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.[6]

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 $C_{18}H_{18}O_3$: 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[6] 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.

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

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CAMBRIDGE, MASSACHUSETTS

RECEIVED OCTOBER 20, 1937

COMMUNICATIONS TO THE EDITOR

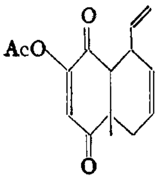
DIENE SYNTHESIS OF POLYCYCLES, WITH OR WITHOUT ANGULAR SUBSTITUENTS, FROM HEXATRIENE

Sir:

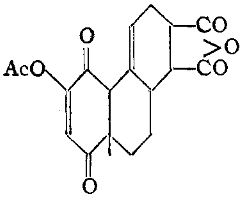
A new approach to the total synthesis of polycyclic compounds similar to the steroids has been investigated in this Laboratory. The method consists essentially in the use of a six-carbon chain containing conjugated double bonds which can be condensed successively with two compounds containing activated 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.

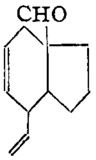
The hexatriene was heated with 5-acetoxy-*p*-toluquinone in alcohol at 90–95°. Removal of alcohol from the reaction products and addition of benzene gave a crystalline substance part of which was removed for analysis. The compound was colorless after recrystallization from benzene and decomposed at 161–162° 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.



I



II



III

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

Animal Husbandry Division
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Lewis W. Butz

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 resulting 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*