

addition of solid potassium hydroxide to a commercial (Rohm and Haas) 25% aqueous solution of dimethylamine. The gas evolved was passed through two drying towers containing solid potassium hydroxide and was then condensed in a receiver cooled by a Dry Ice-acetone bath.) The mixture was refluxed for fifteen minutes after the introduction of all the amine. The condenser was then placed downward for distillation and two-thirds of the benzene was distilled. The residue on cooling deposited 298-316 g. of crude product, m. p. 122-124°. One recrystallization from dry benzene gave 274-291 g. (71-75%) of white microcrystals, m. p. 124-125°.

*Anal.*¹ Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.20; H, 5.53; N, 7.14.

(1) Microanalyses were carried out by Miss Theta Spoor.

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2-Keto-7-*n*-propylhexamethyleneimine and 6-Aminononanoic Acid

2-Keto-7-*n*-propylhexamethyleneimine.—2-*n*-Propylcyclohexanone oxime, m. p. 65-66° (uncor.),¹ 1.7 g., was rearranged in 92% sulfuric acid essentially according to the procedure of Marvel and Eck.²

(1) Vavon and Anziani, *Bull. soc. chim.*, **41** (4), 1638 (1927).

(2) Marvel and Eck, "Organic Syntheses," **17**, 60 (1937).

The relatively high acid concentration has been reported to be conducive to higher yields.³ The product, 2-keto-7-*n*-propylhexamethyleneimine, after being vacuum distilled as the residue from a chloroform extraction of the neutralized reaction mixture, melted at 97-98° (uncor.).

Attempted fractional crystallization of the product from chloroform-petroleum ether resulted in a 97% yield of the lactam, m. p. 100.5-101.5° (uncor.). Only a trace of partially crystalline residue remained.

Anal. Calcd. for $C_9H_{17}ON$: C, 69.68; H, 10.97. Found: C, 69.84; H, 11.13.

6-Aminononanoic Acid.—By hydrolysis of the lactam there was obtained the corresponding amino acid hydrochloride; it did not crystallize. After treating the hydrochloride with silver oxide, 6-aminononanoic acid was isolated, m. p. 198.5-199° (temperature rise of 4°/min.).

Anal. Calcd. for $C_9H_{19}O_2N$: C, 62.39; H, 11.05. Found: C, 62.34; H, 11.01.

The formation of but one isomer during the Beckmann rearrangement of a 2-alkylcyclohexanone oxime is in accordance with previous results.^{4,5}

(3) Hildebrand and Bogert, *THIS JOURNAL*, **58**, 650 (1936).

(4) Wallach, *Ann.*, **389**, 169 (1912).

(5) Ungnade and McLaren, *J. Org. Chem.*, **10**, 29 (1945).

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COMMUNICATIONS TO THE EDITOR

SMALL-ANGLE X-RAY DIFFRACTION STUDIES ON MUSCLE

Sir:

A type of protein fibril (I), distinguished by a certain large structural pattern, has been described for molluscan muscles.^{1,2} Recently another variety of fibril (II) has been identified in the same and other muscles by means of small-angle X-ray diffraction. The relatively widespread occurrence of the type II fibrils is presumptive, although purely circumstantial, evidence that they are related to the fibrous protein, myosin.

Diffractions characterizing both types of fibril have been observed in the following muscles: the adductor muscles of the molluscs *Venus*, *Anodonta*, *Pecten*, *Mya* and *Mytilus*, and the retractor muscle of the sipunculid annelid, *Phascolosoma*. The first three muscles possess both white and tinted portions, the colorless components being more purely type I, the colored ones showing relatively more type II. While these muscles have been variously classified histologically,³ the colored *Pecten* component alone seems definitely cross-striated and not to possess the

(1) R. S. Bear, *THIS JOURNAL*, **66**, 2043 (1944).

(2) C. E. Hall, M. A. Jakus, and F. O. Schmitt, *J. Applied Phys.*, **16**, 459 (1945).

(3) See H. Plenck, *Z. wiss. Zool.*, **123**, 20 (1924).

type I fibrils. The striated frog sartorius and the smooth dog retractor penis muscles also exhibit only the type II diffractions.

The new diffraction system (II) is generally faint, diffuse and susceptible of damage by physical and chemical manipulation of the muscle. The best patterns have been obtained from *Venus* (pink component) and *Mya* muscles, in which type II fibrils are plentiful and are also undoubtedly stabilized by the accompanying type I component. As with other protein fibers,¹ the small-angle diffractions of system II are almost exclusively exhibited near or on the pattern meridian. The diffraction positions correspond to the following calculated spacings⁴: 58, 51, 27.2, 18.7, 13.8, 11.2, 9.2 and 6.9 Å. From such pattern details as sharpness and concentration of intensity with respect to the meridian, it seems probable that the structure involved is similar to that found for system I,² except that the repeating units are much smaller. The following tentative comparisons can be made: Fiber axis periods are 725 (I) and possibly 350 to 420 Å. (II); meridionally accentuated diffractions are orders of 145 (I) in contrast to about 27 Å. (II); and the

(4) I. MacArthur, *Nature*, **152**, 38 (1943), quotes measurements of W. T. Astbury, on frog sartorius muscle, which include all but the first two of the spacings given here.

transverse structural periods are 200 to 325 Å compared to approximately 115 Å. (II).

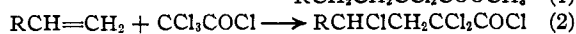
System II is also distinctive in that the apparent calculated spacings change with the cosine of the angle of departure of the muscle axis from perpendicularity to the X-ray beam, indicating that the diffracting elements are two-dimensional. Type I elements are also believed to have a thin dimension,² but apparently this is not fine enough to result in the corresponding diffraction phenomenon.

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RECEIVED AUGUST 9, 1945

ADDITION OF DERIVATIVES OF CHLORINATED ACETIC ACIDS TO OLEFINS

Sir:

The chain reaction whereby the elements of carbon tetrachloride and of chloroform may be added to the double bonds of olefins¹ has been reported.² Furthermore, it has been found that (among other substances) derivatives of chlorinated acetic acids will add to olefins to give excellent yields of the following type of compounds



Octene-1 (32 g.) and methyl dichloroacetate (177 g.) were heated in a flask for four hours at 100° in the presence of diacetyl peroxide (2 g.). About 57 g. remained in the flask after removal of the starting materials at reduced pressure. This material upon distillation gave 29 g. of a fraction which boiled at 74–75° (0.3 mm.) (n_{D}^{20} 1.4561) and a residue (28 g.). It is presumed that the former is methyl α, α -dichlorocaprato (40% yield).

Anal. Calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_2\text{Cl}_2$: Cl, 27.85; mol. wt., 255. Found: Cl, 28.17; mol. wt., 255.

The residue was distilled in a molecular still. From the chlorine content (23.45%) and the molecular weight (357) of the middle fraction, it appears likely that this fraction is a mixture of dimethyl tetrachlorosuccinate (13%), and the condensation product made up of two molecules of octene-1 and one molecule of methyl dichloroacetate (87% = 46% yield on the basis of octene-1 used).

A better yield of the mono addition product and a smaller amount of the higher condensation products (two or more molecules of octene-1 to one molecule of chlorinated acetic acid derivative) were obtained when octene-1 (25 g.) and trichloroacetyl chloride (180 g.) were heated in a

(1) The reaction has also been extended to compounds containing triple bonds; the double or triple bond does not necessarily need to be terminal.

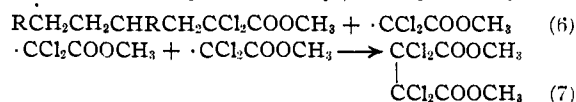
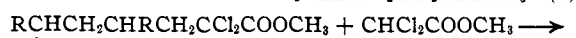
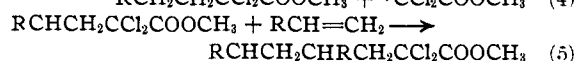
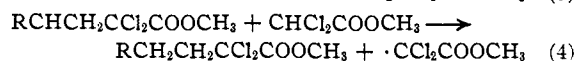
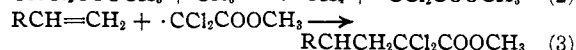
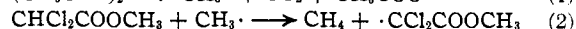
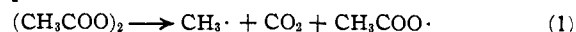
(2) Kharasch, Jensen and Urry, *Science*, **103**, 128 (1945).

flask in the presence of diacetyl peroxide (2 g.) and the reaction mixture was worked up as described above. The yield of α, α, γ -trichlorocapryl chloride (b. p. 123–126°, 0.3 mm., n_{D}^{20} 1.4830) was 81%, based on the octene-1 used.

Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{OCl}_4$: Cl, 48.2; mol. wt., 294. Found: Cl, 48.1; mol. wt., 294.

The condensation of methyl monochloroacetate and octene-1 gave only about a 10% yield of a condensate, based on the octene-1 used.

The reactions cited are assumed to proceed via a free radical chain reaction initiated by the free radicals formed by the decomposition of the diacetyl peroxide.



It is assumed that reactions (5) and (6) are responsible for the formation of the high boiling materials.

Insofar as we know, the propagation of the chain reaction, as indicated in steps (3) and (4), will take place if the radical R in the unsaturated compound is aliphatic and if it is attached to a carbon atom which has a hydrogen atom attached to it. The basis for this statement and the basis for the structures assigned to the compounds formed in this interesting reaction will be presented in the near future in a comprehensive paper now in preparation.

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RECEIVED AUGUST 13, 1945

PRODUCTION OF GLIOTOXIN AND A SECOND ACTIVE ISOLATE BY *PENICILLIUM OBSCURUM* BIOURGE

Sir:

Recently we have been able to isolate gliotoxin, as well as a second heretofore unreported antibiotic, from a culture of *Penicillium obscuro* Biourge. Removal of the two substances from the broth was effected by extraction at pH 2 with benzene. Addition of approximately equal parts of petroleum ether to the concentrated extract resulted in the separation of the crude Isolate 1. Purification was accomplished by repeated crystallizations. The material melted at 192–193°¹

(1) All melting points are corrected.