ALLENES. III. A COMPARISON OF SOME SUBSTITUTED ALLENES WITH PYRETHRONE WITH RESPECT TO THEIR BEHAVIOR TOWARD HALOGENS

FRED ACREE, JR., AND F. B. LAFORGE

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In their investigations on the nature of the unsaturated side chain present in pyrethrolone and its desoxy derivative, pyrethrone, LaForge and Haller (1) observed that, whereas these compounds reacted with one equivalent of bromine in indifferent solvents, yielding dibromo additionproducts, amorphous monobromo compounds and about an equivalent quantity of hydrobromic acid resulted when the reaction was carried out in alcoholic solution. The latter reaction was interpreted as one of substitution, which seemed incompatible with the assumption of the presence of a cumulated system of double bonds as originally proposed by Staudinger and Ruzicka (2) or of the conjugated system as later suggested by Ruzicka and Pfeiffer (3). The reaction-products, on treatment with zinc, yielded the original pyrethrolone or pyrethrone.

As the conjugated system seemed unlikely for other reasons, an investigation of the behavior of compounds with the cumulated system toward halogens became of interest with reference to the results obtained with pyrethrolone and pyrethrone.

In previous communications (4, 5) the preparation of the heretofore unknown 1-phenyl-1,2-butadiene and 1-cyclohexyl-2,3-pentadiene was reported. These compounds and also the known 2,3-pentadiene have been subjected to reactions with halogens carried out in a manner parallel to those performed on pyrethrone by LaForge and Haller.

Reactions of allenes with halogens in indifferent solvents. All the allenes mentioned above absorb one molecular equivalent of bromine or chlorine when treated with dilute solutions of the reagent in carbon disulfide or other indifferent solvents in the cold. The end-point is easily observed by the persistence of the color in the solution. An insignificant quantity of the corresponding halogen acid is always formed during the reaction, but the respective dibromo or dichloro addition-products are readily isolated in good yields.

When 2,3-pentadiene is treated with bromine in chloroform solution in the cold, rapid absorption of one equivalent of the halogen takes place

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with the formation of the 2,3-dibromo-3-pentene in nearly quantitative yield.

The addition of bromine to 1-phenyl-1,2-butadiene furnishes 1-phenyl-2,3-dibromo-1-butene as the main reaction-product. That the halogen has added mainly in the 2.3 position follows from the behavior of the reaction-product on treatment with aqueous alkali. When the reagent is gradually added to a hot aqueous suspension of the dibromo compound in the presence of phenolphthalein indicator, an equivalent of the alkali is neutralized in a few minutes. The reaction-mixture consists of three main products, which may be separated by fractional distillation. The bromine content of the lowest-boiling fraction indicates that it is formed by the loss of hydrobromic acid. It is probably 1-phenyl-2-bromo-1,3-butadiene $(C_{6}H_{5}CH=CBrCH=CH_{2})$. The middle fraction has a lower bromine content, corresponding to the formula $C_{10}H_{11}BrO$. It is formed by substitution of a hydroxyl group for one bromine and is without doubt 1-phenyl-2-bromo-3-hydroxy-1-butene (C₆H₅CH=CBrCHOHCH₃), for on hydrogenation with elimination of the double bond and the bromine, it is converted into 1-phenyl-3-butanol, which was identified as the phenylure-The third fraction, boiling much higher than the others, is probathane. bly a dimolecular compound, $C_{20}H_{20}Br_2O$, formed by the condensation of two molecules of 1-phenyl-2-bromo-3-hydroxy-1-butene with loss of one molecule of water or by some other mechanism. Essentially the same reactions occur when the dichloro substitution-product of 1-phenyl-1,2butadiene, *i.e.*, 1-phenyl-2.3-dichloro-1-butene, is treated in ethanol solution with aqueous potassium hydroxide solution. The main reactionproduct, on hydrogenation, yields a liquid of the same boiling point and refractive index as 1-phenyl-3-butanol. It is oxidized by chromic acid to the corresponding ketone, which was isolated and purified as the semicarbazone, having the melting point recorded for the semicarbazone of 1-phenyl-3-butanone. The addition of halogen to 1-phenyl-1, 2-butadiene therefore takes place at least mainly in the 2.3 position.

Although it has no direct bearing on the subject of this article, it may be mentioned that in the chlorination of 1-phenyl-1-hydroxy-2-chloro-2butene there is a tendency for the halogen to shift away from the phenyl group. This is true when hydrochloric acid is the chlorinating agent, but to a much less extent when thionyl chloride is employed. The 1-phenyl-dichlorobutene (4) prepared by the action of hydrochloric acid on 1-phenyl-1-hydroxy-2-chloro-2-butene is a mixture of 1-phenyl-1,2dichloro-2-butene (C₆H₅CHClCCl=CHCH₃) and 1-phenyl-2,3-dichloro-1-butene (C₆H₅CH=CClCHClCH₃). When the mixture is treated with aqueous alkali, one chlorine is replaced by hydroxyl and the resulting chloro carbinol yields on hydrogenation a mixture of 1-phenyl-1-butanol and 1-phenyl-3-butanol. Oxidation of the mixture with chromic acid yields the corresponding ketones, 1-phenyl-1-butanone and 1-phenyl-3butanone, which are easily separated as their semicarbazones. The phenylurethane of 1-phenyl-3-butanol can be isolated also from the hydrogenation-product before oxidation. When thionyl chloride is the chlorinating agent for the preparation of 1-phenyldichlorobutene, the product is essentially 1-phenyl-2,3-dichloro-1-butene. The dichloro derivative, on aqueous alkaline hydrolysis, is converted into a monochloromonohydroxy derivative. This compound on hydrogenation furnishes 1-phenyl-3-butanol, which can be isolated in good yield as its phenylurethane.

In contrast to the 1-phenyldichlorobutenes, the 1-cyclohexyldichloropentene, which is probably 1-cyclohexyl-2,3-dichloro-3-pentene, prepared from 1-cyclohexyl-2-hydroxy-3-chloro-3-pentene by the action of phosphorus pentachloride, is practically inert toward boiling dilute aqueous alkali. This is also true of the dibromo product obtained by the addition of bromine to 1-cyclohexyl-2,3-pentadiene.

Reactions of allenes with halogen in alcoholic solution. Since the observations of LaForge and Haller (1) were published, a search of the literature revealed articles that relate very closely to the behavior of pyrethrone toward bromine in alcoholic solution. Conant and Jackson (6) and later Jackson and co-workers (7,8) have reported that certain compounds with an ethylene linkage, on treatment with bromine in methanol, react to form methoxybromo addition-products as well as the normal dibromo addition-products. The first reaction takes place with liberation of free

hydrobromic acid according to the scheme $C = C + ROH + Br_2 \rightarrow$

COR-CBr + HBr. Both reactions proceeded at a rather slow rate.

With knowledge of this reaction, it seemed very likely that the unsaturated side chain of pyrethrone had reacted in the same sense as compounds with the simple unsaturation, with formation of alkoxybromo derivatives and free hydrobromic acid and also a certain amount of the dibromo additionproduct. The quantity of free hydrobromic acid formed when pyrethrone was treated with bromine in alcoholic solution indicated that the first reaction predominated. Since reduction of the reaction-product with zinc furnished unchanged pyrethrone in yields that far exceeded the quantity that would be expected from the dehalogenation of the dibromo derivative that might be present, it would be necessary, in order to explain this fact, to assume that the alkoxybromo addition-products reacted with zinc like a dibromo addition-product, with regeneration of the double

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bond. Analogy for such a reaction is found in an article by Dykstra, Lewis, and Boord (9), who reported that α,β -alkoxybromo compounds are readily dehalogenated by zinc with formation of a double bond between the carbon atoms that carried the substituents.

It now became of interest to consider the reactions of compounds with the cumulated system from the standpoint of their behavior toward halogens in methanol solutions. In all cases methoxybromo additionproducts were obtained together with dibromo addition-compounds. Free hydrobromic acid was liberated corresponding to 60-70% of one-half of the bromine added. In contrast to the simple unsaturated compounds, the allenes reacted with bromine in methanol instantaneously in the cold. 1-Phenyl-1,2-butadiene reacted with bromine in methanol to form a methoxybromo addition-compound as the main product. 1-Cyclohexyl-2.3-pentadiene was treated with bromine under the same conditions, and from the reaction-product two fractions could be separated by distillation. Bromine and methoxyl determinations indicated that in the lower-boiling fraction the methoxybromo addition-product predominated while the higher-boiling fraction contained more of the dibromo addition-product. Redistillation of the higher-boiling fraction yielded almost pure dibromo The reaction of 2,3-pentadiene with bromine in methanol compound. proceeded analogously. The products of the reaction were methoxybromopentene and 2,3-dibromopentene, which could be separated by fractional distillation. In no case was the exact relative position of bromine to methoxyl determined, but it seems safe to predict that the structure was $C(OCH_3)CBr=C$ and not $CBrC(OCH_3)=C$.

Addition of bromine to pyrethrone in methanol solution. In the experiments of LaForge and Haller (1) the reaction of pyrethrone with bromine was always carried out in ethanol solution and the reaction-product was not analyzed. The experiment was repeated with methanol as the solvent. After neutralization of the free hydrobromic acid, the reaction-mixture was freed from solvent, and the product, as indicated by the bromine and methoxyl content, was found to consist of a mixture of the bromomethoxy derivative and the dibromide, the former predominating.

Conclusions. Three compounds containing the cumulated system of double bonds react in indifferent solvents with one molecule of bromine to form dibromo addition-compounds. In alcoholic solution bromine reacts with these compounds to furnish monobromoalkoxy addition-products with liberation of free hydrobromic acid.

The reactions of pyrethrone with bromine in both classes of solvent are strictly analogous to those exhibited by the allenes. Its behavior, therefore, is not incompatible with the presence of the cumulated system of double bonds in its side chain, which from the facts now available seems to be the most likely arrangement.

EXPERIMENTAL

Addition of bromine to 1-phenyl-1, 2-butadiene in carbon disulfide solution. Six and one-tenth grams of 1-phenyl-1, 2-butadiene was dissolved in 50 cc. of carbon disulfide to which 15 cc. of water (saturated with sodium sulfate to prevent freezing) was added to absorb the hydrobromic acid, the solution was cooled in an ice-salt mixture, and 6.8 g. of bromine (1 equivalent of Br_2) in 50 cc. of the same solvent was slowly added. After all the bromine had been introduced, the solution was colored yellow by the slight excess of the reagent. The aqueous solution was separated and titrated with 0.1 N alkali, of which 4.1 cc. was required, corresponding to only 0.33 g. of hydrobromic acid. The carbon disulfide solution was washed with 5% sodium carbonate solution and then with water, dried, and the solvent removed under reduced pressure. The residue on distillation yielded 8.25 g. of practically pure product that boiled at 118° (0.5 mm.); n^{25} D 1.6177.

Anal. Calc'd for $C_{10}H_{10}Br_2$: Br, 55.2. Found: Br, 54.0.

The following experiment indicates that the addition of bromine has occurred mainly at the 2,3 position. Eight and two-tenths grams of the dibromo additionproduct was suspended in 20 cc. of water, heated to 100°, and while the suspension was being agitated mechanically a 4.7% aqueous solution of potassium hydroxide was added in small portions at 5-minute intervals. After 28 cc. (cale'd for 1 equivalent of bromine, 34 cc.) had been added, the solution was permanently alkaline. The reaction-products were extracted with ether and, after they had been washed with water and dried, the solvent was removed. On distillation three fractions were obtained.

The first fraction, 1.65 g., boiled at 84-89° (0.5 mm.); n^{27} D 1.6208. It is probably 1-phenyl-3-bromo-1,3-butadiene.

Anal. Calc'd for C10H9Br: Br, 38.27. Found: Br, 38.1.

The second fraction, 1.74 g., boiled at 108-109° (0.5 mm.); n²⁷D 1.5910.

Anal. Calc'd for C10H11BrO: Br, 35.24. Found: Br, 36.5.

This fraction is mainly 1-phenyl-2-bromo-3-hydroxy-1-butene, since on hydrogenation it is converted into 1-phenyl-3-butanol.

One and seven-tenths grams of the second fraction was hydrogenated in 23 cc. of 2.5% ethanol solution of potassium hydroxide with a palladium-calcium carbonate catalyst. In a few minutes 345 cc. of hydrogen was absorbed (calc'd for $2 H_2$, 335 cc.). The ethanol solution was filtered and diluted with water, and the reaction-product was extracted with petroleum ether, which was washed with water, dried, and evaporated. The residue yielded on distillation 0.7 g. of product; b.p. 108-110° (8 mm.); n^{28} D 1.5130. Three-tenths gram of the distillate was allowed to react with 0.24 g. of phenyl isocyanate, and gave 0.37 g. of recrystallized phenylurethane melting at 112-114°. The melting point of the phenylurethane of 1-phenyl-3-butanol is reported as 113° (10). The corresponding derivative of 1-phenyl-1-butanol has not been obtained in crystalline form.

The third fraction, 1.85 g., boiled at 200-210° (0.5 mm.).

Anal. Cale'd for C₂₀H₂₀Br₂O: Br, 36.7. Found: Br, 36.7.

This product is probably a dimolecular compound formed by the condensation of two molecules of the bromohydroxy compound with loss of water.

Addition of chlorine in carbon tetrachloride to 1-phenyl-1,2-butadiene. Five grams (slight excess) of chlorine was passed slowly into a solution of 8.5 g. of 1-phenyl-1,2-butadiene in 50 cc. of purified carbon tetrachloride. There was a slight evolution of

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hydrochloric acid. After removal of the excess chlorine by evaporation, the solution was washed with dilute sodium carbonate solution and dried, and the solvent was removed under reduced pressure. After three fractionations, 5.5 g. of product was obtained, boiling at 130° (13 mm.); n^{28} p 1.5745.

Anal. Calc'd for C₁₀H₁₀Cl₂: Cl, 35.27. Found: Cl, 35.38.

Action of aqueous potassium hydroxide on the dichloro addition-product of 1-phenyl-1,2-butadiene. Five grams of the dichloro compound was suspended in 25 cc. of boiling water and, while the suspension was being agitated with a turbine, 18 cc. of 4.7% aqueous potassium hydroxide was added dropwise over a period of about 1 hour. The reaction-mixture then remained permanently alkaline. The reactionproduct was extracted with ether and, after drying and removal of the solvent, the residue was distilled and separated into two fractions.

The first fraction, 1.09 g., boiled at 70-90° (0.7 mm.); n²⁶D 1.594.

Anal. Calc'd for $C_{10}H_{9}Cl$: Cl, 21.6; for $C_{10}H_{11}ClO$: Cl, 19.4; for $C_{10}H_{10}Cl_2$: Cl, 35.3. Found: Cl, 24.9.

The second fraction, 2.5 g., boiled at 95-100° (0.7 mm.); n²⁶D 1.5730.

Anal. Found: Cl, 26.8.

Both fractions are probably mixtures of all three compounds.

Two and two-tenths grams of the second fraction absorbed 590 cc. of hydrogen in ethanolic potassium hydroxide solution with palladium-calcium carbonate catalyst, and from the reaction-product, in addition to 0.3 g. of distillate boiling at 60° (8 mm.), 0.8 g. of a fraction boiling at $108-111^{\circ}$ (8 mm.), was obtained. Four-tenths gram of this fraction, when treated with 0.32 g. of phenyl isocyanate, yielded 0.62 g. of recrystallized phenylurethane derivative melting at 114° , identical with the corresponding derivative obtained after hydrolysis and hydrogenation of the dibromo addition-product of 1-phenyl-1,2-butadiene.

Another experiment was made in which aqueous ethanol was used instead of water. Eight-tenths gram of the same dichloride fraction as that employed for the preceding experiment was dissolved in 8 cc. of boiling ethanol, and 2.5 cc. of 10% aqueous potassium hydroxide solution was added, producing a permanent alkaline reaction. The solution was diluted with water and the product extracted with ether. The solution was washed and dried and the solvent removed. The residue, on distillation, yielded 0.5 g. of distillate; b.p. 85-90° (0.7 mm.); n²⁹D 1.551. On hydrogenation under the conditions described above 3.25 g. of the product prepared as just described absorbed two moles of hydrogen. The hydrogenated material was isolated by dilution of the reaction-mixture with water and extraction with petroleum ether. On distillation 1.4 g. was obtained; b.p. 118-122° (15 mm.); n²⁷D 1.510. One gram was oxidized in acetic acid solution with a slight excess of chromic acid. The product, isolated from the reaction-mixture by dilution with water and extraction with petroleum ether, was treated with semicarbazide hydrochloride in pyridineethanol solution and yielded 0.4 g. of semicarbazone. After being twice recrystallized from ethanol, it melted at 138-140°, which agrees well with the melting point recorded for the semicarbazone of 1-phenyl-3-butanone (142°) (10).

The 1-phenyldichloropentene prepared by the action of hydrochloric acid on 1-phenyl-1-hydroxy-2-chloro-2-butene ($C_6H_6CHOHCCl=CHCH_8$) (4) is a mixture of 1-phenyl-1,2-dichloro-2-butene and 1-phenyl-2,3-dichloro-1-butene. When 2 g. of the reaction-product was treated with boiling aqueous potassium hydroxide as described above, but with addition of 20 cc. of acetone to facilitate solution, 1.3 g. of distilled material was obtained; b.p. 100-105° (0.7 mm.); n²⁹D 1.5659.

Anal. Calc'd for C₁₀H₁₁ClO: C, 65.75; H, 6.04.

Found: C, 65.20; H, 6.11.

On hydrogenation in ethanolic potassium hydroxide solution with palladium-

calcium carbonate catalyst, 3 g. absorbed 765 cc. of hydrogen (calc'd for 2 H₂, 748 cc.). The hydrogenation-product boiled at $105-110^{\circ}$ (10 mm.); n^{28} p 1.5115.

Anal. Calc'd for C₁₀ H₁₄O: C, 80.00; H, 9.33.

Found: C, 78.4; H, 9.24.

The phenylurethane was prepared from 0.12 g.; yield, 0.15 g.; m.p. 114-115°.

Chromic acid oxidation of 1.5 g. yielded 1.15 g. of product, boiling at $105-108^{\circ}$ (10 mm.); $n^{28}p$ 1.5117.

Anal. Calc'd for C₁₀H₁₂O: C, 81.08; H, 8.10.

Found: C, 77.98; H, 8.48.

Six-tenths gram of the oxidation-product and 0.6 g. of semicarbazide hydrochloride in 6 cc. of ethanol and 0.5 cc. of pyridine were allowed to react. From the solution 0.25 g. of semicarbazone separated, which after recrystallization from ethanol melted at 190°. The melting point of the semicarbazone of 1-phenyl-1-butanone is recorded as 188° (11). From the mother liquor 0.35 g. of recrystallized semicarbazone melting at 145° was obtained. As already stated, the melting point of 1phenyl-3-butanone semicarbazone is recorded as 142°.

When prepared from 1-phenyl-1-hydroxy-2-chloro-2-butene (4) by the action of thionyl chloride, the dichloro derivative is practically all 1-phenyl-2,3-dichloro-1-butene. On hydrolysis with aqueous alkali, 3.6 g. yielded 1.8 g. of product; b.p. 100-105° (0.7 mm.); n²⁸ p 1.5708.

Anal. Calc'd for C₁₀H₁₁ClO: Cl, 19.4. Found: Cl, 19.7.

On hydrogenation of 1.9 g., 490 cc. of hydrogen was absorbed (calc'd for 2 moles, 465 cc.). The hydrogenated product was isolated in the usual manner; yield, 1.1 g.; b.p. $110-112^{\circ}$ (10 mm.); n^{27} D 1.5130.

Anal. Calc'd for C₁₀H₁₄O: C, 80.00; H, 9.33.

Found: C, 79.81; H, 9.38.

The phenylurethane melted at 114°.

Addition of bromine to 1-cyclohexyl-2,3-pentadiene in carbon disulfide. Fifteen cubic centimeters of a cold carbon disulfide solution of 1.6 g. of bromine (1 equivalent of Br_2) was slowly added to a cold solution of 1.5 g. of 1-cyclohexyl-2,3-pentadiene in 15 cc. of the same solvent. There was a slight evolution of hydrobromic acid, which was not measured. The solution was washed with sodium bicarbonate and then with water, and dried. After removal of the solvent under reduced pressure, the residue was distilled; it boiled at 110-115° (1 mm.); $n^{27}D$ 1.5357; yield, 2.6 g.

Anal. Calc'd for C₁₁H₁₈Br₂: Br, 51.6. Found: Br, 51.6.

One and nine-tenths grams of the dibromo compound was suspended in 15 cc. of water and boiled for 5 minutes. The addition of 0.6 cc. of 5% alkali gave an alkaline reaction which did not change after boiling an additional 15 minutes. The recovered product (1.4 g.) distilled at $100-110^{\circ}$ (1 mm.); $n^{26}D$ 1.5340. Therefore, practically no reaction had occurred.

The 1-cyclohexyldichloropentene prepared by the action of phosphorus pentachloride on 1-cyclohexyl-2-hydroxy-3-chloro-3-pentene (5) was likewise inert when subjected to the same treatment. Two and two-tenths grams of the dichloro compound yielded 1.8 g. of recovered product, boiling at 128-130° (10 mm.); n^{sr} D 1.4938. The constants agree with those found for the starting material. No further attempts were made to determine the positions of the halogens in these compounds.

Addition of bromine to 2,3-pentadiene in chloroform solution. Ten cubic centimeters of a chloroform solution containing 1.66 g. of bromine (1 equivalent of Br_2) was added to a solution of 0.75 g. of 2,3-pentadiene (12) in the same solvent. The reaction was carried out with cooling in an ice-salt-bath. The solution was extracted with dilute sodium bicarbonate solution, then with water, and dried. After removal of the solvent, the residue was distilled; b.p. 87-90° (25 mm.); yield, 1.5 g.

Anal. Calc'd for C₅H₈Br₂: C, 26.31; H, 3.50.

Found: C, 26.40, 26.50; H, 3.61, 3.57.

Addition of bromine to 1-phenyl-1, 2-butadiene in methanol solution. A cold solution of 5.4 g. of bromine (calc'd for 1 equivalent of Br_2 , 5.5 g.) dissolved in 30 cc. of methanol was added slowly to a solution of 4.5 g. of 1-phenyl-1, 2-butadiene dissolved in 30 cc. of methanol and cooled in an ice-salt-bath. The bromine was rapidly absorbed until the addition of the last few drops produced a permanent orange color. The reaction-mixture was diluted with an equal volume of water and neutralized to the end-point of phenolphthalein with 24.0 cc. of N aqueous sodium hydroxide solution, corresponding to 71% of the theoretical 33.7 cc. calculated for one-half of the bromine added. The reaction-mixture was diluted with several volumes of water and extracted with ether. The ether solution was washed with water and dried. The residue obtained after removal of the solvent was separated into two fractions by distillation. The first fraction weighed 6.15 g. and boiled at 87-90° (0.5 mm.).

Anal. Calc'd for C₁₁H₁₃BrO: OCH₃, 12.86; Br, 33.2.

Found: OCH₃, 10.2; Br, 38.1.

The second fraction weighed 1.35 g. and boiled at 90-100° (0.5 mm.).

Anal. Calc'd for $C_{10}H_{10}Br_2$: Br, 55.2, OCH₃, 0.0. Found: Br, 52.5; OCH₃, 1.7. Addition of bromine to 1-cyclohexyl-2,3-pentadiene in methanol solution. Four grams of 1-cyclohexyl-2,3-pentadiene was mixed with 30 cc. of methanol, cooled in a freezing mixture, and treated with a solution of 4.3 g. of bromine in 40 cc. of cold methanol (theory for 1 equivalent of Br₂, 4.25 g.). The bromine solution was decolorized instantly until the addition of the last few cubic centimeters, which were absorbed more slowly. The reaction-mixture was diluted with an equal volume of water and neutralized with 16.9 cc. of N aqueous sodium hydroxide to the end-point of phenolphthalein (theory for one-half of the bromine added, 26.87 cc.). The reaction-products were extracted with ether. The ether solution was washed thoroughly with water and then dried. The solvent was removed, and the residue was separated into two fractions by distillation at 0.5 mm. pressure. The first fraction weighed 2.95 g. and boiled at 81-86°; $n_{\rm p}^{\rm m}$ 1.4950.

Anal. Calc'd for C₁₂H₂₁BrO: OCH₂, 11.9; Br, 30.7.

Found: OCH₃, 10.5; Br, 31.6.

The second fraction weighed 2.45 g. and boiled at 93-99°.

Anal. Calc'd for C₁₁H₁₈Br₂: Br, 51.6; OCH₃, 0.0.

Found: Br, 47.8; OCH₃, 2.4.

From another experiment the material corresponding to this second fraction contained 49.7% of bromine.

Addition of bromine to 2,3-pentadiene in methanol solution. Nine-tenths gram of 2,3-pentadiene was dissolved in 5 cc. of absolute methanol, and 2.2 g. of bromine in 10.3 g. of the same solvent was slowly added to the cold solution of the pentadiene. The bromine was instantly absorbed until 8.4 g. of the solution (corresponding to 1.8 g. of bromine or 85% of an equivalent of Br₂) had been added. After the solution was diluted with water, titration showed that hydrobromic acid had been liberated in quantity corresponding to 6.7 cc. of N alkali or 0.54 g. of hydrobromic acid. The reaction-product was extracted with ether, and the ether solution was washed with water and dried. The residue obtained after removal of the solvent yielded two fractions on distillation. This first fraction boiled at 65-70° (27 mm.).

Anal. Cale'd for C₆H₁₁BrO: Br, 44.7; OCH₃, 17.5. Found: Br, 47.3; OCH₃, 14.8. The second fraction boiled at 78-85° (27 mm.).

Anal. Calc'd for C₅H₈Br₂: Br, 70.0; OCH₃, 0.0.

Found: Br, 59.4; OCH₃, 6.5.

Both fractions are mixtures, the bromomethoxy derivative predominating in the first and the dibromo addition-product in the second.

Reaction of pyrethrone with bromine in methanol solution. One and two-tenths grams of pyrethrone was dissolved in 10 cc. of methanol, the solution was cooled in an ice-salt-bath, and 1.2 g. of bromine (1 equivalent of Br_2) in 10 cc. of the same solvent was slowly added. The bromine was rapidly absorbed. Five cubic centimeters of 1.7 N methanolic solution of potassium hydroxide was added, producing a precipitate of potassium bromide. The solution was acidified with acetic acid and the solvent removed under reduced pressure. The residue was dissolved in benzene, and the solution was washed, first with dilute sodium bicarbonate solution and then repeatedly with water, and dried. The benzene was removed under reduced pressure and the residue analyzed for methoxyl.

Anal. Calc'd for C₁₂H₁₇BrO₂: OCH₃, 11.35. Found: OCH₃, 6.6.

The crude product therefore contained about 60% of the bromomethoxy derivative. On distillation, which was accompanied by some decomposition, 1 g. of distillate was obtained, boiling at 140-145° (0.5 mm.). Redistillation yielded 0.8 g. of a slightly yellow oil that boiled at 134-142° (0.5 mm.). A dark residue was left after each distillation. The final product was also a mixture of the dibromo and methoxybromo derivatives.

Anal. Calc'd for $C_{11}H_{14}Br_2O$: Br, 49.7; for $C_{12}H_{17}BrO_2$: Br, 29.3; OCH₃, 11.4. Found: Br, 36.1; OCH₃, 4.9.

WASHINGTON, D. C.

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