rides and the bromides of the rare earth metals it has been found possible to carry out the reaction between lanthanum oxide and ammonium iodide in such a manner that the final product contains about 90% of anhydrous lanthanum iodide.

The essential features of the procedure are as follows. One gram of ammonium iodide is poured into a Pyrex tube, 10 mm. in bore and 60 cm. long, closed at one end. There is then added a mixture of 1 g. of lanthanum oxide and 6 g. of ammonium iodide. The tube is inserted in an electric furnace to a distance of 22 cm., being slightly inclined downward at the outer open end, and is heated at 350°, with an occasional rotation, until no more water condenses in that part of the tube outside the furnace. Four hours are required for complete reaction, whereupon the excess ammonium iodide is removed by sublimation in a high vacuum at 250°. During the whole process the vapor from the ammonium iodide, passing over the product, protects it from reaction with oxygen which would otherwise occur even at low pressures. When no more ammonium iodide condenses outside the heated zone, the tube is sealed and quickly cooled to room temperature.

The product obtained by this method is nearly white with a very slight yellow tinge. Its hydration on exposure to air and the vigor of its reaction with water are indicative of the presence of anhydrous lanthanum iodide. On extraction with water 10% or less is insoluble. The atomic ratio of iodine to lanthanum in this insoluble residue varies from 0 to approximately 0.3. In the solution the ratio is 3, and, since no ammonium ion is present, it corresponds to the formula, LaI_3. Lanthanum iodide was also extracted from the raw product with 95% ethyl alcohol.

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RECEIVED DECEMBER 17, 1936

COMMUNICATIONS TO THE EDITOR

INHIBITION OF THERMAL DECOMPOSITION OF *n*-BUTANE BY NITRIC OXIDE

Sir:

The recent work of Fletcher and Rollefson [THIS JOURNAL, **58**, 2129, 2135 (1936)] has shown that the acceleration of an organic vapor phase decomposition by ethylene oxide, and inhibition of the normal decomposition by nitric oxide give rather conclusive evidence that the decomposition proceeds via a chain mechanism.

We have previously shown [*ibid.*, **58**, 1317 (1936)] that ethylene oxide accelerates the decomposition of propane, *n*- and *i*-butane.

We now find that the decomposition of *n*-butane is strongly inhibited by small amounts of NO, as shown by the following table.

P_0 butane = 200 mm.; temp., 500 ± 1.0°; KCl-coated reaction bulb

P_0(NO), mm.	Init. rate, mm./min.	% Dec. at 120 min.	
		By ΔP	By anal.
0	1.0	26.5	31
20	0.05	7.1	13

The rates as measured by the analysis after 120 minutes indicate that the inhibition is somewhat less than would be concluded from the initial rates. However, the fact that the normal reaction falls off quite rapidly with time, while the inhibited reaction rate increases continuously, can in large part explain this discrepancy. Thus the actual inhibition must lie between a 20/1 ratio of normal to inhibited rate and a 3/1 ratio, as given by the runs to high percentage decomposition. Measurements over a wide range of P_0(NO) indicate a region of maximum inhibition at about 20 mm.

This result, together with the arguments advanced by Hinshelwood [Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **A154**, 335 (1936)] as to the possible causes of an observed inhibition, lead us to the conclusion that the decomposition of butane under these conditions is largely a chain reaction.

Further work is now in progress, attempting to correlate the two effects in a more quantitative manner. It is also hoped to extend the work to lower hydrocarbons, particularly ethane.

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RECEIVED MARCH 11, 1937

CHEMICAL STUDIES ON TOAD POISONS. FURTHER CONTRIBUTIONS TO THE CHEMICAL CONSTITUTION OF MARINOBUFAGIN, CINOBUFAGIN AND GAMABUFAGIN

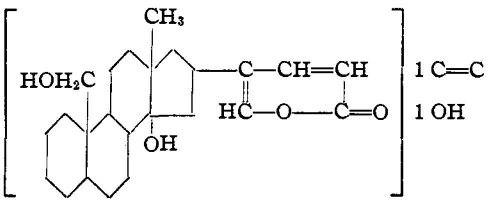
Sir:

Marinobufagin, $C_{24}H_{32}O_5$ [Jensen and Evans, Jr., *J. Biol. Chem.*, **104**, 307 (1934)], and cinobufagin, $C_{26}H_{34}O_6$ [Crowfoot and Jensen, THIS JOURNAL, **58**, 2018 (1936)], are unsaturated hydroxy lactones, cinobufagin being the acetyl derivative of the compound $C_{24}H_{32}O_5$, an isomer of marinobufagin. Tschesche and Offe [*Ber.*, **68**, 1998 (1935)] and independently Jensen [THIS JOURNAL, **57**, 2733 (1935)] showed that cinobufagin on dehydrogenation with selenium yields the Diels hydrocarbon $C_{18}H_{16}$. It has been found that marinobufagin (5 g. used) under the conditions described for cinobufagin [Jensen, *ibid.*, **57**, 2733 (1935)] also yields this hydrocarbon, found m. p. 122–123°, no depression when mixed with methylcyclopentenophenanthrene (m. p. 123–124°). *Anal.* Calcd. for $C_{18}H_{16}$: C, 93.05; H, 6.95. Found: C, 92.92; H, 7.17.

Repetition of catalytic hydrogenation of marinobufagin and cinobufagin has revealed the presence of three double bonds instead of two as previously reported by Jensen and Evans [*J. Biol. Chem.*, **104**, 307 (1934)]; α-hexahydromarinobufagin m. p. 212–213°, β-derivative m. p. 225–227°; α-hexahydrocinobufagin m. p. 230–232°; β-derivative m. p. 210–212°. The found analytical data agree with the calculated. Simultaneously small amounts of acidic products are produced, probably by the opening of the lactone ring. Tschesche and Offe [*Ber.*, **69**, 2361 (1936)] have since reported similar findings.

Ozonization of marinobufagin and cinobufagin (ozone was passed under cooling for three hours through a solution of 1 g. of substance in chloroform, the working up of the reaction product was carried out in the usual manner) was found to yield formic acid, identified by qualitative tests, and glyoxylic acid, identified by color reactions and as the dinitrophenylhydrazone, yellow needles m. p. 190° with decomposition, no depression with the derivative prepared from glyoxylic acid. A small amount of oxalic acid, formed by oxidation of glyoxylic acid, was also found and identified as the calcium salt. These findings indicate the presence of two double bonds in the lactone group, which is a six-membered ring and apparently identical with that in scillaren [Stoll, Hofmann and Peyer, *Helv. Chim. Acta*, **18**, 1247 (1935)]. The third double bond is present in the sterol ring; its exact position is still uncertain.

It has been found that both marinobufagin and gamabufagin contain a —CH_2OH group attached either at C_{10} or at C_{13}, corresponding to one of the angular methyl groups of the sterols. Under the influence of strong acid or alkali this primary alcoholic group is eliminated as formaldehyde. On oxidation with chromic acid marinobufagin gives an aldehyde, the oxidation product giving the typical reactions for an aldehyde group. Evidence has been obtained that a tertiary hydroxyl group is attached at C_{14} in all three principles. Whether or not the third hydroxyl group in marinobufagin is also tertiary is somewhat uncertain, as is its position. Under the influence of acid two hydroxyl groups in marinobufagin are eliminated as water. On the basis of the experimental findings the following structure for marinobufagin is suggested



Analytical data obtained for gamabufagin, acetylgamabufagin and anhydrogamabufagin indicate the empirical constitution of $C_{24}H_{34}O_5$ for gamabufagin, as suggested by Wieland and Vocke [*Ann.*, **481**, 215 (1930)]. Gamabufagin contains only two double bonds, both in the lactone ring. Under the influence of acid gamabufagin loses one molecule of water. Both cinobufagin and gamabufagin have a structure similar to that of marinobufagin.

The author is greatly indebted to Dr. K. K. Chen, Lilly Research Laboratories, Indianapolis, for a supply of the secretion of the Japanese toad.

Owing to the temporary interruption of this