

10% cracking would be about 10^{-6} mole of CH_3 per mole of paraffin hydrocarbon. If it is assumed that the removal of 0.01 mg. of antimony in the form of a mirror can be observed, this would require about 10^{-7} mole of CH_3 . Therefore, the decomposition of approximately one-tenth of a mole of hydrocarbon would be required. It is very probable that the passage of such a substantial amount of hydrocarbon would soon inactivate the mirror due to the products of decomposition and the slight impurities that may be contained in the hydrocarbon before any removal of the mirror could be observed.

It seems plain that at the low pressures used in this work the concentration of free radicals in decomposing petroleum cuts may be very considerable. At the pressures employed in commercial cracking, however, the radical concentration must be very small indeed.

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Ruthruff and G. G. Lamb for their help throughout.

Summary

1. The free radical concentrations, as measured by their combination with a metallic lead surface, were determined in the pressure range 0.25 to 6.0 mm. for the following petroleum hydrocarbon cuts: petroleum "octane," petrolatum "hexane," pentane, butane, and propane.

2. A rapid decrease of free radical concentration with pressure was found but the complexity of the petroleum hydrocarbons did not permit any exact study of the mechanism.

3. Dilution of the hydrocarbon stream with nitrogen and decreasing the surface to volume ratio did not noticeably increase the free radical concentration.

4. The molecular weight of the hydrocarbons studied as sources of free radicals had no apparent effect on the free radical concentration when investigated under comparable conditions.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Maleic Anhydride and Vinyl Hydrindenes

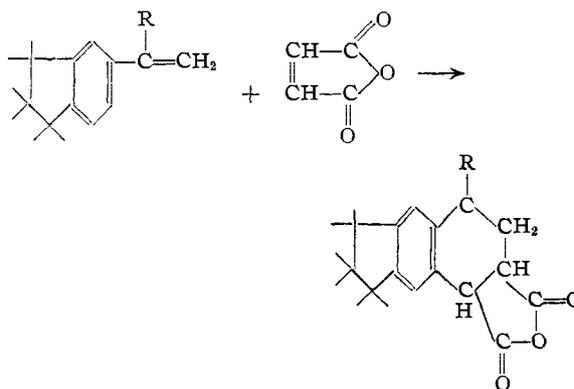
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The conception of stabilized double bonds in condensed ring systems containing one benzene ring was initiated by Mills.¹ In the case of naphthalene and phenanthrene it has been accepted that such bond fixation does occur. For some polynuclear systems, *i. e.*, hydrindene, the problem is completely unsolved although considerable evidence exists on both sides of the question.

It has been shown recently²⁻⁴ that vinyl derivatives of both naphthalene and phenanthrene will add maleic anhydride according to the Diels-Alder reaction. This is extremely interesting in view of the fact that simple benzene derivatives which do not contain a fixed double bond undergo an entirely different type of reaction.⁵ In the single case of *as*-diphenylethylene the normal product is obtained.

With this information as a background, the

corresponding hydrindene problem was studied. If a fixation of the double bonds actually exists in the benzene ring of hydrindene, and if the above reaction with maleic anhydride is characteristic of such fixation, one could expect the formation of the following compound to take place.



On the other hand, if the benzene nucleus in hydrindene is similar to that in styrene a polymer would be formed.

- (1) Mills, *J. Chem. Soc.*, 2510 (1930).
- (2) Bachmann and Kloetzel, *THIS JOURNAL*, **60**, 2204 (1938).
- (3) Bergmann, *ibid.*, **59**, 1443 (1937).
- (4) Cohen and Warren, *J. Chem. Soc.*, 1318 (1937).
- (5) Wagner-Jauregg, *Ber.*, **63**, 3218 (1930).

The synthesis of pure vinyl derivatives of aromatic hydrocarbons, especially when these are liquids, is a difficult task. Almost without exception those which have been reported previously were not analytically pure. This troublesome fact also was evident in attempts to purify 5-vinyl- and 5-isopropenylhydrindene. The latter substance even after seven careful fractionations (the last in the presence of sodium) gave analytical values which were not entirely satisfactory.⁶ These compounds failed to form picrates.

When treated with equivalent amounts of maleic anhydride, both 5-vinyl- and 5-isopropenylhydrindene quantitatively separated as polymers which were not soluble in dilute alkali.

Although the above described polymerization indicates a correspondence between the nuclear system in hydrindene and benzene, it may well be that the rapid rate of polymerization in these cases is overshadowing any tendency of maleic anhydride to add to these molecules.

Experimental

5-Chloromethylhydrindene.—To a mixture containing 118 g. of hydrindene, 125 cc. of formaldehyde (30%), and 212 cc. of concentrated hydrochloric acid and held at a temperature of 60°, was added 139 cc. of concentrated sulfuric acid over a period of seven hours. Stirring was continued for twenty hours and the reaction mixture worked up in the usual way. The yield is 95 g. (57%); b. p. 110–112° (4 mm.).

Anal. Calcd. for $C_{10}H_{11}Cl$: C, 72.04; H, 6.65. Found: C, 72.57; H, 6.63.

5-Hydrindene Aldehyde.—Forty-five grams of 5-chloromethylhydrindene and 36.0 g. of hexamethylenetetramine were refluxed in 1000 cc. of 60% ethanol for six hours. After evaporation of the excess ethanol the mixture was extracted with ether. Purification was readily accomplished by the formation of a sodium bisulfite addition product. The yield of aldehyde was 15 g.; b. p. 135–138° (23 mm.). The structure was proved by the formation of the corresponding anil and carboxylic acid melting at 85–86° and 177°, respectively.⁷

β -(5-Hydrindenyl)-acrylic Acid.—Seventeen grams of 5-hydrindene aldehyde was treated with equivalent amounts of malonic acid and piperidine at 60° for six hours according to Dutt.⁸ The yield was 95%; m. p. 161–162° after one recrystallization from benzene.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.59; H, 6.43; neut. equiv., 187. Found: C, 76.83; H, 6.62; neut. equiv., 189.

(6) The writer is indebted to Mr. J. W. Opie for following the purity of several of these fractions by careful analytical methods.

(7) Gattermann, *Ann.*, **347**, 385 (1906).

(8) Dutt, *J. Ind. Chem. Soc.*, **9**, 309 (1932).

Methyl-5-hydrindenylcarbinol.—Twenty-five grams of sodium chips was added to a boiling solution of 25 g. of acetohydrindene in 250 cc. of absolute ethanol. The reaction was continued for four hours. The excess alcohol was removed by distillation at diminished pressure and 500 cc. of cold water added. After careful acidification, the mixture was extracted with ether, dried, and distilled: yield 72%, b. p. 133° (10 mm.).

Anal. Calcd. for $C_{11}H_{14}O$: C, 80.61; H, 8.73. Found: C, 80.42; H, 8.70.

Dehydration of Carbinol.—When attempts were made to dehydrate 5-hydrindenylmethylcarbinol with formic acid or phenyl isocyanate, a polymer was obtained.

(a) **5-Vinylhydrindene.**—Ten grams of the above carbinol was treated with pyridine and thionyl chloride.⁹ The crude alkyl chloride so obtained was treated at 60° for two hours with 20 cc. of ethanol saturated with potassium hydroxide. Potassium chloride separated in copious amounts. The mixture was thrown into an excess of water and extracted with ether. Fractionation gave 3 g. of a hydrocarbon; b. p. 95–100° (10 mm.). This material reacted immediately with bromine in carbon tetrachloride.

(b) **Decarboxylation of Carboxylic Acid.**—The thermal decomposition of β -(5-hydrindenyl)-acrylic acid in the presence of hydroquinone or copper powder-quinoline gave only about 5% of the hydrocarbon.

Anal. Calcd. for $C_{11}H_{12}$: C, 91.60; H, 8.40. Found: C, 90.79; H, 8.78.

5-Isopropenylhydrindene.—Twenty-five grams of 5-acetylhydrindene was added to a Grignard solution containing 47.0 g. of methyl iodide and 8.0 g. of magnesium. From this reaction was obtained 24.5 g. of the crude carbinol. This was saturated at 0° with dry hydrogen chloride and after standing for three hours at room temperature, the excess gas was removed by vacuum. The residue was treated with 20.0 g. of potassium hydroxide in 100 cc. of ethanol for thirty minutes at 60°. There was obtained 17.0 g. of a hydrocarbon boiling at 84° (2 mm.). This material absorbed the theoretical quantity of bromine in carbon tetrachloride rapidly.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.07; H, 8.93. Found: C, 90.37; H, 8.64.

Reaction with Maleic Anhydride.—One gram of the hydrocarbon in 2 cc. of xylene and an equivalent amount of maleic anhydride were heated at 100°. After ten minutes the solution became foggy and after one hour the precipitation stopped. The material was a hard glossy polymer. The same result was obtained in the case of both hydrocarbons.

Summary

5-Vinyl- and 5-isopropenylhydrindene have been shown to polymerize in the presence of maleic anhydride.

New derivatives of hydrindene are reported.

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(9) Whitmore, *This Journal*, **60**, 2265 (1938).