protein content. For this reason it would be of considerable interest to investigate these two proteins, and if possible to establish some definite relation which they bear to the plant's power of abstracting nitrogen from the air.

The author is indebted to Dr. Edward Records and Dr. Harry W. Jakeman of the Veterinary Department of the University for assistance in connection with the toxicological experiments herein described.

This investigation has been supported by the Adams Fund, a Federal appropriation for scientific research.

RENO, NEV.

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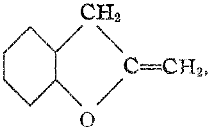
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

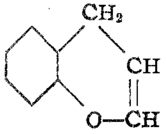
# CYCLIC ETHERS FROM *o*-ALLYL PHENOLS; METHYLENE COUMARANES.

BY ROGER ADAMS AND R. E. RINDFUSZ.

Received January 8, 1919.

*o*-Allyl phenols, which are so easily prepared by the rearrangement of allyl-phenyl ethers, offer an admirable starting point for the production of various cyclic ethers. Claisen[1] has shown, for example, that pyridine hydrochloride converts them quantitatively into methyl coumaranes. The present investigation proves that methylene coumaranes, 

may also be readily produced from *o*-allyl phenols by the following succession of reactions: (1) acetylation of the *o*-allyl phenol, (2) addition of bromine to the double bond, (3) treatment with alcoholic potash. All three reactions run smoothly and good yields are obtained. Moreover, the method has been applied with success to 6 different *o*-allyl phenols so that the reaction is unquestionably a general one.

The research was originally undertaken in an attempt to synthesize the 6-membered unsaturated cyclic ethers of the following general formula, 

, which may be called chromenes from analogy to the name of chromanes[2] given the corresponding saturated ethers. These substances present interest not only because they have not hitherto been synthesized but also because they may be looked upon as the basic substances of the large and important class of natural dyes, the flavones and their derivatives.

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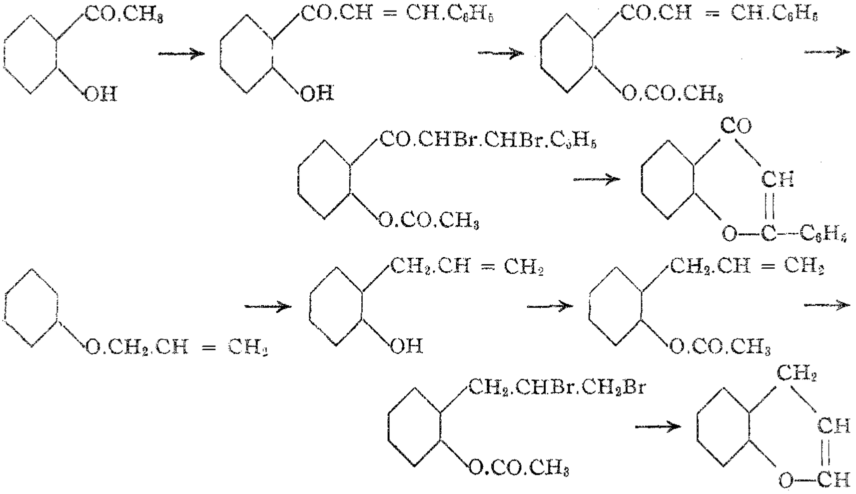
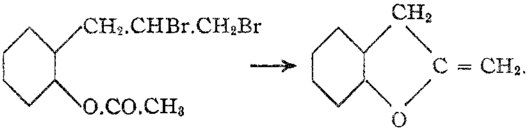
[1] *Chem. Zentr.*, [2] 1213 (1914); *D. R. P.* 279,864.

[2] *Ber.*, 38, 855 (1905); 39, 2856 (1906).

The method of preparation employed in this investigation in an attempt to make chromenes is similar to one of those used by Kostanecki[1] in synthesizing flavones, and if it had gone in exactly an analogous manner would have given chromenes, thus:



The reactions do indeed proceed as indicated up to the last step when methylene coumaranes instead of chromenes are produced:



The mechanism of this last reaction and the proof of the structure of the final substance are described in the following pages.

When acetyl *o*-allyl-phenol dibromide is treated with excess of alcoholic potash or sodium ethylate, an unsaturated cyclic ether is produced, as indicated first by its stability toward and insolubility in alkali, and second by the fact that it decolorizes immediately dilute bromine water or permanganate. Moreover, analysis shows that during this treatment the acetyl group, one hydrogen and two bromines have been eliminated. This decomposition is readily explained by the fact that the alkali causes three reactions to take place, namely, hydrolysis of the acetate to give the potassium salt of the phenol, elimination of potassium bromide to form an ether, and the splitting out of hydrobromic acid to give an ethylene linkage. There are three possible isomeric structures for the final product depending entirely upon which halogen is eliminated as potassium bromide and which hydrogen and bromine as hydrobromic acid, thus:

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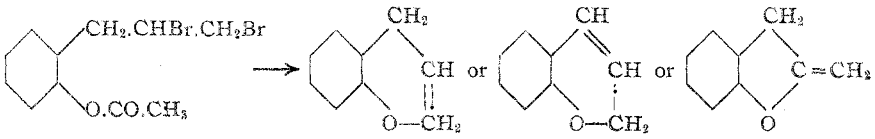
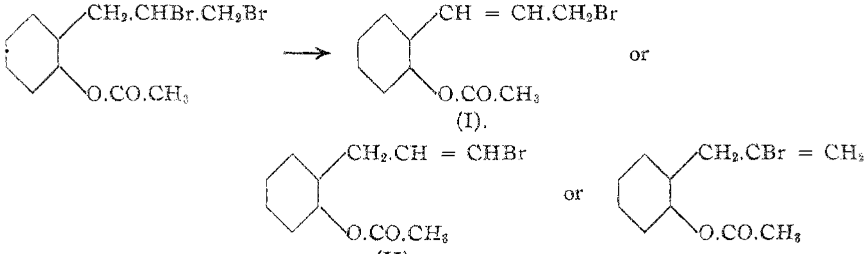
[1] *Ber.*, 31, 696, 1760 (1898).



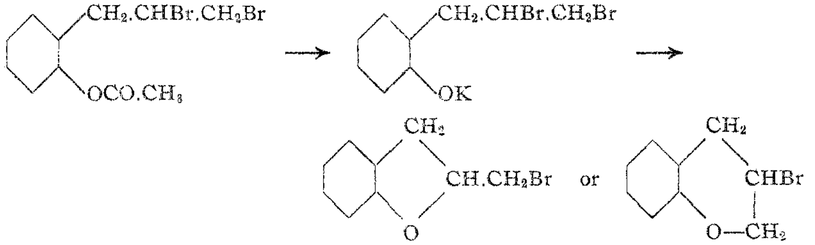
α-Chromene. β-Chromene. α-Methylene coumarane.

By a study of the mechanism of the above reaction, the proof of the formula of the unsaturated cyclic ether is easily determined. If it is assumed that hydrobromic acid is eliminated first, the following intermediates are possible:



(I). (II).

This means that after subsequent hydrolysis of the ester and then elimination of potassium bromide (I) will yield β-chromene, (II) will yield α-chromene and (III) will yield α-methylene coumarane. If, however, the hydrolysis of the ester takes place first, the following intermediates are possible:



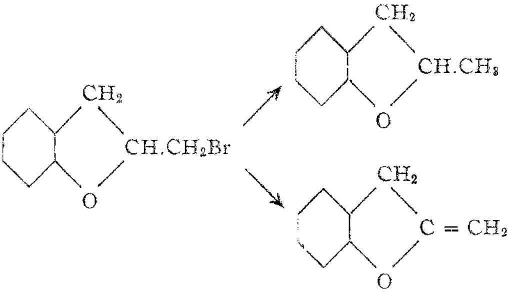
(A). (B).

After elimination of hydrobromic acid (A) will yield α-methylene coumarane and (B) will yield either α- or β-chromene.

In the laboratory, the mechanism was proved by causing just one molecule of sodium alcoholate to react with the acetyl-*o*-allyl-phenol dibromide. Under these conditions, a monobromocyclic ether is actually produced, shown by analysis of the product and its insolubility in alkali. Thus hydrolysis of the ester does take place first and then potassium bromide splits out, so that the problem next resolves itself into proving whether the structure of the monobromo derivative formed is (A) or (B). This was accomplished by elimination of the bromine atom by means of

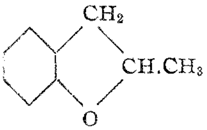
(1) alcoholic potash and (2) reduction. On treatment with alcoholic potash, the same unsaturated cyclic ether is produced as is obtained by excess of alcoholic potash on the acetyl-*o*-allyl-phenol dibromide. By reduction with zinc and hydrochloric acid, the halogen is replaced by hydrogen and one of two different isomeric saturated cyclic ethers may be produced, depending on whether the monobromo compound has the structure (A) or (B). α-Methyl coumarane will result from (A), chromane from (B); both of these are known compounds. In the laboratory, α-methyl coumarane is actually obtained, which proves definitely that the structure of the monobromo compound is (A).

Since there is evidently only one possible way in which halogen acid may split out of the monobromo compound, the structure of the unsaturated cyclic ether is fixed as α-methylene coumarane:

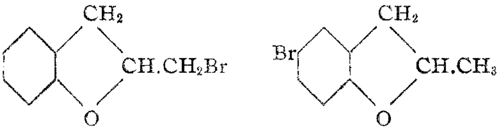


Thus not only is the mechanism of the direct formation of the unsaturated cyclic ether by means of alcoholic potash on the acetyl-*o*-allyl-phenol dibromide completely proved but also the constitution of the compound produced.

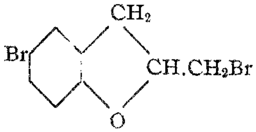
In studying the action of bromine on *o*-allyl phenol, additional proof of the structure of the various cyclic ethers was obtained. Thus the bromination of *o*-allyl phenol even at a very low temperature differs from the bromination of the acetyl-*o*-allyl phenol in that a copious evolution of hydrobromic acid occurs during the reaction. A product is obtained under these conditions which contains three constant boiling fractions. The largest and lowest boiling fraction is α-methyl coumarane, the middle fraction is a mixture of the two isomers *p*-bromo-α-methyl coumarane and α-bromomethyl coumarane, both of which boil at practically the same point, the third and highest boiling fraction is *p*-bromo-α-bromomethyl coumarane.



1st fraction.

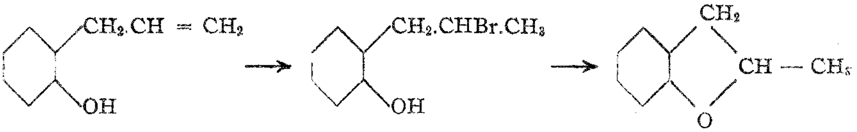


2nd fraction.



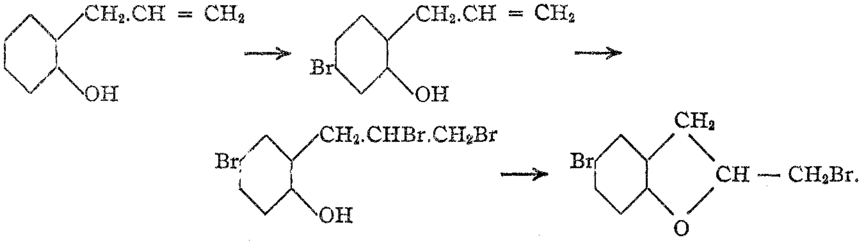
3rd fraction.

The first fraction was identified as α-methyl coumarane by analysis and by comparing it with this substance made from *o*-allyl phenol and pyridine hydrochloride. It is undoubtedly produced in two steps: the hydrobromic acid evolved in the reaction first adds to the double bond of the *o*-allyl phenol; the resulting compound then decomposes into α-methyl coumarane and hydrobromic acid:



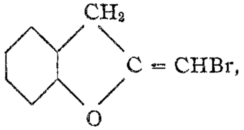
The second fraction analyzed for a monobromo-substituted α-methyl coumarane and the original presumption was that it was a pure compound. Its chemical reactions, however, subsequently showed it to be a mixture of two isomeric monobromo substituted α-methyl coumaranes, one of which contains an active, the other an inactive halogen atom. When the mixture is treated with alcoholic potash, the active bromine compound is changed to an unsaturated halogen-free cyclic ether identical with that obtained by the action of alcoholic potash on the acetyl-*o*-allyl-phenol dibromide, namely, α-methylene coumarane. The unchanged inactive bromine compound is much higher boiling than the halogen-free ether, so it may readily be separated by fractionation. If the mixture is treated with zinc and hydrochloric acid, the active bromine compound is changed to a saturated halogen-free cyclic ether which is α-methyl coumarane. Again, the unchanged inactive bromine compound may readily be separated from the halogen-free cyclic ether because of the difference in boiling point. The above properties of the active bromine compound leave no doubt as to its structure. It is α-bromomethyl coumarane identical with the substance produced by the action of one molecule of sodium alcoholate on acetyl-*o*-allyl-phenol dibromide. The inactive halogen compound in the mixture is *p*-bromo-α-methyl coumarane, identical with the reaction product obtained from *p*-bromo-*o*-allyl-phenol and pyridine hydrochloride or by the bromination of α-methyl coumarane. The active halogen compound is most probably produced by the loss of one molecule of hydrobromic acid from the dibromo addition compound formed from bromine and *o*-allyl phenol, the inactive halogen compound either by direct bromination of the α-methyl coumarane formed as one of the constituents of the reaction mixture, or else bromination of the *o*-allyl phenol to give *p*-bromo-*o*-allyl phenol, then conversion to the substituted methyl coumarane by means of hydrobromic acid, in the same way as the *o*-allyl phenol itself is converted to α-methyl coumarane.

The third fraction analyzed for a dibromo substituted α-methyl coumarane and its reactions prove the structure to be *p*-bromo-α-bromomethyl coumarane. Alcoholic potash converts it into *p*-bromo-α-methylene coumarane, the same compound as is obtained from *p*-bromo-*o*-allyl phenol by successive acetylation, addition of bromine and then treatment with alcoholic potash. Zinc and hydrochloric acid reduce the dibromo compound to *p*-bromo-α-methyl coumarane identical with the reaction product of pyridine hydrochloride and *p*-bromo-*o*-allyl phenol or with the product of the reaction of bromine and α-methyl coumarane. The dibromo compound is probably formed first by the bromination of the *o*-allyl phenol to give the *p*-bromo-*o*-allyl phenol; bromine then adds to this compound and one molecule of hydrobromic acid splits out, thus:



It is particularly significant that in the preparation of the methylene coumaranes, acylation of the phenol is in general necessary before the addition of bromine is carried out. This is to avoid as much as possible not only bromination in the ring which has a great tendency to take place when the free phenol group is present, but also the formation of considerable amounts of complex tarry compounds. The bromination of *o*-allyl phenol just described is a good illustration of the way the reaction runs provided the phenol group is not acylated. In the case of *o*-carboxy-*o*-allyl phenol, acetylation is extremely difficult, in fact no acetyl derivative was obtained in this research. The hydroxyl group has at the same time lost its tendency to cause easy substitution in the ring so that bromination of this phenol goes smoothly and clean products result. Alkylation in place of acylation is not satisfactory since bromination of *o*-allyl anisol gives the same type of complex mixture that *o*-allyl phenol itself gives.

The only reaction of the α-methylene coumaranes studied was the bromination and this was carried out with α-methylene coumarane itself. Hydrobromic acid is continually evolved during the reaction and a monobromo substitution product results. It is not identical with *p*-bromo-α-methylene coumarane, the substance which would undoubtedly be formed if substitution in the ring took place. The halogen is, however, inactive to alcoholic potash or zinc and hydrochloric acid. This leads to the conclusion that the monobromo compound is α-bromomethylene coumarane,



resulting no doubt from the addition of bromine to the double bond, then splitting out of hydrobromic acid. The analogous bromine derivative of *o*-carboxy-α-methylene coumarane was also prepared.

In this investigation, besides α-methylene coumarane, the *o*- and *p*-methyl-, *p*-bromo- and *o*-carboxy-substituted derivatives were made with satisfactory results. The corresponding compound from α-allyl-β-naphthol was synthesized also; the yield in the last step, however, was poor.

Further investigations on various types of cyclic ethers are now in progress.

## Experimental.

**o-Allyl Phenol,** $C_6H_4(OH)^1(C_3H_5)^2$.—Allyl-phenyl ether is prepared from phenol and allyl bromide and rearranged to *o*-allyl phenol according to the general directions of Claisen.[1] During this investigation an article published by Jacobs[2] included a description of this compound. The directions followed in this research for the rearrangement of the allyl-phenyl ether to *o*-allyl phenol differ slightly from those of Jacobs. It was found that if allyl-phenyl ether is refluxed till the temperature, which registers about 190° at first, reaches a constant point of 220°, the product is practically pure *o*-allyl phenol and needs only a vacuum distillation for complete purification.

**Acetyl-*o*-Allyl Phenol,** $C_6H_4(OCOCH_3)^1(C_3H_5)^2$.—*o*-Allyl phenol is refluxed for three hours with two moles of acetic anhydride. The reaction mixture is then distilled under diminished pressure. This gives in 90% yield, a colorless, pleasant smelling oil.

B. p. 123–124° at 20 mm., $d_{24}$ 1.031, $[n]_D^{20}$ 1.508.
Subs., 0.1336: $CO_2$, 0.3712; $H_2O$, 0.0880.
Calc. for $C_{11}H_{12}O_2$: C, 75.6; H, 6.8. Found: C, 75.8; H, 7.2.

**Acetyl-*o*-Allyl-phenol Dibromide,** $C_6H_4(OCOCH_3)^1(C_3H_5Br_2)^2$. — The acetyl derivative of *o*-allyl phenol is dissolved in about 4 times its volume of carbon disulfide and cooled to 0°. The calculated amount of bromine in carbon disulfide is slowly run into the first solution. Practically no hydrogen bromide is given off until the bromine is about two-thirds added, then a very little is evolved. On evaporation of the solvent,

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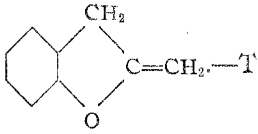
[1] *Ber.*, **45**, 3157 (1912); *Ann.*, **401**, 56 (1913).

[2] THIS JOURNAL, **39**, 2202 (1917).

a dark oil is left which is repeatedly extracted with hot petroleum ether. On cooling the extraction liquors without stirring, the brominated compound settles out as an oil or with stirring in the form of white crystals which on recrystallization from petroleum ether melt at 42°.

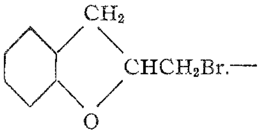
Subs., 0.1824: AgBr, 0.2060.
Calc. for $C_{11}H_{12}O_2Br_2$: Br, 47.7. Found: 48.1.

**α-Methylene Coumarane,** 

.—The dibromo compound obtained above is refluxed with an excess of alcoholic potash or sodium alcoholate for about an hour. The reaction mixture is poured into water and extracted with ether. After drying and evaporating the solvent, a clear colorless oil with a pleasant odor is obtained.

B. p. 93–94° at 20 mm., or 196–197° at 744 mm., $d_{24}$ 1.050, $[n]_D^{22}$ 1.555.
Subs., 0.1337: $CO_2$, 0.3987; $H_2O$, 0.0757.
Calc. for $C_9H_8O$: C, 81.8; H, 6.1. Found: C, 81.5; H, 6.3.

**α-Bromomethyl-coumarane from Acetyl-*o*-allyl-phenol Dibromide,**

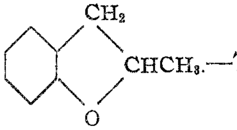


.—30 g. of the acetyl-*o*-allyl-phenol dibromide is dissolved in absolute alcohol and treated with one molecule of sodium alcoholate (made from 2.1 g. of sodium). After heating under a reflux on the steam bath for about an hour, the mixture is diluted with water, extracted with ether, dried over calcium chloride, the solvent evaporated and the product distilled. After redistillation, 12 g. of clear liquid results which turns dark on standing.

B. p. 144–145° at 20 mm., $d_{25}$ 1.453, $[n]_D^{20}$ 1.575.
Subs., 0.2081: AgBr, 0.1858.
Calc. for $C_9H_9OBr$: Br, 37.6. Found: 37.8.

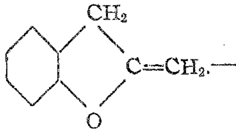
The structure of the compound is without doubt the one given when (1) the mode of preparation, (2) the reduction to α-methyl coumarane, (3) the alcoholic potash treatment to α-methylene coumarane are considered.

**α-Methyl Coumarane from α-Bromomethyl Coumarane,**



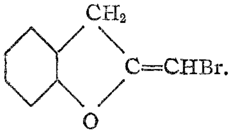
.—The α-bromomethyl coumarane is heated for several hours with zinc and hydrochloric acid (20%) under a reflux condenser on the steam bath. The progress of the reduction may be followed readily since the original oil, which at first settles around the zinc, on reduction is of much less sp. gr. and floats on top of the solution. After the action is complete, the oil is extracted with ether, washed with sodium carbonate and with water, dried over calcium chloride and distilled. The main product boils at 198–199° at 740 mm., $[n]_D^{20}$ 1.533, $d_{24}$ 1.038, thus agreeing perfectly with the properties of α-methyl coumarane.

**α-Methylene Coumarane from α-Bromomethyl Coumarane,**



—The α-bromomethyl coumarane is treated with an excess of alcoholic potash and refluxed for a short time. The mixture is then diluted with water, extracted with ether, washed with water, dried over calcium chloride and distilled It is a colorless oil, b. p. 197–198° at 745 mm., $[n]_D^{22}$ 1.554, $d_{24}$ 1.050.

**α-Bromomethylene Coumarane,**



— α-Methylene coumarane is brominated in carbon disulfide at 0° with the calculated quantity of bromine for addition to the double bond. Hydrobromic acid is given off continuously during the process. After evaporating off the carbon disulfide, the product is distilled, yielding a clear colorless oil which turns dark on standing, b. p. 134–138° at 25 mm., $[n]_D^{20}$ 1.584, $d_{23}$ 1.472.

Subs., 0.1932: AgBr, 0.1693.
Calc. for $C_9H_7OBr$: Br, 37.8. Found: 37.3.

The analysis indicates a monobromo substitution product. On treating this compound with alcoholic potash there is little or no reaction even on boiling; alcoholic silver nitrate gives but a very slow reaction; the compound is not reduced by zinc and hydrochloric acid. These properties lead to the conclusion that the halogen is either in the benzene ring or attached to a carbon atom holding the double bond. If the bromine entered the ring it would most probably give the para derivative since the bromination of α-methyl coumarane yields a para derivative. The *p*-bromo-α-methylene coumarane, however, has been prepared in two ways described later in this investigation and its properties do not coincide with those of the compound produced by bromine on α-methylene coumarane. The compound obtained is therefore very probably α-bromomethylene coumarane.

### Bromination of *o*-Allyl Phenol.

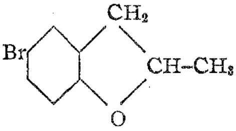
The *o*-allyl phenol is dissolved in carbon disulfide and the calculated amount of bromine in the same solvent is slowly dropped in, the temperature being kept at 0° or below. Hydrobromic acid is evolved to some extent during the entire process and increases in amount if the temperature is allowed to rise. Moreover, if the reaction mixture warms up, considerable tar forms and much trouble is encountered in the fractionation. After all the bromine has been added, the solvent is evaporated off and the viscous black mixture is poured into a large Claissen distilling flask for distillation. This flask should be about twice the size normally used for the volume of liquid at hand since on the first distillation much frothing takes place. Great care must be used to prevent this, and several hours are required for the distillation of the product from 100 g. of *o*-allyl phenol. At a pressure of 20 mm. the first fraction is collected up to 125°, a second fraction from 125 to 146°, a third from 146 to 180°, and finally the last fraction, 180 to 210°. A fractional distillation is carried on till only three main fractions are produced (1) up to 125°, (2) 138–146°, (3) 180 to 210°. The residue left in the flask is a black tar which cools to a hard cake and usually causes the flask to break. The amount of this residue as well as the amount of each of the fractions depends on the conditions during bromination. If the temperature is not kept low during the entire reaction, the lowest fraction and residue will be large; if the bromination mixture is kept well cooled, however, larger middle fractions are produced.

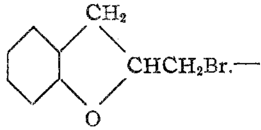
**Fraction 1. α-Methyl Coumarane.**—Fraction 1 is shaken with 10% sodium hydroxide solution in order to remove any unchanged allyl phenol which may be present. This alkaline solution is extracted with ether and the extract dried over calcium chloride. Upon evaporation of the ether and fractionation of the product there is obtained a colorless oil with a rather pleasant odor, b. p. 93–94° at 23 mm., $d_{24}$ 1.032, $[n]_D^{22}$ 1.531.

Subs., 0.1832: $CO_2$, 0.5430; $H_2O$, 0.1259.

Calc. for $C_9H_{10}O$: C, 80.6; H, 7.5. Found: C, 80.8; H, 8.06.

This substance is α-methyl coumarane and has already been prepared by Claissen.[1] A sample made according to his method proved to be identical with the substance obtained above.

**Fraction 2. *p*-Bromo-α-methyl Coumarane,** 

; **α-Bromomethyl Coumarane,** 

.—By further fractionation of the portion boiling at 138–146°, a product boiling fairly constant at about 142° at 20 mm. is obtained. Experiments show that this product

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[1] *Chem. Zentr.*, [2] **1914**, 1213.

is actually a mixture of two substances, *p*-bromo-α-methyl coumarane and α-bromomethyl coumarane. The former contains the halogen atom in the benzene ring with the result that the bromine is not replaceable, while the latter compound holds an aliphatic halogen which may be readily removed.

**a. Treatment of Mixture of Alcoholic Potash.**—If the constant boiling material obtained above is refluxed several hours with alcoholic potash, then poured into water, an oil may be extracted which on careful fractional distillation yields two pure products: (1) a colorless oil boiling at 141–142° at 20 mm., $d_{24}$ 1.414, $[n]^{22}_{\mathrm{D}}$ 1.569, which by analysis and subsequent preparation from *p*-bromo-*o*-allyl phenol and from the bromination of α-methyl coumarane proves to be *p*-bromo-α-methyl coumarane.

Subs., 0.1628: AgBr, 0.1450.
Calc. for $C_9H_7OBr$: Br, 37.8. Found: 37.9.

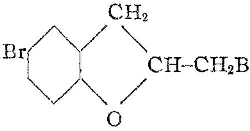
(2) A colorless oil boiling at 196–197° at 744 mm., $d_{24}$ 1.050, $[n]^{22}_{\mathrm{D}}$ 1.554, which by analysis and properties proves to be α-methylene coumarane, already prepared by the action of excess alcoholic potash on acetyl-*o*-allyl-phenol dibromide.

**b. Treatment with Zinc and Hydrochloric Acid.**—If the constant boiling material obtained from Fraction 2 is refluxed several hours with granulated zinc and hydrochloric acid (20%), then extracted with ether, dried and fractionally distilled, two pure products are obtained: (1) *p*-bromo-methyl coumarane, the same substance as one of those resulting from the action of alcoholic potash described above; (2) a colorless oil, b. p. 196–197° at 745 mm., 98–99° at 25 mm., $d_{24}$ 1.038, $[n]^{22}_{\mathrm{D}}$ 1.531, which by analysis and properties proves to be α-methyl coumarane. This was obtained as the low fraction in the product of bromination of *o*-allyl phenol and from the action of pyridine hydrochloride on *o*-allyl phenol.

Subs., 0.1531: $CO_2$, 0.5658; $H_2O$, 0.1246.
Calc. for $C_9H_{10}O$: C, 80.2; H, 7.5. Found: C, 80.2; H, 7.9.

The only structure possible for the second bromine compound in the original mixture which by alcoholic potash goes to α-methylene coumarane and by zinc and hydrochloric acid goes to α-methyl coumarane is α-bromo-methyl coumarane. This substance may be obtained pure by the action of one molecule of alcoholic potash on acetyl *o*-allyl-phenol dibromide and has already been described in this investigation.

Fraction 3. **p-Bromo-α-bromomethyl Coumarane,**



—By careful fractionation of Fraction 3, an oil which turns dark on standing is produced, boiling 189–194° at 20 mm., $d_{24}$ 1.795, $[n]^{22}_{\mathrm{D}}$ 1.607. By analysis and subsequent treatment with alcoholic potash and with zinc and hydrochloric acid, it may be shown to be *p*-bromo-α-bromomethyl coumarane.

Subs., 0.2256: AgBr, 0.2884.
Calc. for $C_9H_8OBr_2$: Br, 54.8. Found: 54.4.

(a) **Treatment with Alcoholic Potash.**—If the pure material from Fraction 3 is refluxed an hour with alcoholic potash, then diluted with water, extracted with ether, dried and distilled, a clear, colorless oil is produced, b. p. 148° at 30 mm., $d_{24}$ 1.483, $[n]_D^{22}$ 1.595. Analysis and subsequent preparation from *p*-bromo-*o*-allyl phenol proves it to be *p*-bromo-α-methylene coumarane.

Subs., 0.1546: AgBr, 0.1414.
Calc. for $C_9H_7OBr$: Br, 38.0. Found: 37.9.

(b) **Treatment with Zinc and Hydrochloric Acid.**—The material is refluxed with zinc and hydrochloric acid (20%) for several hours, extracted with ether, washed with sodium carbonate, dried and distilled. A colorless oil is produced, b. p. 142–144° at 20 mm., $[n]_D^{22}$ 1.570, which is identical with the *p*-bromo-α-methyl coumarane synthesized either by bromination of α-methyl coumarane or by the treatment of *p*-bromo-*o*-allyl phenol with pyridine hydrochloride.

### Experiments with *o*-Allyl Anisol.

In the course of this investigation, the dibromo addition product of *o*-allyl-phenol was desired. Since this was not obtained when bromine was added directly to *o*-allyl phenol, nor by the hydrolysis of acetyl-*o*-allyl-phenol dibromide, an attempt was made to prepare the *o*-allyl-anisol dibromide with the further intention of splitting the ether with aluminum chloride and obtaining the compound wanted. The experiments were unsuccessful but a description of results of the work is given below.

***o*-Allyl Anisol,** $C_6H_4(OCH_3)^1(C_3H_5)^2$.—One mole of *o*-allyl phenol and 1.5 moles of sodium hydroxide are dissolved in water. On addition of a molecule of dimethyl sulfate a reaction begins at once. It is refluxed on the steam bath for several hours. The allyl anisol separates and comes to the top as an oil. It is extracted with ether, washed with sodium hydroxide and with water, dried over calcium chloride and distilled. The yield may be increased by adding more of the base and dimethyl sulfate to the original solution and refluxing again. Yield, 90%.

The product is a colorless, pleasant smelling liquid turning slightly yellow on standing, b. p. 101–102° at 22 mm., $d_{24}$ 0.972, $[n]_D^{22}$ 1.526.

Subs., 0.1784: $CO_2$, 0.5285; $H_2O$, 0.1368.
Calc. for $C_{10}H_{12}O$: C, 81.1; H, 8.17. Found: C, 80.6; H, 8.0.

**Bromination of *o*-Allyl Anisol.**—The allyl anisol is dissolved in carbon disulfide and two atoms of bromine dissolved in the same solvent are slowly added, the temperature being kept at 0°. Hydrobromic acid is given off, mainly toward the end of the process. On evaporation of solvent and distillation, the boiling point of product ranges from 90–205° at 20 mm. and a tar-like residue is left. It is possible to separate the same fractions as those obtained from the bromination of *o*-allyl phenol. The lowest fraction boils chiefly at 94° at 20 mm. and has $[n]_D^{22}$ 1.531, these properties as well as its color and smell checking with $\alpha$-methyl coumarane. The next fairly constant boiling fraction boils from 140–150° at 20 mm. It was not purified further but gives $[n]_D^{22}$ 1.572 which is identical with that of the mixture of *p*-bromo-$\alpha$-methyl coumarane and $\alpha$-bromomethyl coumarane obtained from the bromination of *o*-allyl phenol. There is also a high fraction boiling from 190–205° at 20 mm. which was not further studied.

### Derivatives of *p*-Bromo Phenol.

*p*-Bromo-*o*-allyl phenol is prepared by rearranging allyl-*p*-bromophenyl ether according to the method of Claissen and Eisleb.[1] It melts at 52°, 2° higher than the melting point observed by these investigators.

**Benzoyl-*p*-bromo-*o*-allyl Phenol,** $Br^4C_6H_4(OCOC_6H_5)^1(C_3H_5)^2$.—This is prepared from the phenol by the Baumann-Schotten reaction. 25 g. of the phenol is dissolved in a big excess of 10% sodium hydroxide and 40 g. of benzoyl chloride added. The mixture is then shaken until the smell of benzoyl chloride is gone. It is extracted with ether and washed with water until free from alkali, dried over calcium chloride and the ether evaporated. The product (90% yields) distills completely without decomposition at 234–236° at 25 mm., $[n]_D^{22}$ 1.589, $d_{24}$ 1.308.

Subs., 0.5350: AgBr, 0.3212.
Calc. for $C_{16}H_{13}O_2Br$: Br, 25.2. Found: 25.6.

**Benzoyl-*p*-bromo-*o*-allyl-phenol Dibromide,** $Br^4C_6H_4(OCOC_6H_5)^1(C_3H_5Br_2)^2$.—The benzoyl-*p*-bromo-*o*-allyl phenol is dissolved in carbon disulfide and, after cooling in an ice bath, the theoretical amount of bromine dissolved in about three times its weight of carbon disulfide is slowly run in. A very little hydrogen bromide is given off toward the end of the bromination. When about half of the bromine has been added, the product begins to crystallize out and it has practically all separated by the time all the bromine has been added. The crystals are filtered off and washed with a little petroleum ether and ether. The material is then dissolved in hot ligroin from which it separates on cooling in 70% yields as fine, white crystals which melt at 98.5°.

Subs., 0.1857: AgBr, 0.2192.
Calc. for $C_{16}H_{13}O_2Br_3$: Br, 50.31. Found: 50.23.

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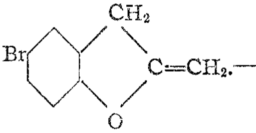
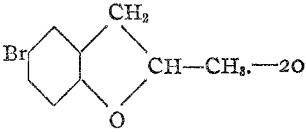
[1] *Ann.*, 401, 38 (1913).

**_p_-Bromo-α-methylene Coumarane,** —The brominated compound just described is treated with an excess of alcoholic potash according to the method already given. The product is a colorless oil boiling at 141–143° at 21 mm., $[n]_D^{24}$ 1.593, $d_{26}$ 1.476.

Subs., 0.2009: AgBr, 0.1797.
Calc. for $C_9H_7OBr$: Br, 38.0. Found: 37.9.

**_p_-Bromo-α-methyl Coumarane,** —20.7 g. of _p_-bromo-_o_-allyl phenol is heated in a flask under a reflux condenser with about 15 g. of pyridine hydrochloride. After about an hour of heating, the mixture is extracted with ether and washed successively with dil. sulfuric acid, water, sodium hydroxide and water. It is then dried over calcium chloride, the ether evaporated and the product distilled. A colorless oil boiling at 144–146° at 23 mm. results, $[n]_D^{20}$ 1.569, $d_{24}$ 1.403.

Subs., 0.3230: AgBr, 0.2883.
Calc. for $C_9H_9OBr$: Br, 37.55. Found: 37.85.

It may also be prepared by the bromination of α-methyl coumarane. Methyl coumarane is dissolved in about 4 times its volume of carbon disulfide, cooled to 0° and treated slowly with the calculated amount of bromine dissolved in carbon disulfide. Hydrobromic acid is given off continuously. After evaporation of the solvent the material is distilled. A clear, colorless oil is obtained, b. p. 139–140° at 18 mm., $d_{24}$ 1.434, $[n]_D^{22}$ 1.569.

## Derivatives of _p_-Cresol.[1]

**_o_-Allyl-_p_-cresol,** $C_6H_3(CH_3)^1(OH)^4(C_3H_5)^5$.—The preparation and rearrangement of _p_-cresol-allyl ether is carried out according to the directions of Claissen and Eisleb.[2]

**Acetyl-_o_-allyl-_p_-cresol,** $C_6H_3(CH_3)^1(OCOCH_3)^4(C_3H_5)^5$.—The _o_-allyl-_p_ cresol is refluxed for two hours with two moles of acetic anhydride. The resulting mixture is fractionated under diminished pressure, giving a colorless oil in 75% yields, b. p. 139° at 22 mm., $d_{20}$ 1.022, $[n]_D^{20}$ 1.507.

Subs., 0.1754: $CO_2$, 0.4876; $H_2O$, 0.1215.
Calc. for $C_{12}H_{14}O_2$: C, 75.82; H, 7.37. Found: C, 75.76; H, 7.71.

**Acetyl-_o_-allyl-_p_-cresol Dibromide,** $C_6H_3(CH_3)^1(OCOCH_3)^4(C_3H_5Br_2)^5$.—The acetylated allyl cresol is dissolved in chloroform, cooled to about 0° and treated slowly with two atoms of bromine. Small amounts of

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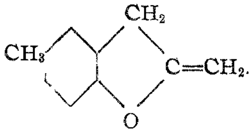
[1] Experimental work by L. F. Krug.

[2] _Ann._, **401,** 56 (1913).

hydrobromic acid are given off toward the end of the bromination. On evaporation of the chloroform, a pink solid remains which crystallizes from 50% alcohol, as long, white needles and melts at 77.5°. Yield, 78%.

Subs., 0.2346: AgBr, 0.2508.
Calc. for $C_{12}H_{14}O_2Br_2$: Br, 45.70. Found: 45.35.

**p-Methyl-α-methylene Coumarane,**



—The dibromide just described is dissolved in absolute alcohol and treated with an equal volume of absolute alcoholic potassium hydroxide. After refluxing for about two hours, water is added and the mixture extracted with ether. The ether solution is dried over calcium chloride, the solvent evaporated and an oil obtained which on purification boils at 113° at 17 mm., $d_{20}$ 1.043, $[n]_D^{20}$ 1.556.

Subs., 0.1739: $CO_2$, 0.5294; $H_2O$, 0.1076.
Calc. for $C_{10}H_{10}O$: C, 82.2; H, 6.85. Found: C, 81.6; H, 6.88.

## Derivatives of *o*-Cresol.[1]

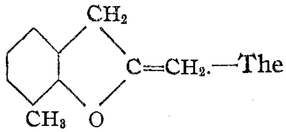
**o-Allyl-o-cresol,** $C_6H_3(CH_3)^1(OH)^2(C_3H_5)^3$.—Preparation and rearrangement of *o*-cresol-allyl ether are carried out as described by Claissen and Eisleb.[2]

**Acetyl-o-allyl-o-cresol,** $C_6H_3(CH_3)^1(OCOCH_3)^2(C_3H_5)^3$.—*o*-Allyl-*o*-cresol is refluxed several hours with two molecules of acetic anhydride. The reaction mixture is fractionated under diminished pressure and the acetylated *o*-allyl-*o*-cresol is obtained in 79% yield as a pleasant smelling colorless oil, b. p. 128° at 14 mm., $d_{20}$ 1.023, $[n]_D^{20}$ 1.507.

Subs., 0.2053: $CO_2$, 0.5712; $H_2O$, 0.1390.
Calc. for $C_{12}H_{14}O_2$: C, 75.82; H, 7.37. Found: C, 75.80; H, 7.57.

**Acetyl-o-allyl-o-cresol Dibromide,** $C_6H_3(CH_3)^1(OCOCH_3)^2(C_3H_5Br_2)^3$.—The bromination is carried out in chloroform at 0°. Upon evaporation of the solvent there is left a reddish yellow viscous liquid which does not solidify. On distillation under diminished pressure, it boils with some decomposition at about 210° at 20 mm. Yield of the crude oil, 91%.

**o-Methyl-α-methylene Coumarane,**



—The crude dibromo compound is dissolved in absolute alcohol and treated with alcoholic potash as in the case of the derivative of *p*-cresol. Yield, 46%. The product is a colorless, pleasant smelling oil, b. p. 101–102° at 15 mm., $d_{20}$ 1.043, $[n]_D^{20}$ 1.553.

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[1] Experimental work by H. W. Moor.

[2] *Ann.*, 401, 36 (1913).

Subs., 0.2056: $CO_2$, 0.6153; $H_2O$, 0.1277.
Calc. for $C_{10}H_{10}O$: C, 82.20; H, 6.85. Found: C, 81.70; H, 6.95.

## Derivatives of β-Naphthol.

**Allyl-β-naphthol,** $C_{10}H_6(OH)^2(C_3H_5)^1$.—Allyl-β-naphthyl ether was made and rearranged according to the directions of Claissen.[1]

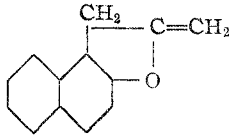
**Acetyl-α-allyl-β-naphthol,** $C_{10}H_6(OCOCH_3)^2(C_3H_5)$.[1]— α-Allyl-β-naphthol is refluxed for three hours with two moles of acetic anhydride and the product fractionated. The acetyl compound is a practically colorless oil boiling at 186–189° at 17 mm., $d_{25}$ 1.111, $[n]_D^{22}$ 1.584. If not carefully distilled, it contains an impurity which causes it to turn green on standing. Yield, 94%.

Subs., 0.1320: $CO_2$, 0.3874; $H_2O$, 0.0771.
Calc. for $C_{15}H_{14}O_2$: C, 79.7; H, 6.2. Found: C, 80.1; H, 6.5.

**Acetyl-α-allyl-β-naphthol Dibromide,** $C_{10}H_6(OCOCH_3)^2(C_3H_5Br_2)^1$.—The bromination is carried out in carbon disulfide at a low temperature. When the bromine is about two-thirds added, the entire mixture becomes of buttery consistency and on adding more bromine, crystals separate. After all the bromine is in, the crystals are filtered from the cold solution and washed with a little carbon disulfide.

The product is crystallized from alcohol, giving beautiful, white, fibrous needles in 60% yield, m. p. 89°.

Subs., 0.1022: AgBr, 0.0990.
Calc. for $C_{15}H_{14}O_2Br_2$: Br, 41.4. Found: 41.2.

**α-Methylene-β-naphtho-dihydrofurane,**  .—Acetyl-α-allyl-β-naphthol dibromide is refluxed with an excess of sodium alcoholate, 3 to 4 atoms of sodium being used. After two to three hours, it is diluted with water, extracted with ether, the ether extract over calcium chloride and distilled. The material decomposes very readily and on several attempts it could be seen boiling and condensing as a clear oil in the flask but was largely decomposed before it came over. A clear oil was obtained, boiling mainly at 188–190° at 17 mm. The distillation is difficult to carry out and much decomposition takes place. A tarry residue is left in the flask which, on extraction with hot petroleum ether, gives white crystals melting at 97°. Only a very small amount was obtained and the product was not identified.

The clear, oily distillate solidified in the receiving flask. It was dissolved in hot alcohol and after cooling it was precipitated as lustrous, white crystals by adding water until a cloudiness appeared, m. p. 55°.

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[1] *Ber.*, 45, 3157 (1912).

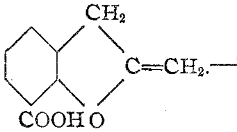
Subs., 0.0408: $CO_2$, 0.1258; $H_2O$, 0.0210.
Calc. for $C_{13}H_{10}O$: C, 85.6; H, 5.5. Found: C, 84.7; H, 5.7.

## Derivatives of Salicylic Acid and Its Methyl Ester.[1]

**2-Hydroxy-3-allyl-methyl-benzoate,** $C_6H_3(COOCH_3)^1(OH)^2(C_3H_5)^3$.—This substance is prepared by the rearrangement of the allyl ether of methyl salicylate.[2] Unlike the other allyl phenols studied, this compound is not acetylated by continued boiling with acetic anhydride.

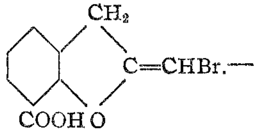
**2-Hydroxy-3-allyl-methyl-benzoate Dibromide,** $C_6H_3(COOCH_3)^1(OH)^2(C_3H_5Br_2)^3$.—The bromination is carried out in carbon disulfide in an ice bath. Two atoms of bromine in carbon disulfide are added with continued stirring. A pasty mass separates which is filtered off with suction and recrystallized with alcohol, forming white, granular crystals, m. p. 72–72.5°.

Subs., 0.1986: AgBr, 0.2121.
Calc. for $C_{11}H_{12}O_3Br$: Br, 45.6. Found: 45.5.

**o-Carboxy-α-methylene Coumarane,** 

—This is obtained by refluxing 2-hydroxy-3-allyl-methyl-benzoate dibromide with excess of alcohol potash for several hours. The methyl ester is hydrolyzed at the same time. Water is added and the impure product (m. p. 144–146°) is precipitated by the addition of hydrochloric acid. There is a yellowish impurity present which may be removed by repeated fractional crystallization from a mixture of ether and petroleum ether, leaving the pure product as fine, white crystals which may be recrystallized from an alcohol and water mixture or sublimed, m. p. 152°.

Subs., 0.2878: $CO_2$, 0.7131; $H_2O$, 0.1272.
Calc. for $C_{10}H_8O_3$: C, 68.2; H, 4.55. Found: C, 67.8; H, 4.95.

**o-Carboxy-α-bromomethylene Coumarane,** 

—1.5 g. of o-carboxy-α-methylene coumarane is dissolved in ether and treated slowly with 1.6 g. of bromine, the temperature being kept at 0°. The ether is partly evaporated off and crystals separate. These are recrystallized from ether and petroleum ether, depositing as white needles, m. p. 222–223°.

Subs., 0.1630: AgBr, 0.1261.
Calc. for $C_{10}H_7O_3Br$: Br, 31.4. Found: 32.9.

The compound does not react with alcoholic potash nor with alcoholic silver nitrate.

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[1] Experimental work by R. H. Gerke.

[2] *Ann.*, **401**, 70 (1913).

**2-Hydroxy-3-allyl Benzoic Acid,** $C_6H_3(COOH)^1(OH)^2(C_3H_5)^3$.—This compound is obtained by the saponification of its methyl ester. 59 g. of the 2-hydroxy-3-allyl-methyl benzoate is dissolved in 300 cc. of absolute alcohol and refluxed for about two hours with 25 g. of potassium hydroxide. The solution is then diluted with water and the product precipitated by the addition of hydrochloric acid. After recrystallization from ether and petroleum ether it melts at 93°.

Upon treatment with acetic anhydride, this compound is recovered unchanged.

**2-Hydroxy-3-allyl-benzoic-acid Dibromide,** $C_6H_3(COOH)^1(OH)^2(C_3H_5Br_2)^3$.—24 g. of the 2-hydroxy-3-allyl-benzoic acid just described is dissolved in carbon disulfide and 21.8 g. of bromine gradually added, the temperature being held near 0°. The product crystallizes out and is filtered with suction. After recrystallization from ether and carbon disulfide, the product is in the form of white needles, m. p. 162.5–163.5°.

Subs., 0.3438: AgBr, 0.3838.
Calc. for $C_{10}H_{10}O_3Br_2$: Br, 47.35. Found: 47.40.

On refluxing this with alcoholic potash *o*-carboxy-α-methylene coumarane results identical with the product obtained by the action of alcoholic potash on the 2-hydroxy-3-allyl-methyl benzoate.

### Summary.

1. *o*-Allyl phenols are converted readily to α-methylene coumaranes by the following succession of reactions: (1) acylation, (2) bromination, (3) treatment with alcoholic potash.

2. Proof of the structure of α-methylene coumarane obtained from *o*-allyl phenol was accomplished by step-wise decomposition of the acetyl-*o*-allyl-phenol dibromide and proof of the structure of the intermediate products. Additional proof resulted from the direct bromination of *o*-allyl phenol.

3. Bromination of α-methylene coumarane yields α-bromo-methylene coumarane.

URBANA, ILLINOIS.

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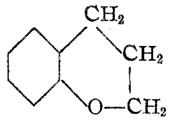
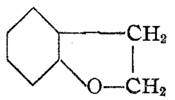
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

# SYNTHESES OF CHROMANES AND COUMARANES.

BY R. E. RINDFUSZ.

Received January 8, 1919.

Although chromane  and coumarane  have been known for a number of years, there has never been a convenient method for their preparation, and only a very few of their derivatives