RADICAL CHLORINATION OF SUBSTITUTED t-BUTYLBENZENES

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Abstract—A series of substituted t-butylbenzenes has been treated with sulfuryl chloride in the presence of benzoyl peroxide at 70° . For six of these compounds, the favored reaction was formation of a substituted neophy radical. While a correlation of data is obtained by application of the Hammett equation, the results may be better described by a field effect approach using a modified Kirkwood–Westheimer treatment.

THE reactions of substituted alkylbenzenes with free radicals has been frequently studied. Attention has been primarily directed toward the evaluation of substituent effects operative in the abstraction of benzylic H atoms. Thus, abstractions by the trichloromethyl radical or Br atom have been carried out on substituted toluenes,^{3,4} ethylbenzenes,^{5,6} allylbenzenes⁷ and cumenes.⁸ Abstraction from substituted toluenes has also been accomplished by the less selective Cl atom.⁹ The results of these studies support a mechanism in which electron donating substituent groups stabilize the benzylic radical intermediate. As the attacking radical is made more reactive, or alkyl substituents are introduced at the reaction site, the substituent dependence of the reaction decreases.

It was felt that an examination of the substituent effects governing formation of a radical in a position β to a substituted Ph group v/ould also be of interest. Such radicals have been generated by the addition of the trichloromethyl radical to the double bond of substituted allylbenzenes.¹⁰ However, the large magnitude of the substituent effect was considered here as evidence for a mechanism involving intramolecular transfer of a complexed radical. These results can hardly be considered as typical.

It was, therefore, decided to examine the abstraction of H atoms from a series of substituted t-butylbenzenes. Unfortunately this reaction will not occur in liquid phase using either Br atoms¹¹ or trichloromethyl radicals.¹² The reaction of t-butylbenzene with sulfuryl chloride to yield neophyl chloride, however, had long been known.¹³ A probable reaction sequence for the benzoyl peroxide initiated reaction is given below.

$$\begin{array}{ccc} O & O \\ \parallel & \parallel \\ C_6H_5C - O - O - CC_6H_5 \rightarrow 2C_6H_5 \cdot + 2CO_2 \end{array}$$
(1)

$$C_6H_5 \cdot + SO_2Cl_2 \rightarrow C_6H_5Cl + SO_2Cl \cdot$$
⁽²⁾

$$SO_2Cl \rightarrow SO_2 + Cl$$
(3)

$$\mathbf{R} - \mathbf{H} + \mathbf{Cl} \cdot \rightarrow \mathbf{H}\mathbf{Cl} + \mathbf{R} \cdot \tag{4}$$

$$\mathbf{R} \cdot + \mathbf{SO}_2 \mathbf{Cl}_2 \to \mathbf{R} - \mathbf{Cl} + \mathbf{SO}_2 \mathbf{Cl} \cdot \tag{5}$$

Subsequent studies have shown that Eq. (3) may be an equilibrium process which can be shifted to the left by excess sulfur dioxide.¹⁴ In such a situation the active abstracting agent would be the SO₂Cl radical in accord with Eq. (6).

$$\mathbf{R} - \mathbf{H} + \mathbf{SO}_2 \mathbf{Cl} \cdot \rightarrow \mathbf{R} \cdot + \mathbf{HCl} + \mathbf{SO}_2 \tag{6}$$

Fortuitously, Russell has shown that the peroxide-induced reaction of sulfuryl chloride with hydrocarbons exhibits the same selectivity as photochlorination when carried out in aromatic solvents.¹⁵ The actual abstracting agent in both cases may well be a complexed Cl atom.¹⁵

EXPERIMENTAL

Materials. Commercial SO_2Cl_2 chlorobenzene and benzoyl peroxide were utilized. All were purified via standard procedures. Bps and refractive indices or m.p. agreed with lit. values.

t-Butylbenzene, p-di-t-butylbenzene, p-bromo-t-butylbenzene, and β -chloro-t-butylbenzene were also commercially obtained. Physical properties agreed with lit. values. GLC showed minimal purities of 99%. Samples of *m*-nitro-t-butylbenzene and *m*-bromo-t-butylbenzene were graciously supplied by Professor M. M. Martin of the University of Michigan.

p-Nitro-t-butylbenzene was prepared by direct nitration of the parent compound according to the method of Nelson and Brown;¹⁶ b.p. 92–94° (1 mm); n_D^{22} 1.5324 (lit¹⁶ n_D^{20} (1.5337).

Ethyl p-t-butylbenzoate was prepared via esterification of the corresponding acid: b.p. 137–139° (11 mm); n_D^{22} 1.5019 (lit¹⁷ n_D^{23} 1.4996).

The methyl ether of p-t-butylphenol was obtained by treating that compound in base with Me₂SO₄: b.p. 99-100° (15.5 mm) (lit¹⁸ 221.4-222.4°); n_{22}^{22} 1.5026 (lit¹⁸ n_{20}^{20} 1.5030). The *meta* isomer was prepared in an analogous manner from the corresponding phenol: b.p. 99-100° (17.5 mm) (lit¹⁹ 65° (2.5 mm)); n_{2}^{22} 1.5028 (lit¹⁹ n_{20}^{20} 1.5033).

p-Chloro-t-butylbenzene was obtained by alkylation of chlorobenzene using the technique of Leser and Fabre:²⁰ b.p. 209° (lit²⁰ 112° (30 mm)); $n_D^{2^2}$ 1.5099 (lit²⁰ n_D^{20} 1.5123).

p-Iodo-t-butylbenzene was prepared from the parent hydrocarbon by treatment with I₂ and HNO₃: b,p. 128-130° (12 mm) (lit²¹ 253-254°); n_D^{22} 1.5682 (lit²¹ n_D^{20} (1.5707).

p-Cyano-t-butylbenzene was synthesized from the corresponding acid *via* conversion to the chloride, reaction with ammonia and dehydration with SOCl₂: b.p. 132–133° (21 mm) (lit²² 243–245°); n_b^{22} 1·5183.

Phenyl-p-t-butylbenzoate was synthesized via the following approach. p-t-Butylbenzoic acid was converted to its acid chloride by action of SOCl₂ in benzene. After distillation, the acid chloride was shaken with phenol in 10% KOH aq. The product was distilled from the reaction mixture: b.p. 165–168° (2 mm). The crude ester solidified on standing and was recrystallized from 95% EtOH; m.p. 60–61°. The IR spectrum showed strong absorption at 1728, 1266, 1190 (doublet) and 1070 cm⁻¹. The NMR showed a Me singlet at 1.36 ppm and a complex pattern of Ph protons from 70 to 8.15 ppm; the areas integrated 1:1. (Found: C, 80-60; H, 7-08. Calc. for C_{1.7}H₁₈O₂: C, 80-31; H, 7-08%).

p-Phenoxyl-t-butylbenzene was prepared from phenyl bromide and *p*-t-butylphenol according to the method of Sartoretto and Sowa :²³ b.p. 115–116° (0-6 mm) (lit²⁴ 172° (14 mm)); m.p. 53–54° (lit²⁴ 54°). (Found : C, 84-66; H, 7-93. Calc. for $C_{16}H_{18}O_2$: C, 84-90; H, 8-02%).

The *m*-phenoxy-t-butylbenzene was prepared in analogous manner to the above:²³ b.p. 145° (6 mm); n_D^{21} 1.5532. The IR spectrum showed strong absorption at 1225, 928, 752, 697 and 690 cm⁻¹. The NMR spectrum showed Me proton absorption at 1.25 ppm and Ph proton absorption in the range 6.5 to 7.5 ppm; the areas integrated 1:1.1. (Found: C, 84.80; H, 7.96. Calc. for C₁₆H₁₈O₂: C, 84-90; H, 8-02%).

2-Methyl-2-(*p*-nitrophenyl)chloropropane was obtained by the direct nitration of β -chloro-t-butyl-benzene.¹⁶ The product was recrystallized from 95% EtOH: m.p. 53–54° (lit¹¹ 60–62°). (Found: C, 56·30; H, 5·97; N, 6·52. Calc. for C₁₀H₁₂ClNO₂: C, 56·21; H, 5·66; N, 6·56%).

2-Methyl-2-(*p*-chlorophenyl)chloropropane was synthesized from *p*-chloro-t-butylbenzene by reaction with SO₂Cl₂¹³ b.p. 74° (0.35 mm) lit²⁵ 123.5° (10 mm)); n_D^{22} 1.5390 (lit²⁵ n_D^{2D} 1.5389). (Found: C, 58.80; H, 605. Calc. for C₁₀H₁₂Cl₂: C, 59.11; H, 5.96%).

All materials had purities in excess of 99% by GLC.

Product determination. Samples of a single t-butylbenzene, SO_2Cl_2 and chlorobenzene in the ratio 4:2:1 were prepared.* Portions of this mixture were placed in individual tubes with benzoyl peroxide, evacuated at dry ice-acetone temp and filled with N₂ before sealing. Reaction was carried out in a mineral oil bath at $700 \pm 0.5^{\circ}$ for 30 min to 15 hr. Based upon hydrocarbon consumed, the reactions were from 7 to 33% completed. The amounts of benzoyl peroxide used were less than 0.5% of the chlorobenzene. The possible error introduced into the experiment by the formation of additional chlorobenzene (Eq 2) is less than the experimental uncertainty. After reaction the samples were analyzed by GLC on a 5% SE30 column. It was shown that in all cases studied the side-chain chlorinated product had a longer retention time than nuclear chlorinated products. Side-chain chlorinated products were formed in greater quantity at 70° .† It was shown using authentic samples that the isomeric *p*-chloro-t-butylbenzene and β -chloro-t-butylbenzene caused the same response on the Varian Aerograph 202B instrument used in these studies. Peak area of all products were taken as being equivalent to the actual quantities present. A material balance between the moles of substituted t-butylbenzene consumed and the chlorinated products formed was maintained in all studies.

Determination and relative rates of reaction. Solutions of two t-butylbenzenes, SO_2Cl_2 and chlorobenzene in an approximate ratio of 1:1:3:1 were prepared. The samples were treated in analogous fashion to those used to determine products. Reaction times varied from 10 min to 4 hr. All substituted compounds were run in competition with the parent hydrocarbon except for *p*-chloro-t-butylbenzene which was run against *p*-cyano-t-butylbenzene. The treatment of data followed formal procedures.^{3,8}

RESULTS AND DISCUSSION

Unlike the examples previously cited, $^{3-10}$ the abstractable H atom of the t-butylbenzenes are completely aliphatic and are not marked by high lability. It was found that substituent groups such as OMe and carboethoxy contain hydrogens which are as easily abstracted as those in the t-Bu group. Compounds containing these substituents were omitted from this investigation when it was observed that *p*-methoxy-tbutylbenzene produced several products. Some of these may have arisen *via* hydrogen abstraction from the OMe group.²⁶

Two other possible types of side reaction exist which might also interfere with the proposed study. The substituted neophyl radicals formed by hydrogen abstraction might undergo rearrangement by Ph migration. These migrations have been observed in reactions which generate neophyl radicals from the corresponding Grignard



(7)

Reagents^{27, 28} and from the decomposition of t-butyl-3-methyl-3-substituted phenylperbutanoates.²⁹ The migration has been shown not to be synchronous with the abstraction of the H atom.³⁰ Seubold has shown that migration tendency is a function of the lifetime of the neophyl radical.³¹ He pointed out that abstraction of a Cl atom from sulfuryl chloride should occur before the neophyl radical has an opportunity to rearrange.

- * Certain solid t-butylbenzenes required the presence of additional chlorobenzene to affect solution.
- † At 40° the opposite was observed. Nuclear products predominated. These may arise by an ionic mechanism if insufficient radical initiation occurs.

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Although possible rearrangement of the primary radical appears unlikely, a serious competing reaction involves chlorination of the aromatic portion of the molecule. Boocock and Hickinbottom noted that approximately 20% of the reaction of t-butylbenzene with sulfuryl chloride yielded nuclear chlorinated products.¹¹ Side-chain reactions should be particularly unfavoured when the substituent contains additional Ph groups. In the reaction of *p*-phenoxy-t-butylbenzene the principle product was identified as 4-t-butyl-4'-chlorodiphenyl ether. The *m*-phenoxy and *p*-carbophenoxy substituted compounds also showed negligible side-chain reaction. Substantial amounts of 4-chlorodiphenyl ether and 4,4'-dichlorodiphenyl ether were also obtained from *p*-phenoxy-t-butylbenzene. These compounds can arise from starting material or the major product by formal displacement of a t-Bu group by a Cl atom. Chlorine atoms will displace bromine atoms from bromobenzene.³² Recently exchange of bromine from bromobenzene by the *p*-toluenesulfonyl radical has also been noted.³³ The displacement of an alkyl group, under similar conditions, however, warrants further study.³⁴

Because of the facile Br-Cl exchange reaction mentioned above, the bromo-tbutylbenzenes also proved unsuitable for this study. *p*-Iodo-t-butylbenzene was also observed to undergo appreciable I-Cl exchange. This was not noted in previous studies.³²

Table 1 presents the percent of side-chain reaction for those compounds ultimately utilized in this study. Side-chain chlorinated products were fully characterized for the parent compound and the p-chloro and p-nitro derivatives by comparison with samples of the pure materials. Relative rates of total reaction were obtained and converted into relative rates of hydrogen abstraction. These data are also found in Table 1.

| TABLE I. RELATIVE RATES OF HYDROGEN ABSTRACTION FROM BY CHLORINE ATOMS AT 70° χ χ σ Side-chain reaction Rel. rate of total rxn of H abstraction | | | | |
|--|-------|-----------------------------|---------------------------|-------------------------------|
| x | σ | % Side-chain reaction | Rel. rate of total rxn | Rel. rate of H abstraction |
| p-t-C₄H₀ | -0197 | 94.5 | 1.07 ± 0.03° | 1.14 ± 0.03 |
| н | 0 | 88.4 | 1.00 | 1-00 |
| p-Cl | 0-227 | 100-0 | 0.71 ± 0.05 | 0·80 ± 0·05 |
| p-CN | 0-660 | 83.6 | 0-51 ± 0-02 | 0.47 ± 0.02 |
| m-NO ₂ | 0-710 | 78-7 | 0-21 ± 0-02 | 0·19 ± 0·01 |
| p-NO ₂ | 0-778 | 81·9 | 0-48 ± 0-04 | 0.45 ± 0.04 |

* Statistically corrected.

An attempt to correlate these data by means of the Hammett equation could be made if the surprisingly unreactive *m*-nitro derivative was not utilized. Omission of this point led to a ρ value of -0.44 ± 0.01 with a correlation coefficient of -0.995. It would appear that the normal tendency of electron donating groups to stabilize

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radicals is still observed even when resonance interactions are eliminated. This is in keeping with recent results of Tedder *et al.* on substituted butanes.³⁵ An attempt had been made prior to obtaining the above value to estimate a ρ value for this reaction. Making use of the relative reactivity of aralkyl hydrocarbons to toluene and the variation in substituent effects for these compounds, a ρ value of -0.70 was crudely estimated as an upper limit for this process. It is felt that the obtained result is in fair agreement with this. The magnitude of the experimental value is also in keeping with a process not involving internal complexation of the attacking radical.¹⁰ Such a situation would not only be very unlikely in a hydrogen abstraction reaction occurring β to the aromatic ring, but should produce a larger substituent dependence.

The deviation of *m*-nitro-t-butylbenzene from the above correlation suggested that transmission of the electronic effect of the substituent might be operative *via* a field effect. Some evidence for this was obtained by noting that the *m*-nitro group exerted a greater deshielding effect on the NMR absorption of the Me protons than the *p*-nitro function. If such a field effect were operative, it could be correlated by the Kirkwood-Westheimer charge-dipole interaction model.³⁶ Application of a modified Kirkwood-Westheimer approach has already proven successful for correlation of free-radical processes in rigid saturated systems.^{37, 38} Calculated relative rates of reaction are obtained by presuming a unit of positive change to be formed in the transition state and determining the interactions with the dipole of the substituent:

$$\log\left(\frac{k_{\rm X}}{k_{\rm H}}\right) = \frac{Ae}{2\cdot3\,kT} \left\{ \left[\frac{\mu\cos\theta}{R^2 D_E}\right]_{\rm X} - \left[\frac{\mu\cos\theta}{R^2 D_E}\right]_{\rm H} \right\}$$
(8)

where A represents the actual fraction of positive charge formed, μ is the group dipole of the substituent, θ the angle between the direction of the group dipole and the extension of the carbon-substituent bond and R the distance between the center of the dipole and the center of the C—H bond being broken. The effective dielectric constant, D_E , is given by the relationship:

$$\frac{1}{D_{\rm E}R^2} = \frac{x}{Dbr} \left\{ -\frac{2[x-\cos\alpha]}{[1-2x\cos\alpha+x^2]^{3\cdot 2}} - \frac{1}{x} \left[\frac{1+\frac{[x-\cos\alpha]}{[1-2x\cos\alpha+x^2]^{1\cdot 2}}}{[1-2x\cos\alpha+x^2]^{1\cdot 2}+x-\cos\alpha} \right] + \frac{1}{x^2} \ln \left[\frac{[1-2x\cos\alpha+x^2]^{1\cdot 2}+x-\cos\alpha}{1-\cos\alpha} \right] \right\} + \frac{1}{x^2} \ln \left[\frac{[1-2x\cos\alpha+x^2]^{1\cdot 2}+x-\cos\alpha}{[1-\cos\alpha]} \right] \right\} + \frac{x}{bD_i r} \left[\frac{[x-\cos\alpha]}{[1-2x\cos\alpha+x^2]^{3\cdot 2}} \right] + \frac{[d\cos\alpha-r]}{D_i R^3}$$
(9)

In Eq. 9, R maintains the definition already given. r is the distance from the center of the molecule to the midpoint of the projection of the dipole on the carbon-substituent bond extension, d is the invariant distance from the center of the molecule to the midpoint of the C—H bond to be broken and b is equal to r + 1.5 Å. This last term is the Tanford modification which attempts to define the actual size of the cavity in which the molecule exists.³⁹ α is the angle between r and d. x is given by the expression

$$x = \left(\frac{rd}{b^2}\right)^{1/2} \tag{8}$$

and may be considered as a measure of the depth of penetration of the dipole and the removable hydrogen below the interphase of the cavity. D and D_i are respectively the dielectric constants of the solvent and the cavity. The latter was given a value of 2.2 equal to that of benzene. D was taken as 10-0, the value for sulfuryl chloride. The geometry for the *para* substituted compounds can be easily defined and is presented in Fig. I. For this system d and α have invariant values of 3.846 Å and 155° respectively.



FIG. 1 Geometry of para-substituted t-butylbenzenes

For meta isomers, rotation about the aromatic carbon-benzylic C bond can give rise to an infinite number of conformations each with different values of α and R. Average values for these terms can, however, be obtained by treating the C—H bond to be broken as its projection on the extension of the aforementioned C—C bond. In such a model d will equal 3.489 Å and α will equal 120°. Table 2 presents the values of r, R, b and x necessary to evaluate D_E for the substituted t-butylbenzenes. The calculated values of $1/R^2 D_E$ and the calculated relative rates are found in Table 3.

| Substituent | م | R | b | x |
|-----------------------------------|------|------|------|-------|
| p-t-C ₄ H ₉ | 3.49 | 7.17 | 4.99 | 0.731 |
| Н | 1.94 | 5.67 | 3.44 | 0-790 |
| p-Cl | 2.25 | 5·97 | 3.75 | 0-781 |
| p-CN | 3.40 | 7.09 | 4.90 | 0.735 |
| p-NO ₂ | 3.18 | 6.86 | 4.68 | 0-748 |
| m-NO ₂ | 3.18 | 5.77 | 4.68 | 0.712 |

TABLE 2. VALUES OF r, R, b and x for substituted t-butylbenzenes

^e Distances are in Å. Values were obtained using the method of Kilpatrick and Morse.⁴⁰

It can be immediately seen the *m*-nitro-t-butylbenzene is no longer an anomalous result. The lessened reactivity of this compound is explicable in terms of an increase in the unfavourable charge-dipole interaction. A recent study of nmr spectra of various t-butylbenzenes indicated somewhat enhanced shielding or deshielding effects for *meta* substituted over their *para* isomers in keeping with this explanation.⁴² A plot of the calculated logs of the relative rates against their experimental counterparts yields a line of slope A. This may be regarded as the possible fraction of positive charge developed in the transition state of the reaction. The value obtained for this system is 0.056 ± 0.004 with a correlation coefficient of 0.995. The degree of carbonium ion character developed in this system is small. Previous studies on the abstraction of

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| μ cos θ* | $\frac{1^{b}}{R^{2}D_{E}}$ | $(k_{\rm X}/k_{\rm H})$ calc | $(k_{\rm X}/k_{\rm H})$ exp |
|----------|---|--|---|
| -0.50 | 4.01 | 0.885 | 0-057 |
| 0-0 | 1.32 | 0-00 | 0.00 |
| 1.58 | 2-63 | - 1·833 | -0-097 |
| 3.90 | 3.97 | -6.830 | -0.328 |
| 3-98 | 3-98 | - 6.988 | -0-347 |
| 3.98 | 6-02 | - 10-590 | -0-721 |
| | μ cos θ ² -0.50 00 1.58 3.90 3.98 3.98 | $\begin{array}{c c} \mu \cos \theta^{\mu} & \overline{R^2 D_{e}} \\ \hline \\ \hline \\ \hline \\ \hline \\ -0.50 & 4.01 \\ 0.0 & 1.32 \\ 1.58 & 2.63 \\ 3.90 & 3.97 \\ 3.98 & 3.98 \\ 3.98 & 3.98 \\ 3.98 & 6.02 \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \end{array}$ | $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ |

TABLE 3. CALCULATED VALUES OF $\log (k_x/k_B)$

In debyes.

* In
$$A^{-2} \times 10^{3}$$

bridgehead hydrogens from substituted adamantanes yielded values of 0.12 and 0.17.^{37, 38} In those cases, however, a tertiary radical was generated. The enhanced stability of tertiary to primary carbonium ions can readily explain the small contribution made by the latter in the t-butylbenzene system.

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REFERENCES

- ¹ Taken in part from the M.S. thesis of Robert L. Harvey.
- ² Alfred P. Sloan Fellow (1969-71). To whom inquiries should be addressed.
- ³ E. S. Huyser, J. Am. Chem. Soc. 82, 394 (1960).
- 4 . C. Walling, A. L. Rieger and D. D. Tanner, Ibid. 85, 3129 (1963);
- ^b R. E. Pearson and J. C. Martin, Ibid. 85, 3142 (1963).
- ⁵ K. H. Lee, Personal Communication.
- ⁶ R. L. Huang and K. H. Lee, J. Chem. Soc. C, 935 (1966).
- ⁷ M. M. Martin and G. J. Gleicher, J. Org. Chem. 28, 3266 (1963).
- ⁸ G. J. Gleicher, *Ibid.* 33, 332 (1968).
- 9 G. A. Russell and R. C. Williamson, Jr., J. Am. Chem. Soc. 86, 2357 (1964).
- ¹⁰ M. M. Martin and G. J. Gleicher, Ibid. 86, 233 (1964).
- ¹¹ J. R. B. Boocock and W. J. Hickinbottom, J. Chem. Soc. 2587 (1961).
- ¹² E. S. Huyser, J. Am. Chem. Soc. 82, 391 (1960).
- ¹³ M. S. Kharasch and H. C. Brown, Ibid. 61, 3089 (1939).
- ¹⁴ G. A. Russell and H. C. Brown, Ibid, 77, 4031 (1955).
- ¹⁵ G. A. Russell, *Ibid.* 80, 5002 (1958).
- ¹⁶ K. L. Nelson and H. C. Brown, *Ibid.* 73, 5605 (1951).
- ¹⁷ A. Senlik, Istanbul Univ. Fen Fak. Mecmuasi C, 26, 67 (1961); Chem. Abstr. 55, 27205 c (1961).
- ¹⁸ W. T. Olson, et al., J. Am. Chem. Soc. 69, 2451 (1947).
- ¹⁹ M. S. Carpenter, W. M. Easter and T. F. Wood, J. Org. Chem. 16, 586 (1951).
- ²⁰ M. Leser and C. Fabre, Bull. Soc. Chim., ser 5, 23, 198 (1956).
- ²¹ E. Boedtker, Ibid. ser 3, 35, 825 (1906).
- ²² E. Kreysler, Ber. Dtsch. Chim. Ges. 19, 1706 (1885).
- ²³ P. A. Sartoretto and F. J. Sowa, J. Am. Chem. Soc. 49, 603 (1937).
- ²⁴ R. Pajeau, C.R. Acad. Sci., Paris, 218, 236 (1944).
- ²⁵ C. Ruchardt, Chem. Ber. 94, 2609 (1961).
- ²⁶ M. Arai, Bull. Chem. Soc. Japan 35, 1272 (1962).
- ²⁷ W. H. Urry and M. S. Kharasch, J. Am. Chem. Soc. 66, 1438 (1944).

- ²⁸ S. Winstein and F. H. Seubold, Jr., Ibid. 69, 2916 (1947).
- ²⁹ C. Ruchardt and H. Troutwein, Chem. Ber. 96, 160 (1963) and Refs cited therein.
- ³⁰ C. Ruchardt, Ibid. 94, 2599 (1961).
- ³¹ F. H. Seubold, Jr., J. Am. Chem. Soc. 75, 2532 (1953).
- ³² B. Miller and C. Walling, *Ibid.* 79, 4187 (1957).
- ³³ N. A. Favstritsky, Ph.D. Thesis, Oregon State University (1969).
- ³⁴ Work in progress.
- ³⁵ H. Singh and J. M. Tedder, J. Chem. Soc. B, 612 (1966) and Refs cited therein.
- ³⁶ J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys. 6, 506 (1938); F. H. Westheimer and J. G. Kirkwood Ibid. 6, 513 (1938).
- ³⁷ P. H. Owens, G. J. Gleicher and L. M. Smith, Jr., J. Am. Chem. Soc. 90, 4122 (1968).
- ³⁸ G. J. Gleicher, J. L. Jackson, P. H. Owens and J. D. Unruh, Tetrahedron Letters 833 (1969).
- ³⁹ C. Tanford, J. Am. Chem. Soc. 79, 5348 (1957).
- 40 M. Kilpatrick and G. Morse, Ibid. 75, 1846 (1953).
- ⁴¹ C. P. Smyth, Dielectric Behaviour and Structure: McGraw-Hill, New York (1955).
- ⁴² H. Sakurai and M. Ohtsuru, J. Organometal. Chem. 13, 81 (1968).