Alkylation Accompanying Depolymerization

By V. N. Ipatieff and Herman Pines

The recent studies of alkylation of aromatic hydrocarbons with olefins using sulfuric or phosphoric acid as a catalyst[1] were extended to dimers and trimers of isobutene and normal butene. It was found that by treating benzene with diisobutene in the presence of 96% sulfuric acid at 0° *t*-butylbenzene, *p*-di-*t*-butylbenzene and hydrocarbons corresponding to tributylbenzenes were obtained.

p-Di-*t*-butylbenzene was formed when *t*-butylbenzene was treated with di- or triisobutene in the presence of sulfuric acid. Similar results take place with dimers of normal butene, *p*-di-*s*-butylbenzene and products corresponding to tri-*s*-butylbenzene were formed.

The same type of reaction takes place when diisobutene reacts with benzene in the presence of aluminum chloride as a catalyst. In the latter experiment, when cyclohexane is used instead of benzene, alkylated cyclohexanes were obtained boiling between 170–250°.

For this type of reaction where a depolymerization and a subsequent alkylation of hydrocarbons take place, the term "depolyalkylation" is proposed.

In order to elucidate the mechanism of this reaction its study is being extended to other types of hydrocarbons and catalysts.

Experimental

The apparatus used consisted of a three-necked flask provided with a reflux condenser, mercury-sealed stirrer and a dropping funnel. The flask was surrounded with an ice-bath to maintain the temperature of the reaction at 0°. A mixture consisting of 140 g. of diisobutene (b. p. 102–104°) and 97 g. of benzene was added slowly to 100 cc. of 96% sulfuric acid. The time of addition of the hydrocarbons was one and one-half hours. The hydrocarbon layer was separated from the sulfuric acid layer, washed with a 15% solution of sodium hydroxide followed by a water-wash. The hydrocarbon layer washed and dried weighed 214 g.; it was fractionally distilled on a Podbielniak high temperature precision still.

The following fractions were separated:

Fraction 164–178°.—On reaction of this fraction with isobutene in the presence of sulfuric acid crystals of *p*-di-*t*-butylbenzene were obtained which melted at 78°. This shows the existence of *t*-butylbenzene in the original fraction.

Fraction 216–250°.—A crystalline product (*p*-di-*t*-butylbenzene) (5.7 g.) was separated from this fraction. On crystallization from hot alcohol it yielded snow-white crystals melting at 78°. The mixed melting point with a synthetically prepared *p*-di-*t*-butylbenzene was the same.

Fraction 149–154° at 9 Mm.—This fraction corresponds to tributylbenzene. *Anal.* Calcd. for $C_6H_3(C_4H_9)_3$: C, 87.80; H, 12.20; mol. wt. 246. Found: C, 87.32; H, 12.38; mol. wt. 236.

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[1] Ipatieff, Corson and Pines, This Journal, 58, 919 (1936); Ipatieff, Pines and Komarewsky, *Ind. Eng. Chem.*, 28, 222 (1936).

On the Formation of a Sulfate Salt of the Antirachitic Vitamin

By Albert E. Sobel, Gilbert Goldstein and Benjamin Kramer

In a previous communication from this Laboratory [Natelson and Sobel, *J. Biol. Chem.*, **109**, 692 (1935)] failure to prepare the potassium sulfate salt of the antirachitic vitamin was reported, although this derivative of ergosterol, cholesterol, phenol and borneol may be easily prepared. These derivatives are prepared by the following reactions

$$\mathrm{ROH + SO_3C_5H_5N \xrightarrow{C_5H_5N} ROSO_3HC_5H_5N}$$
$$\mathrm{ROSO_3HC_5H_5N + KOH \longrightarrow ROSO_3K}$$
$$\mathrm{R = cyclic\ radical}$$

Subsequent to the above paper the conditions for the isolation of the intermediate pyridine salt were developed and applied for quantitative purposes in the case of cholesterol [Sobel, Drekter and Natelson, *J. Biol. Chem.*, **114**, XCVI (1936)]. It was found on further study that the conditions outlined hold for ergosterol as well. The reaction was next applied to calciferol (obtained through the courtesy of the Mead Johnson Company). Two mg. of calciferol was dissolved in 0.5 cc. of 5:1 anhydrous benzene–pyridine mixture in a small centrifuge tube. This was followed by adding 20 mg. of pyridine sulfur trioxide and then heated at 46° for thirty minutes. The reaction mixture was then cooled, 6 cc. of petroleum ether (35–60°) added and allowed to stay in an ice-box overnight. The precipitate was washed with additional amounts of 1 cc. of petroleum ether, in which pure calciferol is extremely soluble. The combined washings were evaporated to dryness under vacuum, and then taken up in 4 cc. of absolute alcohol. Similarly, the precipitate was also taken up in 4 cc. of alcohol. To each of these solutions, 1 cc. of Rosenheim and Callow's [*Biochem. J.*, **25**, 74 (1931)] mercuric acetate reagent was added. The intensity of the yellow color formed was compared. It was found in this manner that 80–90% of the calciferol was in the precipitate and the rest in the washings. The pyridine calciferyl sulfate precipitate was found to be slightly soluble in petroleum ether by employing the above criteria in subsequent experiments. These experiments were confirmed by employing 50 mg. of calciferol and weighing the amount of calciferol in the petroleum ether washings which were washed free of any traces of pyridine sulfur trioxide by water. The precipitate was treated with potassium hydroxide in water (using 4–6 moles of the base for each mole of sulfur trioxide employed in the original reaction) and extracted repeatedly with petroleum ether. The petroleum ether fraction was washed free of potassium hydroxide and taken to dryness. There was no potassium or sulfate in the residue, which was found to contain all the calciferol as shown by the mercuric acetate test and later by gravimetric procedure. These relations were also established by the animal experiments using the technique previously outlined [Natelson and Sobel, above].

Thus, it appears that the potassium hydroxide hydrolyzes the pyridine calciferyl salt whereas in the ergosteryl and cholesteryl salts the pyridine is displaced by potassium in a double decomposition and the extremely insoluble potassium sulfate derivative is formed. The reaction for calciferol may be illustrated

$$\mathrm{StOH} + \mathrm{SO_3C_5H_5N} \xrightarrow{\mathrm{C_5H_5N}} \mathrm{StOSO_3OHC_5H_5N}$$
$$\mathrm{StOSO_3OHC_5H_5N} + 2\mathrm{KOH} \longrightarrow \mathrm{StOH} + \mathrm{C_5H_5N} + \mathrm{K_2SO_4}$$

The reaction was next applied to cod liver oil concentrate. Two grams of the concentrate (containing 73.333 I. U. per g. obtained through the courtesy of the National Oil Products Co.) was dissolved in 4 cc. of pyridine and followed by the addition of 1 g. of pyridine sulfur trioxide, heated at 46° for one hour and 50 cc. of petroleum ether added, and then allowed to stand for three days in an ice-box. A yellowish white precipitate settled which was washed with cold petroleum ether. The precipitate was then treated with potassium hydroxide in the presence of petroleum ether. Two fractions of sterols were obtained, one the insoluble potassium steryl sulfates and the other the petroleum ether soluble fraction. The latter was evaporated down to dryness in the presence of maize oil and used for bio-assay. A vitamin bio-assay was run comparing the activity of this fraction against the original material, the unreacted fraction of the concentrate and the insoluble potassium steryl sulfate. It was found by this criterion that approximately 60% of the original vitamin D content precipitated and was found later in the petroleum ether fraction while the insoluble potassium sulfate does not contain any vitamin D. Thus a simple method for obtaining a high concentration of natural vitamin D was obtained. Further work is in progress at present to isolate a pure vitamin D from natural sources.

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COMMUNICATIONS TO THE EDITOR

SURFACE IONIZATION OF CESIUM ON TUNGSTEN

Sir:

Alterum, Krebs and Rompe [*Z. Physik*, **92**, 1 (1934)], in an article on the surface ionization of cesium on a tungsten filament, have reported obtaining values of 0.21 at 1520°K. and 0.29 at 1830°K. for its degree of ionization. These values are considerably lower than the ones predicted by theory for these temperatures; they also show an increase in the degree of ionization occurring with rising temperature, whereas theory predicts a decrease. The apparatus used by Alterum, Krebs and Rompe was one in which the ionization unit was surrounded by the saturated vapor of cesium. Taylor and Langmuir [*Phys. Rev.*, **44**, 423 (1933)], using the same type of apparatus, previously had obtained values approximating 100% ionization at temperatures as high as 1500°K. Above this temperature the onset of a very large photoelectric current from plate to filament, caused by the action of the light from the filament on an adsorbed layer of cesium on the