

M.Sc. IV
Org. Chem. Spl.
Paper : EC. 1C
Unit : 1

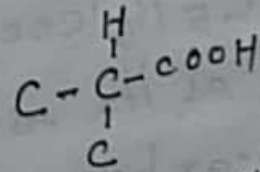
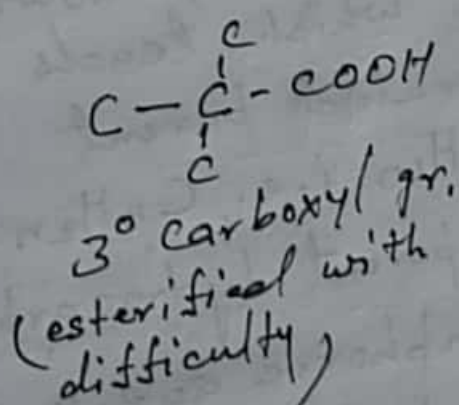
continued - . . . - By Dr. Manju Kumari

Constitution of Camphoric acid : —

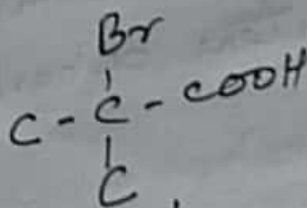
- (i) It is found to be a saturated dicarboxylic acid.
- (ii) Now since its oxidised product camphoric acid has a gem dime. gr. and separate methyl group, camphoric acid and camphor must have three CH_3 -grs. Now therefore the formula of camphoric acid may be shown as $\text{Me}_3\text{C}_5\text{H}_5(\text{COOH})_2$ which leads C_5H_{10} as its saturated parent hydrocarbon. C_5H_{10} i.e., C_nH_{2n} of its saturated parent hydrocarbon suggests that camphoric acid is a cyclopentane dicarboxylic acid.

(iii) Camphoric acid forms monoester very easily but diester with some difficulty indicating that the two $-COOH$ grs. are not similar.

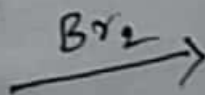
i.e., one is 1° or 2° and the other is 3° . This is confirmed by the fact that camphoric acid forms only monobromoderivatives which is possible only when one of the carboxyl acid is 2° .



2° carboxyl gr.
(easily esterified)



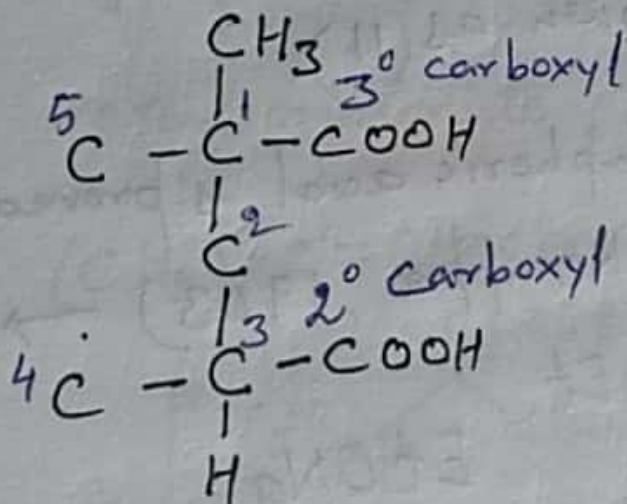
Monobromoderivative



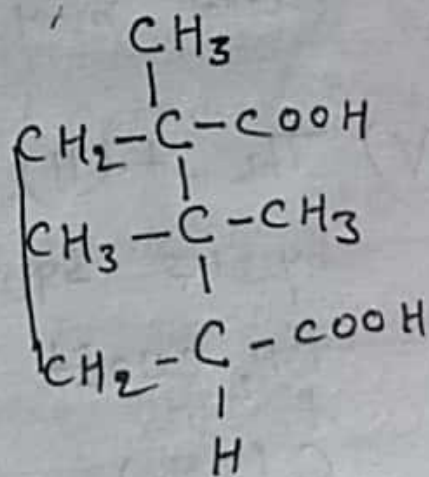
3.

(iv) Camphoric acid is found to be a ring substituted glutaric acid on the basis of Blanc rule which states that on heating with Ac_2O , glutaric acids give anhydrides, adipic acids give cyclopentanones, and pimelic acids give cyclohexanones. Since camphoric acid gives an anhydride, it must be glutaric acid derivative.

So on the basis of the above points, the following part structure must be assigned to camphoric acid (I) —



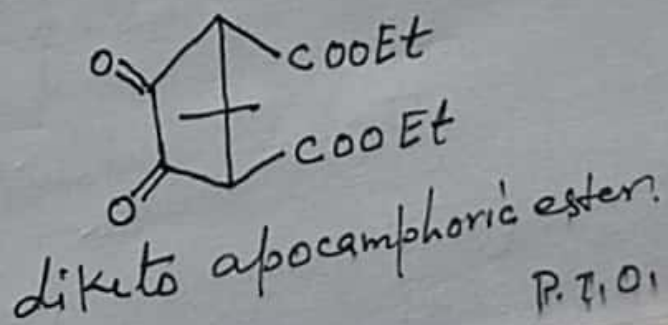
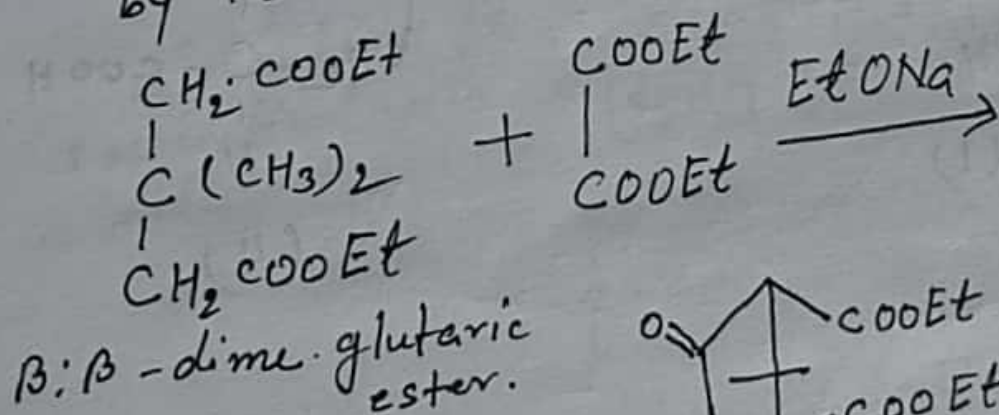
(I)

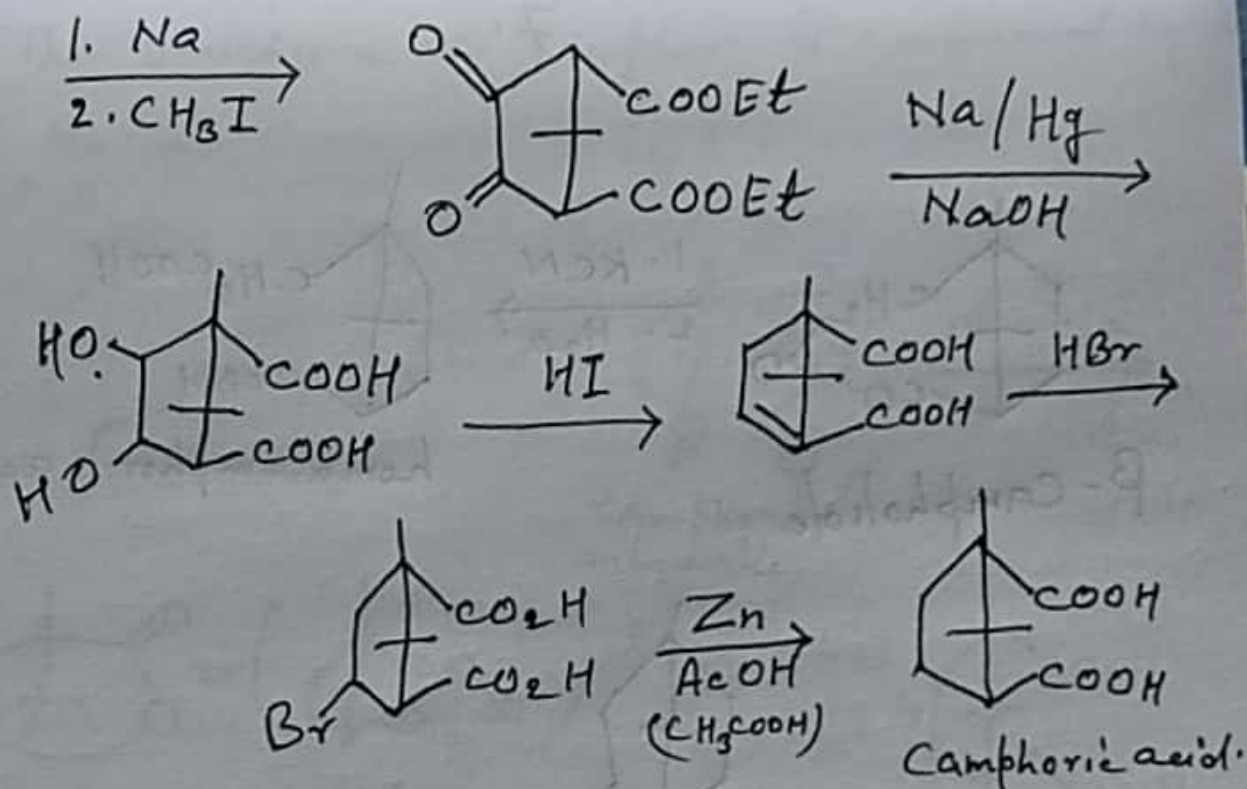


(II)

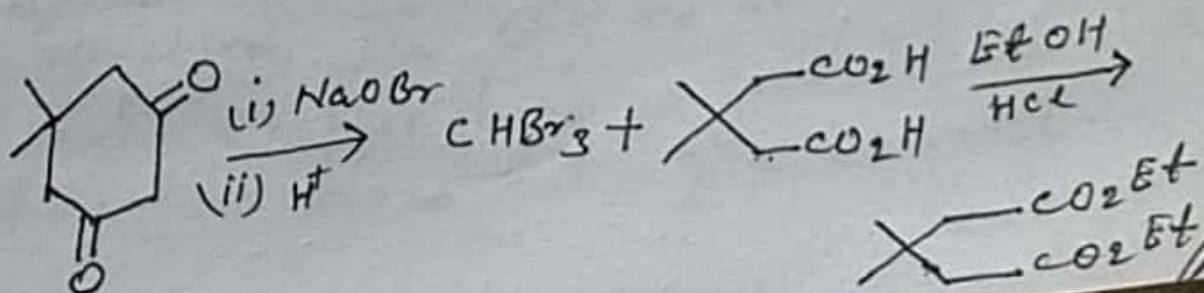
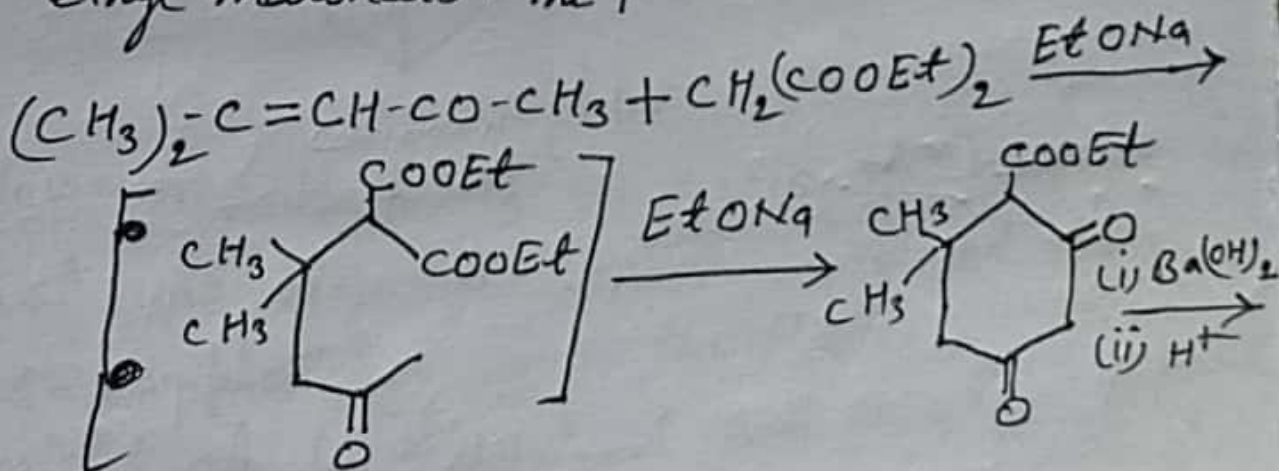
Now as the Camphoric acid is a cyclopentane derivative, C₄ and C₅ must be linked to form a cyclopentane derivative. Furthermore, since camphoric acid has a gem dimethyl group, it must be present on the C-2 in camphoric acid since other C-atoms viz. 4 and 5 are oxidised during oxidation and hence camphoric acid may be shown as (II).

(V) The st. (II) for camphoric acid is proved by its synthesis (Kempka, 1903) →



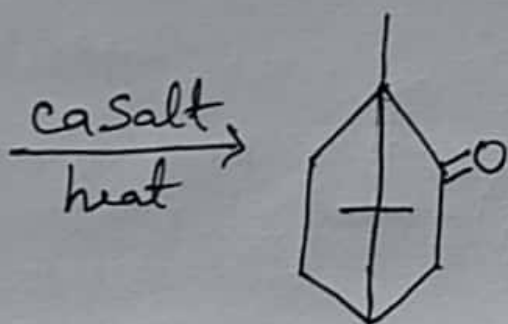
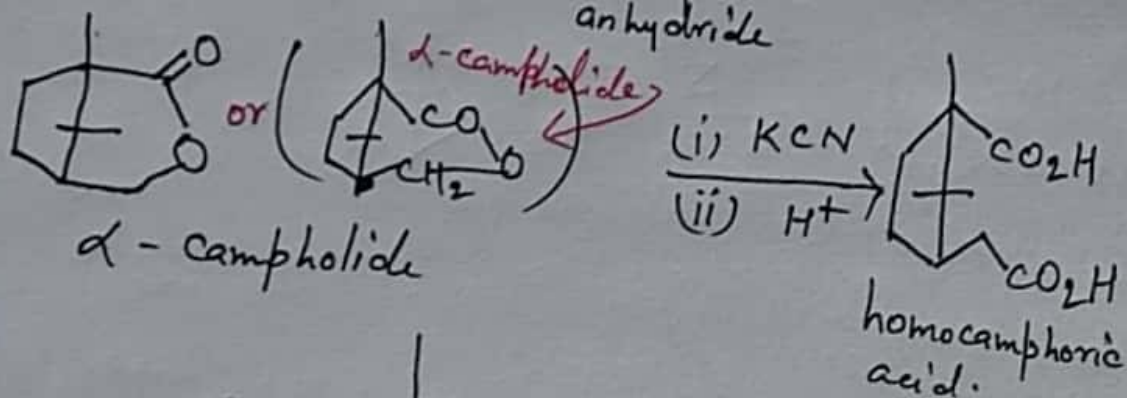
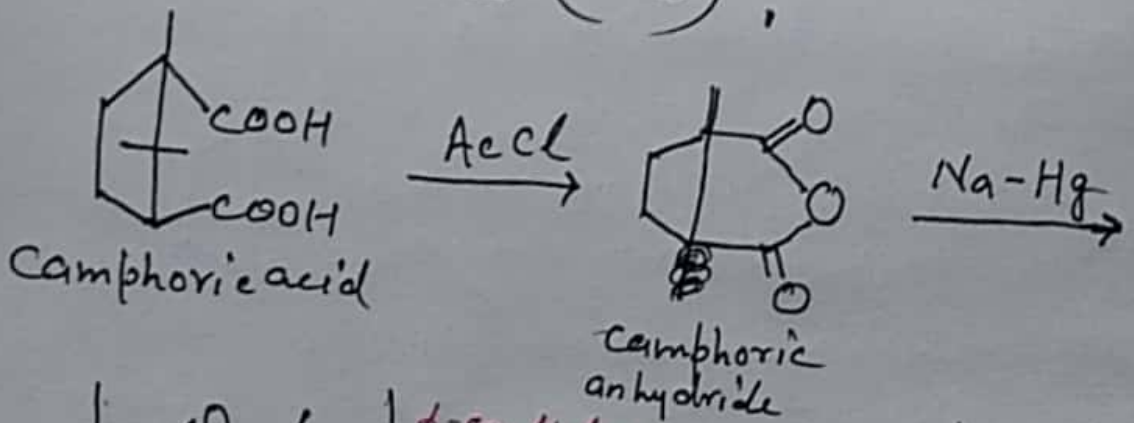


The starting material β : β dimethyl glutaric acid ester had already been synthesized by Komppa (1899) from mesityl oxide and ethyl malonate. The product obtained was —



6.

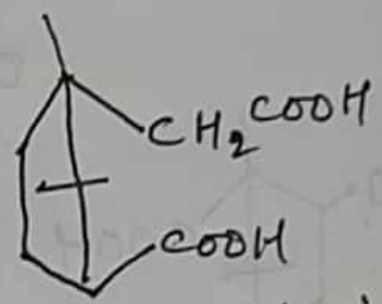
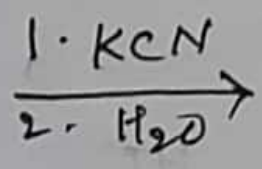
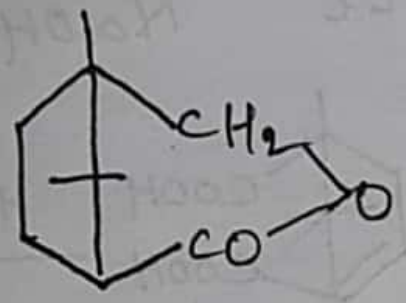
The structure of Camphor is confirmed by Haller, Synthesis (1896) :-



camphor.

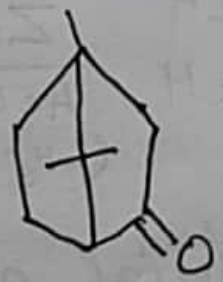
However, Haller's Synthesis of Camphor is not unambiguous since instead of α -campholide, ~~the~~ the β -campholide might also be obtained and thus the compound of structure IV will be obtained which is not Camphor because on distillation with iodine it does not give carvacol.

P.T.O.



homocamphoric acid

β -Campholide



(VI)