

---



---

## COMMUNICATIONS TO THE EDITOR

---



---

### LONG X-RAY DIFFRACTION SPACINGS OF COLLAGEN

Sir:

Various values have been proposed for the unusually large fiber-axis structural periodicity found in collagenous tissues. R. B. Corey and R. W. G. Wyckoff [*J. Biol. Chem.*, 114, 407 (1936)] concluded that their measured meridional spacings indicated a fundamental period of 330 Å., while the results of G. L. Clark and J. A. Schaad [*Radiology*, 27, 339 (1936)] introduced the figure 432 Å., or multiple. Using purely speculative arguments, W. T. Astbury [*J. Int. Soc. Leather Trades Chemists*, 24, 69 (1940)] suggested 838 Å. as the probable value.

Photographs recently obtained in this Laboratory show that the period is in reality close to 640 Å. for air-dried collagenous tissues. Technical improvements comprise principally the use of fine slits with long collimating tubes. The slits, by causing registration of a series of equally spaced line-shaped diffractions, greatly facilitate the resolution and accurate measurement of diffraction orders.

The table shows results obtainable from a typical diffraction pattern of dried beef tendon, citing only the more intense innermost orders of the fundamental period (filtered Cu K $\alpha$  radiation, specimen-to-film distance 26.1 cm.):

Measured diameter, mm.	Bragg spacing, Å.	Order no., <i>N</i>	<i>N</i> times spacing, Å.
15.1	53	12	636
13.8	58	11	638
12.6	64	10	640
11.4	71	9	639
10.0	80	8	640
8.8	91	7	637
7.6	106	6	636
5.0	161	4	644
3.7	217	3	651
2.5	322	2	644

Average 640

The first order (strongest, but difficult to separate completely from the central beam) and every one of the fainter orders to the twentieth can be seen. No lines requiring a period greater than 640 Å. have been observed in this range. Occasional orders can be made out on some films up to the position of about the thirtieth.

The fundamental periods as thus measured are included in the range 638–648 Å. when air-dried native materials (tendon, skin, cornea) from a variety of sources (rat, beef, human) are used, and in all such instances relative order intensities do not change materially. Under certain conditions, however, the positions and intensities can be altered. These effects are being studied and will be reported in due time.

DEPARTMENT OF BIOLOGY AND PUBLIC HEALTH  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE, MASSACHUSETTS      RICHARD S. BEAR  
RECEIVED FEBRUARY 18, 1942

### 1,2-DIPHENYL-3,4-DIHYDRONAPHTHALENE

Sir:

Before the publication of the paper by Bergmann, Eschinazi and Schapiro [*THIS JOURNAL*, 64, 557 (1942)], Dr. Bergmann asked for my explanation of the fact that he found the melting point of 1,2-diphenyl-3,4-dihydronaphthalene to be 94–95° while I had reported [*ibid.*, 61, 608 (1939)] a melting point of 77°. He sent me a sample of his hydrocarbon (m. p. 93–94°) which I have compared with my sample and with the carbinol which he was unable to get. My samples were bottled and put away in October, 1938, at the conclusion of that particular problem. My carbinol which melted at 98–99° in 1938, melts now at 98.5–99°, and the mixture of this compound with Dr. Bergmann's sample melts at 88–94°. The bottle which contained my pure 76.5–77° hydrocarbon in 1938, now contains two distinct varieties of crystals: colorless, transparent plates which melt at 76.5–77° and white, opaque plates melting at 91.5–93.5°. A mixture of my two kinds of crystals melts at 76–94°, a mixture of Dr. Bergmann's compound with my high melting form melts at 90–93°, and a mixture of his compound with my low melting form melts at 75–93°. Recrystallization of my mixture from either methanol or ethanol and ethyl acetate gives the high melting form identical with Dr. Bergmann's compound.

I have just repeated this preparation and again had no trouble in preparing 1-hydroxy-1,2-diphenyl-1,2,3,4-tetrahydronaphthalene by the addition of phenylmagnesium bromide to 1-oxo-2-

phenyl-1,2,3,4-tetrahydronaphthalene. This carbinol is identical with that made three years ago. The addition of a few drops of concentrated hydrochloric acid to a solution of the carbinol in ethanol caused the immediate precipitation of 1,2-diphenyl-3,4-dihydronaphthalene melting at 76°. After three weeks this material changed completely to the high melting form.

My explanation would be that these two forms are physical isomers, and Dr. Bergmann got the high melting form. I got the low melting, less stable form, both at Minnesota and at Vassar, and it is gradually changing to the more stable form after three years.

SANDERS LABORATORY OF CHEMISTRY  
VASSAR COLLEGE  
POUGHKEEPSIE, N. Y.

H. MARJORIE CRAWFORD

RECEIVED OCTOBER 8, 1941

#### THE INTRODUCTION OF TERTIARY BUTYL GROUP INTO ETHYL ACETOACETATE BY MEANS OF BORON TRIFLUORIDE

Sir:

It was shown recently<sup>1</sup> in this Laboratory that ethyl acetoacetate is alkylated by isopropyl alcohol or ether in the presence of boron trifluoride. Other alkylations effected by boron trifluoride were also described recently.<sup>2</sup> It has now been shown that ethyl acetoacetate is alkylated by

(1) Hauser and Breslow, *THIS JOURNAL*, **62**, 2389 (1940).

(2) Hauser and co-workers, Ninth National Organic Chemistry Symposium, December 29-31, 1941, Ann Arbor, Michigan.

*t*-butyl alcohol or *t*-butyl ethyl ether in the presence of boron trifluoride. This reaction should be of special value because of the well-known difficulty of introducing tertiary alkyl groups into active methylenic compounds by the common method in which a base is employed.

In a typical experiment, a mixture of 0.5 mole of *t*-butyl alcohol and 0.5 mole of ethyl acetoacetate was saturated with boron trifluoride at 0°. After standing for six hours at room temperature, the reaction mixture was worked up essentially as described previously.<sup>1</sup> Thirteen grams (14%) of alkylated  $\beta$ -keto ester boiling at 101-102° at 20 mm. was obtained. In this experiment an ester-alcohol exchange apparently occurred, the product analyzing for *t*-butyl  $\alpha$ -*t*-butylacetoacetate (*Anal.* Calcd. for C<sub>12</sub>H<sub>22</sub>O<sub>3</sub>: C, 67.25; H, 10.34. Found: C, 67.38; H, 10.40). The *t*-butyl derivative on ketonic hydrolysis yielded methyl neopentyl ketone which was identified as the semicarbazone and 2,4-dinitrophenylhydrazone.

These experiments will be described in greater detail later. It seems quite likely that the yield of the *t*-butyl derivative can be improved. Studies are now in progress on the introduction of various tertiary alkyl groups into various active hydrogen compounds by means of boron trifluoride or other acidic reagent.

DEPARTMENT OF CHEMISTRY  
DUKE UNIVERSITY  
DURHAM, NORTH CAROLINA

CHARLES R. HAUSER  
JOE T. ADAMS

RECEIVED FEBRUARY 19, 1942

---

## NEW BOOKS

---

**An Introduction to Organic Chemistry.** BY ROGER J. WILLIAMS, Ph.D., D.Sc., Professor of Chemistry, the University of Texas. Fourth edition. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y., 1941. xiii + 628 pp. Illustrated. 14 × 22.5 cm. Price, \$4.00.

Old friends of this time honored text will be pleased to note that it has been brought up to date without essential change either in the character of the subject matter or in its organization. Electronic structure has been stressed to a somewhat greater extent but aspects of the subject involving more advanced training in physical chemistry than the average student usually has, are omitted. Although considerable statistical information is given, detailed discussion of industrial processes is not included.

The work remains, then, neither an advanced theoretical treatise nor a compendium of information, but, true to its title, a well constructed and clearly presented introduction to organic chemistry.

C. E. BOLSER

**Industrial Instruments for Measurement and Control.** BY THOMAS J. RHODES, Engineer, The Procter and Gamble Company. First edition. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York, N. Y., 1941. ix + 573 pp. 282b figs. 15.5 × 23.5 cm. Price, \$6.00.

This addition to the "Chemical Engineering Series" gives an excellent description of the design and a discussion of the theory of instruments for measuring, recording and