upon acetonitrile in the same manner as the experiment just described. It melted at 106–107° (percentage of nitrogen determined, 10.39; calculated, 10.37).

It is absolutely essential that all materials used in these experiments be anhydrous and that care be taken to prevent the introduction of moisture in transferring the addition compounds to the sealed tubes, in order to have success with this reaction.

NATIONAL UNIVERSITY OF CHEKING
CHINA

RECEIVED JANUARY 3, 1944

COMMUNICATIONS TO THE EDITOR

RESYNTHESIS OF DESTHIOBIOTIN FROM DIAMINOPELARGONIC ACID[1]

Sir:

Work in this Laboratory has demonstrated[2] that desthiobiotin, derived from biotin by hydrogenolysis of the sulfide linkage,[3] is equally as effective as biotin in promoting the growth of yeast. Desthiobiotin has been shown to be 4-methyl-5-imidazolidone-2-caproic acid, and is converted by acid or alkaline hydrolysis to ζ,η-diaminopelargonic acid.[3]

In view of the high yeast-growth-promoting activity of desthiobiotin, it became of interest particularly from the standpoint of possible synthetic approaches to desthiobiotin, to investigate the effect of phosgene on the diaminopelargonic acid derived from desthiobiotin, since it has been shown[4] that nearly quantitative yields of biotin can be obtained by treatment with phosgene of the sulfur-containing diamino acid derived from biotin.

Diaminopelargonic acid was prepared in good yield from pure desthiobiotin[2] by hydrolysis with barium hydroxide.[3] The product was isolated as the sulfate, which crystallized in small diamond-shaped plates, micro m. p. 245–246°.

For the treatment with phosgene, 15 mg. of the diaminopelargonic acid sulfate was dissolved in 2 cc. of aqueous 10% sodium carbonate and phosgene gas was passed into the solution until the solution became acid to congo red. The clear solution was concentrated *in vacuo* to a volume of approximately 0.5 cc. Crystalline material separated from the solution and was removed and washed with a few drops of water. The combined washings and mother liquors were extracted continuously with ether for two hours; a small amount of crystalline material separated in the ether extract. The crystalline fractions were combined, dissolved in methanol and filtered, and the filtrate was concentrated to dryness. The residue was crystallized from a few drops of hot water, washed with water, and dried. The yield of product in the form of long, colorless needles, micro m. p. 156–158°, was 7.4 mg. (66% of the theoretical yield).

The reaction product possessed the same crystalline form, solubility, and melting point as desthiobiotin. A mixture of the reaction product with a sample of pure desthiobiotin, micro m. p. 156–158°, showed no depression of the melting point. Furthermore, the resynthesized material possessed the same yeast-growth-promoting activity as desthiobiotin. The diaminopelargonic acid from which it was synthesized, on the other hand, exhibited approximately 10% of the activity of desthiobiotin under the same conditions of assay and at levels which produced half-maximum growth.

It is concluded from these data that the chief product formed by the action of phosgene on the diaminopelargonic acid is desthiobiotin. The yield obtained suggests the use of this reaction as a step in the total synthesis of desthiobiotin.

DEPARTMENT OF BIOCHEMISTRY
CORNELL UNIVERSITY MEDICAL COLLEGE
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RECEIVED JULY 17, 1944

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[1] The desthiobiotin used in this investigation was prepared from natural biotin generously supplied by Merck and Company, Inc. Appreciation is also expressed to Dr. Karl Dittmer and Mrs. Glenn Ellis for carrying out the microbiological assays.

[2] Melville, Dittmer, Brown and du Vigneaud, *Science*, **98**, 497 (1943).

[3] Du Vigneaud, Melville, Folkers, Wolf, Mozingo, Keresztesy and Harris, *J. Biol. Chem.*, **146**, 475 (1942).

[4] Melville, Hofmann and du Vigneaud, *Science*, **94**, 308 (1941).

THE MECHANISM OF THE ALKYLATION OF PARAFFINS WITH OLEFINS IN THE PRESENCE OF ALUMINUM CHLORIDE

Sir:

The previously proposed mechanisms[1] for the catalytic alkylation of paraffins are unsatisfactory either in explaining how the reaction occurs or accounting for the structure of the products obtained. An investigation of the reaction of alkyl chlorides with olefins and of isoparaffins with chloroölefins has now led to the conclusion that the alkylation of isoparaffins with olefins in the presence of aluminum chloride proceeds via the conversion of the paraffin to an alkyl chloride. The mechanism is outlined below for the reaction of isobutane with ethylene. Similar reactions occur with other paraffins and olefins.

The *t*-butyl chloride formed in Eq. 3 starts a new cycle by reacting with ethylene as in Eq. 2. Ethane is produced only in the initiating step and the amount formed will therefore be small.

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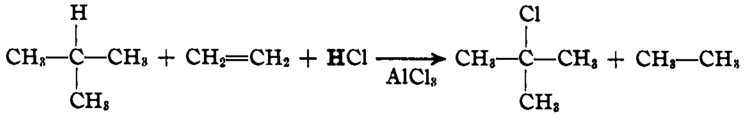
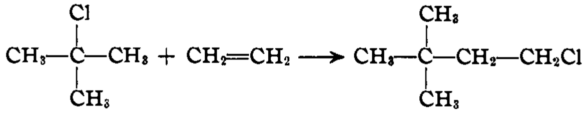
[1] (a) Ipatieff and Grosse, THIS JOURNAL, **57**, 1616 (1935); (b) Birch and Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939); (c) Caesar and Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941); (d) McAllister, Anderson, Ballard and Ross, *J. Org. Chem.*, **6**, 647 (1941).

Eq. 1)



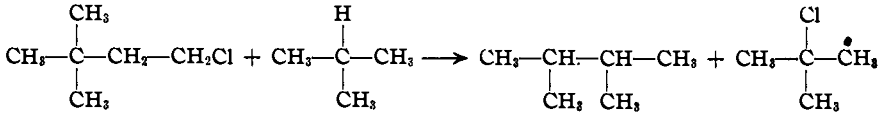
$$CH_3-\overset{H}{\underset{CH_3}{C}}-CH_3 + CH_2{=}CH_2 + HCl \xrightarrow[AlCl_3]{} CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3 + CH_3-CH_3$$

Eq. 2)



$$CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3 + CH_2{=}CH_2 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2Cl$$

Eq. 3)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2Cl + CH_3-\overset{H}{\underset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3 + CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3$$

The more pertinent evidence in support of each of the three steps will be briefly mentioned in this communication.

Eq. 1.—This probably occurs via the formation of ethyl chloride. The reduction of an alkyl halide (*e. g.*, ethyl chloride) to the corresponding paraffin by reaction with another paraffin (*e. g.*, *n*-heptane) in the presence of aluminum chloride has been reported.[2] Ethane and propane have been obtained as by products of the alkylation of isobutane with ethylene and propene,[3] respectively. *t*-Butyl chloride was isolated from the products of the reaction of isobutane with vinyl chloride, allyl chloride or 2-chloropropene at temperatures near 0° or below.

Eq. 2.—A 75% yield of 1-chloro-3,3-dimethylbutane (characterized by conversion to neopentylcarbinol) is obtained by the addition of *t*-butyl chloride to ethylene in the presence of aluminum chloride at −15 to −10°. The addition of *t*-butyl chloride to other olefins occurs in the analogous manner.

Eq. 3.—2,3-Dimethylbutane was found to be the major product of the reaction of 1-chloro-3,3-dimethylbutane with isobutane. The condensation of allyl chloride with excess isobutane yields chloroheptane as the chief product if the reaction is carried out at temperatures near 0° or below, while at higher temperatures reduction to heptane occurs.

The rearrangement of the carbon skeleton which occurs in Eq. 3 is not unexpected since the dehydrochlorination involves the hydrogen atom attached to a carbon atom of a neopentyl group. Dehydrochlorination of 1-chloro-3,3-dimethylbutane yielded a mixture of 2,3-dimethylbutene-1 and -2.

A complete discussion of the mechanism as well as of the reaction of isoparaffins with chloroolefins and of alkyl chlorides with olefins will be given in forthcoming papers.

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[2] Nenitzescu and Dragan, *Ber.*, **66**, 1897 (1933).

[3] Unpublished results from These Laboratories.

NEW BOOKS

Handbook of Chemistry. Compiled and edited by NORBERT ADOLPH LANGE, Ph.D., assisted by GORDON M. FORKER, B.S.(Chem.Eng.), with mathematical tables by RICHARD STEVENS BURINGTON, Ph.D. Fifth edition, revised and enlarged. Handbook Publishers, Inc., Sandusky, Ohio, 1944. xvi + 1777 + 271 + 28 pp. 14 × 20 cm. Price, $6.00.

This excellent handbook, a relative newcomer in the field, has proved very popular with users, as is attested by the need for a fifth edition within ten years from the date of the first. The activity of the compiler is shown by the increase in total pages from 1542 in the first issue to the present 2076. Since the handbook contains over 200 *groups* of related tables, any attempt to list them would be superfluous; this latest edition has six new tables, while thirteen others have been extended or completely rewritten, producing an expansion of 174 pages. In the words of the compiler, it is to be hoped "that its resting place will be on the desk rather than on the book shelf" of many students, engineers and teachers.

ALLEN D. BLISS

A Source Book of Agricultural Chemistry. By CHARLES A. BROWNE, Ph.D., Sc.D., Adviser, Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, etc. (No. 1 of volume 8 of *Chronica Botanica*, edited by Dr. Frans Verdoorn.) Waltham, Mass., the Chronica Botanica Co.; New York City, G. E. Stechert and Co. 290 pp. 32 illustrations. 17.5 × 26 cm. Price, $5.00.

This admirable volume is not precisely what I would have anticipated from the title, "A Source Book of Agricultural Chemistry"—namely, a collection of original literature dealing with agricultural chemistry. It is rather a history of the development of agricultural chemistry frequently documented by quotations from original articles and books, accompanied by brief biographies of their authors.

It is, nevertheless, a "source book" in the sense that it is chiefly concerned with the origins of agricultural chemistry. Six of its seven chapters are devoted to the period ending with Lavoisier and the Chemical Revolution; the seventh and final chapter covers the succeeding half-