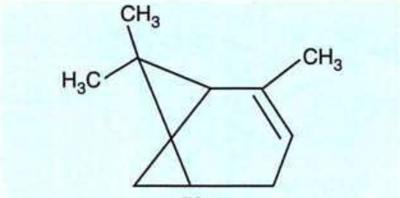
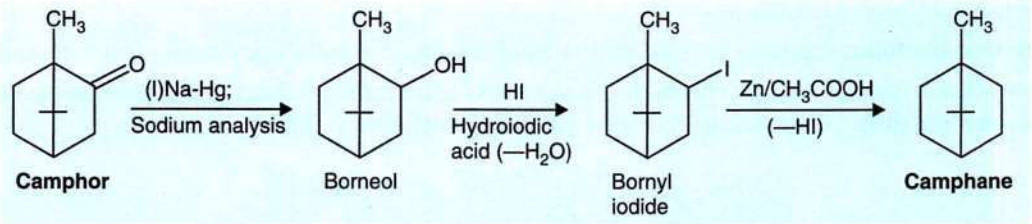
Arbusov and Naumov* have recently established by means of the **Electron Diffraction studies** that **α-pinene** exists predominantly in the ***bridged half-chair type conformation*** as given under:



α-Pinene
[Bridged Half-Chair-Type-Conformation]

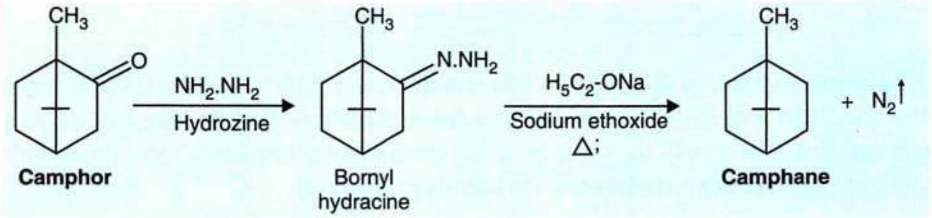
BORANE [or CAMPHANE] GROUP

The '**borane group**' is also referred to as the '**camphane group**' because of the presence of the **saturated bicyclic hydrocarbon** (*viz.*, borane or camphane). Interestingly, it fails to occur in the *natural plant products*; and, therefore, need to be prepared synthetically right from '**camphor**', that eventually constitutes and designates as the most important example of this *particular group/class of compounds*. Thus, we may have the following valid conversions:



That is, conversion of **camphor** to **camphane** *via* **reduction-hydrolysis-dehydration** and **reduction.**

Wolff-Kishner Reduction (or Huang-Minlon Modification):** It also provides an alternative means of preparing **camphane** from **camphor** as given under:



Thus, nitrogen gas (N_2) escapes from the reaction mixture to give **camphane** at the end.

NOTE: '*Camphane*' is a saturated hydrocarbon. It is obtained as a solid substance having a sharp mp 156ºC, and is found to be optically '*inactive*'.

The most important member of the '**Borane Group**' is the classical example of '**Camphor**' which shall now be discussed as under:

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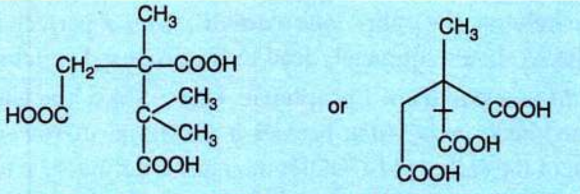
* Arbusov and Naumov : In : Banthorpe DV and Whittaker D, *Chem Rev*, **66** : 643-654, 1966.

** Kishner N : *J Russ Phys Chem Soc,* **43** : 582,1911; Huang-Minlon, *J Am Chem Soc* **68** : 2487,1946



(+)-Camphoronic Acid (I) **(+)-Camphoronic Acid (I)**

Explanation: The various steps involved may be explained as under:

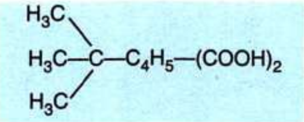
1. Acetoacetic ester on treatment with freshly prepared sodium ethoxide followed by methyl iodide loses 2 moles of methyl iodide to yield **α,α-dimethyl acetoacetic ester.**
2. The resulting product undergoes **Reformatsky Reaction** with ethyl-bromoacetate to produce an **organozonic derivative of α-bromo ester.**
3. Treatment of this product with an acid gives a *diethyl ester derivative*, which upon reaction with **phosphorus tribromide (PBr_3)** followed by KCN yields a **diethyl cyano ester derivative.**
4. Finally, this product on treatment with an alkali and then with an acid yields the *racemate* of **camphoronic acid (I).**

10. Structure of Camphoric Acid [$C_{10}H_{16}O_4$]

The structure of **camphoric acid** may be duly established by means of its elucidation as stated under:

(a) **Molecular Formula:** Its *molecular formula* has been duly established to be $C_{10}H_{16}O_4$.

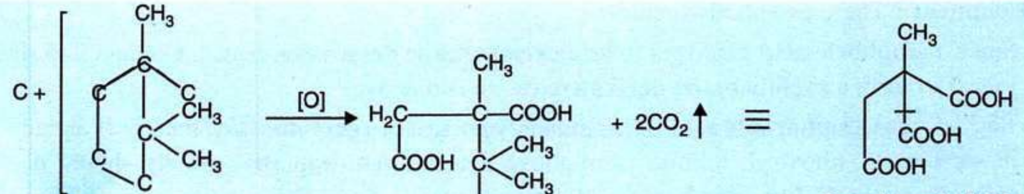
(b) **Saturated Dicarboxylic Acid : Camphoric acid** essentially has a **gem-dimethyl moiety** and an altogether *separate methyl group*; therefore, it should have essentially **3-methyl groups.** Thus, one may express the formula of **camphoric acid** as:



$$(H_3C)_3C{-}C_4H_5{-}(COOH)_2$$

which eventually leads to C_5H_{10} as its **saturated parent hydrocarbon.** Furthermore, the *molecular formula* C_5H_{10} relates to C_nH_{2n} which designates a **saturated hydrocarbon**, and thereby suggests that **camphoric acid** is a **cyclopentane dicarboxylic acid.**

(c) **Oxidation of Camphoric Acid to Camphoronic Acid :** The careful oxidation of **camphoric acid** to **camphoronic acid** may be expressed as under:



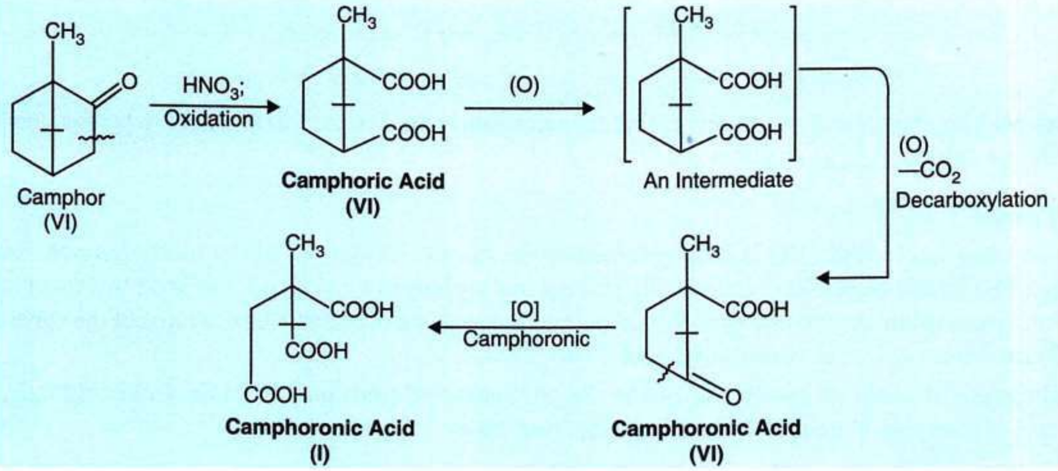
'C'-Skeletion (IV)

Camphoronic Acid (I)

All the above scientific arguments lead to the fact that the following **structure (VII)** for **camphor**, which closely corresponds to the **structure (VI)** above should be the most *probable* and *correct structure*.

Actually, it was Bredt (1893) who duly proposed the following reactions to explain logically the intricate relationship amongst the following *three* compounds:

- **Camphor**
- **Camphoric Acid**
- **Camphoronic Acid**



Camphor (VI)

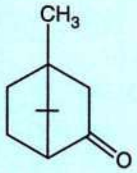
Camphoric Acid (VI)

An Intermediate

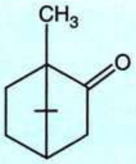
Camphoronic Acid (VI)

Camphoronic Acid (I)

Bredt, later on, proposed judiciously the following structure (VIII) for **camphor**, that eventually explains all the foregoing arguments; however, he rejected **structure (VIII)** in favour of **structure (VII)** for camphor.

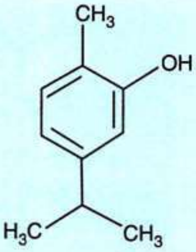


Bedt' Structure for Camphor (VIII) (*Rejected*)



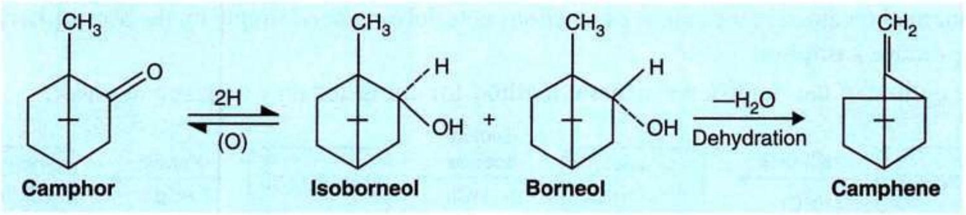
Camphor Structure (VII) (*Accepted*)

Why is the proposed structure (VIII) for Camphor rejected? The simple concrete reason for the outright rejection of **Bredt' structure for camphor (VIII)** being supported by the fact that when camphor is distilled with iodine gives rise to the formation of **carvacrol (IX)**. Thus, the critical formation of **(IX)** may only be explained judiciously with the above structure of **camphor (VII)** and 'not' with **structure (VIII)**.



Carracrol (IX)

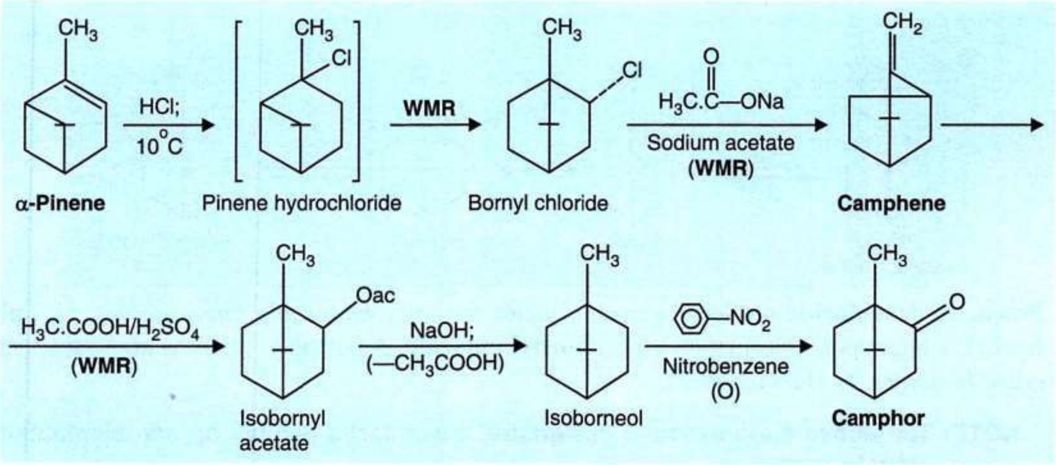
'**isoborneol**' when subjected to *dehydration reaction* usually gives '**camphene**', which on oxidation yields '**camphor**' as shown below:



18. Commercial Manufacture of Synthetic Camphor [or Borneol Camphor]

The large-scale (commercial) manufacture of purely **synthetic camphor** is largely obtained using ***α-pinene*** as the starting material (which is available mostly from the '*turpentine oil*'). In fact, a series of **Wagner-Meerwein Rearrangement*** (**WMR**) effectively come into play that cause an altogether **complete change** in the **C-skeleton.**

Following are the various sequential steps of reactions for the **commercial synthesis of camphor** as detailed under:



Explanation : These steps may be explained as under:

1. **α-Pinene** when treated with HCl at 10°C gives **pinene hydrochloride** (as an *intermediate*) which undergoes the **first WMR** to yield **bornyl chloride.**
2. The resulting product is treated with *sodium acetate* for the **second WMR** to occur and yields **camphene**, which with interaction of CH_3COOH/H_2SO_4 undergoes the **third WMR** to produce **isobornyl acetate.**
3. This product when treated with an **alkali(NaOH)** loses a mole of acetic acid (CH_3COOH) to give **isoborneol**, which upon reaction with *nitrobenzene* undergoes **oxidation** to yield **camphor.**

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* Wagner G : *J Russ Phys Chem Soc.*, **31** : 690, 1899; Meerwein H : *Ann*, **405** : 129, 1914