like substance. This form is believed to be less pure, for solvent or impurities are very likely entrained.

Pyrene.—On recrystallization of the 200–260° fraction from 95% ethanol, a crop of tan crystals, m. p. 142–143°, came down on cooling. A crop of acenaphthylene was obtained from the filtrate on dilution with water. The first crop of crystals was recrystallized from 95% ethanol, and then 100–105° petroleum ether, reaching a constant m. p. 148.5° corr. The picrate was prepared in alcohol, from which long silky, deep red needles separated on cooling.

	M. p., °C.	M. p. picrate, °C.
Compound	148.5 corr.	224 corr.
Pyrene[7]	149	222

Mixed melting points with a sample of pure pyrene did not show any depression, nor did mixed melting points run with the respective picrates.

Summary

1. Acenaphthylene and pyrene were identified in organic matter formed by the pyrolysis of natural gas.
2. Polymers of acenaphthylene differing in molecular weight from those previously described in the literature were found.

TERRE HAUTE, INDIANA RECEIVED APRIL 23, 1936

---

[7] Freund, *Ber.*, **30**, 1383 (1897).

NOTES

The Thermal Decomposition of Acetone

BY A. O. ALLEN[1]

The mechanism of the thermal decomposition of acetone to methane and ketene is at present unsettled, Winkler and Hinshelwood[2] assuming it to be unimolecular, while Rice and Herzfeld[3] have proposed a chain mechanism. In this note evidence is presented which favors strongly the latter view.

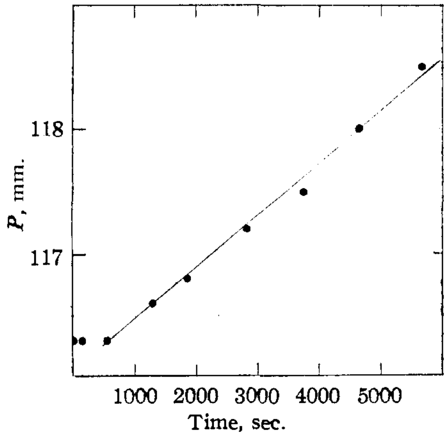


Fig. 1.—Pressure *vs.* time in the decomposition of acetone at 462°.

The reaction was studied by the usual static method, being followed by pressure change. With the object of getting rid of complications due to the decomposition of ketene, the reaction was run at temperatures where it proceeds slowly, and was carried to only about 5% decomposition. A constant-volume manometer with mirror scale was used which could be read to 0.1 mm. This method allows an accurate evaluation of the initial slope of the pressure–time curve, which, assuming two molecules are formed from each molecule of acetone decomposed, will give the true rate of acetone decomposition, uncomplicated by the slow decomposition of the ketene produced.

At the highest temperature used (529°) the reaction proceeded perfectly smoothly. At somewhat lower temperatures it was always found that the measured initial pressure was higher than would be obtained by extrapolation of the pressure–time curve to zero time. This suggested a short induction period, but was at first thought to be due to an incomplete establishment of pressure equilibrium. However, on going to a still lower temperature, it was found that the induction period, though corresponding to only about 0.3% decomposition, was undoubtedly real, lasting some ten minutes at 462° (Fig. 1).

The experiments were then repeated, with the 1-liter reaction vessel packed with short pieces of 10-mm. glass tubing. It was found that packing had three effects: (1) the shape of the rate–pressure curve was entirely changed, the curve of log k (unimolecular) *vs.* log p at any temperature being concave upward, instead of convex as usual;

---

[1] Sheldon Traveling Fellow, 1936. Present address, Department of Chemistry, Victoria University, Manchester, England.

[2] Winkler and Hinshelwood, *Proc. Roy. Soc.* (London), **A149**, 340 (1935).

[3] F. O. Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(2) the apparent rate at high pressures, practically unchanged at 529°, was decreased at lower temperatures, being only about half the normal value at 465°; (3) the induction period was no longer apparent at any temperature.

These effects are practically sufficient to prove the reaction a chain. On the chain hypothesis, the short induction period appears naturally as the time necessary for the chain-carrying radicals to attain their steady-state concentrations; packing shortens the chains, rendering the induction period inappreciable and reducing the rate most at the lower temperatures, where chains of this type are longest.[3] The change of shape of the rate-pressure curve by packing also shows the great complexity of the reaction.

Though packing may lower the apparent rate by promoting condensation reactions, it seems very unlikely that a 50% reduction could be caused in this way. An induction period might conceivably occur if the reaction proceeded through some active form of acetone, in equilibrium with the ordinary form, the active form decomposing unimolecularly; but in this case, if increased surface shortened the induction period it must increase, rather than decrease, the observed rate.[4] Hence the reaction must be a chain.

The most likely mechanism for the reaction is the Rice–Herzfeld one

$$\begin{array}{rcll} CH_3COCH_3 & = & 2CH_3 + CO & (1) \\ CH_3 + CH_3COCH_3 & = & CH_4 + CH_2COCH_3 & (2) \\ CH_2COCH_3 & = & CH_3 + CH_2CO & (3) \\ 2CH_3 & = & C_2H_6 & (4) \\ CH_3 + CH_2COCH_3 & = & C_2H_5COCH_3 & (5) \end{array}$$

The combination of two acetonyl radicals is not included, as the diacetonyl formed would decompose rapidly at the temperatures used;[3] a steady-state concentration of diacetonyl must exist, however, and it is probably the building-up of this compound that causes the induction period. Rice and Herzfeld have attempted to obtain, from this type of mechanism, expressions for the pressure and temperature dependence of the reaction rate. This procedure assumes that the reactions involved have a simple order of one or two; this cannot be the case, unfortunately, for in the range of pressures used, reactions (1), (3), (5) and possibly (4) will have "fallen off" from their high-pressure rates by the well-known theory of unimolecular reactions, and will thus possess no definite order. This effect introduces so many unknown variables into the picture that it seems impossible to make any real progress by further study of the thermal reaction alone.

The author wishes to thank Drs. O. K. Rice and D. V. Sickman for their kind encouragement and helpful suggestions.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
RECEIVED DECEMBER 23, 1935

---

[4] The argument is as follows: Let the reaction scheme be

$$\begin{array}{lll} X = Y \text{ (active)} & & (1) \\ Y = X & & (2) \\ Y = \text{products} & & (3) \end{array}$$

Then $dY/dt = k_1X - k_2Y - k_3Y$. At the steady state, this equals zero, whence $Y = k_1X/(k_2 + k_3)$: observed rate $= k_3Y = k_3k_1X/(k_2 + k_3)$. Then increasing k_3, the only way in which increased surface could decrease Y and hence lower the induction period, will increase the observed rate.

Pumice as a Support for Copper–Chromium Oxide Catalysts in Dehydrogenations[1]

BY RALPH E. DUNBAR, DONALD COOPER AND ROBERT COOPER

Investigations involving the dehydrogenation of various alcohols to the corresponding aldehydes have been reported from time to time.[2] Oxide catalysts, pressed into pellets of approximately 0.15 g. each, have frequently been used.[3] Since the formation of the catalyst into pellets is extremely laborious and time consuming, it seemed advisable to find a suitable support so that the catalyst could be prepared directly for immediate use.

Experimental Part

The best results in the preparation of this catalyst were achieved by precipitating and decomposing with heat the catalyst in the presence of finely divided pumice. Two solutions were prepared as follows: (A) 300 ml. of a solution containing 87 g. of cupric nitrate hexahydrate and 10.4 g. of barium nitrate. The barium nitrate was first dissolved in the least amount of water possible at a temperature near the boiling point of water. The cupric nitrate hexahydrate was then added and the solution diluted to the 300 ml. required. Solution (B) was prepared from 300 ml. of a solution containing 50.4 g. of ammonium dichromate and 75 ml. of a 28% solution of ammonium hydroxide. Solution (B) was added to 177 g. of Italian, acid washed, pumice of size 20. This was allowed to digest for one hour on a steam-bath with frequent stirring. Solution (A) was then heated to 80° and added to solution (B) with thorough stirring. The treatment from this point was identical with that of Connor, Folkers and Adkins[4] except that the final decomposition was carried

---

[1] Original manuscript received April 22, 1935.

[2] Bouveault, *Bull. soc. chim.*, [4] **3**, 119 (1908); Conant, Webb and Mendum, THIS JOURNAL, **51**, 1250 (1929); Adkins, Folkers and Kinsey, *ibid.*, **53**, 2714 (1931); Weston and Adkins, *ibid.*, **50**, 1930 (1928).

[3] Adkins, Kommes, Struss and Dazler, *ibid.*, **55**, 2992 (1933).

[4] Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

out in five portions with very slow, cautious heating and continual stirring. Lazier and Vaughen[5] have found that the final heat treatment very materially affects the activity of the catalyst. The material was then leached with 600 ml. of 10% acetic acid and washed with six 100-ml. portions of water. The catalyst was sifted before use on a twenty-mesh sieve to remove the fine material. The portion that did not pass through the sieve was used for the dehydrogenation of normal butanol. The yields of suitable catalyst average 220 g.

To test the effectiveness of this catalyst we have studied the dehydrogenation of *n*-butanol on a fresh sample of catalyst and on one which had been in use continuously for fifteen hours. Butanol is well suited for such a test because of the consistent yields of aldehyde it affords and the minimum yields of unsaturated hydrocarbon and ester.

The representative results obtained are shown in the following table where 100 g. of *n*-butanol was employed, using equipment similar to that described by Conant[6] and with a catalyst maintained at a temperature of 330–350°.

TABLE I

	Fresh catalyst	Used catalyst
Butyraldehyde, g.	60.2	49.4
Unchanged butanol, g.	2.0	6.5
n-Butyl butyrate, g.	10.0	11.0
Condensation products, g.	1.5	2.0
Gases collected, liters	27.8	24.3
Water, g.	2.5	2.8

The yields given are those actually separated from the reaction mixture, mechanical losses and the weight of the gaseous products accounting for the deficit between the starting material and the products finally recovered. It can be seen that this catalyst gives yields of about 50% even after fifteen to twenty hours of continuous use.

---

(5) Lazier and Vaughen, THIS JOURNAL, **54**, 3080 (1932).

(6) Conant, "The Chemistry of Organic Compounds," The Macmillan Company, New York, 1933, p. 106.

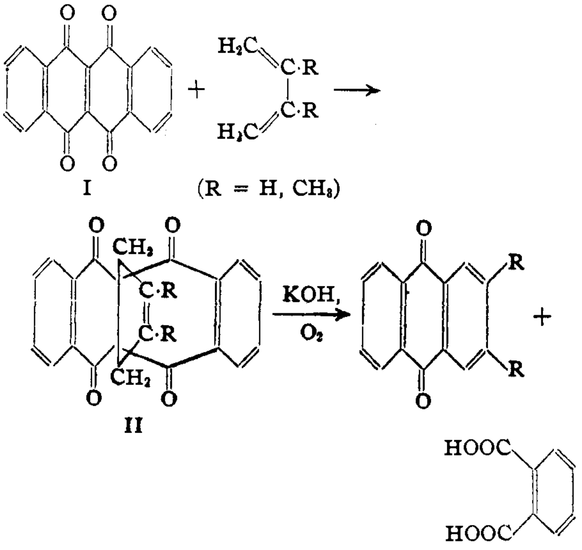
CONTRIBUTION FROM THE
CHEMICAL LABORATORIES OF
DAKOTA WESLEYAN UNIVERSITY
MITCHELL, S. DAK.

RECEIVED MAY 4, 1936

The Addition of Dienes to Naphthacenediquinone

BY L. F. FIESER AND J. T. DUNN

In view of the renewed interest in the chemistry of naphthacene as a result of the discovery[1] that rubrene is a derivative of this hydrocarbon, an account may be given of an observation pertinent to the subject which was made in the course of a further study of the addition of dienes to substituted quinones.[2] Having found that the two alkyl groups of 2,3-dimethyl-1,4-naphthoquinone do not interfere seriously with the course of the Diels–Alder reaction,[2a] it seemed possible that naphthacenediquinone, I,[3] might be capable of adding dienes, for there is evidence that this substance contains a highly active double bond.[4] In the case of butadiene and dimethylbutadiene addition was found to occur rapidly in glacial acetic acid solution at 100°, giving beautifully crystalline, colorless products. That the substances have the expected endocyclic structure II was established by the isolation of characteristic cleavage products. Like other 1,3-diketones which are incapable of enolization,[5] the compounds are quite susceptible to alkaline hydrolysis, giving anthraquinone, or 2,3-dimethylanthraquinone, and phthalic acid. The primary rupture of the molecule evidently gives a tetrahydroanthraquinone which becomes isomerized and oxidized to an anthraquinone under the influence of alkali and air.



Experimental Part

Naphthacenediquinone-2,3-dimethylbutadiene (II, R = CH_3).—A suspension of 1 g. of naphthacenediquinone in 45 cc. of glacial acetic acid containing 2 cc. of 2,3-dimethylbutadiene was heated at 100° for four to five hours, when the initially brown solution had become pale yellow. The solution was boiled to expel unchanged diene, clarified with active carbon, and concentrated to one-fifth its volume. The product separated in a good condition and the yield of once recrystallized material was 1.1 g. (87%). The substance is readily soluble in benzene, glacial acetic acid, chloroform or acetone, and moderately soluble in alcohol or ether. By crystallization from a hot, concentrated solution in acetic acid it was obtained as small colorless, transparent orthorhombic prisms, m. p. 255–256°, while from a cool, dilute solution the substance was

---

(1) Dufraisse and Velluz, *Compt. rend.*, **201**, 1394 (1935).

(2) Previous papers: Fieser and Seligman, (a) THIS JOURNAL, **56**, 2690 (1934); (b) *Ber.*, **68**, 1747 (1935).

(3) Gabriel and Leupold, *ibid.*, **31**, 1272 (1898).

(4) Voswinckel, *ibid.*, **38**, 4015 (1905); **42**, 458 (1909).

(5) Beckham and Adkins, THIS JOURNAL, **56**, 1119, 2676 (1934).

deposited in the form of needles having the same melting point.

Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 78.03; H, 5.27.

Naphthacenediquinone-butadiene (II, R = H) was obtained in a slightly less smooth reaction in 74.5% yield. Crystallized from glacial acetic acid it formed colorless, transparent plates melting at 243–244°.

Anal. Calcd. for $C_{22}H_{14}O_4$: C, 77.17; H, 4.13. Found: C, 77.12; H, 4.36.

Alkaline Cleavage.—Half-gram samples of the addition products were heated on the steam-bath with 15-cc. portions of 25% methyl alcoholic potassium hydroxide for ten to fifteen minutes and the mixture was shaken with air until there were no further color changes. In the absence of air the solid dissolves to a deep red solution and on exposure this becomes green and then yellow and deposits pale yellow needles, sometimes with a greenish tinge. The products were collected and recrystallized from glacial acetic acid containing a little chromic anhydride. From the dimethyl compound there was obtained 0.31 g. (97%) of 2,3-dimethylanthraquinone, m. p. 208–210°, which gave no depression when mixed with a known sample. The parent substance yielded 0.26 g. (93%) of anthraquinone, m. p. 284–285°, similarly identified.

In each case the alkaline mother liquor was acidified and evaporated to dryness. The residue was extracted thoroughly with ether and the ethereal solution extracted with 2% alkali and the product precipitated with hydrochloric acid. The phthalic acid which separated was sublimed and identified in the form of the anhydride (0.09–0.1 g.), m. p. and mixed m. p., 129.5–130.5°.

CONTRIBUTION FROM THE
CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

RECEIVED APRIL 14, 1936

The Oxidation of Methyl α- and β-Naphthyl Ketones

BY L. F. FIESER, H. L. HOLMES AND M. S. NEWMAN

In view of the usefulness of α- and β-naphthoic acid in synthetic operations and the high current price of these materials the preparation of the compounds by the hypochlorite oxidation of the corresponding methyl ketones was investigated. It was found that β-naphthoic acid can be prepared very conveniently by this method. A solution of potassium hypochlorite was prepared by dissolving 250 g. of commercial calcium hypochlorite ("HTH"), containing 65% of the active ingredient, in 1 liter of water, adding a warm solution of 175 g. of potassium carbonate and 50 g. of potassium hydroxide in 500 cc. of water, shaking well, filtering and washing the precipitate. The solution was heated to 55°, stirred mechanically, and 85 g. of methyl β-naphthyl ketone was added, the temperature subsequently being controlled to 60–70° by frequent cooling in an ice-bath. After about one hour the excess hypochlorite was destroyed by adding 50 g. of sodium bisulfite in 200 cc. of water and the solution was cooled and acidified. The colorless acid which precipitated (85 g., m. p. 181–183°) was crystallized while moist from 600 cc. of alcohol, giving 75 g. (87%) of β-naphthoic acid, m. p. 184–185° (corr.).

The methyl naphthyl ketone prepared by Caille's method[1] at temperatures as low as −15°, using either acetyl chloride or acetic anhydride, was found by oxidation to contain at least 30% of the β-isomer. This is in conformity with the observations of St. Pfau and Ofner,[2] who found that methyl α-naphthyl ketone can be isolated easily from the mixture in the form of the picrate. On submitting to hypochlorite oxidation the ketone separated from the mixture by a single crystallization as the picrate, we obtained pure α-naphthoic acid, the yield of once recrystallized material, m. p. 161.5–162.5° (corr.) being 90%. Although this constitutes a practical method of preparing the acid, it is less convenient than to treat α-naphthylmagnesium bromide with carbon dioxide or ethyl carbonate,[3] in the latter case with subsequent hydrolysis. We obtained α-naphthoic acid in 85% yield from the bromide, the Grignard reagent being poured onto solid carbon dioxide.

For comparison with the methyl α-naphthyl ketone isolated through the picrate[2] a sample of the ketone was prepared from methyl α-naphthoate and ethyl acetate, following the procedure of Mosettig and van de Kamp[4] for a comparable case. The constants (corr.) were as follows: b. p. 151.5–152° at 9 ± 0.5 mm., 302° at 760 mm.; $n^{27}D$ 1.6233; picrate, m. p. 119–120°; oxime, m. p. 139.5–140.5°; semicarbazone, m. p. 228.5–229.5°. The picrate isolated according to St. Pfau and Ofner and once recrystallized likewise melted at 119–120° (corr.) and it is concluded that the pure ketone can be obtained in an entirely satisfactory condition by the Friedel and Crafts reaction and separation of the isomers through the picrates.

CONTRIBUTION FROM THE
CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

RECEIVED APRIL 21, 1936

---

(1) Caille, *Compt. rend.*, **153**, 393 (1911).

(2) St. Pfau and Ofner, *Helv. Chim. Acta*, **9**, 669 (1926).

(3) Loder and Whitmore, THIS JOURNAL, **57**, 2727 (1935).

(4) Mosettig and van de Kamp, *ibid.*, **55**, 3442 (1933).

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.

Universal Oil Products Company
Research and Development Laboratories
Riverside, Illinois
Received February 17, 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

$$\mathrm{ROH} + \mathrm{SO_3C_5H_5N} \xrightarrow{\mathrm{C_5H_5N}} \mathrm{ROSO_3HC_5H_5N}$$

$$\mathrm{ROSO_3HC_5H_5N} + \mathrm{KOH} \longrightarrow \mathrm{ROSO_3K}$$

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

---

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

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

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

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.

PEDIATRIC RESEARCH LABORATORY
THE JEWISH HOSPITAL OF BROOKLYN
BROOKLYN, N. Y.
RECEIVED MAY 18, 1936

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