

cooled in an ice-water bath, and three grams of anhydrous aluminum chloride was added slowly. The solution was then warmed in an oil-bath and finally refluxed. After fifteen minutes of refluxing a solid cake formed. Heating was continued for an hour. The reaction mixture was then cooled and poured into ice-cold dilute hydrochloric acid, and the acid solution was extracted several times with ether. The ether extracts were combined and washed with water and 10% sodium carbonate. The phenol was then extracted from the ether solution with 5% sodium hydroxide, and after acidification of the alkaline extract the phenol was extracted with ether. The ether extract was washed with water and dried over sodium sulfate. The ether was removed and the remaining sirup was distilled. The distillate readily crystallized. The substance was recrystallized from benzene-petroleum ether. It melted at 83°. The yield was 1.2 g. It was identified by its optical properties as tetrahydrotubanol.

**Tetrahydrotubaic Acid from Synthetic Tetrahydrotubanol.**—Five-tenths gram of the product obtained on demethylation of 2,6-dimethoxyisoamylbenzene with aluminum chloride in toluene was refluxed in 100 cc. of saturated sodium bicarbonate solution for one hour. The solution was cooled, filtered and acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water and dried. The substance was then twice recrystallized from benzene. It melted at 206°. It was found to be identical with tetrahydrotubaic acid.

### Summary

2,6-Dihydroxyisoamylbenzene was synthesized and found to be identical with tetrahydrotubanol.

On refluxing 2,6-dihydroxyisoamylbenzene with a saturated solution of sodium bicarbonate, tetrahydrotubaic acid (2,4-dihydroxy-3-isoamylbenzoic acid) was obtained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

## The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. III. The Calculation of the Products Formed from Paraffin Hydrocarbons

BY F. O. RICE

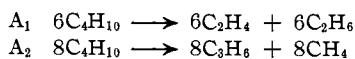
A difficulty in connection with the theoretical treatment of the thermal decomposition of paraffin hydrocarbons from the standpoint of free radicals<sup>1</sup> lies in the behavior of the higher free radicals formed in the primary dissociation as well as those formed by loss of a hydrogen atom from the hydrocarbon in the chain mechanism. Such a radical may either decompose into an olefin and a smaller free radical, or it may react with the surrounding molecules to form a hydrocarbon and generate a new free radical.

It now appears from experimental work carried out in this Laboratory during the past two years that a sharp distinction must be drawn between

(1) Rice, *THIS JOURNAL*, **53**, 1958 (1931).



ethylene and ethane; similarly, the products of  $A_2$  are propylene and methane. This may be summarized as follows



In all such calculations, only the chain cycles are considered and the products resulting from the primary rupture of the molecule into free radicals are neglected; the chain cycles give at once the qualitative composition

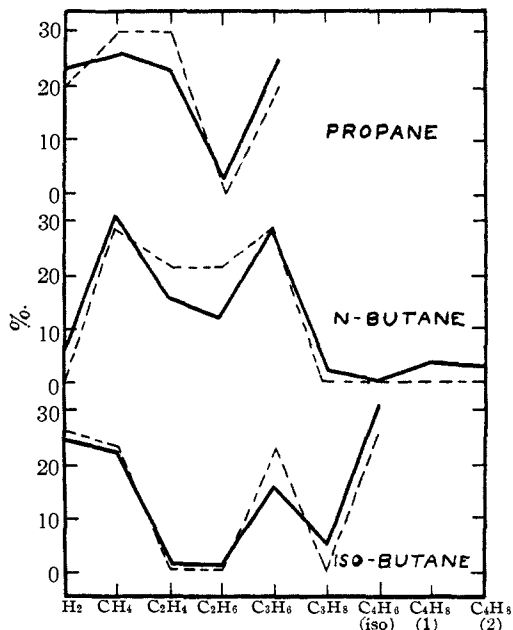
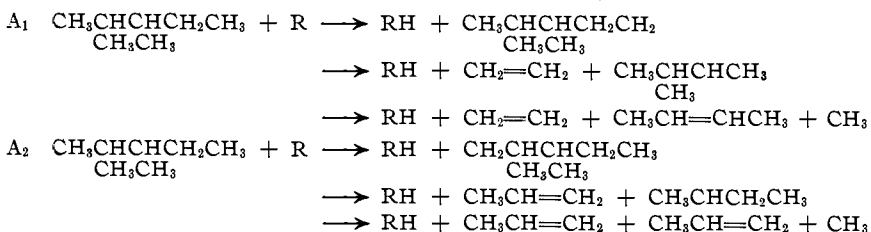


Fig. 1.—Observed (—) and calculated (----) products in the thermal decomposition of hydrocarbons.

of the products; their quantitative composition is found by assigning to each chain cycle a number determined by the number of primary, secondary or tertiary hydrogen atoms associated with the cycle in question, each multiplied by their relative chance of reaction (1:2:10, respectively).

The following are the chain cycles for 2,3-dimethylpentane







similar to that used for paraffin hydrocarbons and the calculated products are in good agreement with the experimental data available.

### Summary

The decomposition products of all paraffin hydrocarbons can be calculated quantitatively by assuming, first, that they decompose according to a chain mechanism; second, that methyl and ethyl groups are the only stable radicals; a larger radical apparently decomposes to yield one or more molecules of an olefin, and either a methyl group, an ethyl group or atomic hydrogen; and third, that the relative chances of reactions of primary, secondary and tertiary hydrogen atoms are 1:2:10, respectively.

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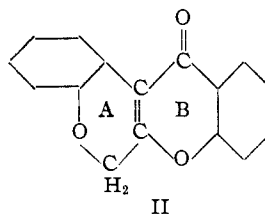
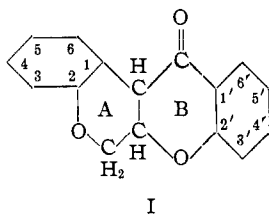
[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

## Rotenone. XXVI. Synthesis of the Parent Substances of Some Characteristic Rotenone Derivatives

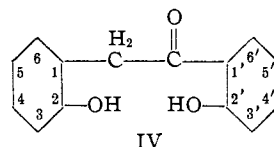
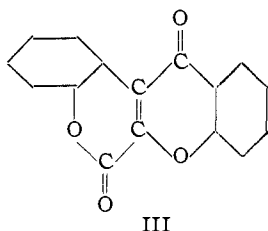
By F. B. LAForge

The investigation presented in this article deals with the synthesis of the parent substances of some of the characteristic rotenone derivatives, derritol, anhydroderritol, derrisic acid, dehydrorotenone and rotenonone.

Rotenone has been shown to be derived from the nucleus I,<sup>1</sup> with substituting groups occupying the positions 4 and 5 and 3' and 4'



Dehydrorotenone has the same substituting groups as rotenone but contains two hydrogen atoms less in the dihydro- $\gamma$ -pyrone system B and is derived from the nucleus II.



(1) LaForge and Haller, *This Journal*, **54**, 810 (1932); Butenandt, *Ann.*, **495**, 17 (1932); Takei, Miyajima and Ono, *Ber.*, **65**, 1041 (1932).