

hour, while stirring the gray solid mass and refluxing. The gray solid gradually became yellow and slightly sticky and stirring with refluxing was continued for one-half hour after the addition of the anhydride was complete. The reaction mixture was worked up in the usual way, giving 0.9 g. of diphenyl and an acidic fraction of 10.2 g. of red oil. The latter was taken up in benzene and 3.6 g. of oily yellow solid was obtained by adding ligroin; the solid was taken up in ligroin and on crystallization a crop of yellow plates (1.9 g.) was obtained, m. p. 94–95° after recrystallization from benzene-petroleum ether. The mother liquor from the first fraction gave 2.3 g. of impure material crystallizing from ligroin, so that total crystalline solid obtained was 4.2 g. (26%). The pure sample gave no depression when mixed with a sample of III prepared by the Friedel-Crafts reaction.

**Reaction of Phenylmagnesium Bromide with Dimethylmaleic Anhydride.** 1. **One Mole of Each.**—The Grignard reagent prepared from 1.2 g. of magnesium and 7.9 g. of bromobenzene (0.05 mole) was added at 0° to 5.7 g. of dimethylmaleic anhydride (0.045 mole) dissolved in 300 cc. of dry ether. Reaction was immediate but not as violent as with maleic anhydride. The acid fraction (6.2 g.) was extracted with hot benzene and a residue of 1.1 g. of 1-phenyl-1-methyl-2-benzoylbutyric acid (V) was collected. The filtrate was treated with petroleum ether and 2.2 g. of solid was obtained; this consisted mainly of starting material and dimethylbenzoylacrylic acid (IV), which were separated by fractional crystallization from water; 0.3 g. of the latter turned up in the neutral fraction, from which it had not been extracted completely by sodium carbonate. The total yield after further fractional crystallization was 1.25 g. V, 0.7 g. IV, and 0.7 g. starting material. Compound IV melted at 92–94° and its identity was established

by mixed melting point with a sample prepared by the Friedel-Crafts reaction.<sup>6</sup>

Compound V is insoluble in hot water, very slightly in hot benzene, soluble in hot acetone, alcohol, and ethyl acetate and crystallizes from alcohol in needles, m. p. 183–185°.

*Anal.* Calcd. for  $C_{19}H_{18}O_3$ : C, 76.6; H, 6.4. Found: C, 76.7; H, 6.5.

**Preparation of IV by the Friedel-Crafts Reaction.**—When the reaction was carried out as described<sup>6</sup> the first product obtained crystallized from benzene-petroleum ether as needles, m. p. 65–67° instead of 94°; on recrystallization from hot water it melted at 92–94° and did not change back into the low melting form on recrystallization from benzene-petroleum ether. Apparently IV can exist in two forms.

2. **Two Moles of Grignard Reagent and One of Anhydride.**—Phenylmagnesium bromide (0.1 mole) was added to 5.7 g. of dimethylmaleic anhydride (0.045 mole) in 150 cc. of dry ether at room temperature. The acidic fraction yielded 3.8 g. of V, no IV and 5.6 g. of a white compound, m. p. 65–68° which seemed to lose solvent, finally melting at 85–94° but not identical with IV; when recrystallized from benzene-petroleum ether the low melting form reappeared, and on drying for four hours at 65° melted at 90–93°. It is soluble in carbonate and bicarbonate solution, almost insoluble in hot water, readily soluble in ether, alcohol, benzene and acetone. Its structure was not investigated further, but it may be stereoisomeric with V.

(6) Lutz and Taylor, *ibid.*, **55**, 1593 (1933).

CHEMICAL LABORATORY OF RADCLIFFE COLLEGE  
CAMBRIDGE, MASSACHUSETTS

RECEIVED OCTOBER 20, 1937

## COMMUNICATIONS TO THE EDITOR

### DIENE SYNTHESIS OF POLYCYCLES, WITH OR WITHOUT ANGULAR SUBSTITUENTS, FROM HEXATRIENE

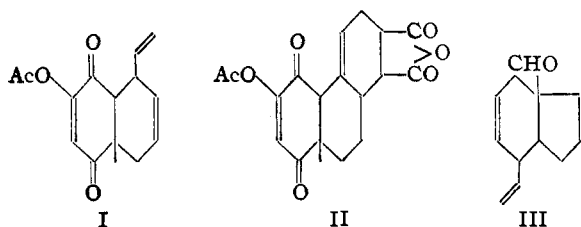
Sir:

A new approach to the total synthesis of polycyclic compounds similar to the steroids has been investigated in this Laboratory. The method consists essentially in the use of a six-carbon chain containing conjugated double bonds which can be condensed successively with two compounds containing activated multiple bonds in the Diels-Alder sense. Thus the six-carbon chain forms the "backbone" of the polynuclear product, *e. g.*, carbons 6–7–8–9–11–12 in the steroid nucleus.

It was anticipated that the simplest chain of this type, 1,3,5-hexatriene, might not serve because the double bonds remaining after the first diene addition might not assume the required conjugated position, and therefore work with 1,3-hexadienes has been planned. Nevertheless condensations with the hexatriene were tried and evidence has been obtained that the primary adduct can add a second molecule.

The hexatriene was heated with 5-acetoxy-*p*-toluquinone in alcohol at 90–95°. Removal of alcohol from the reaction products and addition of benzene gave a crystalline substance part of which was removed for analysis. The compound was

colorless after recrystallization from benzene and decomposed at 161–162° to a yellow solid which melted at 192–195°. *Anal.* Calcd. for  $C_{15}H_{16}O_4$ : C, 69.20; H, 6.20. Found: C, 69.20; H, 6.29. The remainder of the reaction products was heated with maleic anhydride in benzene at 150–160°. At least 25% of the product is a solid which decomposes sharply at 225° in an open capillary tube. It was purified for analysis by three recrystallizations from ether–chloroform. *Anal.* Calcd. for  $C_{19}H_{18}O_7$ : C, 63.66; H, 5.07; molecular weight, 358.1. Found: C, 63.34; H, 5.65; molecular weight (alkalimetric), 345.9. Both the primary and secondary adducts therefore have the expected empirical constitution and I and II are tentatively suggested as the most probable structures. Hexatriene also added cyclopentene-1-aldehyde in alcohol at 90–95°. The products gave a mixture of semicarbazones, one of



which was the derivative of the monocyclic aldehyde (m. p. 209°) and another which melted at 173–175°. The nitrogen content of the latter corresponded to that of a semicarbazone of III. *Anal.* Calcd. for  $C_{13}H_{19}ON_3$ : N, 18.02. Found: N, 17.70.

It is hoped that suitable variations of this procedure will permit the synthesis of natural compounds of the sterol group.

ANIMAL HUSBANDRY DIVISION                      LEWIS W. BUTZ  
NATIONAL AGRICULTURAL RESEARCH CENTER  
BELTSVILLE, MD.

RECEIVED NOVEMBER 23, 1937

#### THE VAPOR PHASE REACTIONS OF CYCLOPROPANE WITH IODINE AND BROMINE

*Sir:*

While it is familiar knowledge to organic chemists that bromine may act upon cyclopropane and its derivatives with resultant ring opening, there appears to be no recorded example of a similar reaction with iodine. On heating mixtures of cyclopropane (at some 300 mm. pressure) and iodine vapor (some 100 mm.) in sealed Pyrex glass bulbs at about 250°, we have observed a reaction result-

ing in almost complete disappearance of the iodine. A marked positive temperature coefficient of the rate was noted. At 250° the half-life was of the order of one hour. Illumination with a 1000-watt tungsten lamp did not increase the rate noticeably. No detectable quantity of hydrogen iodide was formed, and the sole product appeared to be a colorless, oily, high-boiling liquid, stable at room temperature. The refractive index and density of the small quantities obtained agreed with the values recorded for 1,3-diiodopropane [W. Perkin, *J. Chem. Soc.*, 51, 13 (1876); J. H. Gladstone, *ibid.*, 59, 293 (1884)] and it appears that this compound was at least the principal product.

It is reported that 1,3-diiodopropane undergoes partial decomposition at its boiling point (some 227°) with production of iodine [A. Freund, *Monatsh.*, 2, 640 (1881)]. This suggests that the above reaction may be reversible. However, if a vapor phase equilibrium is reached, at 250° it lies chiefly on the side of formation of 1,3-diiodopropane. The failure of intense visible light to enhance the rate indicates that iodine atoms are not responsible for the reaction of cyclopropane and iodine. An association reaction of iodine molecules appears as the most probable mechanism. The quantitative rate studies now under way should allow definite decision.

In agreement with previous investigators [G. Gustavson, *J. prakt. Chem.*, [2] 62, 290 (1900)] we have found a rapid photo reaction of cyclopropane and bromine vapor at room temperature, when illuminated by intense visible light. Only small amounts of hydrogen bromide were formed (corresponding to some 2% of the total bromine reacted), and the principal product was 1,3-dibromopropane, as indicated by its refractive index [J. F. Eykman, *Rec. trav. chim.*, 12, 268 (1893)]. We have also observed a dark reaction between bromine vapor and cyclopropane at some 220°—the rate being similar in magnitude to that for the corresponding iodine reaction. However, large amounts of hydrogen bromide were formed, and the dark reaction appears unsuitable for quantitative study.

Finally, we have observed that cyclopropane and gaseous hydrogen chloride, bromide or iodide undergo at most very slight reaction when heated for several hours at 300° in Pyrex vessels. This is the more remarkable in view of the relatively rapid reactions of cyclopropane with aqueous hydrogen halides [A. Freund and G. Gustavson, *vide*

*supra*] and suggests that the latter reactions proceed by ionic mechanisms. At room temperature there is slow reaction between gaseous hydrogen iodide and cyclopropane in Pyrex vessels. The negative temperature coefficient (*vide* results at

300°) suggests that it is almost certainly heterogeneous.

DEPARTMENT OF CHEMISTRY  
STANFORD UNIVERSITY, CALIF.

R. A. OGG, JR.  
W. J. PRIEST

RECEIVED NOVEMBER 24, 1937

## NEW BOOKS

**Outlines of Theoretical Chemistry.** By FREDERICK H. GETMAN, Ph.D. Sixth Edition by FARRINGTON DANIELS, Professor of Chemistry in the University of Wisconsin. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1937. ix + 662 pp. 170 figs. 15.5 × 23.5 cm. Price, \$3.75.

A measure of scientific progress is the frequency with which new editions of standard text-books are published. In physical chemistry, progress seems to have been most rapid in the sub-atomic field. It is in the clear and concise presentation of these recent findings that Dr. Daniels has made a major contribution to the sixth edition of the always popular "Outlines of Theoretical Chemistry."

In format, the new edition is similar to the earlier issues. All the chapters have been revised, most have apparently been completely rewritten. Important changes are found in the chapters on Thermo-chemistry and Electromotive Force. The chapter on Colloids has a more quantitative aspect and has been amplified by discussions of sedimentation, adsorption, and the ultracentrifuge. Rich in the new chemistry are Chapters XX-XXV which cover the Quantum Theory, Photo-chemistry, Nuclear Structure, Atomic Structure, and Molecular Structure. Here are discussed the neutron, positron, deutron, atomic transmutation, artificial radioactivity, isotopes and deuterium. By condensing tables and omitting some less important discussions, space has been made for this mass of new material without largely increasing the number of printed pages.

Many problems have been added to the book, some of which are to illustrate the practical use of a specific formula or equation, others to test the student's ability to correlate his information. In order to avoid confusing the reader with an undue amount of mathematical detail, the author has placed in an appendix the derivations of the more difficult physical chemical equations. A welcome addition is the list of standard chemical and physical symbols and abbreviations.

From attractive bookplate inside the front cover to the convenient four-place logarithm table inside the back cover, the Sixth Edition of "Outlines of Theoretical Chemistry" is well organized and well executed.

EDWARD P. BARTLETT

**Inorganic Chemistry. A Survey of Modern Developments.** By SIR GILBERT T. MORGAN and FRANCIS HERWARD BURSTALL, The Chemical Research Laboratory, Teddington, Middlesex. Chemical Publishing Company of New York, Inc., 148 Lafayette Street, New York, N. Y., 1937. ix + 462 pp. 14.5 × 22.5 cm. Price, \$6.00.

It is seldom that the title is so exactly descriptive of the contents as is the title of this book. The book truly gives a survey, very complete and informative, to one already adept in chemistry, of the developments in chemical thought and knowledge since the advent of Werner's coordination theory. Indeed the dominant note of this book is coordination. One chapter alone is free of coordination, namely, that on the transmutation of the elements.

An introduction deals with the chemical elements, the structure of the atom and valency, the argument being developed in the main around the law of uniform atomic plan as set forth by Main-Smith. A separate chapter is devoted to hydrogen and deuterium and nine chapters are devoted to a systematic recapitulation of the elements from Group 0 to Group VIII of the periodic arrangement. Mention is made of many interesting developments in the production and utilization of these elements, but by far the greater part of each chapter is devoted to the most varied types of coordination compounds of these elements. To one not already completely acquainted with developments in this field, the vast number of such coordination types comes as a great surprise. Even coordination compounds of the inert gases are convincingly described.

Chapter XII on the transmutation of the elements, natural and artificial, is an exceedingly clear and complete summary of the subject down to the date of publication, and it illustrates the remarkable breadth and accuracy of the authors' information and understanding outside of their own special field of coordination chemistry.

Following are chapters XIII on coordination compounds in nature and in the arts and industries; XIV on corrosion of metals; XV on intermetallic compounds; XVI on the carbides; XVII on metallic carbonyls; XVIII on nitrosyl compounds; XIX on organic derivatives of metals and metalloids. One again receives almost a shock to find the extent to which the coordination conception serves in correlating the varied phenomena of these fields. One hardly