much lower degree of aromaticity for the central ring of II than for the central rings of III or IV.

## Experimental Section

$^{11}B$ nmr spectra were measured with a Varian DP-60 spectrometer using procedures described[20] previously. Melting points are uncorrected. Solvents were purified by standard methods.

**Bis(10,9-borathiaro-10-phenanthryl) Ether (II).** A solution of 2-mercaptobiphenyl[9] (3.0 g, 0.016 mol) in dry methylene chloride (50 ml) was added dropwise to a stirred solution of boron trichloride (3.7 g, 0.032 mol) in dry methylene chloride (100 ml) under nitrogen at −78°. After 3 hr at −78°, followed by 6 hr at 0°, the solution was evaporated under vacuum, the residue dissolved in dry benzene (100 ml), aluminum chloride (0.1 g) added, and the mixture left overnight at room temperature and then filtered. Evaporation under vacuum, treatment with moist ether followed by filtration (to remove boric acid), and evaporation gave a yellow oil which solidified on treatment with petroleum ether (bp 30–60°). Fractional sublimation gave (at 190° (0.03 mm)) II as a white powder, mp 171–172°.

*Anal.* Calcd for $C_{24}H_{16}B_2OS_2$: C, 70.9; H, 4.0; B, 5.4; S, 15.7; mol wt, 406. Found: C, 70.8; H, 4.1; B, 5.4; S, 15.6; mol wt (Rast), 203 (see text).

The proton nmr spectrum in carbon disulfide consisted of multiplets at δ 7.5 and 8.4 (integrated absorptions in the ratio 3:1). The infrared spectrum (KBr disk) showed bands at 1610 (m), 1580 (w), 1480 (w), 1445 (m), 1360 (s), 1335 (s), 1270 (m), 1100 (w), 935 (w), 755 (ms), 750 (s), 735 (m), and 710 (w) K. The ultraviolet spectrum in decalin showed bands at 322 nm (log ε 3.14), 309 (3.18), 278 (3.63). The mass spectrum showed peaks at *m/e* 408 (11.7%), 407 (18.7%), 406 (parent ion, 78%), 405 (67%), 212 (27%), 211 (14%), 186 (30%), 185 (20%), 184 (base ion, 100%), 183 (10%), 152 (17%), and 139 (18%).

**Dibenzothiophene (VIII).** Evaporation of the petroleum ether used to wash II gave a white solid, from which dibenzothiophene (X) (0.6 g, 33%), mp and mmp 98–99° (lit.[23] 99°), was isolated by sublimation at 80° (0.03 mm). The uv and ir spectra were identical with those of an authentic sample (Aldrich Chemical Co.).

**Tris(2′-mercapto-2-biphenylyl)boroxine (IX).** Sublimation of the residue from VIII at 150–160° (0.03 mm) gave IX (0.89 g, 37%) which crystallized from petroleum ether (bp 30–60°) in colorless plates, mp 155–156°.

*Anal.* Calcd for $C_{36}H_{27}B_3O_3S$: C, 68.0; H, 4.3; B, 5.2; S, 15.1; mol wt, 636. Found: C, 68.1; H, 4.4; B, 5.0; S, 15.0; mol wt (Rast), 219 (see text).

The proton nmr spectrum in carbon disulfide showed multiplets at δ 7.1 and 2.95, with integrated absorptions in the ratio 8:1. The infrared spectrum (KBr disk) showed bands at 2560 (w), 1600 (mw), 1560 (mw), 1470 (m), 1450 (m), 1360 (s), 1335 (s), 1300 (m), 1274 (w), 1255 (w), 1240 (w), 1076 (w), 1010 (w), 755 (s), and 695 (s) K.

**Conversion of III to IX.** Solution of III in ethanol, evaporation to dryness, and sublimation of the residue gave IX, identical with an authentic specimen.

**Conversion of III or IX to VIII.** A solution of IX (0.1 g) in ethanolic potassium hydroxide (2.0 ml of 5%) was left overnight when VIII (0.06 g) had crystallized. The total recovery ranged from 60 to 70%. When the reaction was repeated with degassed solvents under oxygen-free nitrogen, no VIII was formed.

**Properties of III.** The proton nmr spectrum of III[5] in carbon disulfide showed multiplets at δ 8.1 and 7.1, ratio of integrated absorptions 3:6. The mass spectrum showed peaks at *m/e* 374 (24.5%), 373 (5.5%), 372 (parent ion, 74%), 371 (42%), 370 (16%), 195 (23%), 194 (base ion, 100%), 192 (13%), 177 (15%), 176 (30%), 175 (15%), 166 (17%), 151 (12%), 150 (15%), 149 (15%), 140 (13%), 138 (12%), 114 (16%), 97 (22%), and 96 (15%).

**Properties of IV.** The proton nmr spectrum of IV[6] in chloroform-*d* consisted of multiplets at δ 8.2 and 7.4, ratio of integrated intensities 1:3. The mass spectrum showed peaks at *m/e* 375 (8%), 374 (parent ion, 25%), 373 (15%), 196 (17%), 195 (base ion, 100%), 194 (25%), 166 (12%), 151 (32%), 150 (23%), 149 (13%), and 140 (15%).

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(23) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, 3, 111 (1938).

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# Nitrogen Ylides. IV. The Role of the Methyl Hydrogen Atoms in the Decomposition of Tetramethylammonium Alkoxides[1]

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**Abstract:** It has generally been assumed that the demethylation of the tetramethylammonium ion by alkoxides to give methyl ethers proceeds by a bimolecular SN2 mechanism. Although proton abstraction from the tetramethylammonium ion by strong bases to give a nitrogen ylide is a well-known process, this process has never been observed in these demethylation reactions. In this study of the decomposition of various tetramethylammonium alkoxides some proton abstraction to give alcohol is always observed, but the ratio of ether to alcohol remains constant (∼4:1), regardless of the steric requirement of alkoxide. By studying the decomposition of tetramethyl-1,1,1-$d_3$-ammonium methoxide, the dimethyl ether product was found to consist of a mixture of $CH_3OCH_3$, $CH_2DOCH_3$, $CHD_2OCH_3$, and $CD_3OCH_3$. The extent of hydrogen scrambling in the ether is greater at low temperature (60°) than at high temperature (200°) suggesting that the precursor of the ether is an ylide which rearranges *via* intramolecular hydrogen exchange. The ylide may then react with methanol by a methylene insertion into the O–H bond to give ether. A discussion of this insertion reaction is presented.

Tetramethylammonium salts generally decompose thermally to give trimethylamine and the corresponding methylated anion. Because there is a high yield of the methylated products and a simple stoichiometry,[2] most of these reactions are reported as proceeding by the nucleophilic attack of the anion on the carbon atom of one of the methyl groups in a simple bimolecular process.[3,4] However, it is known that when a strongly basic reagent, such as potassium amide[5a] or phenyllithium,[5b] is treated with the tetramethylam-

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(1) This research was supported in part by the National Science Foundation (GP-1704) and in part by the National Institutes of Health (GM-14062-01).

(2) A. T. Lawson and N. Collie, *J. Chem. Soc.*, 53, 624 (1888).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 308.

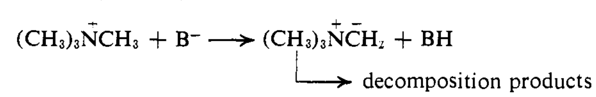
(4) J. Tanaka, J. E. Dunning, and J. C. Carter, *J. Org. Chem.*, 31, 3431 (1966).

Table I. Products Resulting from the Pyrolysis of Tetramethylammonium Alkoxides

| $Me_4N^+X^-$ | | | Temp, °C | Products[a] | | | |
|---|---|---|---|---|---|---|---|
| | | | | Alcohol | Ether | Amine[c] | Ether/amine |
| X = $OCH_3$ | $CH_3OH$[b] | | 80–120 | 0.68 | 0.60 | 0.69 | 0.87 |
| X = $OCH_3$ | $CH_3OH$ | | 80–120 | 0.74 | 0.72 | 0.87 | 0.83 |
| X = $OCH_3$ | $CH_3OH$ | | 80–120 | 1.52 | 1.28 | 1.51 | 0.85 |
| X = $OCH_3$ | $CH_3OH$ | | 80–120 | 1.77 | 1.85 | 2.14 | 0.86 |
| $Me_4N^+X^-$ + | ROM | | | | | | |
| X = F | R = $CH_3$ | M = Li | 200 | 0.44 | 1.30 | 1.56 | 0.83 |
| | R = $CH_3$ | | 200 | 0.57 | 1.63 | 2.13 | 0.77 |
| X = Br | R = $CH_3$ | M = K | 200 | 0.27 | 1.30 | 1.58 | 0.82 |
| X = Br | R = $CH_3$ | M = K | 200 | 0.33 | 1.26 | 1.60 | 0.79 |
| X = Br | R = $(CH_3)_3C$ | M = K | 200 | 0.24 | 1.19 | 1.44 | 0.83 |
| X = Br | R = $(CH_3)_3C$ | M = K | 200 | 0.40 | 1.59 | 2.02 | 0.79 |
| X = Br | R = $(C_2H_5)_3C$ | M = K | 200 | 0.37 | 1.44 | 1.81 | 0.80 |
| X = Br | R = $(C_2H_5)_3C$ | M = K | 200 | 0.54 | 1.64 | 2.12 | 0.77 |

[a] Millimoles. [b] The pure methoxide salt could not be prepared since residual methanol solvent could not be removed from the salt without premature decomposition. [c] The yield of amine amounts to 85–90% of the tetramethylammonium salt used.

monium ion, hydrogen abstraction occurs exclusively, and a nitrogen ylide is formed which may decompose in a variety of ways.[6]



$$(CH_3)_3\overset{+}{N}CH_3 + B^- \longrightarrow (CH_3)_3\overset{+}{N}\overset{-}{C}H_2 + BH \qquad \longrightarrow \text{decomposition products}$$

A determination of tetramethylammonium alkoxide decomposition products does not distinguish between the above-mentioned courses of reaction. While the isolation of alcohol would be most easily explained as resulting from a proton abstraction reaction which forms a nitrogen ylide, the isolation of ether can be explained as resulting from either an SN2 process or from nitrogen ylide formation followed by insertion of the methylene group into the O–H bond of the alcohol. To ascertain the course of these demethylation reactions, the thermal decomposition of various tetramethylammonium alkoxides and tetramethyl-1,1,1-$d_3$-ammonium methoxide was investigated.

## Results and Discussion

**Decomposition of Tetramethylammonium Alkoxides.** The simplest way to determine the extent of proton abstraction during the decomposition of tetramethylammonium alkoxides is to compare the amount of the alcohols corresponding to the various bases with the amount of methylated ethers. If proton abstraction and SN2 processes are competing, the ratio of alcohol to ether is expected to increase as the steric requirement of the base increases. Thus, the pyrolyses of "pure" tetramethylammonium methoxide and of mixtures of tetramethylammonium halides with an alkali metal methoxide, *t*-butoxide, and triethyl carbinolate were investigated.

In Table I the distributions of alcohol, ether, and amine products resulting from the decompositions at various temperatures are reported. Tetramethylammonium methoxide was the only salt prepared in the absence of extraneous alkali metal cations and halide ions, but further studies indicated that these ions did not appear to influence the course of reaction. The methoxide salt could not be isolated in pure form due to extensive solvation of the methoxide ion by methanol, and all attempts to remove this residual methanol led to a premature decomposition of the salt. Thus, the isolation of methanol in the decomposition of "pure" tetramethylammonium methoxide cannot be used as a diagnostic test for proton abstraction. However, in the salt mixture where no residual solvent was present, the isolation of alcohol indicated that at least part of the reaction proceeded by proton abstraction. Interestingly, the steric requirement of the alkoxide ion had little effect on the amount of the alcohol formed, for a 20–25% yield of alcohol based on the yield of trimethylamine was always obtained regardless of whether methoxide, *t*-butoxide, or triethyl carbinolate was used as a base. It should also be noted that in each of these reactions the ether to trimethylamine ratio was less than unity, where, if only an SN2 process had occurred, equal amounts of ether and amine should have been found. Since some alcohol was isolated, we expected that the other normal ylide decomposition products, ethylene or polymethylene, might also be found, but neither of these products was detected. Summarizing, product analysis requires that if all the products are formed *via* an ylide mechanism, the ylide must react by a carbenoid insertion mechanism to give the ether faster than it decomposes to polymethylene; if both ylide and SN2 processes are operating independently, they must give the same products in the same ratio, regardless of the steric requirement of the base.

**Decomposition of Tetramethyl-1,1,1-$d_3$-ammonium Methoxide.** Further insight into the course of the reaction was sought by following the position of the methyl hydrogen atoms of the quaternary ammonium salt through the course of the decomposition.

For example, if tetramethyl-1,1,1-$d_3$-ammonium methoxide is pyrolyzed, the location of the deuterium atoms after the reaction can be determined by submitting the dimethyl ether and methanol fractions to infrared and mass spectral analysis. In the event that an SN2 process occurs exclusively, the products will be dimethyl ether and dimethyl-1,1,1-$d_3$ ether in a ratio of 3 to 1. If a hydrogen abstraction–insertion reaction occurs, a primary isotope effect may be observed and the ratio of dimethyl ether to dimethyl-$d_3$ ether will be greater than 3 to 1. One other possible decomposition route can be envisioned. If the lifetime

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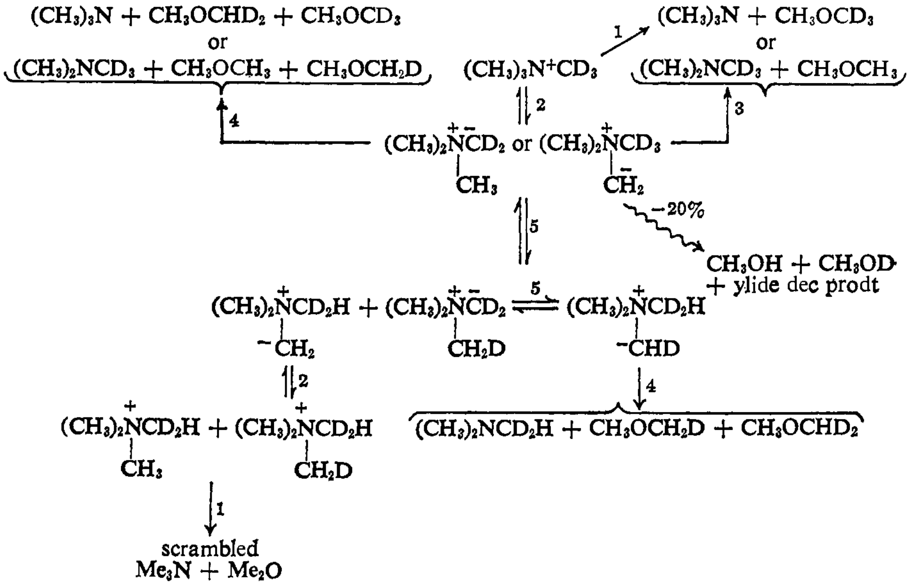
(5) (a) W. K. Musker, *J. Org. Chem.*, 32, 3189 (1967); (b) G. Wittig and M. H. Wetterling, *Ann.*, 557, 193 (1947).
(6) W. K. Musker, *J. Chem. Educ.*, 45, 200 (1968).

**Scheme I.** Possible Decomposition Paths of Tetramethyl-1,1,1-$d_3$-ammonium Methoxide



1, nucleophilic attack by methoxide (SN2)
2, reversible hydrogen (deuterium) abstraction
3, carbenoid insertion without exchange
4, carbenoid insertion (methanol or methanol-*d*)
5, intramolecular rearrangement

of the ylide is long, prior to a reaction to form dimethyl ether, intramolecular hydrogen migration can occur with consequent scrambling of the deuterium and protium. After this equilibration, the ylide can react either by insertion into methanol by a carbenoid pathway or by reprotonation and nucleophilic attack of methoxide to form products. A summary of the individual steps which were considered as possible routes to various deuterated products is given in Scheme I.

To establish the extent of a possible exchange between the tetramethyl-1,1,1-$d_3$-ammonium ion and methanol independent of decomposition, a 2.5 *M* solution of potassium methoxide was refluxed (65°) with the deuterated ammonium salt in methanol for 14 days: *no decomposition or exchange occurred.* This observation may be likened to the negligible solvent exchange of tetramethylammonium deuterioxide in $D_2O$ at 100° for 358 hr.[1,7] However, Leitch[8] recently observed that appreciable hydrogen exchange does occur at 130°.

The results of the pyrolysis of tetramethyl-1,1,1-$d_3$-ammonium methoxide and of mixtures of tetramethyl-1,1,1-$d_3$-ammonium bromide and potassium methoxide are reported in Table II. As before, the salt mixtures were used to obtain higher temperatures and to eliminate all possibility of exchange with residual methanol. The ratio of ether to amine for the "pure" methoxide and the mixtures was similar but a consistently higher ratio was observed for the "pure" methoxide. By comparing the yield of methanol to that of amine *in salt mixtures* where no residual methanol was present, it was concluded that at least 20–25% hydrogen abstraction occurred. To confirm the assumption that hydrogen abstraction occurred in the decomposition of tetramethyl-1,1,1-$d_3$-ammonium methoxide, a sample of hydrogen gas (evolved when the methanol product was treated with potassium metal) was analyzed by mass spectrometry. The mass spectrum showed that much HD and little $D_2$ was present and established conclusively that a hydrogen abstraction process did occur in conjunction with the decomposition.

**Table II.** Pyrolysis of Tetramethyl-1,1,1-$d_3$-ammonium Methoxide

| Temp, °C | Time, hr | Products[a] Methanol | Ether | Amine | Ether/amine |
|---|---|---|---|---|---|
| 55–60 | 76 | 2.75[c] | 1.50 | 1.77 | 0.85 |
| 55–60 | 76 | 2.32[c] | 1.35 | 1.58 | 0.85 |
| 80–90 | 48 | 2.82[c] | 2.42 | 2.77 | 0.87 |
| 80–90 | 48 | 2.81[c] | 2.46 | 2.85 | 0.86 |
| 120 | 24 | 2.07[c] | 1.98 | 2.23 | 0.88 |
| 120 | 24 | 2.02[c] | 1.87 | 2.11 | 0.89 |
| 150[b] | 55 | 0.32[d] | 1.25 | 1.57 | 0.79 |
| 150[b] | 55 | 0.35[d] | 1.34 | 1.68 | 0.80 |
| 200[b] | 48 | 0.38[d] | 1.37 | 1.90 | 0.72 |
| 200[b] | 48 | 0.58[d] | 1.96 | 2.55 | 0.77 |

[a] Millimoles. [b] Equimolar mixtures of tetramethyl-1,1,1-$d_3$-ammonium bromide and potassium methoxide. [c] Since excess methanol solvent could not be removed without decomposition, the methanol/amine ratio in these samples is not a reliable indication of the extent of proton abstraction. [d] The ratio of alcohol to amine in these samples indicates that ~25% of the reaction proceeds by proton abstraction.

The results of the mass spectral analysis of the dimethyl ether fraction indicated that considerable deuterium scrambling had occurred. At temperatures ranging from 60 to 200° (Table III), the amount of mono- and dideuterated ether *decreased* from 25 to 5% of the total dimethyl ether as the temperature was *increased.* At 200° no dimethyl-$d_1$ ether was detected; however, as the pyrolysis temperature was lowered, this product amounts to about 55% of the scrambled dimethyl ether.

The results can be explained by reference to the steps presented in Scheme I. Since a direct nucleophilic displacement (1) and/or a concerted hydrogen abstraction–insertion mechanism (2, 3) gives unscrambled products, no combination of these two modes of attack

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(7) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, 77, 521 (1955).
(8) Dr. L. C. Leitch, personal communication.

**Table III.** Yield of Deuterated Dimethyl Ether Products Obtained from the Decomposition of Tetramethyl-1,1,1-$d_3$-ammonium Methoxide

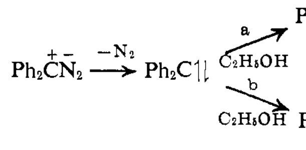
| Temp, °C | Products,[a] % | | |
|---|---|---|---|
| | $CD_3OCH_3$ | $CD_2HOCH_3$ | $CDH_2OCH_3$ |
| 200 | 20.8 | 5.1 | *c* |
| 150 | 17.8 | 6.6 | 4.2 |
| 136[b] | 15.1 | 7.8 | *c* |
| 120 | 15.8 | 8.4 | 6.0 |
| 80 | 12.4 | 11.4 | 10.8 |
| 60 | 11.2 | 11.1 | 14.4 |

[a] Yield determined by mass spectral analysis of the dimethyl ether formed in the reaction. [b] Sealed tube reaction in methanol solvent. [c] None detected.

can adequately account for the observed products. However, a hydrogen abstraction mechanism in which the ylide is formed as a distinct species (2), followed by a carbenoid insertion of a $CD_2$ or $CH_2$ group of the ylide into the O–H bond of methanol (4), can account for both the dimethyl ether and the dimethyl-1,1-$d_2$ ether which were formed in these pyrolyses.

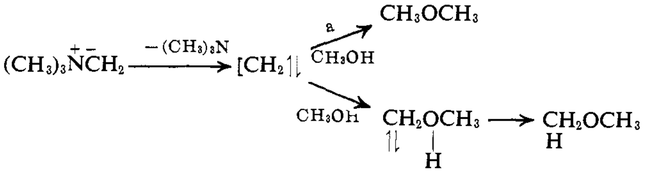
Typical carbene reactions of some nitrogen ylides have been reported. Wittig[9] demonstrated that the ylide resulting from the treatment of trimethyl-*n*-butoxymethylammonium bromide with phenyllithium could be inserted into cyclohexene to give 7-*n*-butoxynorcarane. A carbene was also suggested[10] as a precursor to the ethylene and polymethylene products which form when trimethylammonium methylide is not stabilized by Lewis acids. In an attempt to form ylide adducts of organoboranes, the methylene group was found to insert into the B–C bond of the organoborane.[11] A concerted mechanism was suggested for this process, but a carbene mechanism could not be ruled out.

No examples of methylene insertion by an ylide into an O–H bond have been reported, but O–H insertions have been observed with carbenes obtained from the thermal decomposition of diazo compounds. For example, diphenylcarbene reacts with water and ethanol in acetonitrile at 85° to give diphenylmethanol and diphenyl methylethyl ether.[12] Since the rate of disappearance of diphenyldiazomethane was not affected by the substitution of deuterium oxide for water, a hydrogen abstraction process was not the rate-determining step in the decomposition. Therefore, either a direct methylene insertion into the O–H bond occurred (a) or the reaction progressed by way of an intermediate complex (b), followed by an intramolecular hydrogen transfer.



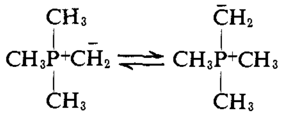
It was suggested[12] that the insertion occurred with singlet diphenylcarbene before it could undergo spin inversion to the more stable triplet state. In the absence of hydroxylic solvents, the singlet carbene decays to the triplet and the major product is tetraphenylethylene.

We feel that the mechanism of the reaction between the ylide and methanol to give the dimethyl ether may be analogous to the mechanism proposed for the reaction of diphenylcarbene with ethanol to give ether. In a like manner, in the absence of hydroxylic species, the



ylide reacts to give ethylene and polyethylene, suggesting that the singlet carbene undergoes spin inversion to the triplet carbene and then reacts by a radical process. This decomposition route has been observed in the decomposition of tetramethylammonium amide in liquid ammonia at 45°.[5] No methylation occurred, and the products were ethylene and polyethylene.

An explanation for the formation of dimethyl-$d_1$ ether at lower temperature can be offered by postulating intramolecular hydrogen migration (5) in the ylide prior to the formation of products. A similar intramolecular hydrogen migration in trimethylphosphonium methylide has recently been observed by nmr spectroscopy.[13] The two sets of doublets present at room temperature merge to a singlet at 100° showing that all the hydrogen atoms become equivalent at elevated temperature. An intramolecular equilibration was proposed to account for this observation.



$$CH_3\overset{CH_3}{\underset{CH_3}{P^+}}\bar{C}H_2 \rightleftharpoons CH_3\overset{\bar{C}H_2}{\underset{CH_3}{P^+}}CH_3$$

From these observations of the products of the decomposition of tetramethyl-1,1,1-$d_3$-ammonium methoxide, we cannot definitely confirm that an ylide was involved in the step leading to the formation of the dimethyl ether since ylide formation and rearrangement could have been completely independent of the decomposition reaction. However, in order for an SN2 process to occur, the ylide must be reprotonated prior to reaction (2, 1), and this two-step process seems unlikely at 200° in the absence of solvent.

The temperature dependence of the distribution of deuterated ethers indicates that either an SN2 process occurs prior to ylide rearrangement or an abstraction–insertion process occurs faster than rearrangement as the temperature is increased. However, the observation that even at 200° some dimethyl-1,1-$d_2$ ether was formed indicates strongly that some ylide was produced.

We have used the fact that neither scrambling nor reaction occurred in the presence of methanol at reflux temperature (65°) to rule out a solvent exchange process which was independent of reaction, although the lower effective base strength of methoxide in methanol could have accounted for this unreactivity. However, when a methanolic solution (~1 *M*) of tetramethyl-1,1,1-$d_3$-ammonium bromide and potassium methoxide was heated to 135° in a sealed tube for 24 hr, both the

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[9] G. Wittig and D. Krauss, *Ann.*, 679, 34 (1964).

[10] V. Franzen and G. Wittig, *Angew. Chem.*, 72, 417 (1960).

[11] W. K. Musker and R. R. Stevens, *Tetrahedron Letters*, 995 (1967).

[12] D. Bethall, D. Whittaker, and J. D. Callister, *J. Chem. Soc.*, 2466 (1965).

[13] H. Schmidbaur and W. Tronich, *Angew. Chem.*, 79, 412 (1967).

solvent exchange reaction and the decomposition reaction to give dimethyl ether and trimethylamine were observed. The decomposition reaction was found to be 60% complete at this time. If it is assumed that the only deuterium found in the solvent after reaction resulted from a deuterium abstraction from the quaternary ammonium salt by methoxide, followed by an insertion of the $CD_2$ group into methanol to give dimethyl-1,1-$d_2$ ether, it would be expected that the methanol solvent would contain 0.36% methanol-$d$ (Table III). However, an analysis of the methanol solvent showed that it contained 1.8% methanol-$d$. Since this value is much higher than expected for an abstraction–insertion reaction, an exchange process, independent of the decomposition reaction, must have occurred. It may be argued that the ethers were formed in an SN2 process and that the formation of methanol-$d_2$ occurred by an independent ylide process, but it is not necessary to propose competing mechanisms. In the analysis of the dimethyl ether product, no dimethyl-$d_1$ ether could be detected, but dimethyl-1,1,1-$d_3$ ether and dimethyl-1,1-$d_2$ ether were formed in almost identical amounts as observed in the decomposition reactions without solvent (Table III) suggesting that the mechanism of formation of these ethers in solution and in the dry salt is similar. However, since dimethyl-$d_1$ ether was not formed, it can be concluded that intramolecular exchange in the ylide was minimized in the presence of a protonic solvent and that the solvent exchange process did not approach equilibrium prior to ether formation. Therefore all the products can be accounted for by the reaction of the ylide with solvent as presented in Scheme I, steps 2–4. Thus, reactions which involve the demethylation of quaternary ammonium salts by strong bases must take into account the role of the metal hydrogen atoms. The positive charge which is generally attributed to the nitrogen atom is certainly felt by the hydrogen atoms of the methyl group.

It is worth noting that when the demethylation of tetraalkylammonium salts is carried out in the presence of anionic substances which are strong nucleophiles, but weak bases, an SN2 process predominates to the exclusion of proton abstraction processes.[14] Thus, thiophenoxide ion reacts with the triethylmethylammonium ion in the dry state and also in nonprotonic solvents to give primarily demethylated products. No evidence for the presence of ethylene—the Hofmann elimination product—was reported.[14]

## Experimental Section

The infrared spectra were obtained using a Beckman IR-12 spectrometer, and the mass spectra were obtained with a C.E.C. Model 21-104 spectrometer. Gas chromatographic analyses were carried out with an Aerograph Model-A-90-P3 chromatograph.

**Preparation of Tetramethylammonium Fluoride.** A solution of 185 ml of 1.15 *M* tetramethylammonium hydroxide was titrated with a 2.75 *M* solution of hydrogen fluoride to the methyl red end point. The bulk of the water was removed on a rotary evaporator, and 20 ml of anhydrous methanol was added. The methanol was removed by vacuum distillation, and the product was dried by heating to 140° under high vacuum for 24 hr. The yield of tetramethylammonium fluoride was 20 g (215 mmol).

**Preparation of Lithium Methoxide.** Into a dried, three-necked flask fitted with a condenser and a dry nitrogen inlet, was distilled 225 ml of methanol which had been treated with 8.0 g of magnesium metal turnings under nitrogen. The reaction of 5.0 g of lithium metal with the dry methanol was carried out at slow reflux by the intermittent addition of small pieces of lithium wire through the condenser and cooling of the reaction mixture in an ice bath. The bulk of the methanol was removed on a rotary evaporator and complete drying was accomplished by heating the white powder to 95° under high vacuum for 24 hr. The yield of lithium methoxide was 25 g (658 mmol). The equivalent weight by HCl titration to a phenolphthalein end point was 37.9 (calcd 37.9).

**Preparation of Tetramethylammonium Methoxide.** Into a dried, 100-ml flask containing a magnetic stirrer, drying tube, and 75 ml of dry methanol, were added 1.52 g (40 mmol) of lithium methoxide and 3.72 g (40 mmol) of tetramethylammonium fluoride. The solution was stirred vigorously at reflux temperature for 12 hr. The precipitated lithium fluoride was removed by centrifuging, and the clear slightly yellow solution of tetramethylammonium methoxide was decanted into a dried, 100-ml flask. The bulk of the methanol was removed on a rotary evaporator leaving a slightly yellow crystalline solid coating on the walls of the flask. The product was further dried by heating to 40° under high vacuum for 24 hr. The titration of three samples of the product with HCl to a phenolphthalein end point gave an equivalent weight of 135.7 (calcd 105.2) indicating that 1 mol of solvent was trapped in the salt.

**Pyrolysis of Tetramethylammonium Alkoxide Salts. General Procedure.** All pyrolysis were carried out on a standard vacuum line having a three-trap manifold. The sample to be pyrolyzed was placed in a small tube connected to the vacuum line. The reaction system was closed off from the pump and opened to a manometer so that the evolution of gaseous products could be monitored.

The temperature of the reaction tube was then gradually raised using an oil bath until the evolution of gases was evident by a change in pressure. As the products of the pyrolysis gradually filled the system, they were bled off into a trap cooled in liquid nitrogen. Evolution of products from the various pyrolyses occurred at temperatures ranging from 60 to 200° and over periods of time ranging from 4 to 76 hr depending upon the particular salt or mixture of salts being pyrolyzed. Heating was continued until the evolution of gaseous products ceased or became extremely slow.

The procedure for pyrolysis of equimolar mixtures of tetramethylammonium halides and alkali metal alkoxides was modified to increase the yield of products by placing the mixture in a sealed glass tube which was completely immersed in a heated oil bath for 24-hr periods. The sealed tubes with breakable side arms were opened on the vacuum line and the products bled into the trap, cooled in liquid nitrogen. The total yield of products was obtained by allowing the gases and volatile liquids to expand into a previously calibrated volume.

The products of the pyrolysis of tetramethylammonium methoxide were methanol, dimethyl ether, and trimethylamine. These products were quantitatively separated by interaction with a potassium mirror to remove methanol, which was measured both by hydrogen isolation and by pressure difference. The remaining amine and ether were treated with an equal volume of hydrogen chloride gas to give the amine hydrochloride salt, which was weighed. The amount of ether was obtained both by pressure difference and by isolation after passing the mixture of unreacted hydrogen chloride and dimethyl ether *repeatedly* through a U tube containing cotton saturated with quinoline.

**Pyrolysis of Equimolar Mixtures of Potassium *t*-Butoxide and Tetramethylammonium Bromide.** The pyrolysis of the mixture was carried out in an evacuated sealed glass tube at 200° for 24 hr. The tube was opened on the vacuum line and the gaseous liquid products were bled into a trap cooled in liquid nitrogen. Most of the trimethylamine was removed from the product mixture by fractionation through a trap cooled in a Dry Ice–acetone bath. The remaining products were condensed into a previously weighed, 1-ml bulb fitted with a stopcock. Samples of the material in the bulb were then removed with a syringe and subjected to quantitative gas chromatographic analysis using a 5-ft aluminum column packed with 20% TCEP supported on 60–80 mesh Firebrick at a temperature of 85°. The *t*-butyl alcohol and methyl *t*-butyl ether were identified by comparison with retention times of known samples on the same column and by comparison of infrared spectra of known samples with material collected from the chromatograph. Exactly the same procedure was used for pyrolysis of mixtures of potassium trimethylcarbinolate and tetramethylammonium bromide except that the column temperature used for the separation of triethylcarbinol and methyl triethylcarbinylmethyl ether was 145°.

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[14] M. Shamma, N. C. Deno, and J. F. Remar, *Tetrahedron Letters*, 1375 (1966).

**Preparation of Dimethyl-1,1,1-$d_3$ Ether.** A U tube fitted with ball joints at each end and containing 5.75 mmol of metallic potassium was loosely filled with glass wool in a nitrogen atmosphere and attached to the manifold of a vacuum line. The bottom of the tube was heated slowly with a flame, causing the potassium to vaporize and condense on the glass wool and on the sides of the tube, thus distributing it over a large surface area in a thin layer. The U-tube was cooled in liquid nitrogen, and 6 mmol of dried methanol was condensed into it. The tube was then closed from the rest of the system and the methanol was allowed to vaporize and react with the potassium film.

At numerous intervals the hydrogen formed in the reaction was removed through a trap cooled in liquid nitrogen which retained unreacted methanol but allowed hydrogen to pass through the vacuum pump. The unreacted methanol was then recondensed in the U tube containing potassium until all metallic surfaces were replaced by a white film of potassium methoxide. After all the potassium had reacted, the tube was evacuated and heated to 100° to drive out excess methanol.

After again cooling in liquid nitrogen, 5 mmol of methyl-$d_3$ bromide was condensed into the U tube which was opened to a cyclic system connected to a Toepler pump. The methyl-$d_3$ bromide was vaporized and recycled for 4 hr through the U tube containing glass wool coated with potassium methoxide, where it slowly formed potassium bromide and dimethyl-1,1,1-$d_3$ ether.

A third U tube was filled with quinoline-saturated cotton, evacuated, and opened to the system containing the mixture of unreacted methyl-$d_3$ bromide and dimethyl-1,1,1-$d_3$ ether. This mixture was recycled continuously through the quinoline-saturated cotton until the total pressure in the system decreased no more. During this operation the methyl-$d_3$ bromide salt of quinoline could be seen forming on the cotton.

After 4 hr, the purified dimethyl-1,1,1-$d_3$ ether was removed from the recycling system to another part of the vacuum line where it was repeatedly passed through a Dry Ice-acetone bath at −78° to remove traces of quinoline vapor. After this treatment the infrared spectrum of the dimethyl-1,1,1-$d_3$ ether (3 mmol) showed no peak at 1000 cm$^{-1}$ characteristic of methyl-$d_3$ bromide. A deuterium analysis of the ether showed it to contain 47.9 mol % deuterium.

**Preparation of Dimethyl-$d_6$ Ether.** Dimethyl-$d_6$ ether was prepared in exactly the same way as that described for the preparation of dimethyl-1,1,1-$d_3$ ether except that the potassium film was first reacted with methyl-$d_3$ alcohol to get deuterated potassium methoxide. The infrared spectrum of the product showed no absorption in the carbon–hydrogen stretching region (3000 cm$^{-1}$) and no absorption at 1000 cm$^{-1}$ indicating that it was free of undeuterated material and methyl-$d_3$ bromide.

**Preparation of Tetramethyl-1,1,1-$d_3$-ammonium Bromide.** Into a previously evacuated tube on the vacuum line was condensed 9 mmol of methyl-$d_3$ bromide and 10 mmol of trimethylamine. The temperature of the tube was raised to −78° by the use of a Dry Ice–acetone bath and the previously frozen gases liquified in the bottom of the tube. After 4 hr, the liquid mixture turned white and tetramethyl-1,1,1-$d_3$-ammonium bromide was observed in the bottom of the tube.

**Preparation of Tetramethyl-1,1,1-$d_3$-ammonium Fluoride.** Into 75 ml of dried methanol contained in a 100-ml, round-bottomed flask was mixed 4.30 g (25.5 mmol) of tetramethyl-1,1,1-$d_3$-ammonium bromide, 4.40 g (14 mmol) of silver sulfate, and 2.42 g (14 mmol) of barium fluoride. The reaction flask was fitted with a condenser and covered with aluminum foil to prevent photodecomposition of silver bromide. The mixture was stirred at reflux temperature for 12 hr, filtered to remove silver bromide and barium sulfate, treated with 0.5 g of activated carbon to remove the yellow color of the solution, and refiltered to remove the carbon. The bulk of the solvent was removed on a rotary evaporator and complete drying was accomplished by heating under high vacuum to 90°. The yield of the white hygroscopic tetramethyl-1,1,1-$d_3$-ammonium fluoride was 2.60 g (27.1 mmol).

**Preparation of Tetramethyl-1,1,1-$d_3$-ammonium Methoxide.** A solution of lithium methoxide (27 mmol) in methanol (50 ml) was prepared in a dry 100-ml, three-necked flask. A solution of 2.6 g (27 mmol) of tetramethyl-1,1,1-$d_3$-ammonium fluoride in 20 ml of dry methanol was added slowly from a dropping funnel. As the fluoride salt was added, a white solid precipitated. After the addition of the fluoride salt the mixture was allowed to stir at reflux temperature for 12 hr.

The lithium fluoride precipitate was removed by centrifuging and the clear liquid layer was decanted into a round-bottomed flask. Most of the solvent was removed on a rotary evaporator at reduced pressure. Further drying was accomplished by heating the slightly yellow crystalline solid to 40° under high vacuum. Titration of two samples of the product with dilute HCl to a phenolphthalein end point gave an equivalent weight of 138.8 indicating that 1 mol of methanol was trapped in the salt.

**Pyrolysis of Tetramethyl-1,1,1-$d_3$-ammonium Methoxide.** The pyrolysis of the partially deuterated salt was carried out exactly as described for the undeuterated material except that the temperature of the reaction was kept constant and was not increased at the end of the reaction. Complete reaction at a given temperature was assured by allowing the reaction to continue until no further evidence for the evolution of gases was seen on the manometer over a 1-hr period. The reaction times for the deuterated salts varied from 24 to 76 hr depending on temperature. The results are summarized in Table III.

**Pyrolysis of Equimolar Mixtures of Tetramethyl-1,1,1-$d_3$-ammonium Bromide and Potassium Methoxide.** Since tetramethyl-1,1,1-$d_3$-ammonium methoxide melted with rapid decomposition at 80 to 90°, an attempted pyrolysis of this material at temperatures above 120° would be somewhat meaningless since the salt would decompose long before it reached the higher temperature. Therefore, equimolar mixtures of tetramethyl-1,1,1-$d_3$-ammonium bromide and potassium methoxide were prepared and samples of the mixture were pyrolysed in sealed tubes in the same way as described for the other mixtures. The results are summarized in Table III.

**Reaction of Tetramethyl-1,1,1-$d_3$-ammonium Bromide with Potassium Methoxide in Methanol (65°).** In 4 ml of dry methanol was dissolved 0.78 g (4.9 mmol) of tetramethyl-1,1,1-$d_3$-ammonium bromide and 0.72 g of potassium methoxide (10.3 mmol). This solution was allowed to reflux with stirring under a nitrogen atmosphere for 14 days. At the end of this time, no characteristic methanol-$d$ absorption at 840–880 cm$^{-1}$ was observed in the infrared spectrum of the methanol solvent ruling out any exchange that may have occurred in the preparation of the tetramethyl-1,1,1-$d_3$-ammonium methoxide at low temperature. To determine the limit of detection of methanol-$d$, it was found that 2% methanol-$d$ in methanol clearly showed the characteristic peak at 840–880 cm$^{-1}$.

**Reaction of Tetramethyl-1,1,1-$d_3$-ammonium Bromide with Potassium Methoxide in Methanol (135°).** In 1.3 g of anhydrous methanol was dissolved 0.32 g (2 mmol) of tetramethyl-1,1,1-$d_3$-ammonium bromide and 0.28 g (4 mmol) of potassium methoxide. The solution was mixed for about 10 min and the precipitated potassium bromide was filtered under nitrogen. The filtrate containing tetramethyl-1,1,1-$d_3$-ammonium methoxide and a little dissolved potassium bromide was placed in a small brass tube fitted with a gas valve capable of withstanding pressures in the range of 10–25 atm without leakage. The tube was then cooled in liquid nitrogen, evacuated, and heated to 135° for 24 hr.

The tube was attached to the vacuum line and the valve was opened to allow the products to condense into a trap cooled in liquid nitrogen. Fractionation of the products through a −78° trap partially separated the dimethyl ether and trimethylamine products from the excess methanol. The ether and amine fraction were separated by the usual method to give 1.22 mmol of dimethyl ether but only 0.4 mmol of trimethylamine, indicating that some amine remained dissolved in the excess methanol. Calculations from the weight of the methanol fraction indicated a total of 40.5 mmol of product and solvent methanol.

A portion of the solvent methanol from the reaction was treated with potassium, and the hydrogen evolved was analyzed for deuterium by mass spectrometry. The mass spectrum showed that the hydrogen contained 3.5% H-D and a negligible amount of $D_2$. Since a total of 40.5 mmol of solvent and product methanol was collected after the reaction was stopped, a total of 0.73 mmol of $CH_3OD$ (3.5/2% of 40.5) must have been formed in the reaction.

**Absence of Stevens Rearrangement during the Decomposition of Tetramethyl-1,1,1-$d_3$-ammonium Methoxide.** A 10-g sample of tetramethyl-1,1,1-$d_3$-ammonium methoxide was pyrolyzed at 90°, and the products were passed through a trap cooled in a Dry Ice–acetone bath which condensed most of the methanol but allowed trimethylamine and dimethyl ether to pass. The amine and ether mixture was condensed with an equal volume of methyl bromide to quaternize the amine. The quaternary ammonium salt which formed was treated with freshly prepared silver oxide in water to form the quaternary ammonium hydroxide.

After filtering the precipitated silver bromide and drying under vacuum the hydroxide was pyrolyzed at 150°. As the products of the pyrolysis formed, they were passed into a trap cooled in a pentane slush bath at −130°. The trace of vapor which passed through the −130° trap showed no absorption at 950 $cm^{-1}$ indicating the absence of ethylene.

**Analysis for Total Deuterium in Dimethyl Ether. Infrared Analysis.** Since the carbon–deuterium bond absorbs in the infrared near 2100 $cm^{-1}$, it was decided to use this band to spectrophotometrically determine the extent of carbon–deuterium bonding in the dimethyl ether obtained from the various pyrolyses at different temperatures. Initially, mixtures of undeuterated and deuterated dimethyl ether were prepared with known concentrations of deuterium. These mixtures were then placed in a gas cell at the same pressure and the absorbance spectrum was recorded for each mixture between 1850 and 2400 $cm^{-1}$. The area under the curves for the sample was determined using a planimeter and a plot of peak are against the percentage of carbon–deuterium bonds present was prepared. The known mixtures were prepared from purified samples of dimethyl ether, dimethyl-1,1,1-$d_3$ ether, and dimethyl-$d_6$ ether.

The standardization graph was prepared in the expected range of per cent deuterium from zero to 16% at a relatively high pressure in the cell so that the areas under the peaks would be large even at low concentrations of deuterium and the error in determining areas would be reduced. The spectra of samples of ether from the pyrolyses were recorded using the same cell at the same pressure as the standard samples and the area under the respective peaks were determined. Using the graph prepared from known mixtures it was found that all the samples contained between 11.3 and 11.9% deuterium. The spectrophotometric results were consistent with a deuterium analyses by the falling-drop method.

**Mass Spectral Analysis.** The mass spectra of undeuterated and half-deuterated dimethyl ether were obtained for comparison with the spectra of the partially deuterated mixtures (Table IV). Examination and comparison of the spectra of undeuterated and half-deuterated ethers provided a basis for some simplifying assumptions which allowed for a rather quantitative analysis of the ether products (Table IV). The spectrum of dimethyl ether showed no peak above *m/e* 46 except a trace of *m/e* 47 whereas the dimethyl-1,1,1-$d_3$ ether showed large peaks at *m/e* 48 and 49. Since the molecular weights of mono- and dideuterated ethers are 47 and 48, respectively, it was assumed that they would contribute little to the characteristic dimethyl-1,1,1-$d_3$ ether peak at *m/e* 49, and, therefore, that the peak at *m/e* 49 in the spectrum of the product ether was due only to dimethyl-1,1,1-$d_3$ ether. Using a sample of pure dimethyl-1,1,1-$d_3$ ether to get the sensitivity of the spectrometer to this material, the per cent of this trideuterated ether was calculated.

**Table IV.** Relative Peak Intensities (*m/e* 42–52) in the Mass Spectra of Samples of Dimethyl Ether[a]

| *m/e* | $CH_3$-$OCH_3$ | $CH_3$-$OCD_3$ | 80° [b] | 135° [c] | 120° [b] | 200° [b] |
|---|---|---|---|---|---|---|
| 42 | 9 | 4 | 8 | 7 | 7 | 7 |
| 43 | 30 | 12 | 27 | 29 | 22 | 23 |
| 44 | 15 | 8 | 22 | 20 | 14 | 13 |
| 45 | 1720 | 22 | 1114 | 1400 | 1060 | 1135 |
| 46 | 781 | 26 | 887 | 683 | 781 | 718 |
| 47 | 23 | 641 | 412 | 240 | 368 | 313 |
| 48 | 2 | 1085 | 220 | 223 | 235 | 264 |
| 49 | 0 | 754 | 93 | 115 | 119 | 156 |
| 50 | 0 | 38 | 3 | 4 | 5 | 6 |
| 51 | 0 | 4 | 0 | 1 | 1 | 1 |
| 52 | 0 | 3 | 0 | 0 | 0 | 0 |

[a] All peak intensities are normalized to the spectrum of $CH_3OCH_3$ taken at a pressure of 49.86 μ. [b] Reaction mixture. [c] Sealed tube.

After the amount of dimethyl-1,1,1-$d_3$ ether in the mixture was determined, the peaks corresponding to this substance were subtracted from the original spectrum leaving a spectrum which contained all ether other than dimethyl-1,1,1-$d_3$ ether and having no peak above *m/e* 48. Assuming that all of the peak at *m/e* 48 was due to dimethyl-1,1-$d_2$ ether and that the sensitivity of the instrument to dimethyl-1,1-$d_2$ ether was the same as to dimethyl-1,1,1-$d_3$ ether, the amount of dimethyl-1,1-$d_2$ ether was calculated.

Since the total deuterium in the sample is known from elemental analysis and from the infrared data, the amount of deuterium determined as the tri- and dideuterated ether could be subtracted from this total to give the amount of deuterium present as dimethyl-$d_1$ ether. The yield of each of these ethers is presented in Table III.

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# Mass Spectrometry. I. Evidence for Phenyl, Hydrogen, and Methyl Migrations in the Unimolecular Decomposition of Acetophenone Azine Induced by Electron Impact

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**Abstract:** Evidence is reported in the mass spectrum of acetophenone azine for the occurrence of phenyl, methyl, and hydrogen rearrangements. Multicentered rearrangements are involved in a number of the fragmentations, although in at least two instances the data appear to be consistent with both 1,5 and 1,3 migrations of methyl and phenyl. The driving force for these rearrangements appears to be electron delocalization in both reactant and product ions and the formation of stable neutral molecules.

Mass spectral studies have been reported for a number of nitrogen-containing derivatives of aldehydes and ketones.[4] Such studies assume importance for two reasons. First, considerable attention has been paid

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(4) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, Chapter 10, and references cited therein.

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