n-butyllithium solution was added to 59 g. (0.15 mole) of 4,4′-dibromobiphenyl ether dissolved in 400 cc. of benzene. The solution was refluxed for 30 min., cooled, and added to 129 g. (one mole) of dimethyldichlorosilane. After refluxing for an additional 3 hr., the mixture was filtered, the excess chlorosilane and solvents were stripped from the filtrate, and Claisen distillation of the residue yielded a pale yellow oil, b.p. 200–205°/mm., weight 38 g. (71% yield). The oil crystallized on standing to a white waxy solid, m.p. 27–28°.

Anal. Calcd. for $C_{16}H_{20}Cl_2OSi_2$: Cl, 20.2; Si, 15.7. Found: Cl, 20.0; Si, 15.7.

Reaction of 4,4′-dibromobiphenyl ether with lithium. An organolithium reagent was prepared in the usual manner from 7 g. (one mole) of lithium wire, 75 g. (0.23 mole) of 4,4′-dibromobiphenyl ether, and 300 cc. of ether. An aliquot of this solution was taken for titration, and the solution was found to contain 0.25 mole of organolithium reagent. After cooling and filtering from excess lithium, the solution was poured rapidly onto a Dry Ice–ether slurry. The ether layer was washed and extracted with dilute potassium carbonate solution. Acidification of the aqueous solution gave a sticky yellow precipitate, weight 20 g. This material dried to a brittle resin, m.p. 150–170°.

MATERIALS ENGINEERING DEPARTMENTS
WESTINGHOUSE ELECTRIC CORPORATION
EAST PITTSBURGH, PA.

A New Synthesis of Menthofuran

H. FRITEL AND M. FETIZON

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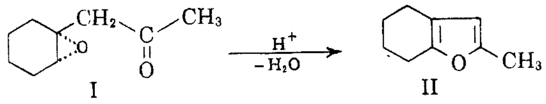
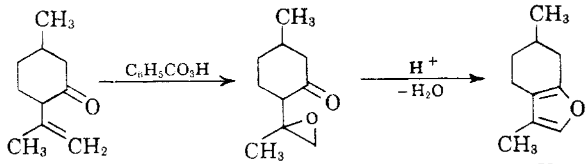
In a recent paper[1] it was shown that keto epoxides such as I could be cyclodehydrated readily to furans when heated with a catalytic amount of acid:



I II

A similar synthesis has been performed on epoxyacetals resulting from a Darzens reaction on ketoacetals.[2]

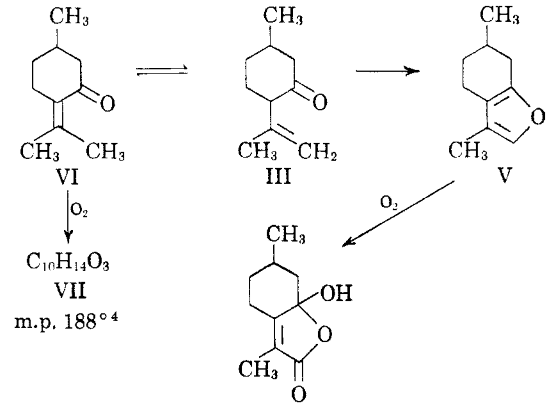
This reaction has been extended now to the keto epoxide (IV), prepared by the action of perbenzoic acid on isopulegone (III). Menthofuran (V) was obtained in poor yield and shown to be identical with an authentic sample, prepared from pulegone according to the method of Treibs.[3] Cyclodehydration of IV occurs under very mild conditions, which are not essentially different from biological ones.



III IV V

Autoxidation of pulegone[4] (VI) or pennyroyal oil[5] gives, among other compounds, a substance (VII), the melting point of which agrees with that of the lactone (VIII), isolated from the products of autoxidation of menthofuran[6]. The structure of VIII has been elucidated recently, but the identity of VII and VIII has not been verified completely.[6]

The results described in this note strengthen the hypothesis of biosynthesis of menthofuran *via* isopulegone:



VIII m.p. 188–189°[6]

EXPERIMENTAL

(*A*) To a solution of perbenzoic acid (0.04 mole) in chloroform, was added 4.32 g. of isopulegone.[7] The solution was kept at 0° and the course of the reaction was followed by titration of the unreacted peracid in aliquots. After completion of the reaction (14 hr.) the solution was washed with 10% sodium carbonate, saturated sodium chloride, dried and concentrated under reduced pressure. The residual oil was refluxed for 10 min. with a mixture of 20 ml. of water, 20 ml. of methanol, and 1 ml. of concentrated sulfuric acid, neutralized and steam distilled; the distillate was extracted with ether and worked up as usual. The yield of pure product was 0.55 g. (13%), b.p. 97–98°/22 mm., n_D^{22} 1.4805.[6,8,9]

The infrared spectrum was identical with that of authentic menthofuran. Menthofuran gives a wine-like characteristic color when treated with chloranil.

Maleic anhydride adduct: m.p. 134°, undepressed when mixed with an authentic sample.[8]

(*B*) When cyclodehydration of the keto epoxide was carried out at room temperature (14 hr.), the yield of menthofuran was lower (5%).

ECOLE POLYTECHNIQUE
PARIS, FRANCE

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