estimated by using the extrapolated value for the 1-bromomethyl compound at 25° and the ratio of the chloro to bromo compound at 100°. By this means a value of 1.0×10^{-9} sec.$^{-1}$ is obtained. This value is probably larger than the true value, since the energy of activation for the chloro compound is expected to be larger than for the bromo compound and thus the ratio of the rate constants of the bromo to chloro compound larger at 25° than at 100°. Comparing the estimated value for the 1-chloromethylnaphthalene (1.0×10^{-9}) with the rate constant for 4-methoxylchloromethylnaphthalene (3.8×10^{-4} sec.$^{-1}$), it is observed that 4-methoxy-1-chloromethylnaphthalene reacts about 380,000 time faster than 1-chloromethylnaphthalene. Similar calculations for the benzene system shows that 4-methoxybenzyl chloride solvolyzes about 10,000 times faster than benzyl chloride in acetic acid. This is in agreement with other systems reported.[14]

p-Methoxybenzyl tosylate solvolyzes 25,000 times faster than the unsubstituted compound in 76.6 mole per cent. aqueous acetone, *p*-methoxybenzyl chloride solvolyzes 10,000 times faster than benzyl chloride in 67 vol. per cent. aqueous acetone, and *p*-methoxybenzhydryl chloride solvolyzes 5,000 times faster than benzhydryl chloride in methanol. Thus the ratio is about 60 times larger in the naphthalene system than in the benzene system.

This value serves to emphasize the strong resonance effect of the methoxy group in 4-methoxy-1-chloromethylnaphthalene. These observations show the same effects as the acidity measurements of nitronaphthols,[16] nitronaphthylamines,[12] nucleophilic displacement in nitrobromonaphthalene[15] and the oxidation–reduction potentials of naphthoquinones.[16]

In the remaining compounds reported here, one substituent is located on each of the rings of the naphthalene system. The relative reactivities of these compounds are listed in Table IV. In comparison to 4-methoxy-1-bromomethylnaphthalene, all these compounds are unreactive, indicating that the resonance effect of substituent groups transmitted through both rings of the naphthalene system is small compared to resonance effects transmitted through one ring of the same system. This is in accord with observations found in the acidity constants of nitronaphthols[1] and nitronaphthylamines[2] and in the nucleophilic displacement of bromine from 5-nitro-1-bromomethylnaphthalene.[15]

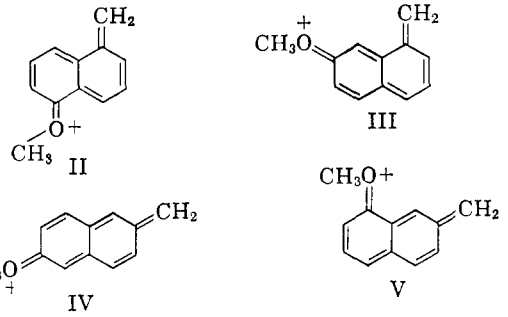
It can be seen in the resonance hybrids II–V that both rings of the system have been stripped of their benzenoid character. These structures, therefore, must be of high energy, and their contribution to the stabilization of the intermediate will be small.

TABLE IV

RELATIVE REACTIVITIES OF SOME x-METHOXY-y-BROMOMETHYLNAPTHALENES

x	y	In acetic acid		In 80% aq. acetone	
..	1	1	..	1	..
..	2	0.4	1	0.7	1
5	1[a]	2.5	..	1.4	..
6	1	1.2	..	..	..
7	1	18.3	..	9.4	..
6	2	..	65.4	..	18.2
8	2	..	4.4	..	1.7

[a] Shoesmith and Rubli report[9] a ratio of 2 in aqueous alcohol.



In contrast to previous investigations, such as the acidity of nitronaphthols,[1] nitronaphthylamines[2] and nucleophilic displacements of bromonitronaphthalenes,[15] in which the nitro group would influence the reaction center inductively or electrostatically in the same direction as the resonance effect, the methoxy group acts to enhance the rate in solvolysis reactions if resonance with the reaction center is possible, but inhibits reaction inductively or electrostatically.

The compounds listed in Table II can be divided into two groups: those in which it is theoretically possible to write resonance structures involving both substituents, and those in which this cannot be done.

In acetic acid, 6-methoxy-2-bromomethylnaphthalene solvolyzes 65 times faster than 2-bromomethylnaphthalene, 7-methoxy-1-bromomethylnaphthalene 18 times faster than 1-bromomethylnaphthalene, while 5-methoxy-1-bromomethylnaphthalene is only 2.4 times faster than its parent compound. The first two compounds show some increase in the reactivity over the respective unsubstituted compounds, but the 1,5-compound shows little, if any, enhancement due to interaction.

There are two possible explanations for this observed difference in the relative rates: the nature of the resonance structures in which the methoxy group interacts with the positively charged intermediate formed in the reaction, and a steric effect caused by a *peri*-hydrogen atom.

An examination of the resonance structures II, III, IV reveals that, in the intermediate from 6-methoxy-2-bromomethylnaphthalene, both rings are *p*-quinoid; in the intermediate from 7-methoxy-1-bromomethylnaphthalene, one ring is *p*-quinoid and one is *o*-quinoid; and in the intermediate from

(13) N. Hall and M. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932).
(14) A. Streitwieser, Jr., *Chem. Revs.*, **36**, 571 (1956).
(15) K. C. Schreiber and I. Isgur, unpublished results.
(16) V. K. LaMer and L. E. Saber, *J. Am. Chem. Soc.*, **44**, 1954 (1922).

5-methoxy-1-bromomethylnaphthalene, both rings are *o*-quinoid. It is also seen that the 5-methoxy-1-bromomethylnaphthalene is the only compound which can be affected by a *peri*-hydrogen atom.

The standard oxidation potentials for 1,2-naphthoquinone and 1,4-naphthoquinone are 0.555[17] and 0.467 v.,[16] respectively. Therefore, the *p*-quinoid 1,4-naphthoquinone is easier to form than the *o*-quinone 1,2-naphthoquinone. Willstätter[18] isolated and characterized 2,6-naphthoquinone; attempts to prepare the 1,5- and 1,7-compounds have been unsuccessful. These facts support the belief that the methoxy group of 6-methoxy-2-bromomethylnaphthalene exhibits the greatest effect because of the *p*-quinoid nature of both rings in the intermediate.

Another possible explanation would be steric inhibition of resonance by the *peri*-hydrogen atom. The methoxy group will exhibit an important resonance effect only if it is coplanar and with the aromatic ring system. In an α-position of naphthalene there are two possible coplanar conformations. However, the α-hydrogens are also coplanar, and they prevent a *peri* substituent from assuming one of the copolanar positions, reducing the resonance interaction of the substituent. In order to understand this problem better, acetolysis of 8-methoxy-2-bromomethylnaphthalene was studied. If there is no *peri*-hydrogen interference in this compound, it would be expected that the methoxy group would exhibit a resonance effect of the same order of magnitude as the methoxy group in 7-methoxy-1-bromomethylnaphthalene since both compounds have the same type of intermediate, in which one ring is *o*-quinoid and one ring is *p*-quinoid. 8-Methoxy-2-bromomethylnaphthalene solvolyzes only 4.4 times faster than 2-bromomethylnaphthalene in acetic acid. This decreased effect in 8-methoxy-2-bromomethylnaphthalene and 5-methoxy-1-bromomethylnaphthalene has, therefore, been attributed to some steric inhibition of resonance by the *peri*-hydrogen atom.

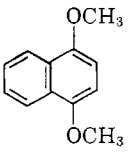
The concept of *peri*-hydrogen interference has been postulated by Sutton[19] to explain some apparently anomalous results in dipole moment studies. The results of the determinations are listed in Table V.

TABLE V

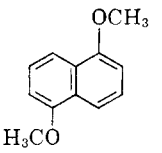
Compound	Dipole moment, D.
Quinol dimethyl ether	1.73
1,4-Dimethoxynaphthalene	2.09
1,5-Dimethoxynaphthalene	0.67
9,10-Dimethoxyanthracene	1.73

The dipole moment of quinol dimethyl ether arises from the moment about the two O–CH_3 bonds. Since there is free rotation about the O–C_{ar} bond, the methoxy groups can assume an infinite number of positions, the observed dipole moment being the summation of the dipole moments for all the possible structures.

If there were free rotation in the naphthalene compounds, their moments should be the same as quinol dimethyl ether. Because of steric interference in the 1,4-dimethoxynaphthalene, the *cis* structure as shown by structure VI makes a greater contribution, and the dipole moment is greater than that of quinol dimethyl ether.



VI



VII

On the other hand, the contribution of structure VII for 1,5-dimethoxynaphthalene is more important and thus the dipole moment is less than in quinol dimethyl ether.

Only one compound, 6-methoxy-1-bromomethylnaphthalene, was studied which cannot stabilize the positive charge by resonance in the oxygen of the methoxy group. Surprisingly, it solvolyzed somewhat (1.2) faster than the parent compound. Further studies on this question are being conducted.

Although the rate measurements in this study were carried out in both acetic acid and 80% aqueous acetone, the results used in the discussion were taken from the acetolysis data. The results in 80% aqueous acetone show the same effect but to a lesser extent.

Acetolysis reaction of benzyl systems are generally considered to be limiting in nature, *i.e.*, there is formation of a carbonium ion intermediate. Hydrolysis reactions in mixed solvents, expecially when the water content is small, are generally considered to be partially limiting in nature. The greater the carbonium ion character of the intermediate, the more pronounced will be the effect of the substituent. Therefore, the acetolysis data were used in the Discussion.

An attempt was made to measure the rates of reaction in formic acid. The study had to be discontinued because the methoxy substituted compounds were essentially insoluble in this solvent. The unsubstituted bromomethylnaphthalene compounds dissolved in this solvent with great difficulty. The initial rate constants obtained for 1-bromomethylnaphthalene and 2-bromomethylnaphthalene were 8.66×10^{-5} and 8.44×10^{-6} sec.$^{-1}$, respectively. This reaction is considered to be limiting in nature.

Since 6-methoxy-2-bromomethylnaphthalene reacted faster than the other compounds, the product run described in the Experimental Section was carried out to see if any abnormal products, formed by cleavage of the methoxy group, were produced under conditions of the kinetic experiments. However, only normal product was found in the product run.

(17) L. Fieser and M. Fieser, *J. Am. Chem. Soc.*, **56**, 1565 (1934).
(18) R. Willstätter and J. Parnas, *Ber.*, **40**, 1406 (1907).
(19) K. H. Everhard and L. E. Sutton, *J. Chem. Soc.*, 2132 (1949); 16 (1951).

Dependence of *cis*-Effect on Ring Size--Magnitude of Steric Interaction of Phenyl Rings in *cis*-1,2-Diphenylcyclopentane and Demonstration of Restricted Rotation

By D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. E. Knipmeyer

As a result of a series of oversights in the process of publication, the original paper with this title *J. Am. Chem Soc.*, **83**, 4838 (1961), was printed without its three illustrations. The missing models and spectra are now printed herewith.

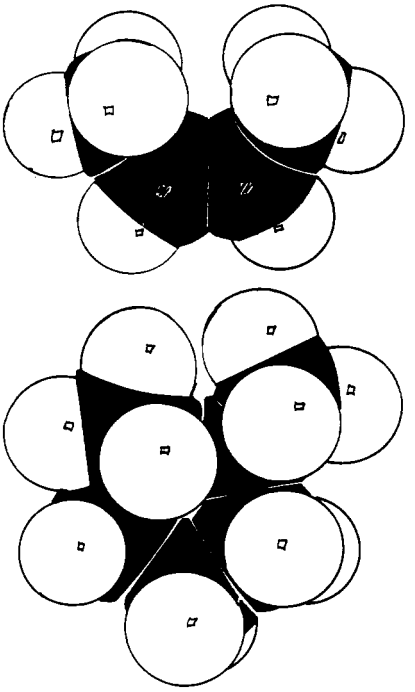


Fig. 1.—*cis*-2-Butene (top) and *cis*-1,2-dimethylcyclopentane.

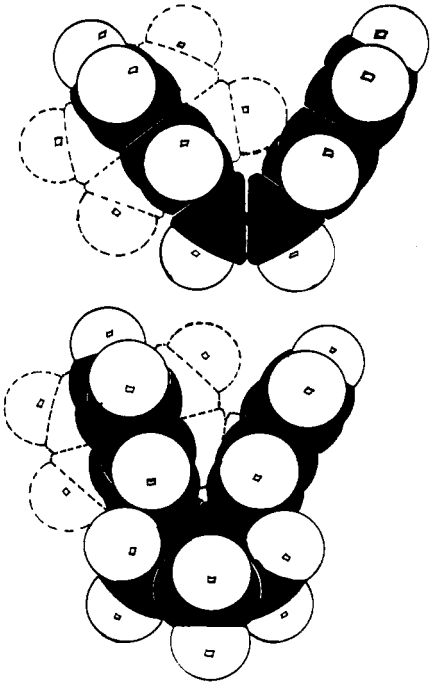


Fig. 2.—*cis*-Stilbene (top) and *cis*-1,2-diphenylcyclopentane (bottom): the dotted lines show the spacial requirements of a phenyl ring rotated 90° from its original position.

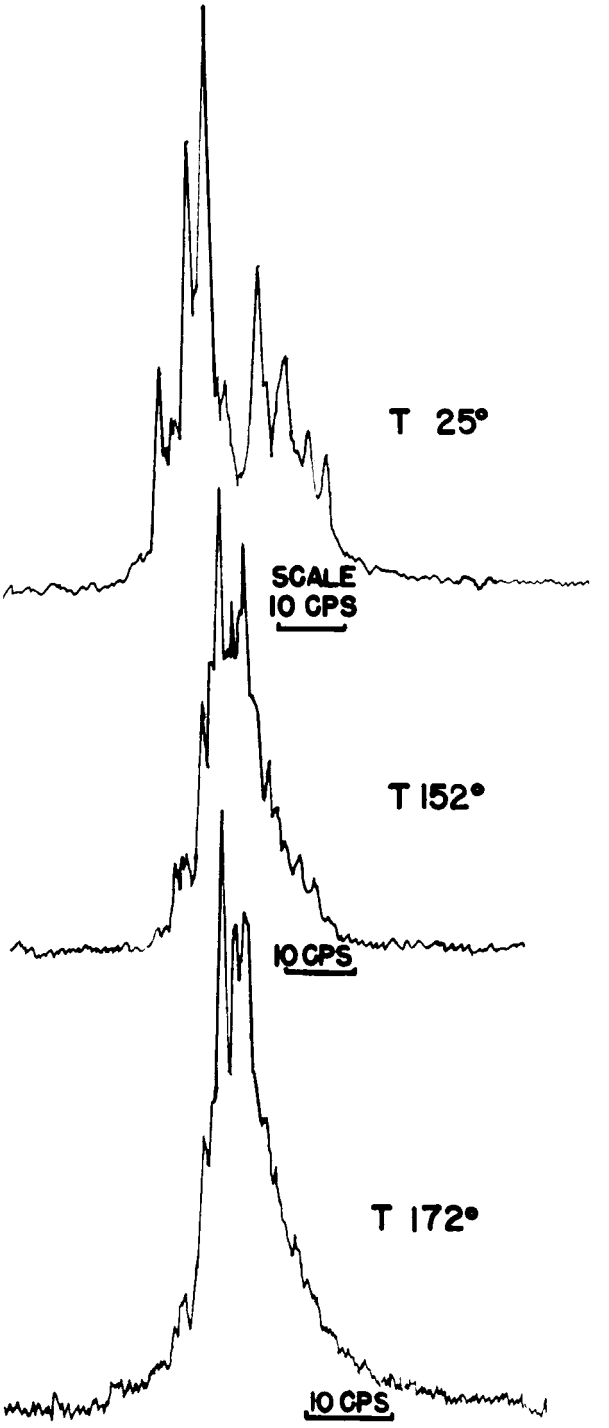


Fig. 3.—Effect of temperature on the aromatic proton spectrum of *cis*-1,2-diphenylcyclopentane.

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