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TREAT BALDWIN JOHNSON

1875—1947

A Biographical Memoir by HUBERT BRADFORD VICKERY

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Biographical Memoir

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Treat B. Johnson

TREAT BALDWIN JOHNSON* 1875-1947

BY HUBERT BRADFORD VICKERY

Yale University has been unusually fortunate among American centers of learning in the number of men who first attended as students and, after graduation, remained for the rest of their lives to become distinguished teachers and investigators. Treat Baldwin Johnson was one of these. He was graduated from the Sheffield Scientific School of Yale in 1898 and received the Ph.D. degree in organic chemistry in 1901. He had been a laboratory assistant during his graduate study and continued in this capacity until 1902 when he was appointed instructor. Promotion to the grade of assistant professor came in 1909 and to a full professorship in 1914. His outstanding attainments in science were recognized by the University in 1028 by an appointment as Sterling Professor of Chemistry, a position he held until his retirement in 1943. These dates are the brackets that enclose a lifetime of service to his University and to organic chemistry.

Johnson was born in Bethany, Connecticut, a small village situated among the hills a few miles northwest of New Haven, on March 29, 1875. His father, Dwight Lauren Johnson, who was born in the nearby town of Prospect in 1847, was a descendant through two successive Garry Johnsons of the daughter of a David Clark who served in New York during the Revolution. Johnson's mother was Harriet Adeline Baldwin who was born in Woodbridge in 1845, the descendant in the sixth generation of a Richard Baldwin who came from England in 1638 and settled in Milford, Connecticut, where he married Elizabeth Alsop of New Haven in 1642. The family names in successive generations, Mitchell, Hotchkiss, and Buckingham on

^{*} The writer is most grateful to Mrs. Johnson who put family records and a file of bound reprints at his disposal. The bibliography is essentially as it was compiled for the Academy by Johnson himself in 1941 but has been completed from Chemical Abstracts. The kind assistance of Professor A. J. Hill in connection with records in the Sterling Chemistry Laboratory of Yale University is gratefully acknowledged.

Johnson's mother's side, and Doolittle, Hotchkiss, and Clark on his father's side, are still common in the vicinity of New Haven and belong to families of the highest repute. Johnson's genealogy is significant in that it goes far to explain his integrity, his singleness of purpose, his industry, and above all, his strong sense of personal obligation to serve his University and his fellow townsmen. These forebears were sound people, farmers and merchants for the most part with the heritage of their English yeoman ancestry, men and women of sturdy independence, thrifty, God-fearing and law-abiding citizens of the communities in which they lived. It is from such people that leaders spring.

Treat Johnson was the oldest of a family of three boys; a sister, the youngest of the family, died in infancy. The boys were brought up on their father's farm in Bethany, sharing in the daily chores and living the life of country boys everywhere. Treat attended the local ungraded country school where he soon attracted the interest of his teachers. The father of one of these teachers, a neighboring farmer, urged upon Johnson's father the desirability of giving his son an opportunity for a more advanced education. The decision was evidently a difficult one and was arrived at with characteristic Yankee uncommunicativeness. Late one September afternoon in 1890, after the boy had spent the day mowing with his uncle, his father appeared in the meadow and directed him to go to the house and get ready to go to Ansonia. He found that his mother had already packed his clothes and, a few hours later, he was deposited in Ansonia with orders to report to the high school the following morning. In this somewhat unceremonious way was Treat Johnson's higher education begun. His comment on the incident in later years was equally brief: "Some experience!"

Lest this story should give a false impression of the relationship between Treat Johnson and his father, it is of interest that, back in the early twenties, a brightly-painted ox neck-yoke hung over the fireplace in Johnson's summer cottage in Bethany. To visitors who inquired about it, Johnson would proudly explain that with that neck-yoke, his father had earned the money to send him to college.

Johnson's private life was a quiet one. He married Emma Estelle Amerman of Woodside, Long Island, in 1904 and for years occupied an apartment not far from the University. They had no children, and occasionally spent summers in travel or, in later years, in automobile trips to Maine or Nova Scotia. Early in the twenties, they built a small summer cottage on what had been his father's farm on Luke Hill in Bethany and, in 1928, erected a permanent home there. The view across the valley is one of the most beautiful in the state. Later, the cottage was occupied by a caretaker, and a small building was erected to house a private laboratory where an assistant helped with many personal investigations. In the item in "Who's Who", Johnson records himself with pardonable pride as "Director, Bethwood Research Laboratory, Bethany, Conn." and this, together with one other affiliation, stands at the head of a list of memberships that includes some of the most distinguished scientific societies in the world.

Light is shed upon Johnson's character by the order in which these apparently small matters are recorded. The other affiliation mentioned is that he was President of the Bethany Library Association, and it is clear that he regarded this at least as important as his professional connections. He had been active in the organization of the local library association and in the building of the library, and was also helpful in establishing an endowment fund for its support. In addition he served his native town as chairman of a committee which planned and built a new school and furnished one of the class rooms at his own expense. But what was, perhaps, his most significant civic service was the presentation in 1936 to the church he had attended as a boy of the Harriet Baldwin Memorial Church House in memory of his mother.

As an undergraduate in the Sheffield Scientific School of Yale University, Johnson came under the influence of H. L. Wheeler,¹ then well started on his career in the field of the synthesis of organic nitrogen compounds. Instruction in organic

^a Elected to Academy 1909.

chemistry was also provided by W. J. Comstock, physical chemistry was taught by B. B. Boltwood² and analytical chemistry by H. L. Wells.³ The new Sheffield Chemical Laboratory had been first occupied in 1895, and the teaching and research were largely in the hands of a group of enthusiastic young men. R. H. Chittenden 4 entered upon his duties as Director of the School in 1808 at the beginning of a period of reorganization and expansion of the facilities that soon placed the School in the forefront of American institutions devoted to the teaching of science.

Johnson received an appointment as a laboratory assistant in 1898, the year he obtained his undergraduate degree, and also the year in which, in collaboration with Wheeler, he published his first scientific paper. He entered the graduate school of the University in the fall and received the degree of Ph.D. in 1901 by which time he had been co-author with Wheeler of five more papers and sole author of one. In 1902, he was appointed as instructor in organic chemistry. Nine papers with Wheeler were published during the next two years but, from 1904 on, this collaboration became less and less frequent, and Johnson's name appears on most of the subsequent papers as senior author with a long succession of graduate students which, at the time of his retirement, had reached the astonishing number of ninety-four.

Johnson's early investigations dealt with the reactions of variously substituted ureas and thioureas and their use in the synthesis of hydantoins and thiohydantoins. In 1903, Wheeler and Merriam described a new synthesis of uracil and of thymine. The method consisted of the condensation of methylpseudothiourea with the sodium salt of formylacetic ester to give thiouracil and with formylpropionic ester to give thiothymine. The thiopyrimidines were easily desulfurized with acid and the procedure, as a whole, was far more elegant than that previously described by Fischer.

These substances had attracted attention as a result of the investigations of Kossel and his associates in Germany upon

^a Elected to Academy 1911. ^a Elected to Academy 1903.

^{*} Elected to Academy 1890.

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nucleic acid from which both pyrimidines had been obtained. In addition. Kossel and Neumann in 1894 had isolated from thymus nucleic acid a base of unknown structure which they named cytosine and, more recently, Kossel and Steudel had found the same base in nucleic acid from sturgeon testicles. They considered it to be in all likelihood a third pyrimidine. Wheeler and Johnson, in 1903, after consideration of various possibilities, prepared 2-amino-6-oxypyrimidine⁵ and 2-oxy-6-aminopyrimidine. They were able to show that the natural base described by Kossel was identical with the second of these isomeric substances. Although Kossel had assigned correct structural formulae to all three of the natural pyrimidines, it was Fischer's synthesis of uracil and thymine, confirmed by Wheeler and Merriam, and Wheeler and Johnson's synthesis of cytosine that completed the proof.

By an interesting coincidence, T. B. Osborne⁶ at the Connecticut Agricultural Experiment Station in New Haven, at about the same time, had obtained a new nucleic acid from wheat embryo 7 and had demonstrated that the purines adenine and guanine were present in the preparation in equimolecular proportions. He had also been able to isolate uracil, but had failed to demonstrate the presence of cytosine. In order to compare the properties of their synthetic uracil with material from a natural source. Wheeler and Johnson asked Osborne for a sample of his preparation from wheat nucleic acid. Unfortunately, or perhaps fortunately as it turned out. Osborne had used up all of his material for analytical studies, but he was able to give them the mother liquors from which the uracil had been separated. Wheeler and Johnson at once looked for cytosine in this solution and, as a result of their experience with this substance, promptly succeeded in isolating it. The preparation was shown to be identical with their synthetic material as well as

 $^{^{5}}$ To prevent confusion with titles in the bibliography, the numbering of the pyrimidine ring employed by Johnson has been retained. Present day nomenclature assigns Johnson's position 3 the number 1 and this substance would be 2-amino-4-oxypyrimidine.

^{*} Elected to Academy 1910. ⁷ Osborne, T. B., and Harris, I. F., Ztschr. f. physiol. Chem., 36, 85 (1002).

with a preparation obtained from spleen by Levene⁸ and furnished by him for comparison. Cytosine was thus shown to be a natural base present in nucleic acid of both animal and plant origin. There is little doubt that Johnson's lifelong interest in pyrimidines was aroused by these successes.

Complete justification of his devotion came in 1935 when thiamine, the first of the vitamins of which the structure was elucidated, was shown by Williams 9 to contain a substituted pyrimidine ring as a part of its structure and was subsequently successfully synthesized 10 in at least three different laboratories practically simultaneously. It chances that the exact degradation product of thiamine, 2,5-dimethyl-6-amino-pyrimidine had not been prepared either by Wheeler or by Johnson although several substances closely related to it had been synthesized. However, the existence of an extensive literature on the pyrimidines, much of it the work of Johnson and his students, enabled Williams to identify and synthesize the new substance with a minimum loss of time and effort.

Beginning in 1903, many of the students who worked with Johnson were assigned problems on the synthesis of various pyrimidines. The motivation of these investigations at the start, aside from the simple interest in the preparation of new compounds, was Johnson's concern with the problem of the composition and structure of nucleic acid. An example of this is furnished by the work (1908) on the action of fuming nitric acid on thymine and uracil. Thymine is converted into oxynitrohydrothymine, while uracil, under the same conditions, is not reduced but gives 5-nitrouracil, a substance which is almost insoluble in alcohol. Inasmuch as the thymine derivative is extremely soluble in alcohol, a method to separate these two substances was devised which could be applied to the separation of the mixture of uracil and thymine found among the decomposition products of nucleic acid.

Another important accomplishment of this period was the dis-

^{*} Elected to Academy 1916.

⁹ Williams, R. R., J. Am. Chem. Soc., 57, 229 (1935); elected to the Academy 1945. ¹⁰ Williams, R. R., and Cline, J. K., J. Am. Chem. Soc., **58**, 1504 (1936).

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covery in 1907 of a specific color test for uracil and cytosine that is not given by thymine. The test consists in the addition of bromine water followed by an excess of barium hydroxide. A purple or violet precipitate furnishes positive indication of the presence of one or both pyrimidines. The test can be so conducted as to be sensitive to a milligram of the substance. The mechanism of the reaction was worked out; both uracil and cytosine are converted by bromine to dibromohydrouracil which is decomposed in the presence of dilute alkali to isodialuric acid. This at once rearranges to dialuric acid with the loss of the elements of water. Both isodialuric acid and dialuric acid give blue precipitates with barium hydroxide. The blue compound, on being acidified and freed from barium, becomes colorless and the solution deposits crystals that were identified as alloxantin.

A further illustration of Johnson's interest in naturally occurring pyrimidines is furnished by the investigation of orotic acid. This substance was isolated from milk in 1905 by Biscaro and Belloni who assigned to it a structure containing a sevenmembered ring. To Wheeler, Johnson and Johns in 1907, it appeared far more likely that the substance was a pyrimidine carboxylic acid, and they thereupon undertook the preparation of uracil-5-carboxylic acid. The properties of this substance were compared with those in the description of orotic acid given by the Italian workers. Although there were many points of resemblance, there were discrepancies in the melting points of the acid and of its derivatives. Wheeler, at the same time, prepared uracil-4-carboxylic acid (an ester of which had already been described by Müller) finding that this substance also differed from orotic acid as described by the Italian workers. Research on the problem was therefore dropped. However, Bachstez in Italy in 1930, repeated the preparation of orotic acid from milk as well as the synthesis of uracil-4-carboxylic acid and was able to demonstrate that the natural material, when adequately purified, is identical with this pyrimidine. Johnson thereupon (1931, with Schroeder) returned to the study and was able to improve the synthesis so that uracil-4carboxylic acid became a readily available substance. It was found that the corresponding aldehyde, which could be prepared by methods developed in 1915 by Johnson and Cretcher, was easily oxidized to the acid. The identification of the synthetic substance with natural orotic acid supplied to them by Bachstez was confirmed.

In 1911, perhaps in part because of the success of the investigations of Osborne at the Connecticut Agricultural Experiment Station in the protein field, Johnson's attention was turned to the consideration of proteins and amino acids, and especially to the hydantoins which may be regarded as derivatives of the amino acids and which are, at the same time, closely related to the pyrimidines. The first paper that specifically mentions proteins in the title (with Burnham) offered an interesting speculation on the possible presence of thiopolypeptide groupings in proteins as an explanation of that part of the sulfur of proteins not present as cystine. At that time, the presence of methionine in proteins had not been recognized. Other speculative possibilities were given in a later paper, and one of his students was set the task of preparing thioamides and thiopeptides to illustrate his views. The work on hydantoins led to the preparation of 3,5-dichlorotyrosine (Wheeler, Hoffmann and Johnson 1911), the analogue of the naturally occurring iodine compound which had been prepared synthetically by Wheeler and Jamieson in 1905; also to the preparation of thiotyrosine (with Brautlecht 1912) and of N-methyltyrosine (with Nicolet 1012). A particularly significant paper was that with O'Brien (1912) on the synthesis of phenylalanine. This procedure was a modification of the Erlenmeyer synthesis starting with hippuric acid whereby benzoylthiohydantoin is formed by condensation with potassium thiocyanate. The hydantoin is reduced with tin and hydrochloric acid and simultaneously hydrolyzed with the formation of phenylalanine. The synthesis required only three operations as compared with four or more by other published methods and employed readily available and cheap reagents. Glycine could also be used if hippuric acid were not available, since it can readily be converted into the same thiohydantoin and used for the synthesis.

Johnson's approach to protein chemistry was strictly that of an organic chemist interested in problems of organic structure.

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A series of papers in 1915 dealt with the synthesis of o-tyrosine (with Scott) and with the problem of the effect of nitric acid on proteins (with Hill). This investigation led to the demonstration of the presence of nitrotyrosine in nitrated silk fibroin.

Work on the products of the destructive distillation of silk fibroin *in vacuo* (with Daschavsky 1919) showed that phenols and amines are produced. Accordingly, the decarboxylation of tyrosine was studied (1925) and an elegant method to accomplish this was developed. The amino acid was heated to 260° in solution in a mixture of diphenylamine and diphenylmethane. The mixture remained liquid when cooled and deposited tyramine in a yield of 95 per cent when diluted with benzene.

Two other syntheses of amino acids were described. In 1930 (with Law), he prepared thiothyronine; this is the sulfurcontaining analogue of thyronine which, in turn, is produced by the deiodination of thyroxine and had been described by Harington. In 1939, the synthesis of α -aminopelargonic acid was described.

In 1922, a series of investigations directly related to biochemistry was begun as the result of arrangements with the National Tuberculosis Association whereby not only funds but liberal supplies of cultures of tuberculosis bacilli were made available for chemical investigation. The first of these studies (with Brown) led to the isolation of thymine and cytosine from the nucleic acid of the organism as well as to improved methods for the preparation of the specific nucleic acid. Later, (1925, with Coghill), 5-methylcytosine was demonstrated to be present in this nucleic acid. This success stimulated the elaboration of plans for a comprehensive study of the chemical composition of tuberculosis bacilli. The proteins of the cells were investigated by Coghill in 1926 and again by Renfrew in 1928. However, a new direction was given to the research by R. J. Anderson,¹¹ who joined the group in the Sterling Laboratory in 1926, and took over the investigation of the lipides of tuberculosis bacilli with results now widely known. For several years, Johnson continued investigation on tuberculosis bacilli as well as upon

¹¹ Elected to the Academy 1946.

other species of bacteria giving special attention to the nitrogenous compounds and carbohydrates; but the main supervision of the research upon bacteria was transferred to Anderson.

Several other investigations of substances of biochemical importance should be mentioned. The substance divicine was discovered by Ritthausen in 1879 in the form of a glucoside, vicine, in vetch seeds and was reinvestigated by him in 1899. It was a base, and the empirical formula published suggested to Johnson that it might be a pyrimidine. Johnson and Johns (1914) accordingly prepared 2,5-diamino-4,6-dioxypyrimidine and 4,5-diamino-2,6-dioxypyrimidine and compared their properties with the description of divicine given by Ritthausen. They inclined to the view that divicine is the 4,5-diaminoderivative. However, Levene at the same time prepared the natural substance and obtained a positive identification with 2,5diamino-4,6-dioxypyrimidine.

A second accompanying glucoside isolated by Ritthausen and designated convicine was studied by Fisher and Johnson in 1932. The pyrimidine nucleus was shown to be 4-iminodialuric acid.

The general increase in interest in synthetic drugs in the third decade of the present century was reflected in Johnson's laboratory by such investigations as those which led, with Manske, to the synthesis of ephedrine (1929) and to the preparation of various hydantoins with hypnotic properties (with Herbst, 1932). However, by far the most important of these investigations, in view of the later results, was that with Lane in 1921. It was found that the antiseptic strength of resorcinols substituted in the 4-position with alkyl groups increased with the molecular weight of the *n*-alkyl group. The comparisons were made with respect to the antiseptic value of resorcinol itself and were carried as far as the *n*-butyl derivative. The fundamental method employed to prepare these substances was an original modification of the Gattermann synthesis; in the hands of others, the series was extended with the result that the germicidal effect was found to be maximal with the n-hexyl derivative. The outcome was the commercial production of hexylresorcinol under patent rights, and Johnson's share of the profits was substantial. The business acumen he inherited from his Yankee forebears stood him in good stead, for this relationship led to the accumulation of a comfortable personal fortune.

Such investigations as those just mentioned did not in any way interfere with the fundamental research on pyrimidines carried on under Johnson's direction. On the contrary, these side excursions, for that is what they actually were, frequently represented the choice of a problem by a student or associate who had special interests, or were investigations carried out under grants of funds for research in special fields such as the chemistry of silk. This project was generously supported for many years by Cheney Brothers of South Manchester, Connecticut, and, later, by the Textile Foundation. Johnson had the disposal of many such fellowships over the years.

The pyrimidine work continued throughout Johnson's life. In 1941, the last year of his full activity in the laboratory, ten of the twelve papers published were contributions to pyrimidine chemistry. With the exception of a few years, notably in the mid-twenties when the major attention was given to the work on tuberculosis bacilli, from one to as many as ten papers on pyrimidine chemistry were sent off annually to the journals. The maximum output occurred in 1930 when twenty-six separate contributions were made; there were many years when from ten to twenty papers of which about one-third dealt with pyrimidines were submitted for publication.

Johnson was accustomed to numbering the papers on pyrimidines. Beginning with an early (1898) paper of Wheeler and with the Wheeler and Merriam paper of 1903 on the synthesis of uracil and thymine as number 2, the series was continued until 1944; Johnson's last published paper was number 182 in the pyrimidine series, and his complete bibliography numbers 358 titles.

In addition to the strictly academic research with graduate students and fellows, Johnson for years carried on personal investigations with the aid of paid assistants, in later years at the Bethwood Laboratory in Bethany, and the results of a number of these were patented, the rights being assigned to

one or another company for commercial exploitation. In all, some fifteen patents were issued to him in addition to several to his co-workers. Most of these patents dealt with such substances as thiazoles, diphenyl sulfides and sulfonic halides.

It is unfortunate that Johnson never took the time to summarize his investigations in pyrimidine chemistry in the form of a monograph. There are only a few publications of the review type. The earliest is his speech of acceptance of the Nichols Medal of the New York Section of the American Chemical Society in 1918 in which the history of pyrimidine chemistry is briefly given together with a clear account of the investigations at Yale up to that time. Far more extensive, although somewhat restricted in its scope, is the review of the amino and aminooxy derivatives of the pyrimidines which was prepared in 1933 in cooperation with Professor Dorothy A. Hahn of Mount Holyoke College. This article of more than one hundred pages was published in Chemical Reviews.

A broader treatment of the pyrimidines under the title "The Chemistry of the Pyrimidines, Purines and Nucleic Acids" was prepared as a chapter in the first edition of Gilman's "Organic Chemistry" in 1938.

Johnson was elected to the National Academy in 1919, the year after he received the Nichols Medal. He was a member of the National Research Council, the American Chemical Society, the American Society of Biological Chemists, the Connecticut Academy of Arts and Sciences, the American Institute of Chemists of which he was president 1926-1927, as well as of a number of other professional societies. He was a member of the Board of Trustees of the Sheffield Scientific School from 1920 to 1941, acting as secretary from 1923 to 1941 and as a member of the Executive Committee from 1921 to 1941. He was also a member of the Board of Trustees of Yale-in-China for many years.

As a teacher, Johnson was a profound influence in American chemistry. His lectures were clear, simple, abundantly illustrated, and scholarly. They were delivered in a manner that enabled the students to take copious notes and were in every way memorable. To be sure, the occasional unregenerate

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student would keep score on the number of times the word "functions", or the even more typical Johnsonianism "functionate", was used in the course of the hour. The phrase "for example" is said, on one occasion, to have been used 127 times! To Johnson, complex organic molecules were often "constructions" and were so called because that is the way he thought of them. But, aside from a few appealing mannerisms of speech such as these, the matter was sound, solid organic chemistry. His students left Yale to go on to professional positions often of the highest eminence. They took with them the memory of a kindly, simple-mannered man whom they all regarded as a friend.

KEY TO ABBREVIATIONS USED IN BIBLIOGRAPHY

Am. Chem. J. = American Chemical Journal

Am. Dyestuff Reptr. = American Dyestuff Reporter

Am. Rev. Tuberc. = American Review of Tuberculosis

Ann. Coll. Symp. = Annual Colloid Symposium

Berichte deutsch. chem. Gesell. = Berichte der deutschen chemischen Gesellschaft

Biochem. Zeit. = Biochemische Zeitschrift

Chem. Rev. = Chemical Reviews

Ind. Eng. Chem. = Industrial and Engineering Chemistry

J. Am. Chem. Soc.= Journal of the American Chemical Society

J. Biol. Chem. = Journal of Biological Chemistry

Proc. Nat. Acad. Sci. = Proceedings, National Academy of Sciences

Rec. Trav. chim. = Recueil des Travaux chimiques des Pays-Bas

Zeit, f. physiol. Chem. = Zeitschrift für physiologische Chemie

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| 2,020,650 | Nov. 12, 1935 | "Thiazole Substituted by a Primary Alkyl- amino Group." (Assigned to Win- throp Chemical Company, Inc., New York City, N. Y.) |
| 2,030,373 | Feb. 11, 1936 | "Derivatives of Thiazoles and Process of Preparing the Same." (Assigned to Winthrop Chemical Company, Inc., New York City, N. Y.) |
| 2,065,808 | Dec. 29, 1936 | "Hydroxy Diphenyl Sulphide Derivatives." (Assigned to Sharp and Dohme, Inc., Philadelphia, Pa.) |
| 2,146,744 | Feb. 14, 1939 | "Process of Preparing Sulphonyl Halides and Sulphonic Acids from Pseudothi- oureas." (Assigned to Röhm and Haas Company, Philadelphia, Pa.) |

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| Number of Patent | Date Granted | Title |
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| 2,147,346 | Feb. 14, 1939 | "Sulphonic Halides." (Assigned to Röhm and Haas Company, Philadelphia, Pa.) |
| 2,171,241 | Aug. 29, 1939 | "Silk." (Assigned to Textile Foundation, Washington, D. C.) |
| 2,174,856 | Oct. 3, 1939 | "Process of Producing Sulphonyl Halides." (Assigned to Röhm and Haas Com- pany, Philadelphia, Pa.) |
| 2,216,515 | Oct. 1, 1940 | "Production of Nitro-Mercapto-Diphenyl- amines." (Assigned to Sharp and Dohme, Inc., Philadelphia, Pa.) |
| 2,350,900 | June 6, 1944 | "Aminodiphenylsulfides." (Assigned to Sharp and Dohme, Inc., Philadelphia, Pa.) |