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# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 76

OCTOBER 20, 1954

NUMBER 20

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## MARSTON TAYLOR BOGERT

1868--1954

The news of the death of Marston Taylor Bogert, Professor Emeritus of organic chemistry in Columbia University and for many years one of its distinguished scientists and teachers was received with sorrow, not only by the faculty and former students, but also by a host of friends both in this country and abroad.

Professor Bogert was born in Flushing, New York, April 18, 1868. On his father's side he came from a long line of Dutch ancestors, the first of whom came from Schoonderwoerd near Leerdam, Holland, in 1663. As a boy he attended the Flushing Institute, a private school where he received some instruction in elementary chemistry. At the age of eighteen, he followed the tradition of the family by coming to Columbia College, as had his three brothers and his father, the latter being a member of the class of 1846. As an undergraduate student he specialized in languages, both ancient and modern, and the training he thus acquired has been evident in the clarity of his diction both in his writing and public addresses in later years. He not only was an excellent student as attested by his Phi Beta Kappa key and on graduation being offered a fellowship in the German Department. His brilliancy as a student allowed him to take a prominent part in extracurricular activities. During his freshman year he was captain of the class crew that beat Harvard, and his prowess as champion tennis player continued to be evident during his years as a member of the faculty. During his senior year he not only was the class president but was chosen as one of "the three most deserving students of the graduating class." He also was given the added honor of being selected as Chairman of the Student Body at the installation of the University's new president, Seth Low.

As a science requirement for the A.B. degree from Columbia College, young Bogert listened to

Professor Chandler's lectures on general chemistry. These lectures appear to have impressed him to such a degree that after his graduation from the College and spending the summer travelling in Europe, he decided to resign his fellowship in the languages and to enter the School of Mines as a major in chemistry. After four years in the latter school, he received the Ph.B. degree in 1894.

In the School of Mines his ability as a student again stood out, and on the death of Professor Charles E. Colby, during Bogert's senior year, Professor Chandler asked him, first as an assistant and then as a tutor, to take over the instruction in organic chemistry. At that time, 1894, Columbia was in the transition period of becoming a great university. The Columbia catalogue offered, for the first time, four courses in organic chemistry, three of them being for candidates for the A.M. and Ph.D. degrees, and it fell on Bogert's young shoulders to carry on the instruction in these advanced courses. His ability for the task was quickly recognized as is evident from his rapid rise from instructor, 1897-1901, Adjunct Professor, 1901-1904, to Professor of Organic Chemistry in 1904, a position which he filled up to his retirement in 1939.

During his forty-three years as teacher and guide to scores of advanced students in their researches for the doctorate, he was the author or co-author of over four hundred contributions on organic chemistry to various scientific journals. These publications extended over a wide field in synthetic organic chemistry, dealing with terpenes, essential oils, alkaloids, arsenicals, drugs, vitamins and perfumes.

Professor Bogert's activities in the University extended far beyond the laboratory and lecture room. He was a member of the University Council, 1909-1911, 1916-1917 and 1922-1929; Columbia representative on the Board of the New

York College of Pharmacy, 1930-1936; member of the Board of Managers of the New York Botanical Gardens, served on many committees of the faculty, alumni, and maintained friendly associations with teachers in other fields. He belonged to the honor societies of Phi Beta Kappa, and Sigma Xi, to the college fraternity, Delta Phi, and took an active part in installing Phi Lambda Upsilon at Columbia. Some of the scientific organizations beyond the campus to which he belonged were: The American Association for the Advancement of Science, the American Philosophical Society, The National Academy of Sciences, National Institute of Social Sciences, American Academy of Arts and Sciences, the American Institute of the City of New York, the Washington Academy of Sciences, the American Institute of Chemists and the Century Association.

In recognition of his many helpful and constructive services and as a scientist, Columbia awarded him the Sc.D. degree at its Sesqui-Centennial Anniversary in 1929, the Egleston Medal in 1939, the Chandler Medal in 1949 and Large Scroll of the Alumni Association of the Graduate Schools "for having distinguished himself as a professor, lecturer, author and chemist" in 1936. At its 25th anniversary Clark University honored him with the degree of LL.D.

In 1927, Nicholas Murray Butler, President of Columbia and Chairman of the Carnegie Endowment for International Peace wanted a lecturer on science to serve as an ambassador of international good will and designated Professor Bogert as the first Visiting Carnegie Professor of International Relations at Charles University in Prague.

Among the local chemists in New York, he took an active part in establishing the Chemists' Club in 1908, serving as its first secretary and later as its president. It also fell to his lot to be the last surviving charter member of the Club. To commemorate his name, recently the Club has set aside one of the rooms in the spacious and well-appointed Club house on East 41st Street as the "Bogert Room." Due to his perennial good humor and ready wit he was often called upon to act as toastmaster at dinners and social gatherings held by the chemists in New York.

He was an enthusiastic supporter of the American Chemical Society and a constant attendant at its national meetings. For several years he was one of its councillors and during 1907 and 1908 served as its president. During the latter incumbency Dr. Bogert skillfully guided the Society through a serious situation, in which the industrial chemists threatened to form their own organization, by authorizing the publication of the *Journal of Industrial and Engineering Chemistry*, which has proved to be an important journal of the Society. Also, during his presidency of the Society, President Roosevelt asked him to take part in conferences on the Conservation of Natural Resources. In the second of these conferences, Dr. Bogert addressed all four divisions, Forests, Lands, Minerals and Water, emphasizing the contribution of chemistry toward the solution of many of their technical problems.

In appreciation for all of these activities, as well as for his high scientific attainments, the American Chemists awarded him their highest honors, the Nichols Medal of the New York Section of the American Chemical Society in 1905, and the Priestley Medal by the National Society in 1938. To this list of honors also should be added medals from the American Institute of Chemists and the American Society of Cosmetic Chemists.

Professor Bogert took an active interest in chemistry abroad. He was a member of the American Advisory Committee of Honor at the 7th Meeting of the International Congress of Applied Chemistry held in London in 1909, president of the American Section at the 8th Meeting of the Congress held in Washington and New York in 1912. At its 10th meeting held in Rome in 1938, he was elected president of the International Union of Pure and Applied Chemistry. The two World Wars seriously disorganized the work of the Union and in 1946 Dr. Bogert spent several weeks in London attending conferences in which he took a leading part in its revival. He continued as president of the Union until 1947 when the first postwar conference was held in London.

The Society of Chemical Industry also was one of Dr. Bogert's special interests and at the time of his death had been for many years its Senior Past President. In addition he served as President of the American Section of the Société de Chimie Industrielle in 1920-1921, held memberships in the Chemical Societies of France, Italy, Switzerland, Poland and Holland, and was a member of the International Commission in honor of Amedeo Avogadro, under the patronage of King Victor Emmanuel III of Italy. He was an Honorary Fellow of the Royal Society of Edinburgh, Fellow of the London Chemical Society and the Royal Society of Sciences and Letters of Bohemia. In appreciation of all his foreign activities, his friends abroad made him Commander of the Order of the White Lion of Czechoslovakia and Charles University honored him with a medal, and the degree N.R.D. (Natumum Rerum Doctor), while Comensky University of Bratislava honored him with its medal.

During World War I, Dr. Bogert was granted leave from the University and spent his time in Washington where he headed the Chemical Warfare Service of the Army with the rank of Colonel. In the latter capacity he served as Assistant Director of the Gas Warfare Service, member of the Executive Board of the National Research Council, Member of the Advisory Committee of the War Trade Board and the Advisory Board of the Signal Corps. In the Second World War he was a member of the Chemical Industry Branch of the War Production Board.

In 1893, Bogert married Charlotte E. Hoogland, and two daughters, Annette B. (Mrs. Frank B. Tallman) and Elise B. (Mrs. F. K. Huber) survive. For many years he and his family spent the summers at their commodious summer home in Maine, situated on the shores of Belgrade Lakes and surrounded by a large tract of beautiful woodland. There he and Mrs. Bogert found time to entertain

many week-end friends, while in the forenoons of the week days Dr. Bogert was found in the woodshed, which had been fitted up as an office, writing for publication, accounts of experimental results and data accumulated during the past academic year by himself and his collaborating research students. The afternoons were given over to fishing and hunt-

ing, sports of which he was especially fond, as shown by his membership in the Megantic Fish and Game Club and in the Hunter's Fraternity of America.

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## Studies in Steroid Total Synthesis. I. Resolution of a Bicyclic Intermediate

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RECEIVED FEBRUARY 11, 1954

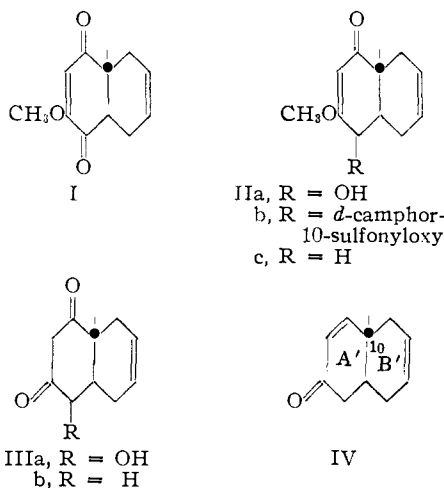
A method for converting Woodward's *dl-trans*-1,4-diketo-2-methoxy-10-methyl- $\Delta^{2,6}$ -hexahydronaphthalene (I) into the optically pure enantiomorphs of *trans*-2-keto-10-methyl- $\Delta^{2,6}$ -hexahydronaphthalene (IV) in 55-60% over-all yield is described. Stereo-selective reduction of I yielded the monohydric alcohol IIa which was resolved *via* its *d*-camphor-10-sulfonate esters. The pure diastereoisomers were reductively cleaved to (+) and (-)IIc and thence reduced to the optically active forms of the Woodward bicyclic ketone (IV) with lithium aluminum hydride followed by vigorous acid hydrolysis.

A resolution step is a requirement of any scheme for the total synthesis of naturally occurring steroids. Maximum economy of materials and effort is achieved if resolution can be effected at the earliest possible stage, *i.e.*, at the time of, or closely following, the introduction of the first stable asymmetric center. Present published syntheses of non-aromatic steroids do not contain this feature.<sup>1</sup> When resolution is accomplished it has been done fairly late in the synthetic sequence.

In the present paper we wish to report modification of the Woodward<sup>2</sup> total synthesis to include resolution at the bicyclic stage coupled with an improved method for converting I to IV. Specifically, the racemic Woodward *trans*-adduct (I)

has been smoothly and stereo-selectively reduced using zinc and aqueous acetic acid to give *dl-trans*-1-hydroxy-4-keto-2-methoxy-10-methyl- $\Delta^{2,6}$ -hexahydronaphthalene (IIa) in approximately 90% yield. That IIa is the correct structure for the reduction product was indicated by cryoscopic molecular weight determination in benzene, infrared spectrum, conversion in good yield to monoesters (acetate, benzoate, *p*-toluenesulfonate) and hydrolysis under mild conditions to a  $\beta$ -diketone IIIa which was soluble in aqueous carbonate and gave a strong ferric chloride test. Subsequent conversions have confirmed these conclusions. Presumably the reduction gives an  $\alpha$ -OH although the configuration at C-1 has not been definitely established. Attempts to isolate an epimeric alcohol were unsuccessful. Zinc and acetic acid have been used by numerous investigators to reduce Diels-Alder adducts of this type.<sup>3a,b</sup> In most instances<sup>3a</sup> the conjugated double bond rather than a carbonyl group was reduced. However, Butz and Butz<sup>3b</sup> have reported the reduction of the C-1 carbonyl group of *cis*-1,2,4-triketo-10-methyl- $\Delta^6$ -octahydronaphthalene in low yield. Nes and Mason<sup>4</sup> observed some reduction of the C-20 carbonyl group of 3 $\alpha$ -hydroxy-21-acetoxy-11,20-diketo-12-bromo- $\Delta^{1,16}$ -pregnene after treatment with zinc and aqueous acetic acid for 2 hours. Resolution of IIa was accomplished readily by conversion to the *d*-camphor-10-sulfonate esters and separation of the resulting diastereoisomers by fractional crystallization from acetone. Both diastereoisomers have been isolated in good yield (85-90%) with optical purity in excess of 98% in each case.

It was found that sulfonate esters of IIa could be reductively cleaved by zinc and acetic acid to give high yields of *trans*-4-keto-2-methoxy-10-methyl- $\Delta^{2,6}$ -hexahydronaphthalene (IIc) plus the zinc salt of the sulfonic acid. Thus reductive cleavage of the tosylate or the mixture of crude diastereo-



(1) R. Robinson, *et al.*, *J. Chem. Soc.*, 676 (1946); 1855 (1949); 361 (1953), resolved a tricyclic intermediate while Sarett, *et al.*, *THIS JOURNAL*, **74**, 1393, 1397, 1401, 1406, 4974 (1952); **75**, 422 (1953); and Woodward (see reference 2) resolved very near the end of their respective syntheses. W. S. Johnson, *et al.*, *THIS JOURNAL*, **75**, 2275 (1953), and A. L. Wilds, *et al.*, *ibid.*, **72**, 5794 (1950); *ibid.*, **75**, 4878 (1953), have prepared racemic non-aromatic steroids by total synthesis but as yet have not indicated resolution has been effected. It should be noted that in the Johnson synthesis a stable asymmetric center is not present until a tetracyclic system has been prepared, thus resolution prior to that stage is impossible.

(2) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *THIS JOURNAL*, **74**, 4223 (1952).

(3) (a) L. H. Sarett, *et al.*, *ibid.*, **74**, 1393 (1952); K. Alder and G. Stein, *Ann.*, **501**, 247 (1936); C. K. Chuang and C. T. Han, *Ber.*, **68**, 876 (1935); (b) E. W. J. Butz and L. W. Butz, *J. Org. Chem.*, **8**, 497 (1943).

(4) W. R. Nes and H. L. Mason, *THIS JOURNAL*, **73**, 4765 (1951).