The Basicity and C^{13}–H Coupling Constants of Certain Acetals, Ketals, and Ortho Esters[1]

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The approximately linear correlation of the infrared stretching frequency of the O–D bond of deuteriomethanol with the basicity of hydrogen-bonding partners has been employed to estimate the values of pK_a for the conjugate acids of certain acetals, ketals, and ortho esters: 2,2-dimethoxypropane, -5.2; methyl orthoacetate, -6.5; methyl orthocarbonate, -8.4. Values of pK_a for the conjugate acids of a series of *para*-substituted benzaldehyde diethyl acetals are near -5.7 and are independent of the nature of the polar substituent. These values provide support for the earlier conclusion that acid-catalyzed hydrolysis of acetals and ketals occurs with pre-equilibrium substrate protonation and that acid-catalyzed hydrolysis of ortho esters does not. The C^{13}–H coupling constants for methyl *t*-butyl ether, 2,2-dimethoxypropane, and methyl orthoacetate are near 126 cps.

A substantial body of evidence requires the conclusion that acid-catalyzed hydrolysis of acetals, ketals, and ortho esters occurs with rate-determining unimolecular decomposition of these substrates following or accompanying their protonation.[4-6] Thus, the immediate products which result from the rate-determining steps are the carbonium ions derived from the substrates and, in consequence, the transition states must possess appreciable carbonium ion character. Herein lies a principal point of lack of understanding for these reactions: what is the relationship between substrate reactivity and substrate-derived carbonium ion stability? If one examines a closely related series of substrates, the intuitive expectation that carbonium ion stability and substrate reactivity should be parallel quantities is realized. For example, the second-order rate constants for hydrolysis of a series of benzaldehyde diethyl acetals,[7] methyl orthobenzoates,[8] and diethyl acetals and ketals derived from aliphatic carbonyl compounds[9] are increased by electron-donating polar substituents. Thus, those substrates yielding the most stable carbonium ions react most rapidly. The situation is, however, not so straightforward if intersystem comparisons are made. Ethyl orthocarbonate is less reactive than ethyl orthobenzoate which is less reactive than ethyl orthoformate which is less reactive than 2,2-dimethoxypropane.[6] For these substrates, reactivity is inversely related to expected carbonium ion stabilities. Several possible explanations for this behavior have been examined.[4] Certain of these depend on the relative and absolute basicities of these substrates. In addition to shedding light on questions of the relationship between structure and reactivity for the hydrolysis of acetals, ketals, and ortho esters, substrate basicities are relevant to the problem of the timing of proton transfer relative to cleavage of the covalent carbon–oxygen bond.[6]

The acid lability of the substrates of interest precludes direct measurement of the extent of protonation in aqueous solution as a function of medium acidity. As an alternative, we have employed the position of the O–D stretching frequency of deuteriomethanol in the infrared as a measure of the basicity of the weak oxygen bases to which it hydrogen bonds.[10,11] Not only is the magnitude of the frequency shift for each of the compounds relative to an appropriate nonbasic standard a measure of relative basicity but approximate values of pK_a for the conjugate acids may also be obtained by use of a relationship between $\Delta\mu$ and pK_a derived from work of Gordy.[10]

The order of basicities for compounds closely related to certain of those employed in this study has been previously examined by West and his collaborators[12] employing the O–H stretching frequency of phenol as a measure of basicity. For those compounds involved, results obtained in this study are in qualitative agreement with those obtained earlier.

In an effort to obtain further evidence concerning stabilization of polyalkoxy compounds of the type of interest here by double bond–no bond resonance, we have measured appropriate C^{13}–H coupling constants.

Experimental Section

Materials.—Diethyl acetals of substituted benzaldehydes were synthesized from commercially obtained aldehydes and triethyl orthoformate in the presence of ethanolic HCl as described by Fife and Jao.[7] Methyl orthocarbonate was prepared in low yield from chloropicrin and sodium methoxide by a slight modification of the method described for synthesis of the corresponding ethyl compound.[13] Methyl orthoacetate, 2,2-dimethoxypropane, and *t*-butyl methyl ether were obtained from the Eastman Organic Chemical Co., and were redistilled prior to use. Deuteriomethanol was obtained from International Chemical and Nuclear Corp., and was also redistilled prior to use. All compounds exhibited boiling points consistent with those reported in the literature. Purity of all compounds employed in basicity measurements was checked by recording infrared and proton magnetic resonance spectra. In no case was there evidence of impurities including the carbonyl compounds which would have resulted from partial hydrolysis.

Infrared measurements were made with the aid of a Perkin-Elmer Infracord spectrometer employing Irtran-2 cells with a path length of 0.05 mm. Positions of the O–D vibrational bands near 3.85 μ in the presence of each of the compounds of interest were determined ± 0.01 μ with spectra calibrations made with the aid of three peaks (3.508, 5.138, and 6.238 μ) in the spectrum of a polystyrene standard. Measurements were made in systems containing only deuteriomethanol and the oxygen base of interest; that is, no outside solvent was employed.[14,15] For each

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[4] E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1966).

[5] A. M. Wenthe and E. H. Cordes, *J. Am. Chem. Soc.*, **87**, 3173 (1965), and pertinent references cited therein.

[6] C. A. Bunton and R. H. DeWolfe, *J. Org. Chem.*, **30**, 1371 (1965).

[7] T. H. Fife and L. K. Jao, *ibid.*, **30**, 1492 (1965).

[8] H. Kwart and M. B. Price, *J. Am. Chem. Soc.*, **82**, 5123 (1960).

[9] M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **77**, 5590 (1955).

[10] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

[11] L. P. Hammett, *J. Chem. Phys.*, **8**, 644 (1940).

[12] R. West, L. S. Whatley, and K. J. Lake, *J. Am. Chem. Soc.*, **83**, 761 (1961).

[13] J. D. Roberts and R. E. McMahon, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 457.

[14] W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

[15] W. Gordy and S. C. Stanford, *ibid.*, **9**, 204 (1941).

compound investigated the position of the O–D vibrational band was established for three concentrations of CH_3OD (0.25, 0.5, and 1.0 M), in order to ensure that spectral shifts were not the result of self-association of deuteriomethanol. In all cases, peak positions were observed to be independent of the concentration of deuteriomethanol. In addition, for each concentration of deuteriomethanol with each compound studied, three to five individual spectra were recorded over a time interval of 1 to 3 days. In all cases, the position of the O–D band of interest was observed to be time independent assuring that substrate hydrolysis did not occur at an appreciable rate. All measurements reported in this paper were obtained at an ambient temperature near 23°. A series of measurements was also made approximately 3° above and below this temperature to ensure that small temperature variations did not significantly affect the results; no such effects were noted. All peak positions are compared to a standard obtained from solutions of 0.5 M deuteriomethanol in benzene (3.73 μ). This value is in good agreemnet with that previously obtained by Gordy.[14,15]

C^{13}-H coupling constants were measured on neat samples by linear measurement on spectra recorded with a Varian Associates A-60 nmr spectrometer. A window of 500 cps was employed. The experimental values are considered to be reliable to ±1 cps.

Results

In Table I, the positions of the O–D stretching band of deuteriomethanol dissolved in benzene and in a series of weak oxygen bases are recorded. The wavelength shift from benzene for the oxygen bases ($\Delta\mu$) decreases in the order ether > ketal > ortho ester > orthocarbonate.[12] Since the greater the shift of the O–D stretching band the greater the basicity of the solvent, it follows that these species decrease in basicity in this order as well. The basicity of benzaldehyde diethyl acetal is similar to that of the ketal 2,2-methoxypropane and is not experimentally distinguishable from those of the *p*-methyl, *p*-chloro, and *p*-methoxy derivatives. Thus, it is clear that basicities for substituted benzaldehyde diethyl acetals are an insensitive function of polar substituents.

TABLE I

BASICITIES OF A SERIES OF WEAK OXYGEN BASES

Compd	Position of O–D stretching band of deuteriomethanol, μ	$\Delta\mu$	pK_a[a] (measured)	pK_a[b] (estimated)
Benzene	3.73	...	...	...
Carbon tetrachloride	3.73	...	...	...
Methyl *t*-butyl ether	3.87	0.14	−3.7	...
2,2-Dimethoxypropane	3.85	0.12	−5.2	−4.6
Methyl orthoacetate	3.82	0.09	−6.5	−6.4
Methyl orthocarbonate	3.80	0.07	−8.4	−8.5
Benzaldehyde diethyl acetal	3.84	0.11	−5.7	−5.8
p-Methylbenzaldehyde diethyl acetal	3.84	0.11	−5.7	...
p-Methoxybenzaldehyde diethyl acetal	3.84	0.11	−5.7	...
p-Chlorobenzaldehyde diethyl acetal	3.84	0.11	−5.7	...

[a] Obtained from the linear relationship between $\Delta\mu$ and pK_a of ref 10. [b] Estimated on the basis of polar substituent effect as outlined by Bunton and DeWolfe in ref 6.

From the data of Table I, it is possible to estimate the values of pK_a for the conjugate acids of each of the oxygen bases from a linear plot of $\Delta\mu$ for CH_3OD against pK_a constructed from the best data available since the original work of Gordy.[10] The calculated values of pK_a for the compounds of interest here are included in Table I. These values should be taken with some reservations since deviations from the $\Delta\mu$ *vs.* pK_a plot are as great as ±2 pH units for certain oxygen bases.[10] However, the values of pK_a obtained from this relationship are similar to those estimated by Bunton and DeWolfe (Table I) on the basis that the effect of polar substituents on the basicity of oxygen and nitrogen bases is similar.[6] At any event, the variations in pK_a from compound to compound are certainly real and the magnitudes of the changes are considered to be quantitatively reliable owing to the modest structural differences involved. The pK_a for the conjugate acid of methyl *t*-butyl ether is similar to those of other ethers measured by the same technique,[10] but is somewhat more negative than the value (−2.9) obtained by the solvent-extraction glpc method.[16]

The C^{13}–H coupling constants for both the methyl and methoxy functions of methyl acetate, methyl *t*-butyl ether, 2,2-dimethoxypropane, and methyl orthoacetate have been measured and the results are collected in Table II. The value for the methoxy function of methyl acetate is in excellent agreement with a previously published determination.[17]

TABLE II

C^{13}–H COUPLING CONSTANTS

Compd	J_{methyl}, cps	J_{methoxy}, cps
Methyl acetate	130	147
Methyl *t*-butyl ether	125	140
2,2-Dimethoxypropane	127	142
Methyl orthoacetate	126	144

Discussion

Measurements of the basicities of acetals, ketals, ortho esters, and orthocarbonates reported herein are relevant to two points of uncertainty regarding the hydrolysis of these substrates: first, the relationship of structure and reactivity, and, second, the timing of proton transfer relative to cleavage of covalent bonds to carbon. The entire question of the mechanism of hydrolysis of these substrates has been recently discussed in depth.[4]

As indicated above, the order of reactivity for the hydrolysis of ketals, ortho esters, and orthocarbonates is opposite to the expected order of stabilities of the corresponding carbonium ions, the immediate products of the rate-determining step.[4] While several explanations have been proposed to account for this surprising result,[4,6,18,19] we direct attention to two: the direct influence of basicity differences, and the importance of substrate stabilization. The hydrolysis of all substrates under consideration here is dependent on acid catalysis. If this catalysis is of the specific acid type, involving pre-equilibrium substrate protonation, the observed second-order rate constants will be the product of the association constants for the protonation reactions and of the unimolecular rate constants for decomposition of the protonated species. While the latter quantity should certainly increase with increasing

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(16) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **84**, 1680 (1962).

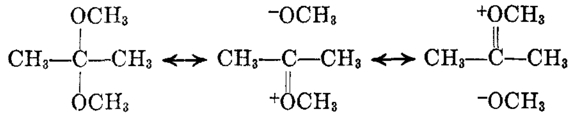
(17) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959).

(18) J. Hine, *J. Am. Chem. Soc.*, **85**, 3239 (1963).

(19) R. H. DeWolfe and J. L. Jensen, *ibid.*, **85**, 3264 (1963).

carbonium ion stability, the former will not since the alkoxy functions, which stabilize the carbonium ions through electron donation by resonance, have an electron-withdrawing polar effect. This effect is clearly seen in the pattern of relative basicities of these substrates (Table I and ref 12). To what extent do the basicity differences account for the observed order of reactivity? In the first place, the basicities differ, as one goes from ketal to orthocarbonate, by only three orders of magnitude. Since 2,2-dimethoxypropane is about 10^3 times as reactive as methyl orthocarbonate,[9,20] the differences in basicity are barely adequate to account for the magnitude of the rate difference and certainly cannot explain why the opposite order of reactivity is not, in fact, observed. In the second place, it is likely that, for some of the substrates at least, the protonation reaction is not a pre-equilibrium process.[6] We return to this point below.

Hine has suggested that the observed order of reactivities may be accounted for in terms of substrate stabilization due to double bond–no bond resonance.[18] Since there exist only two such structures for ketals, six for ortho esters, and 12 for orthocarbonates, it is possible that substrate stabilization by such resonance might be more important than transition-state stabilization by electron donation through resonance, thus accounting for the observed order of reactivities. The data presented herein suggest, but do not prove, that double bond–no bond resonance is not of great importance in the stabilization of ketals, ortho esters, and orthocarbonates. If the opposite were the case, it would show up in the basicities of the substrates since such resonance would be lost or largely lost in the conjugate acids.[21] Thus, the differences in basicities between ketals and ethers, between ortho esters and ketals, and between ortho esters and orthocarbonates should be much greater than can be accounted for in terms of polar effects alone. In Table I, the observed values for pK_a's of the conjugate acids of the compounds of interest are compared with values calculated on the basis of polar effects alone according to the method of Bunton and DeWolfe.[6] The agreement between the two sets of values is exceptionally good, suggesting that polar effects are adequate to account for observed basicities and, hence, that double bond–no bond resonance is of minor importance at best.



$$CH_3-\overset{OCH_3}{\underset{OCH_3}{C}}-CH_3 \longleftrightarrow CH_3-\overset{^{-}OCH_3}{\underset{\overset{\|}{^{+}OCH_3}}{C}}-CH_3 \longleftrightarrow CH_3-\overset{\underset{\|}{^{+}OCH_3}}{\underset{^{-}OCH_3}{C}}-CH_3$$

Determination of the magnitude of C^{13}–H coupling constants is a second indirect method for probing the importance of double bond–no bond resonance in the compounds of interest here. It is well established that the magnitude of these constants is related to the electronegativity of the atom to which the group of interest is attached.[17,22] One might suppose that, if double bond–no bond resonance is of increasing importance in the series ethers > ketals > ortho esters, the oxygen-bonded carbon atom might assume increasing carbonium ion character. Thus, we have determined the C^{13}–H coupling constants for the methyl functions of a series of compounds in which methyl groups are successively replaced by methoxy groups (Table II). These coupling constants are clearly smaller than that for the methyl group of methyl acetate, which is adjacent to a site of considerable carbonium ion character, and do not vary systematically within the series. This result provides no support for or against double bond–no bond resonance. The coupling constants for the methoxy functions of the same compounds (Table II) have also been determined and these do exhibit a definite trend with increasing methoxy group substitution. It is difficult to know if this reflects an increase in the electronegativity of the adjacent oxygen due to double bond–no bond resonance. The symmetry of the resonance structures suggests that such resonance would not lead to this effect but this conclusion is far from firmly based.

The measured basicities of a series of *para*-substituted benzaldehyde diethyl acetals are independent, within the limited sensitivity of this method, of the nature of the polar substituent (Table I). This observation suggests that measured values of ρ for the acid-catalyzed hydrolysis of these substrates,[7] of substituted phenyl-1,3-dioxolanes,[7] and of substituted methyl orthobenzoates[8] do not contain a large contribution from polar effects on the protonation reactions. The similarity of basicity of the *p*-methoxy derivative with the remaining compounds seems slightly surprising since it contains a second site of appreciable basic character. However, the pK_a of anisole is near -6.5,[10,15] suggesting that the ether site of *p*-methoxybenzaldehyde diethyl acetal may be considerably less basic than the acetal site.

The second main point in conjunction with these results concerns the timing of proton transfer relative to cleavage of the carbon–oxygen bond of the protonated substrates. The existence of general acid catalysis for ortho ester and orthocarbonate hydrolysis suggests that the specific acid-catalyzed reaction may be, in fact, general acid catalysis by the hydrated proton.[9,6] Bunton and DeWolfe have estimated the rate constants for the transfer of a proton from solvent to ketals, ortho esters, and orthocarbonates based on their calculated basicities (see above) for these compounds and the excellent assumption that the reverse reactions are diffusion controlled.[6] While the calculated rate constant for proton transfer to ketals is much greater than the over-all rate constant for the reactions, consistent with pre-equilibrium proton transfer, those for ortho esters and orthocarbonates are not, suggesting that proton transfer is either a separate reaction and partially rate determining or is concerted with breakage of the covalent bond to carbon. Our results, which lend quantitative support to the estimated basicities, strengthen these conclusions.

Registry No.—Benzene, 71-43-2; carbon tetrachloride, 56-23-5; methyl *t*-butyl ether, 1634-04-4; 2,2-dimethoxypropane, 77-76-9; methyl orthoacetate, 1445-45-0; benzaldehyde diethyl acetal, 774-48-1; *p*-methyl-

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[20] J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[21] Actually, a limited number of double bond–no bond structures may be written for the conjugate acids. These correspond, however, to the immediate products of decomposition of these species on the pathway to complete hydrolysis.

[22] P. Haake, W. B. Miller, and D. A. Tyssee, *J. Am. Chem. Soc.*, **86**, 3577 (1964).

benzaldehyde diethyl acetal, 2403-59-0; *p*-methoxybenzaldehyde diethyl acetal, 2403-58-9; *p*-chlorobenzaldehyde diethyl acetal, 2403-61-4; methyl orthocarbonate, 1850-14-2; methyl acetate, 79-20-9.

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Chemical and Physical Properties of Some Rotational Isomers of α-Haloacetanilides. A Novel Unreactive Halogen System[1]

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A number of 2′,6′-dialkyl-2-halo-N-methylacetanilides have been shown to exist in two rotomeric forms, although the major isomer I is present in such predominate amount (85–>95%) that detection of the minor isomer II is sometimes possible only by spectral means. When one of the *ortho* substituents is *t*-butyl, I and II can each be isolated in pure, crystalline form. Structural assignments for the isomers are made on the basis of previous anilide studies, shielding effects of the anilide ring on the halomethyl group, and solvent-induced (benzene) chemical shifts observed for the NCH_3 group. From these considerations the XCH_2 group in I is assigned a position *cis* and, with *ortho* substitution, nearly orthogonal to the anilide ring; in II this group is *trans* to the aromatic ring. Although crystal lattice energy is sufficient in maintaining isomeric integrity, solutions of I and II interconvert to an equilibrium mixture *via* first-order processes. The rates of interconversion are dependent upon solvent type, with either polar or hydrogen-bonding solvents inhibiting interconversion. Steric effects are important in influencing rates as found by the decrease in order, Cl > Br > I, with, however, the greatest effect on rate from increasing *ortho* substitution by *t*-butyl groups. Equilibrium constants are not markedly affected, although there is a small increase in II with increased substitution. Differential alkylation rates are easily noted between I and II upon reaction with piperidine or pyridine. Compound II reacts relatively fast, *via* SN2 processes in analogy to the spatially related secondary anilides III. The XCH_2 group in *ortho*-substituted I is hindered to facile approach of nucleophile. Consequently, reaction of I with amine is largely governed by a slow first-order rate-determining conversion to II, with subsequent fast alkylation by the latter isomer. As a result of the novel unreactive halogen system found in I, tertiary anilides comprised of most or all of this isomer will alkylate at considerably slower rates than secondary anilides. This effect of rotational isomerism on inhibiting alkylation rates appears to be partially operative even with tertiary anilides that rapidly equilibrate.

N-Alkyl groups in tertiary amides were found to be nonequivalent,[2] and certain of these materials, as a result of assymmetry and hindered rotation about the carbonyl carbon–nitrogen bond, are capable of existing as mixtures of *cis* and *trans* isomers. There have been a large number of reports further elucidating this phenomenon and extending the study to various different amide systems. Nonequivalence of N-alkyl groups or observance of *cis–trans* isomerism has been reported for certain N,N-disubstituted amides,[3] N-methylcyclohexylacetamide,[4] N-methyl carbamates,[5] N-alkyl lactams,[6] and certain anilides.[7] In these studies physical methods, particularly proton magnetic resonance, were utilized to elucidate configuration, equilibrium position, and energy barrier about the C(O)–N bond for isomeric mixtures of these compounds.

With the recent isolation into one or both of their pure forms, the phenomenon of rotational isomerism in amides has ceased to be a property observed only by spectral means. Thus, "*trans*"-N-methyl-N-benzylthioformamide[8] and a rotational isomer of N-benzyl-N-methylmesitylenecarboxamide[9] have been isolated pure from their respective isomeric mixtures. The more stable N-benzyl-N-methylmesitylenethiocarboxamide was separated into both pure rotational isomers,[10] as was the very hindered N-benzyl-N-methyl-2,4-6-tri-*t*-butylbenzamide.[11] In these cases, the less sterically hindered isomer was predominate, a finding well in keeping with previous studies of aliphatic tertiary amides.

Investigation of these phenomena in anilides, the subject of this report, has not always revealed such a consistent picture. Formanilide has been shown to exist in solution in both forms, but the sterically favored "*trans*" anilide (carbonyl oxygen *trans* to ring) was the predominate isomer only at low concentration.[12] Acetanilide appears to exist in only one form and, from infrared and X-ray analysis, the carbonyl oxygen is *cis* to the ring;[13] a similar configuration is reported for 2,6-diiodoacetanilide.[14] On the other hand, N alkylation appears to reverse the structure of the major isomer, although a minor isomer can be present. X-Ray examination and nmr analysis of N-methylacetanilide show carbonyl oxygen *trans* to the ring, while the minor component in solution possesses the *cis* configuration.[14] Nmr investigation of N-methyl- and N-ethylformanilide indicated a similar pattern.[15] Finally, 2,6-diiodo-N-methylacetanilide was shown to behave similarly, with the amide plane orthogonal to that of benzene. Moreover, these authors[14] claimed that the major and minor isomers could be separated, although no details were given.

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(1) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract O-194.

(2) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(3) L. A. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **85**, 3728 (1963).

(4) R. M. Moriarty, *J. Org. Chem.*, **28**, 1296 (1963).

(5) T. M. Valega, *ibid.*, **31**, 1150 (1966).

(6) R. M. Moriarty, *ibid.*, **29**, 2748 (1964).

(7) T. H. Siddall, III, *ibid.*, **31**, 3719 (1966).

(8) W. Walter, G. Maerten, and H. Rose, *Ann.*, **691**, 25 (1966).

(9) A. Mannschreck, *Tetrahedron Letters*, 1341 (1965).

(10) A. Mannschreck, *Angew. Chem. Intern. Ed. Engl.*, **4**, 985 (1965).

(11) H. A. Staab and D. Lauer, *Tetrahedron Letters*, 4593 (1966).

(12) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Tetrahedron*, **20**, 1811 (1964).

(13) C. J. Brown and D. E. C. Corbridge, *Acta Cryst.*, **7**, 711 (1954).

(14) B. F. Pedersen and B. Pedersen, *Tetrahedron Letters*, 2995 (1965).

(15) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Tetrahedron*, **22**, 1825 (1966).