

SOLVENT EFFECTS ON THE RELATIVE ACIDITIES OF ALKYL SUBSTITUTED BENZOIC ACIDS

溶劑對於烷基苯甲酸之酸性之影響

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Acid dissociation constants of nine acids, benzoic acid and eight *meta* and *para* alkyl substituted benzoic acids have been determined in carbonate free water, in 14.80 wt.%, 35.85 wt.%, and 64.18 wt. % aqueous methanol, in 20.20 wt. % and 44.46 wt. % aqueous ethanol, in 12.15 wt. %, 24.00wt. % and 50.45 wt.% aqueous acetone, and in 10.91 wt.% butyl cellosolve, at 25°C by measuring the pH's of solutions of the acids, which have been partially neutralized with aq. sodium hydroxide.

The present study was made in an attempt to gain some insight into the influence of the solvent on the relative electron releasing capacities of alkyl groups. The role that the solvent plays in shifting the balance between the two apparent mechanisms for electron release by alkyl groups has not been explored until recently. That the solvent can shift this balance was strikingly illustrated in 1952 by Berliner, Beckett, Blommers, and Newman¹ in a study of the rates of alkaline hydrolysis of *p*-alkylethylbenzoates in aqueous ethanol and in aqueous acetone.

The present study provides evidence that the relative acidities of alkyl substituted benzoic acids, and therefore the relative electron releasing capacities of alkyl substituents on benzoic acid depend on the nature of the ionizing medium.

The results indicate that in this system the *meta*-alkyl benzoic acids show

the predominant influence of the inductive effect in all solvents. On the other hand, hyperconjugative electron release by the *para*-alkyl groups is predominant in the solvents of high water content, i.e., high dielectric constant, and the inductive effect has control of relative acid strengths in the less aqueous solvents. The behavior of the *para*-substituted acids was interpreted in terms of a variation in "solvation assistance to hyperconjugation"

The facts do not appear to be compatible with the interpretation that the Baker-Nathan effect is the result of the stereochemistry of the alkyl groups, instead they support the view that the Baker-Nathan effect, i.e., hyperconjugation.

The fact that apparent electron release by the alkyl groups from the *para* position is greater than that from the meta position of benzoic acid is anticipated on the basis of the simultaneous operation of two mechanisms for electron release from the *para* alkyl groups; the *meta* alkyl groups are exerting essentially only one electronic effect on the reaction center.

EXPERIMENTAL

preparation of the solvent

Absolute methanol², absolute ethanol,³ absolute acetone,⁴ and absolute butyl cellosolve⁵ were prepared as in the literature.

*Preparation of 0.1052 N carbonate free aqueous sodium hydroxide.*⁶ was prepared from C. P. sodium hydroxide.

Preparation of 0.05M potassium biphthalate.^{7,8}

In a 500 ml. volumetric flask, 5.1054 g. of potassium biphthalate (Merck reagent grade) was dissolved and then diluted to volume with boiled distilled water and reserved for use in standardizing the pH meter. The pH of this buffer solution is 4.01.

Benzoic acid, p-methylbenzoic acid, p-ethylbenzoic acid, p-isopropylbenzoic acid, p-t-butylbenzoic acid were obtained by several crystallizations of the commercial products until further crystallizations did not raise the melting points.

m-Ethylbenzoic acid was prepared in the following way:

*p-Ethylacetanilide.*⁹ *p*-Ethylaniline was distilled under vacuum and the main fractions from two distillations were used for the acetylation, b.p. 74°/3mm. and 78°/5 mm. Thirty ml. of acetic anhydride was added dropwise to a solution of 24 g.

(0.2 mole) of the amine in 50 ml. of benzene in a casserole, while cooling in ice and stirring. The mixture was then heated to boiling and was allowed to stand at room temperature for evaporation. Crude product, a quantitative yield, 33 g., m. p. 92–93°C. was obtained. (Lit. m.p. 90.2–90.7,¹⁰ 94¹¹).

2-Bromo-4-ethylacetanilide.¹² A solution of 16.4 g (0.1 mole) of acetanilide in 32 ml. of glacial acetic acid was placed in a three-necked, round-bottomed flask provided with a thermometer, a stirrer, a dropping funnel, and a gas-outlet tube. Into this was dropped slowly 5.13 ml. (0.1 mole) of bromine at around 60°C over a period of an hour. Then 10 ml. of glacial acetic acid was added, and the mixture further stirred for 40 min. It was then poured in a thin stream into a solution of 1.25 g. of sodium bisulfate in 500 ml. of cold water with stirring. The precipitated bromide was separated by suction filtration, yield, 19.5 g. (80%), m.p. 91–92°. (lit. m. p. 92°)¹³

2-Bromo-4-ethylaniline hydrochloride. Ten grams (0.0412 mole) of 2-bromo-4-ethylacetanilide in 25 ml. of ethanol was refluxed with 30 ml. of conc. hydrochloric acid for four hours. The reaction mixture was poured into a 125 ml. Erlenmeyer flask and concentrated to about two-thirds of its original volume by heating. The mixture deposited crystals on cooling, which were collected, 8.4 g. (86%), m.p. 209–210° (decomp). It was crystallized from dilute ethanol several times more and yielded a constant melting product, m.p. 194–201°C.

3-Bromo-ethylbenzene.¹⁴ A solution of 12.9 g. (0.0544 mole) of the amine salt in 54.4 ml. of water and 13.7 ml. of conc. hydrochloric acid in a 500 ml., three-necked, round-bottomed flask equipped with stirrer, dropping funnel, and thermometer was cooled to 3°. To this solution, 4.36 g. (0.063 mole) of sodium nitrite in 27.2 ml. of water was added dropwise with stirring. The temperature of the solution was kept at 2° to 3° during the addition. After all of the nitrite solution was added the solution was stirred for another 40 min. The solution was filtered and was transferred to a larger, round-bottomed flask standing in an ice bath. One hundred fifty grams of 30% hypophosphorous acid solution was added. The cold solution was stirred for one hour and stood in a refrigerator for two days and at room temperature for an additional day. A red colored oil was separated and dissolved in ether, and the aqueous layer was extracted with ether thoroughly, the combined ether solutions were washed with water, 5% sodium hydroxide solution, and again with water and dried over calcium chloride. The ether was removed, and the

residual oil was distilled under vacuum as a colorless oil, b. p. 61-62°/4 mm., 6.7 g. (72%).

3-Ethylbenzoic acid.¹⁵ In a one-liter, three-necked, round-bottomed flask equipped with an efficient reflux condenser, a dropping funnel and a mercury sealed stirrer, 2.4 g. (0.1 mole) of magnesium turnings was placed. A calcium chloride drying tube was attached to the top of the condenser. After adding the magnesium turnings, the drying tube was attached directly to the flask, and the bottom of the flask was brushed carefully and thoroughly with luminous flame to remove all trace of moisture. After the flask had cooled, the drying tube was removed and attached to the top of the condenser. A 10 ml. portion of a solution of 18.5g. (0.1mole) of the bromide in 50 ml. of anhydrous ether, previously dried and distilled over n-butyl magnesium bromide, was added to magnesium turnings and stirred for fifteen minutes. No reaction was observed. After addition of a small crystal of iodine and stirring with gentle heating for ten minutes, reaction commenced. The rest of the bromide solution was added at such a rate that the reaction mixture was kept boiling gently for a one hour period. After the addition, the dropping funnel was rinsed with 5 ml. of anhydrous ether, and stirring was continued for an additional hour at the reflux temperature. The Grignard reagent was poured into about 40 g. of dry ice slowly with stirring, and stirring was continued until all of the dry ice had evaporated. Sixty grams of ice was added, followed by 30ml. of water and 9 ml. of conc. hydrochloric acid, and the mixture was stirred until most of the solid had dissolved and the solution had separated into two layers. The ether layer was separated and the aqueous layer was extracted with ether twice, the combined ether layers were washed with 50 ml. of water and 5 ml. of conc. hydrochloric acid. The washed ethereal solution was extracted with 10% sodium bicarbonate solution until the extract contained no 3-ethylbenzoic acid. The combined extract was acidified with conc. hydrochloric acid and extracted with ether, removal of the ether left white crystals, 6.4 g., 44%, m.p. 44-46°. Further crystallizations gave a pure product, m.p. 45.8-46.6°.

m-Isopropylbenzoic acid was prepared in the following way:

*A mixture of o-m-, and p-nitrocumenes.*¹⁶ A mixture of 57 ml. of conc. sulfuric acid and 54.2 ml. of water was added dropwise to 120g. (1 mole) of cumene with stirring at about 45°. The mixture was then stirred

vigorously for two hours, the temperature being held between 10 and 20°. To the reaction mixture 300ml. of water was added, and the organic layer was separated. The aqueous layer was extracted with ether, and the ether washed with water, 5% sodium bicarbonate, and again with water and dried over magnesium sulfate. It was distilled under vacuum and the fractions 117-119°/12 mm. was collected.

A mixture of o-, m-, and p-cumidines. Thirty and five-tenth grams (0.18 mole) of the nitrocumenes was dissolved in 100 ml. of absolute ethanol and was boiled with about 2g. of Raney nickel for a few minutes to remove any catalyst poisons. Raney nickel was prepared according to the method of Mozingo.¹⁷ The reaction mixture was cooled, and the catalyst was filtered off. Six grams of fresh Raney nickel was added, and the hydrogenation was performed for about two hours. The reaction mixture was filtered with suction. It was first distilled using a water suction pump, and then was redistilled under higher vacuum at 78°/2 mm.

A mixture of o-, m-, p-isopropylacetanilides. A solution of 27 g. (0.2 mole) of o-, m-, and p-cumidines and 45 ml. of benzene in an evaporating dish was cooled in ice bath and 30 ml. of acetic anhydride was added dropwise from a dropping funnel. After the addition, the reaction mixture was heated to boiling. It was then removed from the heat and the mixture was allowed to stand at room temperature for evaporation. The crude product, 32 g., 90% yield, was recrystallized from acetic acid, 25.9g., 81%, m.p. 102.5-104.5°.

*Bromination products of o-, m-, and p-isopropylacetanilide.*¹⁸ A solution of 35 g. (0.2 mole) of the acetanilide in 80 ml. of glacial acetic acid was placed in a three-necked, round-bottomed flask equipped with a thermometer, a stirrer, and a dropping funnel. The mixture was heated to about 60° and 10.3 ml. (0.2 mole) of bromine was added dropwise with stirring over a period of two hours. The mixture was then stirred for an additional 40 min. and allowed to stand overnight at room temperature. It was then poured in a thin stream with stirring into a cold solution of 2.5 g. of sodium bicarbonate in 100 ml. of water. The bromides were collected by filtration, yield, 52.7 g., quantitative, which on crystallization from dilute acetic acid gave 39.7 g. of the bromides, m.p. 92.3-99.3°.

A mixture of bromocumidine hydrochlorides. A solution of 36 g. (0.14 mole) of the bromide, 72 ml. of ethanol, and 72 ml. of conc. hydrochloric acid was

refluxed for four hours. The reaction mixture was transferred to an Erlenmeyer flask and evaporated to two-thirds of its volume. Crystals formed on cooling and were collected by suction filtration, 29.6 g. (85% yield), m.p. 175-188° (decomp.)

3-Bromo-isopropylbenzene.¹⁹ A solution of 75.2 g. (0.3 mole) of the mixture of the amine hydrochlorides, 75 ml. of conc. hydrochloric acid, and 300 ml. of water in a one-liter, three-necked, round-bottomed flask equipped with a stirrer, dropping funnel, and a thermometer was cooled to 3° in an ice bath. To this solution, a solution of 84 g. (1.2 moles) of sodium nitrite in 150 ml. of water was added slowly with stirring. During the addition, the temperature was kept at 2-4°. After the addition of the nitrite solution, the mixture was stirred for an additional 40 min. The mixture was then filtered and was transferred into a large, round-bottomed flask standing in an ice bath. To this mixture, 900 g. (4.09 moles) of 30% hypophosphorous acid was added, and the reaction mixture was stirred for one hour. It was then kept in a refrigerator for two days and stood an additional day at room temperature. The red-colored oil which formed was separated and dissolved in ether. The aqueous layer was extracted with ether thoroughly. The combined ether extracts were washed with water, 5% sodium hydroxide solution, and again with water, and dried over calcium chloride. The ether was removed, and the residual oil was distilled under vacuum, b.p. 79-80°/8 mm., 29.7 g. (50% yield). This procedure was followed twice more on the same scale and repeated once on a half scale.

3-Isopropylbenzoic acid. In a one-liter, three-necked, round-bottomed flask equipped with a dropping funnel, a mercury-sealed stirrer, and a reflux condenser, 2.4 g. (0.1 mole) of magnesium turnings were placed. A 10 ml. portion of solution of 19.9 g. (0.1 mole) of 3-bromo-isopropylbenzene in 50 ml. of anhydrous ether, previously dried and distilled over *n*-butyl magnesium bromide, was added to the magnesium turnings and stirred for ten minutes. The reaction commenced on gentle heating for five minutes. The heater was removed, and the rest of the bromide was added at such a rate that the reaction mixture continued to boil gently over a period of 55 minutes. After the addition, the funnel was rinsed with 5 ml. of anhydrous ether, and stirring was continued for an additional hour. The reaction mixture was poured slowly into about 40 g. of dry ice with stirring, and stirring was continued until all of the dry ice had evaporated. Sixty grams

of ice was added, followed by 30 ml. of water and 9 ml. of conc. hydrochloric acid, and the mixture was stirred until most of the solid dissolved, and the mixture had separated into two liquid layers. The aqueous layer was extracted twice with ether, the combined ether extracts were washed with 50 ml. of water and 5 ml. of conc. hydrochloric acid. The ethereal solution was then treated with 50 ml. of 25% sodium hydroxide solution three times. The alkaline aqueous washings were treated with 0.5 g. of charcoal and filtered by suction. The solution was then acidified with conc. hydrochloric acid and extracted with ether. The ether was distilled and the residual oil was dissolved in ethanol, treated with water and kept in a refrigerator. The crystals formed amounted to 6.7 g. (40% yield), m.p. 40-46°. The pure crystals melted at 49.8-50.8°.

*m-t-Butylbenzoic acid.*²⁰ A solution of 5 g. (0.03 mole) of *m-t*-butyltoluene and 15 g. (0.1 mole) of potassium permanganate in 75 ml. of pyridine and 50 ml. of water was heated to boiling for one hour. The reaction mixture was allowed to cool and the manganese dioxide was reduced to soluble manganous ion with sodium bisulfite solution. The reaction mixture was extracted with ether, and the ether solution was washed with water and dried over magnesium sulfate. The ether was removed, and white crystals remained, 1.33 g. (25.8% yield) of the benzoic acid was obtained, m.p. 122.5-125.0°. It was crystallized from dilute ethanol four times to constant melting point, m.p. 127.0-127.5°.

RESULTS AND DISCUSSION

Results

Acidic dissociation constants of benzoic acid and eight meta and para alkyl substituted benzoic acids have been determined in water and in nine aqueous organic solvents at 25°, by measuring the pH's of solutions of these acids which had been partially neutralized with sodium hydroxide. A Beckman Model G pH meter was used for the pH determinations.

The pK_a 's of the acids were calculated from the measured pH's using the Henderson Equation

$$pK_a = pH + \log[\text{conc. of salt}]/[\text{conc. of acid}],$$

a simplified relationship between the pK_a of a weak acid and the pH of its partially neutralized solution, which is applicable to acids of dissociation constant not greater than about 10^{-10} in the region of 50% neutralization,

where hydrolysis of the salt is negligible. A minimum of six independent measurements was made for each acid in each of the ten solvents, with two exception: *m*- and *p*-*t*-butyl benzoic acids have such low solubilities in water that their acidity constants in this solvent could not be determined in the present study.

The pK_a 's established in the present study are summarized in Table I.

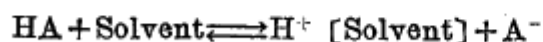
Table I. Mean pK_a 's of *m*- and *p*- alkylbenzoic acids at 25°C

Solv.	Water	10.91 %BCel	12.15 %Acet	14.80 %MeOH	20.20 %EtOH	24.00 %Acet	35.85 %MeOH	44.40 %EtOH	50.45 %Acet	64.18 %MeOH
Diel. Const.	78.54	—	71.72	71.72	66.88	64.55	61.52	52.30	47.92	47.92
Mol. Fract.	0.000	0.018	0.041	0.090	0.090	0.090	0.240	0.240	0.240	0.503
Org. Comp. H	4.20	4.69	4.69	4.43	4.72	4.99	5.07	5.73	6.00	5.90
<i>p</i> -Me	4.34	4.91	4.74	4.64	4.91	5.20	5.22	5.92	6.20	6.10
<i>p</i> -Et	4.35	5.00	4.73	4.63	4.91	5.20	5.25	5.92	6.27	6.10
<i>p</i> -Pri	4.34	5.11	4.73	4.63	4.91	5.21	5.22	5.92	6.27	6.10
<i>p</i> -But	4.40	5.21	4.72	4.61	4.91	5.22	5.21	5.92	6.27	6.10
<i>m</i> -Me	4.25	4.89	4.68	4.58	4.82	5.12	5.19	5.83	6.18	6.00
<i>m</i> -Et	4.29	4.94	4.69	4.59	4.87	5.12	5.19	5.83	6.21	6.00
<i>m</i> -Pri	4.31	5.12	4.70	4.60	4.89	5.13	5.20	5.90	6.25	6.01
<i>m</i> -But	4.28	5.21	4.71	4.59	4.90	5.18	5.21	5.92	6.28	6.03

Discussion

(1) Changes in Acid Strength with Changing Solvent.

A solvent can affect the acidity of an acid through its electrical and chemical properties. Neutral acids are dependent on the electrical properties of a solvent in that the products of ionization of the acid are charged, in contrast to the undissociated molecule.



The charged species created by the ionization process will be increasingly stabilized relative to the undissociated molecule as the polarity of the solvent increases. It is expected, and has been uniformly observed, that an increase in dielectric constant of the solvent increases the dissociation constant of an uncharged acid.

The dielectric constants (at 25°C) of the solvents used in this study vary

in the order $\text{HOH} > 14.80\% \text{ MeOH} = 12.15\% \text{ Acetone} > 20.20\% \text{ Et OH} > 24.00\% \text{ acetone} > 35.85\% \text{ Me OH} > 44.40\% \text{ Et OH} > 64.18\% \text{ Me OH} = 50.45\% \text{ Acetone}$. Examination of the data in Table I shows that each of the nine acids studied exhibits a general increase in acidity with an increase in dielectric constant of the solvent. Each acid is weakest in 50.45% acetone and is most strongly acidic in pure water. Although the variation in acidity of each compound is primarily dependent on the polarities of the solvent, the data in the solvent pairs methanol-water and acetone-water indicate that proton affinities of the solvents are also playing a role. The dielectric constant is identical for 14.80% Methanol and 12.15% Acetone. However, the dissociation constants for the acids are consistently greater in 14.80% Methanol than in 12.15% Acetone; benzoic acid is more acidic by 0.26 pK units in the aqueous methanol and the substituted acids by 0.1 pK units.

(2) Apparent Relative Electron Releasing Capacities of the Alkyl Groups

The data in Table I can further be summarized as follows:

i) All of the alkyl substituted acids are weaker acids than benzoic acid in any one solvent. This is anticipated in view of the fact that alkyl groups are always observed to be electron releasing relative to hydrogen. Therefore substitution of an alkyl group for hydrogen on the nucleus of benzoic acid should diminish acid strength.

ii) In general, the four *meta* substituted acids are collectively *more acidic* than the *para* substituted acids in a given solvent. Making an assumption that electronic effects alone are responsible for this difference, it indicates that the alkyl at the more remote *para* position have *greater electron releasing* ability than those at the *meta* position to the COOH group.

iii) Based on the same assumption, that the difference in the acidities of the benzoic acids reflects the difference in electron releasing capacities of the alkyl groups, the results show that the alkyl groups substituted in the *meta* positions release electrons in an inductive effect order in all solvents, with a little leveling in 14.80% methanol and 64.18% methanol; the alkyl groups substituted in the *para* positions show a great variation in relative electron releasing capacities, depending on the solvent used. A *Baker-Nathan order* of electron release is observed in 14.80% methanol and in 12.15% acetone, i.e., the most highly aqueous mixed solvents, with the exception of the aqueous butyl cellosolve. A straight inductive effect order is obtained in 24.00% acetone

and in 10.91% butyl cellosolve. *Mixed* orders are observed in water and in 35.85% methanol. *No differences* in electron releasing abilities among the alkyl groups is observed in 20.20% ethanol, 44.40% ethanol, and 64.19% methanol. In 50.45% acetone leveling is complete, except that the *p*-methyl group is considerably less electron releasing than the remaining three *p*-alkyl groups. Of the organic solvents added to water in the present study, methanol is the most effective in bringing out the Baker-Nathan order; this order is still observed when up to 24 mole percent. of methanol is added to water. The Baker-Nathan order is not observed from 9 mole percent. upward of acetone and ethanol, nor in highly aqueous butyl cellosolve, in which the mixed order is converted to a straight inductive effect order.

Interpretation

The present study provides evidence that the relative acidities of alkyl substituted benzoic acids, and therefore the relative electron releasing capacities of alkyl substituents on benzoic acid depend on the nature of the ionizing medium.

The results indicate that the *meta*-alkyl benzoic acids show the predominant influence of the inductive effect in all solvents. On the other hand, hyperconjugative electron release by the para alkyl groups is predominant in the solvents of high water content, i.e. high dielectric constant, and the inductive effect has control of relative acid strengths of the *para*-alkyl benzoic acids in the less aqueous solvents. These facts are interpreted as follows. A variation in "solvation assistance to hyperconjugation"²¹, can account for the behavior of the *para*-substituted acids. The hydrogen-bonding properties of solvents should vary with the basicity of the solvents. Water is definitely more basic than the organic solvents employed in this study²² and it is believed to solvate the α -hydrogen's of the alkyl groups²³. Moreover, water is even more basic, when mixed with small amounts of these organic solvents than it is in the pure state²³. It is in water and the most highly aqueous water-methanol and water-acetone mixtures that the Baker-Nathan sequence of acidities of the *p*-alkyl benzoic acids can be observed. As the mixed solvents become richer in organic component, the organic component may partially take over as the solvator for the α -hydrogen's of the alkyl groups. The organic components of the solvents are less capable of H-bonding than water molecules. However, the decrease in relative importance of hyperconjugation in the less highly aqueous

solvents also appears to be due to the absolute enhancement of the inductive effect in these solvents. This enhancement of the inductive effect can be explained by decreased dissipation of the electrostatic electronic effect of the alkyl substituent into the solvent, in favor of increased transmission through the benzene nucleus in the less polar solvents. In other words, a solvent can assist the transmission of the inductive effect through the ring. Such an interpretation would correlate with the Schwarzenbach and Egli relationship²⁴, which states that polar substituents operating by an electrostatic mechanism will show increased transmission of their electronic effects through the benzene ring in less polar solvents.

The facts do not appear to be compatible with the interpretation (preferred by some authors) that the Baker-Nathan effect is the result of the stereochemistry of the alkyl groups, namely: a change in steric interference to solvent stabilization of the ionic intermediate due to a change in the bulk of the alkyl group²⁵; changing steric release in the transition state; a variation in steric hindrance to ring solvation; and increasing steric inhibition of bond contraction with increasing size of the alkyl group.²⁶ Instead, the present work supports the view that the Baker-Nathan effect is identical with the hyperconjugation effect.

The fact that apparent electron release by the alkyl groups from the *para* position is observed to be greater than that from the *meta* position of benzoic acid is anticipated on the basis of the simultaneous operation of two mechanisms for electron release from the *para* alkyl groups; the *meta* alkyl groups are exerting essentially only one electronic effect on the reaction center.

REFERENCES

1. Berliner, E., Beckett, M. C., Blommers, E. A., Newman, B. J. Am. Chem. Soc., **74**, 4949 (1952).
2. Fieser, L. F., "Experiment in Organic Chemistry," 2nd Edition, D. C. Heath and Company, Boston, Mass., 1941, p. 360.
3. Maryott, A. A., J. Am. Chem. Soc., **63**, 3079 (1941).
4. Conant, J. B. and Kirner, W. R., J. Am. Chem. Soc., **46**, 245 (1924).
5. Halford, J. O., *ibid.*, **53**, 2944 (1931).
6. Kolthoff, I. M. and Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," 3rd Edition, The Macmillan Company, New York, 1955. p. 527.

7. Hitchcock, D.I. and Taylor, A. C., J. Am. Chem. Soc., **59**, 1812 (1937).
8. Dole, M., Glass Electrode, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 284.
9. Fiessr, L.F., Ref. 2, p. 398.
10. Berliner, E. and Berliner, F., J. Am. Chem. Soc., **76**, 6179 (1954).
11. Oline, E. L. and Roid, E.E., *ibid.*, **49**, 3150 (1927).
12. Johnson, J.R. and Sandborn, L.T., "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N.Y., 1941, p. 133.
13. Kodo, H. and Uyeo, S., Chem. Ber., **70B**, 1096 (1944).
14. Kornblum, N., "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Chapt. 7, p. 262.
15. Kharasch, M. S. and Reinmuth, O., "Grignard Reactions of Nonmetallic Substances," Pretice-Hall Inc., New York, N. Y., 1954, p. 913.
16. Gilman, H., J. Org. Chem., **19**, 1067 (1954).
17. Mazingo, R., "Org. Syntheses," **21**, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 15.
18. Carpeter, M.S., Easter, W.M., and Wood, T.F., J. Org. Chem., **16**, 586 (1951).
19. Marvel, C. S., Johnston, H.W., Neier, J. W., J. Am. Chem. Soc., **66**, 914, (1944)
20. Schlatter, M.J. and Clark, R.D., J. Am. Chem. Soc., **75**, 316 (1953).
21. Shiner, V.J., and Verbanic, C. J. Am. Chem. Soc., **79**, 369 (1957).
22. Braude, E.A., J. Chem. Soc., 1971 (1948).
23. Schubert, W.M., J. Am. Chem. Soc., **79**, 910 (1957).
24. Schwarzenbach, A. and Egli, H., Helv. Chim. Acta, **17**, 1183 (1934).
25. Price, C.C. and Lincoln, D.C. J. Am. Chem. Soc., **73**, 5836 (1951).
26. Spinner, E. J. Chem. Soc., 1590 (1956); see also Dewar, M.J.S., "Hyperconjugation," Ronald Press, N. Y., 1962.