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UMI

SOME REACTIONS OF

P-METHOXY-DIPHENYLBUTADIENE

A THESIS

SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE

BY

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ATLANTA, GEORGIA

JUNE 1941

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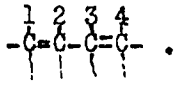
CHAPTER I

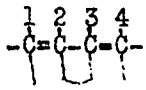
THEORETICAL

Ever since Thiele introduced his theory of addition to conjugated unsaturated compounds, numerous investigators have pointed out that it does not cover all the experimental facts.[1]

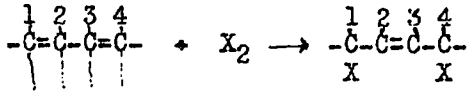
In brief, Thiele postulated residual valencies[2] resulting from the excess of affinity left from the union of carbon to carbon:



Due to the close proximity of the 2,3-carbon atoms the residual valencies neutralize each other leaving only the 1,4-positions free.



Thus any addenda to the conjugated compound would give the 1,4-addition product. As the addenda would require more affinity than that offered by the residual valencies, the double bonds would be ruptured and a new double bond would form at the 2,3-position.[3]



It has been shown that universal 1,4-addition to conjugation,

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[1]Henry Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, I, 575-576.

[2]J. B. Cohen, "Organic Chemistry for Advanced Students," Longmans, Green, and Co., New York, I, 145.

[3]Henry Gilman, op. cit.

as Thiele postulated, does not occur;[1] consequently much experimentation has been done to show the true nature of addition to conjugated compounds.

This investigation was undertaken in order to determine the position of addition of bromine to 1-para-methoxy-phenyl-4-phenylbutadiene.

Ingold has predicted that compounds of this nature would add bromine in the 3,4-position;[2] so that a brief resume of his theory will not be out of place.

Ingold[3] divided addition to unsaturated compounds into three classes: (1) both parts of the compound added are stable anions: e.g., Cl_2, Br_2, OHCl, etc., which may enhance or retard anionotropic mobility; (2) an anion-cation grouping: e.g., HCl, HBr, HCN, etc., which may also enhance or retard anionotropic mobility; and (3) a cation-cation grouping: e.g., H_2.

Starting from the demonstration that one atom of halogen adds initially,[4] Ingold[5] postulates the following series of reactions for butadiene:

$$\underset{(I)}{CH_2{=}CH{-}CH{=}CH_2} + Br_2 \longrightarrow \underset{(II)}{CH_2Br{-}\overbrace{\overset{+}{C}H{-}CH{=}CH_2}} + Br^-$$

$$CH_2Br{-}\overset{+}{C}H{-}C{=}CH_2 + Br^- \longrightarrow CH_2Br{-}CHBr{-}CH{=}CH_2$$

$$CH_2Br{-}CH{=}CH{-}\overset{+}{C}H_2 + Br^- \longrightarrow CH_2Br{-}CH{=}CH{-}CH_2Br$$

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[1]Straus, Ber., 42, 2866 (1909).
[2]Ingold and Smith, J. Chem. Soc., 2753 (1931).
[3]Ingold and Burton, J. Chem. Soc., 904 (1928).
[4]Francis, J. Am. Chem. Soc., 47, 2344 (1925); Terry and Eichelberger, J. Am. Chem. Soc., 47, 1067 (1925).
[5]Ingold and Burton, op. cit.

The part of the molecule of (II) under the bracket is the anionotropic system which is activated by the CH_2Br-grouping to give the 1,2 and 1,4 ions. As CH_2Br- has just about the same effect as hydrogen as an activating agent, both the 1,2 and the 1,4-dibromides of butadiene should be formed. Farmer and co-workers[1] have isolated and characterized the two dibromides.

Phenylbutadiene[2] adds chlorine in the 3,4-position in accordance with Ingold's prediction.[3]

$$C_6H_5CH{=}CH{-}CH{=}CH_2 + Cl_2 \longrightarrow C_6H_5CH{=}CH{-}CHCl{-}CH_2Cl.$$

The phenyl group, a stronger electronegative group than the CH_2Cl-group, prevents the anionotropic shift; therefore the 3,4 dichloride is formed almost exclusively.

Ingold[4] has also predicted that conjugated substituted diphenylbutadiene compounds with substituents having unshared pairs of electrons should add bromine in the 3,4-position, because the unshared electrons may be displaced consecutively throughout the conjugated system to build up a region of high electron density on the fourth carbon atom. For example, 1-para-bromophenyl-4-phenylbutadiene would react in this manner:

$$:\ddot{Br}C_6H_4{-}CH{=}CH{-}CH{=}CHC_6H_5 + Br_2 \longrightarrow BrC_6H_4CH{=}CH{-}CHBr{-}CH{-}BrC_6H_5.$$

The bromophenyl-group, being a more electronegative group than the phenyl group, prevents the anionotropic shift; and only

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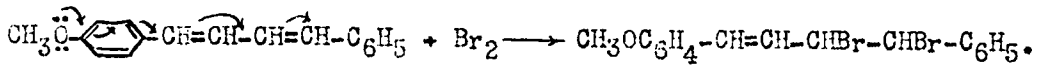
[1]Farmer, Lawrence, and Thorpe, J. Chem. Soc., 729 (1928).
[2]Muskat and Huggins, J. Am. Chem. Soc., 51, 2496 (1929).
[3]Ingold and Burton, op. cit.
[4]Ingold and Smith, op. cit.

the 3,4-dibromide will be formed. Yokely[1] has shown that para-bromodiphenylbutadiene does add bromine in the 3,4-position.

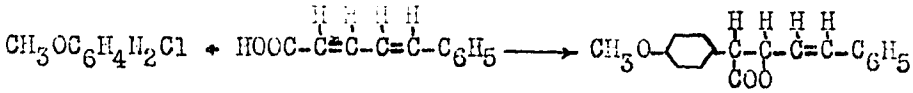
Proctor,[2] working with the corresponding para-chloro compound, got a 3,4-dichloride. This result is also in complete accord with Ingold's theory.

Similarly, 1-para-methoxy diphenylbutadiene should add bromine in the 3,4-position:

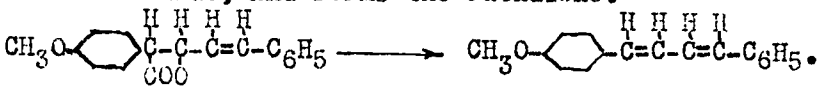


Para-methoxy diphenylbutadiene was prepared by the method of Meerwein[3] and also by the method of Kuhn and Winterstein.[4]

Meerwein's method is based upon the fact that aromatic diazo compounds will react with α,β-unsaturated carbonyl compounds to give unsaturated hydrocarbons.



The lactone, formed as an intermediate,[5] breaks down, loses carbon dioxide, and forms the butadiene.



This method gave 16% yields of the para-methoxy compound as compared to 25% yields of the para-nitro-diphenylbutadiene and 40% yields of the substituted stilbenes prepared by Bergmann

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[1]Yokely, "Studies in the Butadiene Series: Addition of Bromine and Hydrogen Bromide to 1-para-Bromo-phenyl-4-phenyl-butadiene," Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1939.

[2]Proctor, "The Preparation and Chlorination of 1-para-Chloro-phenyl-4-phenylbutadiene," Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1932.

[3]Meerwein, Buchner, and Emster, J. Prakt. Chem., 152, 237 (1939).

[4]Robinson, "Organic Synthesis," John Wiley and Sons, New York, 1935.

[5]Meerwein, Buchner, and Emster, op. cit.

and Weinberg[1] and Meerwein and co-workers[2] respectively. The product is difficult to purify, as a great deal of tarry material along with some dye is formed as a by-product of this reaction.

Kuhn and Winterstein's[3] method gave a product which was easily purified, but, on account of difficulties experienced in obtaining enough para-methoxyphenylacetic acid to prepare workable quantities of the butadione, the method was abandoned. By condensing a small quantity of para-methoxyphenylacetic acid with cinnamic aldehyde,[4] a product was obtained which was identical with the product obtained by Meerwein's method. When the two products were mixed they gave the same melting point.

To secure evidence of the structure of the butadiene a sample was condensed with maleic anhydride in benzene. Some difficulty was experienced in obtaining a product as condensation took place only after refluxing for sixteen hours.

The maleic anhydride condensation, the so called diene synthesis of Diels and Alder,[5] has been accepted as a means of identification of conjugated compounds, and, as such, it is used here. Occasionally, however, maleic anhydride will condense with compounds other than the butadienes.

Besides maleic anhydride, maleic acid, acrolein, or naphthaquinone might have been used, the condensation usually taking place in the 1,4-position.

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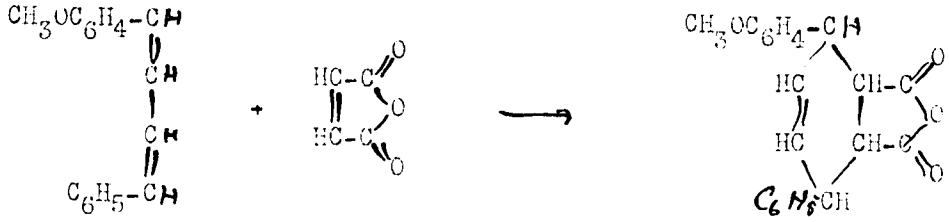
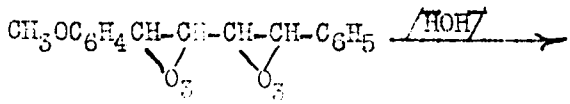
[1]Bergman and Weinberg, J. Org. Chem., 6, 134 (1941).
[2]Meerwein, Buchner, and Emster, op. cit.
[3]Robinson, op. cit.
[4]Ibid.
[5]Allen, J. Chem. Ed., 10, 494 (1933).



When a sample of the diene was saturated with bromine, a fine white powder was isolated from the reaction mixture. Upon repeated recrystallization, this powder melted at 190° with much decomposition. The analyses for bromine were higher than the calculated value for the tetrabromide of para-methoxy-diphenyl-butadiene.

To gain further knowledge of the structure of the butadiene prepared, a portion of it was treated with an excess of ozone; and the solution resulting from the hydrolysis of the ozonide was analyzed qualitatively for the fragments.

The decomposed ozonide should give benzaldehyde, para-methoxy benzaldehyde, and glyoxal or the corresponding acids.



(1) C_6H_5CHO

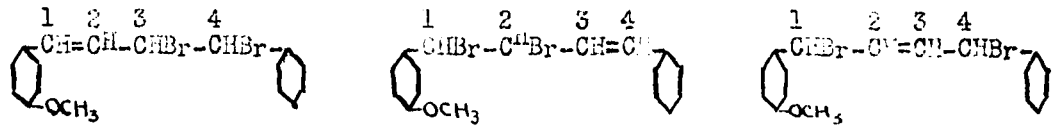
(2) $CH_3OC_6H_5CHO$

(3) CHO CHO

Oxalic acid was identified; and, after oxidation of an oily residue, para-methoxybenzoic acid was isolated. No benzoic acid or benzaldehyde was found.

The result of the ozonalysis, along with the maleic anhydride derivative, gives evidence of the conjugated structure of para-methoxy-diphenylbutadiene.

There are three possible dibromides for para-methoxy-diphenylbutadiene, which, upon ozonalysis and subsequent hydrolysis, should give characteristic decomposition products.



(I) (II) (III)

Compound (I) should give para-methoxy benzaldehyde and α,β-dibromohydrocinnamic aldehyde or the corresponding acids.

Compound (II) should give benzaldehyde and α,β-dibromo-para-methoxyhydrocinnamic aldehyde or the corresponding acids.

Compound (III) should give α-bromohomoanisaldehyde and α-bromophenyl acetaldehyde or the corresponding acids.

A sample of the butadiene was treated with one mole of bromine in the cold, but on standing the solution darkened and gave off white fumes. The recrystallized product (m.p. 123°-127°) gave bromine analyses that were higher than the theoretical.

Another sample was brominated, and the solvent was removed immediately. Again decomposition was observed, and some of the original butadiene was recovered.

Yet another sample was brominated and ozonized directly without removal of the solvent. None of the fragments expected were isolated from the hydrolyzed ozonide.

A portion of the diene was treated with one mole of bromine; and, without removal of the solvent, it was oxidized with potassium permanganate after the manner of Farmer and Scott.[1]

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[1]Farmer and Scott, J. Chem. Soc., 172 (1929).

The oil resulting from this reaction was treated with hydrogen peroxide with no visible effect. The fragments expected from the oxidation of the dibromide were not obtained. This is probably due to the instability of the dibromide.

The literature records the fact that the methoxycinnamic acids and esters react abnormally with bromine, giving substitution products instead of addition products. Davies and Davies,[1] working with the meta-methoxycinnamic acid derivatives; Hanson and Williams,[2] using the ortho-methoxy- and the para-methoxycinnamic acids; and Riemer and Tobin,[3] working with the 2,4-dimethoxycinnamic acids, all obtained large amounts of substitution products, along with the addition products, when these compounds were treated with halogen.

Some time ago, Straus,[4] working with similar acids, found that the highly activating methoxy group fostered substitution instead of addition. He noted that the amount of the substitution products was increased by the position and number of methoxy groups. In many cases he isolated the substitution product.

In view of Straus' work, it would be expected that para-methoxy diphenylbutadiene would react with bromine by substitution more readily than by addition. The experimental results, while far from complete, apparently support this conclusion.

The prediction that bromine would add 1,2 to paramethoxy-diphenylbutadiene[5] could not be verified as the dibromide was unstable.

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[1]Davies and Davies, J. Chem. Soc., 602 (1928).
[2]Hanson and Williams, J. Chem. Soc., 1059 (1930).
[3]Riemer and Tobin, J. Am. Chem. Soc., 52, 341 (1930).
[4]Ibid.
[5]Ingold and Smith, op. cit.

CHAPTER II

EXPERIMENTAL

Preparation of 1-para-Methoxyphenyl-4-Phenylbutadiene. -- The butadiene was prepared after the manner of Meerwein.[1] The cinnamylidene acetic acid used was prepared according to Riiber's method.[2]

Para-anisidine (44 g.) was suspended in 200 cc. of 20% hydrochloric acid and diazotized at 0° with sodium nitrite (18 g.) in 40 cc. of water. The diazo solution was added dropwise to the cinnamylidene acetic acid (32 g.) suspended in 350 cc. of acetone which had been cooled to 5°. Then cupric chloride (10.6 g.) and sodium acetate (55 g.) in 50 cc. of water were added. Nitrogen was evolved at once, and the solution developed a deep purple color. After stirring for one hour at 15°, the reaction mixture was steam distilled until the distillate became clear. The solution was filtered while hot, and the non-volatile tarry residue was dissolved in hot glacial acetic acid. The solution was filtered while hot; and, when cool, the precipitated diene was filtered off. The precipitate was recrystallized several times from an alcohol-benzene mixture. The product isolated melted at 159°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.4, H, 6.8. Found: C, 86.6, 86.7, 86.6; H, 7.1, 7.3, 7.0.

The butadiene was also prepared by the method of Kuhn and Winterstein.[3] The para-methoxy-phenylacetic acid used was

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[1]Meerwein, Buchner, and Emster, J. Prakt. Chem., 152, 237 (1939).
[2]Riiber, Ber., 37, 2272 (1904).
[3]Robinson, op. cit.

prepared by the method of Cain, Simonsen, and Smith.[1]

Para-methoxy-phenylacetic acid (11 g.), cinnamic aldehyde (9 g.), acetic anhydride (10 cc.), and lead monoxide (7.5 g.) were refluxed together for five hours in a flask protected from atmospheric moisture by a calcium chloride tube. The dark, hot solution was poured into a beaker and allowed to stand overnight. The grayish mass was moistened with alcohol, filtered, and recrystallized twice from toluene. A mixture of this product and the substance prepared by Moorwoin's method melted at 159°.

Condensation with Maleic Anhydride. -- Maleic anhydride (0.41 g.) was dissolved in 35 cc. of benzene and filtered into a long neck flask containing para-methoxy-diphenylbutadiene. The mixture was refluxed for sixteen hours, concentrated, and the precipitate was recrystallized three times from toluene. The pure product melted at 186°. The yield was almost quantitative.

Anal. Calcd. for $C_{21}H_{18}O_4$: C, 75.4; H, 5.4. Found: C, 75.0, 75.3; H, 5.3, 5.7.

Attempted Preparation of the Tetrabromide of para-Methoxy-Diphenylbutadiene. -- A sample (1.5 g.) of the diene was dissolved in chloroform, cooled to 0°, and bromine was added in excess. Ligroin (b.p. 65°-70°) was added, and, after standing for one hour, the solution was filtered. After recrystallization several times from ligroin, a white powder melting at 190° with much decomposition was obtained. The yield of the recrystallized product was small.

The results of the analyses are approximately the same as the calculated value for the percent of bromine in para-bromo-diphenylbutadiene.

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[1]Cain, Simonsen, and Smith, J. Chem. Soc., 103, 1035 (1935).

Anal. Calcd for $C_{17}H_{16}OBr_4$: Br, 57.5. Found: Br, 64.8, 65.0, 65.4.

Anal. Calcd for $C_{16}H_{13}Br_5$: Br, 66.4

Ozonolysis of para-Methoxy-Diphenylbutadiene. -- A sample of the butadiene was dissolved in chloroform and ozone was passed through the solution which was cooled in a salt-ice bath. After eight hours of ozonization, the chloroform was removed by suction, and 5 cc. of dilute potassium hydroxide in 25 cc. of water were added; the mixture was warmed on a water bath for one hour.

The alkaline solution was extracted several times with ether, the extract was dried over sodium sulfate (anhydrous), and the ether was removed by suction. The oil which remained was dissolved in a slight amount of alcohol and 2 cc. of dilute potassium hydroxide and 2 cc. of 30 % hydrogen peroxide were added. The solution was warmed on the water bath for fifteen minutes, and the alcohol was removed by evaporation.

The alkaline mixture was acidified, and the white precipitate was recrystallized from water and from dilute alcohol. The fluffy solid melted at 184°. Mixing the unkown with a known sample of para-methoxy-benzoic acid caused no change in the melting point of the known acid.

The alkaline solution from the decomposition of the ozonide was acidified with sulfuric acid, made alkaline with ammonium hydroxide, and then acid with acetic acid. Boric acid (2 g.) was added. After warming and stirring to dissolve the solid, 5 cc. of calcium chloride solution were added, and the solution was set aside for ten minutes with occasional stirring. Then the solution was heated to boiling, filtered, and the precipitate was washed with hot water until all the reducing material was removed.

Five cc. of hot dilute sulfuric acid were poured on the filter paper, and the filtrate was collected in a test tube. A drop of dilute potassium permanganate solution was bleached instantly by the hot acid solution. This proved the presence of oxalic acid.

No other substances were isolated from the ozonization.

Attempted Preparation of the Dibromide of para-Methoxy-Diphenylbutadiene. -- In the dark, bromine (3.36 g.) dissolved in 25 cc. of chloroform was added dropwise through a separatory funnel to a chloroform solution of the butadiene (5 g.) protected by a calcium chloride tube. The butadiene solution was kept at 0° through-out the addition of bromine after which it was allowed to stand over night. The solution darkened, and upon removal of the solvent a black residue was obtained. Repeated recrystallizations from chloroform by the addition of ligroin (b.p. 65°-70°) yielded a small amount of tan powder melting at 123°-130° with decomposition. The analyses showed that the powder was not the dibromide.

Anal. Calcd. for $C_{17}H_{16}OBr_2$: Br, 40.4. Found: Br, 47.5, 45.9, 45.6.

Another sample was treated with bromine in the same manner as before with the exception that the chloroform was removed immediately with the aid of an oil pump. Repeated recrystallization of the black residue yielded a small amount of the original butadiene.

To another sample, slightly more than the calculated amount of bromine was added, and the cold solution was ozonized directly for eight hours. After removing the solvent by suction, the oily ozonide was decomposed by adding 25 cc. of water and by

warming on a water bath. The water solution was extracted several times with ether, and the extract was dried over anhydrous sodium sulfate. The oil left after the removal of the ether was dissolved in dilute alcohol, and 2 cc. of 30% hydrogen peroxide were added. The oil showed no visible change after the oxidation and was not analyzed.

Another portion of the diene (1.2876 g.) was brominated in the manner stated, and an equal volume of cold acetone was added to the chloroform solution. After the method of Farmer and Scott,[1] potassium permanganate (3.932 g.) and magnesium sulfate (3.932 g.), dissolved in 60 cc. of water, were added dropwise with vigorous shaking to the chloroform-acetone solution. The mud formed was filtered, and the acetone was removed by bubbling a rapid stream of air through the solution. The chloroform was removed by evaporation. The oily material obtained here was combined with the material isolated from the mud.

The mud was suspended in water acidified with sulfuric acid, and enough sodium bisulfite to bring the mud into solution was added. The acid mixture was extracted with ether and the extract neutralized with a few drops of saturated sodium bicarbonate solution. Then the ether was dried over anhydrous sodium sulfate and later was removed by suction. The oil which was obtained showed no visible change after treatment with 2 cc. of 30% hydrogen peroxide. It was not analyzed further.

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[1]Farmer and Scott, op. cit.

CHAPTER III

SUMMARY

1. A brief resume of Thiele's theory has been given.

2. It has been shown that Thiele's theory is not universal in application.

3. A brief review of a part of Ingold's theory of addition to unsaturation has been given.

4. The preparation of para-methoxy-diphenylbutadiene has been reported.

5. The preparation of a maleic anhydride derivative of para-methoxy-diphenylbutadiene has also been reported.

6. It has been shown that the bromides of para-methoxy-diphenylbutadiene are unstable in chloroform even in the cold.

7. Straus' prediction concerning the effect of the methoxy-group on unsaturated compounds has been supported.

CHAPTER IV

BIBLIOGRAPHY

Books

Cohen, J. B. Organic Chemistry for Advanced Students, Vol. I. New York: Longman and Green, and Co., 1928.

Gilman, H. Organic Chemistry, Vol. I. New York: John Wiley and Sons, Inc., 1938.

Hielbron, I. Dictionary of Organic Compounds, Vols. I-III. New York: Oxford University Press, 1934.

Robinson, J. R. Organic Synthesis, Vol. XVI. New York: John Wiley and Sons, Inc., 1935.

Waters, W. A. Physical Aspects of Organic Chemistry. New York: D. Van Nostrand Co., 1936.

Watson, H. S. Modern Theories of Organic Chemistry. Oxford: Clarendon Press, 1937.

Periodicals

Allen, C. F. H. "The Diene Synthesis of Diels and Alder," Journal of Chemical Education, Vol. 10 (1933), pp. 494-497.

Bergmann, F., and Weinberger, Z. "Remarks on the Synthesis of Substituted Stilbenes and ortho-Phenylbutadienes," Journal of Organic Chemistry, Vol. 6 (1941), pp. 134-39.

Cain, J. C., Simonsen, J. L., and Smith, C. "Synthesis of Unsymetrical Derivatives of Deoxybenzoin," Journal of Chemical Society, Vol. 103 (1919), pp. 1035-1039.

Davies, H., and Davies, W. "The Bromination of Meta-Methoxy Cinnamic Acid," Journal of the Chemical Society, part I (1928), pp. 602-605.

Farmer, E. H., Lawrence, C. D., and Thorpe, J. F. "Properties of Conjugated Compounds, Part IV. The Formation of Isomeric Additive Dibromides from Butadiene," Journal of the Chemical Society, Part I (1928), pp. 729-739.

Farmer, E. H., and Scott, W. D. "Properties of Conjugated Compounds, Part VI. The Dibromination Products of Cyclic Butadienes," Journal of the Chemical Society, Part I (1929), pp. 172-180.

Francis, A. W. "Active Agents in Bromination," Journal of the American Chemical Society, Vol. 47 (1925), pp. 2340-2347.

Hanson, N. W. and Williams, D. M. "The Addition of Halogen to Unsaturated Acids and Esters. Part III. The Velocity of Bromine Addition," Journal of the Chemical Society,

Part I (1930) pp. 1059-1063.

Ingold, C. K., and Burton, H. "Mobile Ion Tautomerism, Part I. A Preliminary Study of Conditions of Activation of the Three Carbon System and a Discussion of Results in Relation to Modes of Addition to Conjugated Systems," Journal of The Chemical Society, Part I (1928), pp. 904-921.

Ingold, C. K., and Smith, H. E. "Mode of Addition to Conjugated Unsaturated Systems. Part III. Further Remarks and Observations Bearing on the Mechanism of Addition of Halogens and Hydrogen Halides," Journal of the Chemical Society, Part II (1931), pp. 2752-2765.

Meerwein, H., Buchner, E., and Emster, K. van. "Reaction of Aromatic Diazo Compounds upon α, β-Unsaturated Carbonyl Compounds," Journal fur Praktische Chemie, Vol. 152 (1939), pp. 237-266.

Muskat, I. E., and Huggins, K. A. "Studies of Conjugated Systems. I. The Chlorination of Phenylbutadiene," Journal of the American Chemical Society, Vol. 51 (1929), pp. 2496-2503.

Riemer, M., and Tobin, E. "The Bromination of 2,4-Dimethoxycinnamic acid," Journal of the American Chemical Society, Vol. 52 (1930), pp. 341-347.

Riiber, C. N. "Ueber die Constitution des Bisphenylbutadienes," Berichte Der Deutschen Chemischen Gesellschaft, Vol. 42 (1909), pp. 2866-2885.

Terry, E. M., and Eichelberger , L. "Halogenation of Fumaric and Maleic acids -- Walden's Inversion," Journal of the American Chemical Society, Vol. 47 (1925), pp. 1067-1078.

Unpublished Material

Proctor, C. A. "The Preparation and Chlorination of 1-p-Chloro-phenyl-4-Phenylbutadiene." Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1932.

Yokley, O. E. "Studies in Conjugated Systems: The Addition of Bromine and Hydrogen Bromide to 1-p-Bromo-phenyl-4-Phenyl-Butadiene." Unpublished Master's Thesis, Department of Chemistry, Atlanta University, 1939.