ORGANIC AND BIOLOGICAL CHEMISTRY

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Novel Heterocyclopentadienes. II

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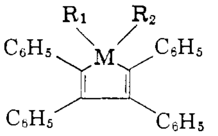
The dimerization of diphenylacetylene by lithium metal has been investigated and shown to yield an active dilithium compound which may be used in the preparation of heterocyclic materials by condensation with metallic (or metalloid) dihalides. A series of monocyclic heterocyclopentadienes having the general structure I has been prepared. In this series, M equals S, P, As, Sb, C, Ge or Sn. The substituents R_1 and R_2 may be absent in the case of a divalent hetero atom or may be alkyl, aryl or halide in the case of tri- or tetravalent hetero atoms. Spiro compounds have been prepared having the general structural formula II in which M is either Ge or Sn.

In the course of our studies on general reactions of organolithium compounds with metallic halides, we have investigated a reaction which leads to the preparation of heterocyclopentadienes. Our previous communication[1] describes briefly the preparative route to such compounds. We are giving here the details of the experimental procedure and the extension of these reactions to the preparation of a series of heterocycles. The general formula (I) is

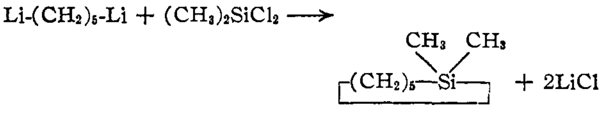


I

where R_1 and R_2 are alkyl, aryl, halides, a second ring (a spiro compound), or one or both may be missing.

This type of heterocyclic compound (except where M = S, N, O or Se) had not been described in the literature prior to our initial communication.[2] We have prepared such heterocyclopentadienes with hetero atoms such as sulfur, phosphorus, arsenic, antimony, germanium and tin. The preparative scheme also has been applicable to the making of the hydrocarbon analogs, tetraphenylcyclopentadiene and pentaphenylcyclopentadiene.

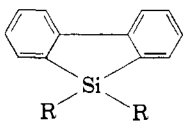
Heterocyclic compounds of many elements are known. With several exceptions, notably nitrogen, oxygen and sulfur, a limited number of types of ring containing only carbon and one hetero atom are known. The most common method of forming heterocyclic organometallic compounds is the use of the reactive metal dihalide and difunctional Grignard or organolithium reagent. The preparation of cyclopentamethylene derivatives of various elements is illustrated by the reaction[3]



$$Li\text{-}(CH_2)_5\text{-}Li + (CH_3)_2SiCl_2 \longrightarrow \underbrace{(CH_2)_5\text{—}\overset{CH_3\ CH_3}{Si}}\text{—} + 2LiCl$$

Exactly analogous cyclotetramethylene derivatives are known for phosphorus,[4] arsenic,[4] antimony[4] and boron.[5]

Aside from the saturated rings mentioned above, another common class of heterocyclic compounds are the nine substituted fluorene analogs often derived from 2,2′-dilithiobiphenyl. The 5,5′-disubstituted dibenzosiloles are known, *e.g.*



where R may be alkyl, aryl or chloro as well as the 5,5′-spirobi-(dibenzosiloles).[6] Similar compounds have been reported for phosphorus,[7] arsenic[4] and antimony.[4]

Not only is the extension of the synthesis described herein interesting from the point of view of preparing a wide variety of heterocyclopentadienes, but the chemistry of the rings so produced seems worthy of further investigation. The work presently described involves the use of a single dilithio derivative as a starting material with a variety of metal di- and polyhalides. The preparation of rings by other schemes is currently being investigated and will be reported later in conjunction with the chemistry of the heterocycles so produced.

Discussion

The dimerization of diphenylacetylene with lithium has been reported.[8,9] Two possible products may result from this reaction. One of these, 1,4-dilithiotetraphenylbutadiene, is the desired starting material in our reaction scheme. However, a second material which upon quenching produces 1,2,3-triphenylnaphthalene also has been obtained. The conditions leading to each of these were specified by Smith and Hoehn's work.[8] We have found that the undesirable ring closure to the naphthalene derivative occurs with greater frequency than they predict. Under the conditions of our dimerization we were unable to run the reaction to 100% conversion, regardless of the pro-

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[1] F. C. Leavitt, T. A. Manuel and F. Johnson, THIS JOURNAL, **81**, 3163 (1959).

[2] Another route to the tetraphenylmetaloles recently has been described; E. H. Braye and W. Hubel, *Chemistry & Industry*, 1250 (1959). Also, one reference to phospholes has appeared; E. Howard and R. E. Donadio, Abstracts, American Chemical Society 136th Meeting, Atlantic City, N. J., p. 100-P.

[3] R. West and E. G. Rochow, *Naturw.*, **40**, 142 (1953).

[4] F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth and Silicon," Interscience Publishers, Inc., New York, N. Y., 1950.

[5] K. Torssell, *Acta Chem. Scand.*, **8**, 1779 (1954).

[6] H. Gilman and R. D. Gorsich, THIS JOURNAL, **80**, 1883 (1958).

[7] G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).

[8] L. I. Smith and H. H. Hoehn, THIS JOURNAL, **63**, 1184 (1941).

[9] W. Schlenk and E. Bergmann, *Ann.*, **463**, 71 (1928).

portions of reagents. Consequently, all of our dimerizations were carried out to the extent of approximately 60% conversion to the dilithiobutadienyl derivative. Using this precaution, the desired linear dilithium derivative was obtained. Since both possible organolithium compounds are highly colored it was always necessary to quench an aliquot to verify the fact that tetraphenylbutadiene was the sole product.

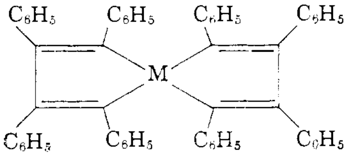
The mechanism of the dimerization has not been previously defined. We propose a mechanism similar to that of Szwarc[10] which leads to an ion radical. In Szwarc's system, an electron exchange takes place from a sodium–naphthalene complex to styrene, producing the styryl radical-ion. In the case of the lithium and diphenylacetylene, an electron donation from lithium to the diphenylacetylene would produce an essentially olefinic ion radical. The ionic portion could be stabilized by combination with the lithium cation in a more or less covalent structure. However, the radical would exist only long enough to couple with a second radical yielding the 1,4-dilithiotetraphenylbutadiene. While the polymerization through either an ionic or free radical process is a possibility, the steric requirements for such polymerization are prohibitive.

This mechanism does not account for the observed ring closure to yield the naphthalene derivative. A minimum amount of work toward elucidation of this mechanism has been carried out. However, the interesting fact remains that a mixture of tetraphenylbutadiene with triphenylnaphthalene never has been obtained upon quenching any dimerization. The organic products are either tetraphenylbutadiene or triphenylnaphthalene. It appears, therefore, that at some stage in the dimerization an increase in the concentration of an intermediate species allows it to act in a catalytic fashion to cause the ring closure.

The geometrical configuration of this butadiene derivative is not defined. Of the three possibilities, *i.e.*, *cis-cis*, *cis-trans* and *trans-trans*, the presence of the *cis-cis* isomer seems to be most consistent with the observed behavior. The apparent ease of ring formation and difficulty in preparing bis-substituted organometallic tetraphenylbutadiene derivatives[11] are both most readily explained assuming a *cis-cis* configuration.

Interest in the production of polymeric materials led us to try the condensation of stoichiometric quantities of sulfur dichloride with the dilithiobutadienyl derivative. Initial reactions produced crystalline products rather than polymeric materials. The product was identified as tetraphenylthiophene. Although tetraphenylthiophene was not a novel substance, having been previously described,[12] it did serve as a basis for study of a series of compounds having the conjugated diene structure plus one hetero atom. The extension of this reaction to include other metal and metalloid dihalides was successful in the case of the phosphorus, arsenic, antimony, germanium and tin derivatives. All of the heterocyclopentadienes of this series have been high melting crystalline materials, with little tendency toward ready oxidation when crystalline.

The extension of this reaction to prepare spiro compounds has been successful in the case of the germanium and tin. A 2:1 molar ratio of the dilithiobutadiene with tetrahalides of the hetero atom provided a path to compounds with the general structure II where M is Ge or Sn.



II

Analogous condensation reactions lead to the hydrocarbon cyclopentadienes as well. When benzal chloride and dibromomethane were substituted for metallic dihalides, pentaphenylcyclopentadiene and tetraphenylcyclopentadiene, respectively, were produced.

As indicated above, the R_1 and R_2 groups in the generalized formula for the class of heterocyclopentadienes described herein may be halide atoms. It is presumed that in the course of the preparation of spiro compounds, at one stage the dihalide of the tin or germanium derivatives does indeed exist. Isolation of this type compound was attempted, but the reactivity of the intermediate made identification difficult. The experimental details of the dichloride preparations are not included. A series of reactions involving the germanium derivatives yielded products on which it was extremely difficult to obtain reproducible elemental analyses. However, the example using a trihalide was more successful. Equal molar quantities of the dilithio butadienyl derivative and arsenic trichloride were condensed to yield the 1-chloro-2,3,4,5-tetraphenylarsenole. The experimental details are included in this paper. Further reaction of the heterocyclic halide with phenyllithium or phenyl Grignard yielded in both cases the previously prepared pentaphenylarsenole. This indicates that the intermediate monochloride was present and groups other than phenyl may be attached with ease. The full extent of the variables in this reaction have not been covered by any means.

This reaction scheme, although seemingly generally applicable, has not as yet led to all the readily obtainable products. The silicon analog is an obvious omission. The unsuccessful experiments have not been included; many have been attempted. However, the products have been ill-defined and do not add anything to the general study of the reaction. In the case of silicon, particularly, the failure to obtain the heterocycle is outstanding inasmuch as all the surrounding elements in the periodic table, *i.e.*, carbon, phosphorus, germanium have been incorporated in such a structure. The possibility of a ring of this type being thermodynamically unstable seems to be ruled out by the recent appearance of an article describing a compound probably having such a

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(10) M. Szwarc, M. Levy and R. Milkovich, This Journal, 78, 2656 (1956).

(11) Unpublished results from this Laboratory.

(12) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952.

ring structure.[7] No satisfactory explanation is available for the failure of the silicon dihalides to enter into the desired condensation reaction. In all experiments that were run with silicon dihalides, good yields of tetraphenylbutadiene were recovered, indicating that quantities of the dilithio derivative were unreacted at the time of quenching.

The chemistry of the heterocycles themselves is currently being investigated and will be reported in the future. Braye and Hubel[2] have indicated that the compounds do not appear to be aromatic from studies of these reactions on analogous materials prepared in their laboratories. Also, the participation of the unpaired electrons on the phosphorus atom in the resonance system of the ring is not likely in view of the fact that the ring will form as readily when the phosphorus is in a pentavalent state, *i.e.*, phenyldichlorophosphine oxide yields the pentaphenylphosphole oxide in good yield. Pentaphenylphosphole may be oxidized in solution under rather rigorous conditions to the phosphole oxide.

Experimental

All melting points are uncorrected. The yields of the heterocycles are based on available 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (LTPBD). The dimerization leading to LTPBD was never run to completion. Concentration of LTPBD was based on an assumed 60% dimerization.

Preparation of 1,4-Dilithio-1,2,3,4-tetraphenylbutadiene (LTPBD).[8]—A solution of 2.0 g. (11.2 mmoles) of diphenylacetylene (tolan) in 50 ml. of anhydrous diethyl ether was prepared. To this solution was added 0.078 g. (11.2 mmoles) of lithium shot. The lithium was prepared by melting the required quantity in mineral oil, rapidly shaking, cooling, and rinsing with anhydrous ligroin. The reaction vessel was then flushed with dry nitrogen, rapidly stoppered, and shaken at room temperature for 16 hours. Within the first few hours, a deep scarlet color developed in the solution indicative of the presence of the dilithium compound. After 16 hours, the conversion to the dilithio dimer was approximately 60%. This was determined by quenching with MeOH and weighing the tetraphenylbutadiene. The Gilman Color test I[13] was positive after the initial color development in the solution.

Preparation of Tetraphenylthiophene.—A solution of 1.16 g. (11.2 mmoles) of SCl_2 (practical grade) in 30 ml. of anhydrous diethyl ether was closed by a piece of pure gum rubber sheeting securely stretched across the opening and a dry nitrogen purge introduced *via* a hypodermic needle. A previously prepared LTPBD solution then was removed from its container *via* a hypodermic syringe. This was made possible by inserting the needle through rubber sheeting stretched over the neck of the flask in which the dimerization took place. The hypodermic syringe technique allowed excess lithium to be left in the flask. A homogeneous scarlet solution of the dilithium compound was removed and added dropwise through the rubber dam into the SCl_2 solution. There was an immediate reaction observed in the clear SCl_2 solution indicating the ionic nature of the reaction. The tetraphenylthiophene dropped out to give a yellow slurry. This reaction was carried out at room temperature. However, lowering the temperature to −25° did not appreciably affect the rate or the yield of the reaction.

Upon completion of the LTPBD addition, the reaction mixture was stirred for approximately 20 minutes. The Gilman test I was negative throughout the reaction in the flask containing the SCl_2. After this period of time, the nitrogen atmosphere was discontinued and the ether removed off under vacuum. The residual solids were extracted with methylene chloride yielding a yellow solution. By gradual addition of methyl alcohol, the crystallization of tetraphenylthiophene could be accomplished. Upon recrystallization from methylene chloride–methanol mixtures, colorless needles of tetraphenylthiophene were prepared; yield 50%, m.p. 189–190°.

Anal. Calcd. for $C_{28}H_{20}S$: C, 86.4; H, 5.2; S, 8.2; mol. wt., 388. Found: C, 86.2; H, 5.2; S, 8.6, mol. wt. (mass spec.), 388.

Preparation of 1,1-Dimethyl-2,3,4,5-tetraphenylstannole.—The above procedure was repeated with the use of dimethyltin dichloride as the source of the hetero atom. A yellow slurry again developed and was treated as above. Recrystallization from methylene chloride–methanol mixtures produced colorless needles of the 1,1-dimethyl-2,3,4,5-tetraphenylstannole, m.p. 192–193°, yield 67%; mol. wt. calcd. 505, found (Rast) 518.

Anal. Calcd. for $C_{30}H_{26}Sn$: C, 71.3; H, 5.2. Found: C, 71.4; H, 5.2.

Preparation of Pentaphenylphosphole.—The standard method of preparation was involved, the source of the phosphorus atom being phenyldichlorophosphine. The recrystallized product was in the form of yellow needles, m.p. 256–257°, yield 68%; mol. wt. calcd. 464, found (Rast) 512, mol. wt. (mass spec.), 463.

Anal. Calcd. for $C_{34}H_{25}P$: C, 88.1; H, 5.4; P, 6.65. Found: C, 88.2; H, 5.5; P, 6.55.

Preparation of Pentaphenylarsenole.—The above procedure was repeated using phenyldichloroarsine as the source of the hetero atom. The recrystallized yellow needles had a m.p. of 215–216°, no molecular weight determination was run; yield 93%.

Anal. Calcd. for $C_{34}H_{25}As$: C, 80.3; H, 4.9; As, 14.75. Found: C, 79.5; H, 4.9; As, 14.5.

Preparation of Pentaphenylstibiole.—The method described above was used with the source of the hetero atom being phenyldichlorostibine. The recrystallized product was yellow and needle-like, m.p. 160°, yield 52%.

Anal. Calcd. for $C_{34}H_{25}Sb$: C, 73.4; H, 4.5; Sb, 22.0. Found: C, 72.7; H, 4.5; Sb, 22.1.

Preparation of Octaphenyl-1,1′-spirobistannole.—The procedure described above was used. However, the ratio of reactants was changed to 2 moles of the dilithium compound per mole of $SnCl_4$. The reaction conditions and recrystallization technique were the same. The product was a spirobistannole having a melting point 281–282°, yield 62%.

Anal. Calcd. for $C_{56}H_{40}Sn$: C, 80.9; H, 4.8. Found: C, 80.7; H, 4.7.

Preparation of Octaphenyl-1,1′-spirobigermanole.—The standard procedure was again followed, using 2 moles of the dilithium compound per mole of $GeCl_4$. Yellow needles having a melting point of 258–260° were produced, yield *ca.* 22%.

Anal. Calcd. for $C_{56}H_{40}Ge$: C, 85.6; H, 5.05; Ge, 9.3. Found: C, 85.7; H, 4.9; Ge, 9.55.

Preparation of 1,1′-Divinyl-2,3,4,5-tetraphenylstannole.—The standard procedure was carried out using divinyldichlorotin as the source of the hetero atom. The product had a melting point of 158–159°, yield 69%.

Anal. Calcd. for $C_{32}H_{26}Sn$: C, 72.6; H, 4.9. Found: C, 71.9: H, 4.9.

Preparation of Hexaphenylstannole.—The above-described procedure was carried out using diphenyldichlorotin as a starting material. The product was crystalline, having a melting point of 173–174°, yield <20%.

Anal. Calcd. for $C_{40}H_{30}Sn$: C, 76.3; H, 4.8; Sn, 18.9. Found: C, 76.1; H, 4.7; Sn, 19.3.

Preparation of Tetraphenylcyclopentadiene.—The ability to prepare pure hydrocarbons by this technique was demonstrated by using dibromomethane as the halide in this system; m.p. 182–184° (lit.[14] 177–178°), yield 66%.

Anal. Calcd. for $C_{29}H_{22}$: C, 94.1; H, 5.9. Found: C, 94.3; H, 5.8.

Preparation of Pentaphenylcyclopentadiene.—The above technique was used with benzal chloride as the starting material. The resulting crystalline product had a melting point of 258–259° (lit.[15] m.p. 250°), yield was 51%.

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(13) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

(14) E. B. Auerbach, *Ber.*, **36**, 936 (1903).

(15) K. Ziegler and B. Schnell, *Ann.*, **445**, 278 (1925).

Anal. Calcd. for $C_{35}H_{26}$: C, 94.1; H, 5.9. Found: C, 93.9; H, 6.0.

Preparation of Pentaphenylphosphole Oxide.—The source of the hetero atom was phenyldichlorophosphine oxide. The same reaction scheme as described above led to a crystalline material having a melting point of 292–293° in 70% yield. This was identified as the phosphole oxide by comparison with an authentic sample prepared in our laboratories by another method.[11]

Anal. Calcd. for $C_{34}H_{25}OP$: C, 85.0; H, 5.25; P, 6.45. Found: C, 84.8; H, 5.1; P, 6.34.

Preparation of 1-Chloro-2,3,4,5-tetraphenylarsenole.—The standard procedure was repeated using arsenic trichloride. One mole of the dilithium compound was added per mole of trichloride and the resulting monochlorotetraphenylarsenole was obtained from an acetone–ligroin solvent system in the form of yellow needles, m.p. 182–184°. As opposed to the other recrystallization techniques, no methanol or other alcohols were used. The combination of the difficulties in purifying the sample and the problems inherent in an analysis of organometallic halides did not allow an unequivocal analysis for this product.

Anal. Calcd. for $C_{26}H_{20}AsCl$: C, 72.2; H, 4.3; Cl, 7.6. Found: C, 69.7; H, 4.5; Cl, 6.4.

Preparation of the monochlorotetraphenylarsenole was repeated without an isolation step. This was further treated with phenyllithium in anhydrous diethyl ether at room temperature for 30 minutes. A 35.4% yield (based on LTPBD) of pentaphenylarsenole was recovered. It was identified by melting point (214–215°), mixed m.p. (214–215°) and infrared as identical with an authentic sample. A similar preparation was carried out with an excess of phenylmagnesium bromide in anhydrous tetrahydrofuran. This reaction mixture was refluxed for 2 hours and a yield of 35.2% (based on LTPBD) of pentaphenylarsenole was recovered. Again, identification was based on melting point and infrared spectra.

Attempted Preparation of Mercuric Heterocycles.—A similar reaction was run with $HgCl_2$. An 8% yield of tetraphenyl-1,3-butadienylene-bis-mercury chloride, m.p. 245–248° with decomposition, was obtained. No other mercury-containing compounds were isolated.

Anal. Calcd. for $C_{28}H_{20}Cl_2Hg_2$: C, 40.6; H, 2.4; Hg, 48.5; Cl, 8.6. Found: C, 40.75; H, 2.55; Hg, 48.4; Cl, 8.25.

[Contribution from the Department of Chemistry, University of Toronto, Toronto 5, Canada]

The Spectral and Chemical Properties of α-Silyl Ketones

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The ultraviolet and infrared absorption spectra of several α-silyl ketones and one α-germyl ketone are reported and reveal that the carbonyl groups of these ketones are abnormally polar. The reactions of some of these ketones with typical Grignard reagents have been investigated. The data are interpreted as evidence for the existence of partial bonding between the silicon and carbonyl-oxygen atoms in α-silyl ketones.

One of the outstanding features about benzoyltriphenylsilane,[1] the first α-silyl ketone prepared, is its yellow color, a property not possessed by its carbon analog β-benzpinacolone, nor by the only other α-silyl ketone reported, acetyltriphenylsilane.[2] The yellow color implies that silicon is acting as a chromophore, a phenomenon previously unknown. It therefore appeared to be of interest to prepare a variety of α-silyl ketones in order to study their ultraviolet and infrared spectra, as well as their chemical reactions.

The spectra of these compounds, as well as of benzoyltriphenylgermane, β-benzpinacolone and a few related aliphatic and aromatic ketones, are presented in Tables I and II.

It is immediately apparent that all the α-silyl phenyl ketones are colored, and in fact that their spectra are practically identical in the ultraviolet and in the carbonyl regions of the infrared, regardless of the nature of the groups attached to the silicon atom.

By analogy with the ultraviolet absorption spectra of acetophenone[3] where the band at 325 mμ has been assigned to carbonyl absorption, that at 280 mμ to phenyl absorption and that at 242 mμ to the benzoyl group,[4] we assign the low-intensity, long wave length band of the α-silyl ketones to absorption by the carbonyl group and the high-intensity, short wave length band to absorption by the benzoyl group present in these compounds. The compounds show no absorption in the 280–295 mμ region. By comparing suitable spectra (*e.g.*, acetone, acetophenone and benzoyltriphenylsilane) it is possible to assign additive bathochromic shifts of the carbonyl band caused by the introduction of groups adjacent to

Table I

Ultraviolet Spectra of α-Silyl and Other Ketones[d]

Compound	Carbonyl mμ	Carbonyl ε	Phenyl mμ	Phenyl ε	Benzoyl mμ	Benzoyl ε
$Ph_3SiCOPh$	403(s)	264			258	15,500
	417	300				
$Ph_2MeSiCOPh$	403(s)	210			256	12,200
	417	235				
$PhMe_2SiCOPh$	403(s)	200			255	13,900
	415	216				
$Me_3SiCOPh$	402 (d)	117			252	11,700
	413 (d)	118				
$Ph_3SiCOMe$[a]	360 (d)	324	260	1510		
	372 (d)	366	265	1490		
	389(s)	239	272	1060		
$Ph_3GeCOPh$	403(s)	262			257	17,100
	415	306				
Ph_3CCOPh	329	299	293	782	253	11,600
$PhCOMe$[b]	325	50	280	1000	242	13,000
$MeCOMe$[c]	279	15				

[a] We are indebted to Dr. Henry Gilman, Iowa State College, for a sample of this compound. Subsequently, G. E. LeGrow in this Laboratory prepared additional material from triphenylsilyllithium and acetyl bromide in 4% yield following the published method (ref. 2). [b] See ref. 3. [c] See ref. 4. [d] (s) = shoulder, (d) = doublet.

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(1) A. G. Brook, This Journal, **79**, 4373 (1957).

(2) D. Wittenberg and H. Gilman, *ibid.*, **80**, 4529 (1958).

(3) G. Scheibe, F. Backenholer and A. Rosenberg, *Ber.*, **59**, 2617 (1926).

(4) E. A. Braude and F. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955.