

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., THE RESEARCH DEPARTMENT, AMOCO CHEMICALS CORP., WHITING, INDIANA]

Mass Spectra of *ortho*-Substituted Diarylmethanes

BY SEYMOUR MEYERSON,^{1a} HARALD DREWS,^{1b} AND E. K. FIELDS^{1b}

RECEIVED JUNE 19, 1964

Mass spectra of *o*-methyl diarylmethanes show a characteristic intense peak corresponding to the rearrangement 1. Precise parallels occur in the spectra of *o*-hydroxydiarylmethanes and *o*-methyl diaryl ethers. The reaction is another member of a large class of ionic unimolecular rearrangement-dissociation processes that are highly sensitive to molecular structure and insensitive to interchange of O, CH₃, and other such atoms and groups.

Among the prominent features of mass spectra of hydrocarbons generally—and for that matter, of derivatives containing any of the common heteroatoms other than nitrogen—is a pattern of alternating intensities: high at odd mass numbers, low at even. This pattern has been rationalized on the basis that hydrocarbon ions of odd mass number contain even numbers of electrons that can be paired to yield relatively stable configurations.² Ions of even mass number, on the contrary, contain odd numbers of electrons and so are all free radicals. Moreover, a fragment ion arising by fission of a single bond in a hydrocarbon molecule necessarily has an odd mass number. Formation of a fragment ion of even mass number must involve fission of at least two bonds and often bond-making also; thus entropy considerations might well discriminate against such ions. Against this background, any even-mass-number peak of intensity close to or greater than that of adjacent odd-mass-number peaks is anomalous and suggests that

groups.⁴ Spectra of the first two such products investigated, those derived from dimesityl and di-*p*-xylyl sulfones, clearly ruled out the originally suspected biaryls. The spectrum of the former showed an intense peak at mass 132, corresponding to a C₁₀H₁₂⁺ ion; that of the latter showed a similarly intense peak at 118, corresponding to C₉H₁₀⁺. Each of these ions contains one carbon atom more than an aryl group of the original sulfone; thus, the two aryl groups appeared to be bonded *via* a side-chain carbon atom rather than directly. Further investigation confirmed the diarylmethane structure so inferred. Moreover, the products from pyrolysis of dimesityl and di-*p*-xylyl sulfones were both found to be *o*-methyl diarylmethanes, and the decomposition process that gave rise to the C₁₀H₁₂⁺ and C₉H₁₀⁺ ions to be characteristic of this class of compounds.

Table I shows partial spectra of diphenylmethane and eleven methylated derivatives. Included in the spectra are the parent and parent less CH₃ ions and all frag-

TABLE I
PARTIAL SPECTRA OF METHYLATED DIPHENYLMETHANES, ArCH₂Ar'

Mass	Ion	Positions of methyl groups in												
		Ar ...	2	2,4	2,5	2,6	3,4	2,4,6	2,5	3,4	2,4,6	2,4,6	2,3,4,5	
		Ar'	3	4	3	2	4	3,5	3,4	3,5	2,4,6	2,3,4,5	
		Molecular weight	168	182	210	210	210	224	224	224	238	252	280	
Parent	Parent	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
Parent less 15	Parent less CH ₃	14.2	134	159	159	133	139	159	130	218	130	1346	114	
104	C ₈ H ₈ ⁺	...	46.4	140	
118	C ₉ H ₁₀ ⁺	40.9	96.6	89.8	107	
132	C ₁₀ H ₁₂ ⁺	95.6	88.7	224	...	
146	C ₁₁ H ₁₄ ⁺	229	

some special factors favor the reaction giving rise to the ion in question. Investigation of such rearrangement-dissociation processes—analogueous to the photochemist's "molecular" decompositions—has proved especially fruitful in revealing underlying relationships between mass spectra and molecular structure, and thus in facilitating construction of a systematic chemistry of gaseous ions.^{3a,b} Incidentally, many of these processes find close parallels in radiolytic, photolytic, and pyrolytic systems.^{3a}

Such a process was indicated by an intense even-mass-number peak in the spectra of products from pyrolysis of *o*-methyl diaryl sulfones. These sulfones eliminate sulfur dioxide on pyrolysis to give hydrocarbons composed of the elements of the two aryl

ment ions of even mass number having intensities greater than 35% that of the parent ion. In the unsubstituted compound, the parent ion yields the most intense peak. In the derivatives, loss of CH₃—to give most likely a phenyltropylium ion, by analogy with loss of CH₃ from xylene to give tropylium⁵—produces an intense peak, often the most intense in the spectrum. Relative intensity of the parent less CH₃ ion is markedly higher in the spectrum of the 3,4-, 3',4'-tetramethyl compound, the only one with no *ortho* substitution, than in any of the other spectra studied. The reason lies apparently in the absence of competition in this one case from the rearrangement-dissociation process evidenced by intense even-mass-number peaks. One such peak appears in the spectrum of each *ortho*-substituted compound. In each case it has a mass 13 units greater than that of the original

(1) (a) American Oil Co.; (b) Amoco Chemicals Corp.

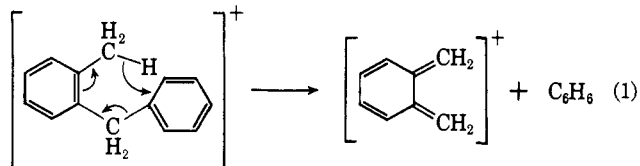
(2) M. Magat, *Discussions Faraday Soc.*, **10**, 113 (1951).

(3) (a) S. Meyerson and J. D. McCollum, *Adv. Anal. Chem. Instrumentation*, **2**, 179 (1963); S. Meyerson, *J. Phys. Chem.*, **68**, 968 (1964). (b) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 107f.

(4) H. Drews, E. K. Fields, and S. Meyerson, *Chem. Ind. (London)*, 1403 (1961).

(5) S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

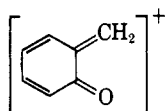
ortho-substituted aryl group. Moreover, in each case the spectrum contains a metastable peak^{3a} that establishes the parent ion as an immediate precursor of the even-mass-number fragment ion (1).



To confirm the *o*-methyl group as the source of the migrating hydrogen atom, we measured the spectra of *o*-methyl diphenylmethane unlabeled and singly deuterated in the methyl group. The pertinent spectral data, given in Table II, show that deuterium retention in the $C_8H_8^+$ ion is approximately 66%, in agreement with the value expected if the migrating atom comes solely from the methyl group and no isotope effect is involved.

The precise structure written for the resultant ion is arbitrary; it could be formulated just as plausibly as benzocyclobutene. The structure of the apparently similar $C_8H_8^+$ ion produced by loss of C_2H_4 from tetralin is also not certain, but available data furnish some basis for a choice in that case. The dominant primary decomposition reaction of 2-methyltetralin under electron impact is loss of C_3H_6 to give $C_8H_8^+$, the same product as in the unsubstituted compound; that of 1-methyltetralin, on the contrary, is loss of CH_3 , with loss of C_2H_4 appearing as a minor competing process.⁶ Thus, loss of C_2H_4 from tetralin almost certainly occurs by rupture of the two β carbon-carbon bonds. An energetics argument, based on the appearance potential of the $C_8H_8^+$ ion in the spectrum of tetralin, has been advanced for the *o*-quinodimethane structure in preference to that of benzocyclobutene.⁷ Elimination of ethylene from tetralin is most simply formulated as occurring by a reverse Diels-Alder reaction, apparently a favored path in molecules that satisfy the structural requirements.⁸⁻¹⁰

The even-mass-number peak that distinguishes *ortho*-substituted from non-*ortho*-substituted diarylmethanes has a precise parallel in diaryl ethers.¹¹ The underlying reaction has been formulated analogously; thus, the ionic product from *o*-tolyl ethers, for example, is represented as



Both reactions fall into a larger class of *ortho* rearrangements typified by respective loss of H_2O , CH_3OH , and H_2O from *ortho*-methylated aryl acids, derived methyl esters,^{12,13} and benzyl alcohols.¹⁴

A structure problem originating in another investi-

(6) H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 453.

(7) H. Wincel and Z. Keçki, *Nukleonika*, **8**, 216 (1963).

(8) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961).

(9) K. Biemann, *Angew. Chem. Intern. Ed. Engl.*, **1**, 98 (1962).

(10) H. Audier, M. Fétizon, and W. Vetter, *Bull. soc. chim. France*, 1971 (1963).

(11) R. I. Reed and J. M. Wilson, *Chem. Ind. (London)*, 1428 (1962).

(12) F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959).

(13) T. Aczel and H. E. Lumpkin, *ibid.*, **33**, 386 (1961).

(14) T. Aczel and H. E. Lumpkin, *ibid.*, **32**, 1819 (1960).

TABLE II
LABEL RETENTION IN $C_8H_8^+$ FROM
2-METHYL-*o*-DIPHENYLMETHANE
A. Partial spectra, 70 e.v.

Mass	Ion ^a	Relative intensity	
		Unlabeled	Labeled
103	$C_8H_7^+$	8.5	3.6
104	$C_8H_8^+$	47.4	19.6
105	$C_8H_9^+$	11.0	30.5
106	10.6
Parent	$C_{14}H_{14}^+$	100.0	100.0

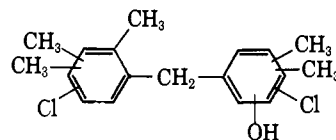
Retention = 30.5/47.4 = 64%

B. Voltage dependence at electron energies near appearance potential

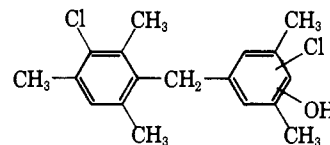
Nominal electron energy, e.v.	8.5	8.9	9.4	9.8	10.2	10.6
Peak height, arbitrary scale units						
104	0.3	0.8	1.2	1.9	2.7	3.7
105	1.0	1.7	2.3	3.7	5.3	7.3
Label retention, %	83	68	66	66	66	66

^a Formulas listed correspond to unlabeled ions of indicated masses.

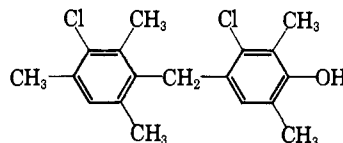
gation¹⁵ furnished an opportunity to test the usefulness of the correlation and raised a question which, in turn, led to extension of the correlation to still another class of related compounds. The major product from a reaction of 2-chloromesitylene with peroxytrifluoroacetic acid and boron fluoride gave a mass spectrum with parent peaks at masses 322-324-326, with an isotopic distribution indicating a dichloro compound. The molecular weight was right for a dichloromonohydroxypentamethyldiphenylmethane, as suggested by other evidence. The most abundant ion occurred at masses 166-168 (1 chlorine atom), indicating an *o*-methyl diarylmethane and establishing the formula



o-Methyl substitution in the second ring would lead to intense peaks at masses 168-170 (1 chlorine atom); only a tiny peak occurs at 170, ruling out such a structure. Peaks at 169-171 (1 chlorine atom) correspond to loss, without rearrangement, of the first aryl group— $C_6HCl(CH_3)_3$. If the mesitylene carbon skeleton is assumed to remain unchanged, the possible structures can be narrowed to

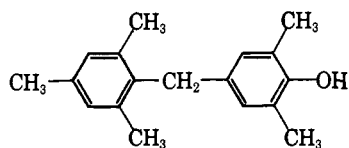


If an *o*-hydroxyl group resembles—and is able to compete effectively with—*o*-methyl in facilitating the rearrangement-dissociation,¹⁶ only one structure remains



(15) C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963); H. Hart, C. A. Buehler, A. J. Waring, and S. Meyerson, *J. Org. Chem.*, in press.

in satisfactory agreement with evidence from n.m.r. and infrared spectroscopy.¹⁵ Similar evidence led independently to the structure assignment



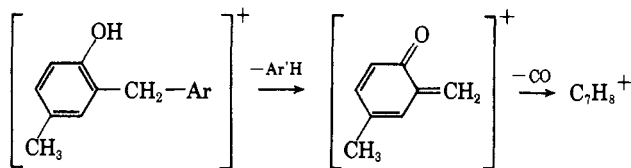
for the dechlorinated derivative.¹⁵ Partial spectra of both are shown in Table III. Again, both spectra contain metastable peaks establishing the parent ions as precursors of the even-mass-number fragment ions.

TABLE III
PARTIAL SPECTRA OF CHLOROMESITYLENE OXIDATION
PRODUCT AND DECHLORINATED DERIVATIVE

Mass ^a	Ion	Molecular weight ^a	
		332	254
Parent	Parent	100.0	100.0
Parent less 15	Parent less CH ₃	32.0	94.1
Parent less 35	Parent less Cl	47.9	...
132 ^b	C ₁₀ H ₁₂ ⁺	...	227
166	C ₁₀ H ₁₁ Cl ⁺	448	...

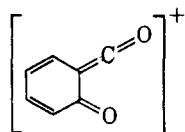
^a Heavy-isotopic peaks attributed to ions containing ³⁷Cl are omitted. ^b As in Table I, all even-mass-number peaks are shown that have intensities greater than 35% that of the parent ion.

To test the ability of *o*-hydroxyl to replace *o*-methyl as the hydrogen donor group, spectra were measured of 2-hydroxy-5-methyl- and 2-hydroxy-5-chlorodiphenylmethanes. These are shown in Table IV. Each spectrum contains the expected even-mass-number peak—as well as the associated metastable peak, not shown in the table—plus a second intense even-mass-number peak corresponding to further loss of a neutral particle of 28 mass units. The reaction sequence is apparently



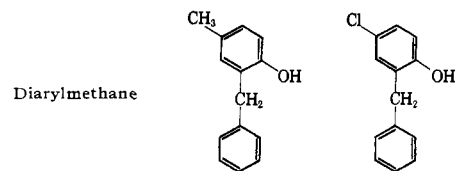
although a contribution from loss of C₂H₄ cannot be ruled out. Subsequent loss of CO from the primary product was suggested also by the spectra of *o*-methyl-diaryl ethers,¹¹ and is to be expected by analogy with

(16) In substituted benzoate esters, for example, either a hydroxyl or methyl group in the *ortho* position can furnish the hydrogen atom needed for the analogous reaction. Thus, the mass spectra of alkyl salicylates are characterized by an intense peak at mass 120, attributed to an ion with the structure



[See E. M. Emery, *Anal. Chem.*, **32**, 1495 (1960).]

TABLE IV
PARTIAL SPECTRA OF *o*-HYDROXYDIARYLMETHANES



Mass ^a	Ion	Molecular weight	
		198	218
Parent	Parent	100.0	100.0
Parent less 15	Parent less CH ₃	37.0	0.8
Parent less 35	Parent less Cl	...	76.9
92 ^b	C ₇ H ₈ ⁺	39.1	...
112	C ₆ H ₆ Cl ⁺	...	40.3
120	C ₈ H ₈ O ⁺	65.2	...
140	C ₇ H ₆ ClO ⁺	...	78.0

^a See footnote a, Table III. ^b See footnote b, Table III.

ions of similar structure in other systems.¹⁷⁻¹⁹ The peak arising from this secondary reaction is analytically useful in that it signals the presence of an oxygen atom, either in the *ortho* substituent or as the connecting link between the two aryl groups.

The reaction is thus common to diarylmethanes and diaryl ethers containing an *o*-methyl or -hydroxyl substituent. It is another member of a large class of ionic unimolecular rearrangement-dissociation reactions that are essentially unaffected by interchanging O, CH₂, and, no doubt, other groups such as NH and S.^{3a,b} These reactions, which seem to be energetically favored, are highly sensitive to molecular structure. Whether such a reaction will occur in a specific instance is determined largely by whether the molecule satisfies the geometric requirements needed to form the appropriate bridged cyclic intermediate or transition state.

Experimental

Materials.—Table V summarizes the preparation and physical properties of the diarylmethanes studied. Method 1 consists of benzylation of an aromatic hydrocarbon by a benzylic halide in the presence of a mild Lewis acid, usually ferric chloride or zinc chloride²⁰; aluminum chloride leads to extensive transbenzylation. Method 2 consists of the pyrolysis of a methylated diphenyl sulfone.⁴

In addition to the preparation listed, compound 1 was purchased from Matheson Coleman and Bell. Compound 5 was obtained as the forecut from distillation of compound 3 on a 100-plate spinning-band column, and was purified by gas chromatography. The mass spectrum clearly indicated the 2,6,3'-structure rather than the 3,5,3'-, which might have been expected to be favored by steric considerations. Compound 6 was separated by fractional distillation from the pyrolysis products of di-*o*-xylyl sulfone. It was derived evidently from the 3,4,2',3'-isomer in the tetramethyldiphenyl sulfone mixture. Compound 7 was formed by reaction of *p*-xylyl bromide with mesitylene, catalyzed by zinc chloride in acetic acid. The mass spectrum of the pyrolysis product of mesityl *p*-xylyl sulfone indicated a mixture of the two predictable⁴ isomeric tetramethyldiphenylmethanes. The peak at mass 132 was attributed to compound 7 and its spectral contributions were removed; the residual spectrum was attributed to compound 8. Compound 9 was formed along with other isomers by the condensation of formaldehyde with *o*-xylene, catalyzed by toluenesulfonic acid.²¹ The dixylylmethanes were

(17) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

(18) J. H. Beynon and A. E. Williams, *Appl. Spectry.*, **14**, 156 (1960).

(19) J. D. McCollum and S. Meyerson, *J. Am. Chem. Soc.*, **85**, 1739 (1963).

(20) C. Serres and E. K. Fields, *ibid.*, **82**, 4685 (1960).

(21) J. G. Hendrickson and F. T. Wadsworth, *Ind. Eng. Chem.*, **50**, 877 (1958).

TABLE V
 PREPARATION AND PROPERTIES OF DIARYLMETHANES

Compound number	Positions of methyl groups	Method of preparation ^a	Literature reference	Yield, mole %	Boiling point, °C./Torr	Melting point, °C.
1	...	2	5	20	...	26
2	2	a	3-4
3	2,4,3'	1	22	30	123 (1)	...
		2	5	41	106 (0.5)	...
4	2,5,4'	1	22	69	104 (0.5)	...
		2	5	50	106 (0.5)	...
5	2,6,3' ^b	1	22	10	123 (1)	...
6	3,4,2'	2	5	8	98 (0.2)	...
7	2,4,6,4' ^b	1	22	60	...	50-52
8	2,5,3',5' ^b	2	5	20	127 (1)	...
9	3,4,3',4'	a	23	18	113-115 (2)	32-34
10	2,4,6,3',5'	1	22	52	...	67
		2	5	95	...	67
11	2,4,6,2',4',6'	a	23	66	198-200 (10)	96-97
12	2,3,4,5,2',3',4',5'	..	16	150
13	4-OH-3,5,2',4',6'	..	16	121-123
14	2,3'-Cl ₂ -4-OH-3,5,2',4',6'	..	16	143-144
15	2-OH-5	..	c	..	184-186 (13)	...
16	2-OH-5-Cl	..	c	..	198-199 (13)	48.5

^a See text. ^b New compound. ^c See K. Kindler, German Patent 824,058, December 10, 1951.

separated from more highly condensed material by distillation. Compound 9, being the highest-melting isomer, crystallized first and was isolated in about 99% purity, as estimated by gas chromatography. Compound 11 was similarly prepared from mesitylene and formaldehyde.²¹ Compounds 12 and 14 resulted from reactions of peroxytrifluoroacetic acid with prehnitene and chloromesitylene, respectively.¹⁵ Compound 13 was obtained by dechlorination of compound 14.¹⁵ Compounds 15 and 16 were purchased from Aldrich Chemical Co.

Preparation of *o*-Methyl-*d*-diphenylmethane. *o*-Benzylbenzoic acid was prepared by reduction of *o*-benzoylbenzoic acid with zinc dust and ammonium hydroxide.²² The yield of white acid, melting at 114-115°, was 26%; in addition, there resulted a 50% yield of the lactone of 2-carboxybenzhydrol.

***o*-Benzylbenzyl Bromide.**—Refluxing 7.3 g. (0.0344 mole) of *o*-benzylbenzoic acid and 1.31 g. (0.0344 mole) of lithium aluminum hydride in 150 ml. of ether for 1 hr. gave, after the usual work-up, 3.2 g. (51%) of *o*-benzylbenzyl alcohol as a colorless oil. Treatment with concentrated hydrobromic acid²³ converted it to *o*-benzylbenzyl bromide, m.p. 44-45°, in 69% yield.

***o*-Methyl-*d*-diphenylmethane.**—A mixture of 1.31 g. (0.005 mole) of *o*-benzylbenzyl bromide and 0.44 g. (0.01 mole) of lithium aluminum deuteride in 50 ml. of ether was stirred and refluxed 3 hr. The mixture was cautiously treated with 10% sulfuric acid; the ether solution was dried and evaporated, leaving 0.9 g. (98%) of *o*-methyl-*d*-diphenylmethane, melting at 5-6°. The literature melting point for the undeuterated *o*-methyl-diphenylmethane is 6.61°²⁴; our undeuterated compound, obtained by the above reduction using lithium aluminum hydride, melted at 3-4°.

Nuclear magnetic resonance spectra of the unlabeled and labeled *o*-methyl-diphenylmethanes were measured in deuteriochloroform with tetramethylsilane as the internal standard in the cavity of a Varian DP 60 machine. The peaks in τ -units for the unlabeled compound were: aromatic hydrogens at 2.94, methylene hydrogens at 6.14, and methyl hydrogens at 7.89. The ratio of the integrated areas was 9:2:3. The hydrogens of the labeled compound gave peaks at the same τ -values, and were in the ratio 9:2:2. Thus, the deuterium atom was clearly in the methyl

group and no exchange with the hydrogens of the methylene group had occurred during the reduction with lithium aluminum deuteride.

Mass Spectrometry.—Mass spectra were measured with 70-v. electrons on a modified²⁵ Consolidated Model 21-103c instrument with the inlet system at 250°. Low-voltage measurements were made with the repeller plates at an average potential of 3 v.; actual settings, adjusted for maximum ion current, were 3.80 v. on the inner repeller and 2.20 v. on the outer one.

Corrections for naturally occurring heavy isotopes—as well as for the isotopic impurity, 5.6% of the unlabeled species, estimated at low voltage²⁶—have been made only on the data in Table II. Such correction is required in calculating label retention.⁶ Low-voltage measurements—below the appearance potential of C₈H₉⁺—were made to eliminate possible interference from unlabeled C₈H₉⁺ ions and to check for possible dependence of label retention on ionizing voltage.²⁷ The 70-v. spectra show that the label is retained quantitatively in the C₈H₉⁺ ion. The finding that retention is independent of ionizing voltage supports the assumption that C₈H₉⁺ arises by only one path. The apparently high retention at 8.5 v. could be caused simply by uncertainties in reading the small peak heights.

Acknowledgment.—We are indebted for the preparation of 2,4,6,4'-tetramethyldiphenylmethane to J. G. Hendrickson; of the 2,5,3',5'-isomer to D. H. Meyer; of the 3,4,3',4'-isomer to C. Serres, Jr.; and of 2,3,4,5,2',3',4',5'-octamethyl-, 4-hydroxy-3,5,2',4',6'-penta-methyl-, and 2,3'-dichloro-4-hydroxy-3,5,2',4',6'-penta-methyldiphenylmethanes to C. A. Buehler and Harold Hart, of Michigan State University. The assistance of D. K. Albert with gas chromatographic purification and of E. M. Banas with n.m.r. spectroscopy is gratefully acknowledged.

(25) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, 7th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.

(26) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950); R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950).

(27) S. Meyerson, *J. Chem. Phys.*, **34**, 2046 (1961); S. Meyerson, T. D. Nevitt, and P. N. Rylander, in "Advances in Mass Spectrometry," Vol. II, R. M. Elliott, Ed., Pergamon Press, London, 1963, p. 313; S. Meyerson and H. Hart, *J. Am. Chem. Soc.*, **85**, 2358 (1963).

(22) R. Scholl and W. Neovius, *Ber.*, **44**, 1080 Anm. (1911).

(23) N. J. Leonard, A. J. Kresge, and M. Oki, *J. Am. Chem. Soc.*, **77**, 5078 (1955).

(24) I. H. Lammeck, Jr., and P. H. Wise, "Nat'l. Advisory Comm. Aeronaut. Tech. Note 2230," 17 pp. (1950); *Chem. Abstr.*, **45**, 6609h (1951).