of patents on such polymerization of olefinic compounds have appeared. In continuing the theoretical studies[3] of olefin polymerization in this Laboratory, we have been led to investigate the action of boron trifluoride on alcohols, a type of reaction which has not been reported previously. This is of particular interest since this halide is believed to yield true polymerization products by its action on isobutylene at low temperatures.[4]

We have found that the action of boron trifluoride on isopropyl alcohol proceeds with the formation of polymerized products and from the reaction mixture we have isolated substantial yields of tetrapropylene.

Boron trifluoride (1400 g.) was dissolved in 2 kg. of isopropyl alcohol with external cooling and the resulting solution was heated in a loosely-capped bomb at 100°. The reaction proceeded spontaneously with liberation of much boron trifluoride and other gases (propylene, the dimer, etc.). The contents of the bomb consisted of an upper layer of colorless polymer and a lower aqueous layer. The former was removed, washed free of acid, dried over anhydrous potassium carbonate and fractionated through a 12-plate distilling column of the type used in this Laboratory.[5] Figure 1 shows the course of the distillation. The tetrapropylene, b. p. 94–105° at 30 mm., $n^{20}D$ 1.4358–1.4406, is about 20% of the 1200 g. of polymer formed from two kilograms of isopropyl alcohol. Investigation of the products is in progress.

(3) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).
(4) I. G. Farbenindustrie, British Patent 401,297.
(5) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

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RECEIVED FEBRUARY 23, 1939

COMMUNICATIONS TO THE EDITOR

THE TOTAL SYNTHESIS OF THE SEX HORMONE EQUILENIN

Sir:

Although certain sex hormones such as estrone have been prepared from other naturally occurring compounds possessing similarities in structure, the total synthesis of none of them has yet been reported. We have now succeeded in accomplishing the total synthesis of the sex hormone equilenin, and in view of Marker's conversion of equilenin to estrone by reduction [THIS JOURNAL, **60**, 1897 (1938)] it follows that the total synthesis of both equilenin and estrone has been accomplished.

The reactions which were used are fairly obvious ones and the successful preparation of the hormone depended principally on developing the proper conditions for making the reactions proceed. As a matter of fact, some features of the method had been explored by other investigators without success. The starting point was the known 7-methoxy-1-keto-1,2,3,4-tetrahydrophenanthrene, prepared from 1-naphthylamine-6-sulfonic acid (Cleve's acid).

An eleven-step synthesis converted this compound to equilenin. First of all this ketone was condensed with methyl oxalate to give a 1-keto-2-glyoxalate derivative which by elimination of carbon monoxide yielded 7-methoxy-1-keto-2-carbomethoxytetrahydrophenanthrene. As early as 1932 Haworth [*J. Chem. Soc.*, 1125 (1932)] prepared the corresponding ethyl glyoxalate from 1-keto-tetrahydrophenanthrene but was unable to eliminate carbon monoxide without decomposing the compound. Under the proper conditions we were able to obtain the 2-carbomethoxy ketone in 89–91% yields. This compound readily was converted to the important intermediate, 7-methoxy-1-keto-2-methyl-2-carbomethoxytetrahydrophenanthrene (m. p. 84.5–86°) in excellent yield. From this point more or less standard procedures were employed to build up the five-membered ring. The Reformatsky reaction followed by dehydration and reduction of the unsaturated acid served to introduce an acetic acid group in the 1-position. As was expected, the product consisted of two racemic mixtures. These readily were separated into the *cis* (m. p. 228–230°) and the *trans* (m. p. 208–210°) 7-methoxy-1-acetic acid-2-methyl-2-carboxytetrahydrophenanthrene. Each of the acids was car-

ried through the remaining steps, which consisted first in lengthening the acetic acid chain to a propionic acid chain through the Arndt–Eistert reaction. The dimethyl ester of the *trans*-7-methoxy-1-propionic acid-2-methyl-2-carboxytetrahydrophenanthrene (m. p. 101–102°) was cyclized by sodium and the product was converted to *d,l*-equilenin by the usual hydrolysis and decarboxylation, including the hydrolysis of the methoxy group. The synthetic equilenin crystallized from benzene in thin colorless plates which melted at 265–267° (natural equilenin, 258°) to a red liquid. The structure of the synthetic equilenin was established definitely by its conversion to 3′,3′-dimethyl - 7 - methoxy - 1,2 - cyclopentenophenanthrene, identical with the compound obtained from natural equilenin by the procedure of Cohen, Cook and Hewett [*J. Chem. Soc.*, 445 (1935)], the method employed by these investigators to establish the structure of equilenin. The synthetic equilenin was resolved by converting it to its *l*-menthoxyacetic ester, from which was isolated the ester which proved to be identical (mixed melting point) with the *l*-menthoxyacetic ester (m. p. 172–174°) of natural equilenin.

DEPARTMENT OF CHEMISTRY W. E. BACHMANN
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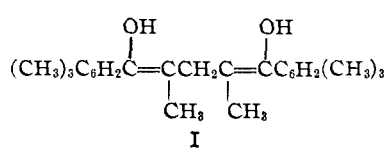
RECEIVED MARCH 28, 1939

1,2-DIARYLACETYLENE GLYCOLS. A NEW TYPE OF ENE-DIOL

Sir:

The isolation of the dienol I in solid form[1] suggested that an ene-diol such as 1,2-dimesitylacetylene glycol (II), being more highly conjugated,



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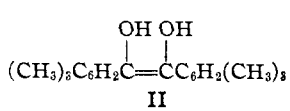

II

might possess still greater stability. This has proved to be true. The ene-diol is formed by the action of the binary mixture, Mg + MgI_2,[2] on dimesityl diketone or 2,4,6-trimethylbenzoyl chloride.

(1) Fuson, Ross and McKeever, THIS JOURNAL, **61**, 414 (1939).
(2) Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

The ene-diol is a white solid (plates) which melts at 144–145° in a nitrogen-filled sealed tube.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.02; H, 8.01.

It can be kept indefinitely in an atmosphere of dry nitrogen but when exposed to air autoxidizes rapidly even in the solid state, giving the corresponding benzil. The ene-diol rearranges to 2,4,6,2′,4′,6′-hexamethylbenzoin under the influence of hydrochloric acid or piperidine. It reduces Tollens' reagent as well as cupric acetate solution at 0°. It is immediately oxidized by sodium 2,6-dichlorobenzeneoneindophenol. The isomeric benzoin does not react with Tollens' reagent or cupric acetate solution in the cold nor with the indophenol even when heated.

2,4,6-Triethylbenzoyl chloride gives a similar but even more stable ene-diol when treated with the binary mixture.

These ene-diols are unique in that in them the ene-diol grouping is not conjugated with a carbonyl group.[3] However, it is conjugated with two aromatic nuclei. This consideration suggested that the remarkable stability of the new ene-diols might be shared by their vinylogs derived from ketones of the types $RCO(CH{=}CH)_nCOR$ and $RCO(C_6H_4)_nCOR$. Evidence of this already has been brought forward by Lutz and Reveley,[4] who report the existence in solution of an ene-diol obtained by the reduction of 1,2-di-(2,4,6-trimethylbenzoyl)-ethylene.

A detailed report of our work will be presented in the near future.

(3) See Barnes and Green, *ibid.*, **60**, 1549 (1938).
(4) Paper presented at the Baltimore meeting of the American Chemical Society, April 4, 1939.

UNIVERSITY OF ILLINOIS REYNOLD C. FUSON
URBANA, ILLINOIS JOSEPH CORSE

RECEIVED MARCH 23, 1939

PANTOTHENIC ACID AND THE FILTRATE (CHICK ANTI-DERMATITIS) FACTOR

Sir:

An extensive series of investigations on pantothenic acid, a factor stimulating the growth of yeast, has been conducted by Williams and coworkers, culminating in the preparation and elementary analysis of the calcium salt.[1] Properties so far described for the filtrate[2] (chick anti-derma-

(1) Williams, Weinstock, Rohrmann, Truesdail and Meyer, THIS JOURNAL, **61**, 454 (1939).
(2) (a) Lepkovsky and Jukes, *J. Biol. Chem.*, **114**, 109 (1936); (b) Jukes, *ibid.*, **117**, 11 (1937); (c) Woolley, Waisman, Mickelsen and Elvehjem, *ibid.*, **125**, 715 (1938).