low-boiling petroleum ether; m. p. 151–153°. A mixed melting point with an authentic sample of mesitoic acid was not depressed. The yield appeared to be practically quantitative.

Reaction with Mesitylmagnesium Bromide.—The Grignard reagent, made from 1 g. of magnesium and 8.8 g. of bromomesitylene in 25 cc. of ether, was added dropwise to 1 g. of mesitoic anhydride dissolved in 10 cc. of ether and 25 cc. of benzene. As the drops of Grignard reagent struck the nitrile solution, a dark red coloration was produced. After being stirred for ten minutes, the reaction mixture was decomposed with ice and acetic acid. The organic layer was separated and washed with water and dilute hydrochloric acid. It was then steam distilled; the residual material was recrystallized from alcohol. It melted at 136–137° and proved to be dimesityl ketone

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

REYNOLD C. FUSON
JOSEPH CORSE
NORMAN RABJOHN[2]

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(2) Röhm and Haas Research Assistant.

RECEIVED JULY 14, 1941

2-Methyl-5-hydroxybenzimidazole

Five grams of 3,4-di-(acetylamino)-1-acetoxybenzene in a mixture of 100 cc. of alcohol and 7.5 cc. of concentrated hydrochloric acid was refluxed for two hours. The alcohol was removed by distillation, the residue dissolved in 50 cc. of water, neutralized with sodium carbonate, and cooled. The solid (2.3 g.) was crystallized from 1% sodium hydrosulfite, using decolorizing charcoal. One and three-tenths grams of white crystals was obtained. The dried compound (monohydrate of 2-methyl-5-hydroxybenzimidazole) lost water at 110–115°, resolidified and melted at 187–188°. When dried to constant weight *in vacuo*, at 100°, the anhydrous compound melted at 187.5–188.5°.

Anal. Calcd. for $C_8H_8ON_2 \cdot H_2O$: N, 16.86; H_2O, 10.84. Found: N, 17.03; H_2O, 11.06. Calcd. for $C_8H_8ON_2$: N, 18.91. Found: N, 18.77.

This compound was also prepared from 1-acetylamino-2-amino-4-acetoxybenzene by refluxing 10 g. in a mixture of 20 cc. of concentrated hydrochloric acid and 10 cc. of water for two hours.

DEPARTMENT OF CHEMISTRY
COLLEGE OF PHARMACY
UNIVERSITY OF ILLINOIS
CHICAGO, ILLINOIS

S. D. GERSHON
G. L. WEBSTER

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Ethyl γ-(2-Carboethoxy-2-cyclohexanone)-butyrate and Some Related Compounds

Alkylation of 2-carboethoxycyclohexanone with ethyl γ-bromobutyrate by the standard procedure for β-ketonic esters[1] gave ethyl γ-(2-carboethoxy-2-cyclohexanone)-butyrate in 48.5% yield; b. p. 166–168° at 2 mm.; $n^{20}D$ 1.4630.

Anal. Calcd. for $C_{15}H_{24}O_5$: C, 63.40; H, 8.45. Found: C, 62.99; H, 8.64.

This keto-ester gave a 2,4-dinitrophenylhydrazone derivative which after two recrystallizations from 60% alcohol melted at 84–85°.

Anal. Calcd. for $C_{21}H_{28}O_8N_4$: C, 54.30; H, 6.03. Found: C, 54.15; H, 6.04.

Hydrolysis of this ester with dilute sodium hydroxide followed by treatment with acid and loss of carbon dioxide gave the known[2] γ-(2-ketocyclohexanyl)-butyric acid, m. p. 59–60° in 61% yield.

Reduction of 55 g. of the keto-ester in 75 cc. of absolute alcohol over Raney nickel[3] at 125° and 2500 lb. pressure gave 40.5 g. of the corresponding hydroxy ester; b. p. 164–166° at 2 mm.; $n^{20}D$ 1.4672.

Anal. Calcd. for $C_{15}H_{26}O_5$: C, 63.00; H, 9.10. Found: C, 62.93; H, 9.01.

A Zerewitinoff determination showed 0.982 active hydrogens per mole.

2,4-Dinitrophenylhydrazone of Cyclopentylidenecyclopentanone.—Cyclopentylidenecyclopentanone prepared by the method of Wallach[4] gave a brick-red 2,4-dinitrophenylhydrazone which after crystallization from alcohol melted at 228–229°.

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.25; H, 5.45. Found: C, 58.33; H, 5.53.

1-(Hydrindylidene)-4-pentene.—Condensation of 66 g. of α-hydrindone and the Grignard reagent from 1-bromo-4-pentene[5] gave 53 g. of the corresponding tertiary alcohol which could not be distilled without loss of water. Distillation gave 48.5 g. of the diene, b. p. 119–121° at 3 mm.; $n^{22}D$ 1.5518.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.30; H, 8.70. Found: C, 90.65; H, 9.19.

1-(3-Phenylhydrindylidene)-4-pentene.—Similarly from 3-phenylindanone there was obtained 1-(3-phenylhydrindylidene)-4-pentene; b. p. 190–191° at 5 mm.; $n^{20}D$ 1.6110.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.40; H, 7.60. Found: C, 92.40; H, 7.77.

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(1) See "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 243.

(2) Hückel and Naab, *Ann.*, **502**, 136 (1933).

(3) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

(4) Wallach, *Ber.*, **29**, 2963 (1896).

(5) Gaubert, Linstead and Rydon, *J. Chem. Soc.*, 1972 (1937).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

C. S. MARVEL
LESTER A. BROOKS

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Hexacyclohexoxydisiloxane, $(C_6H_{11}O)_3Si\text{-}O\text{-}Si(C_6H_{11}O)_3$

In connection with the preparation of the ethyl esters derived from some of the silicon oxyhalides, described by us elsewhere in THIS JOURNAL,[1] the extension of the work to include other silicon esters has been undertaken in this Laboratory. The first of these esters obtained was prepared from cyclohexanol and Si_2OCl_6.

To 11 g. of Si_2OCl_6 (b. p. 137°) dissolved in 50 cc. of anhydrous ether in a round-bottomed flask, 27 g. of cyclohexanol was added slowly and, after complete addition, the

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(1) Schumb and Holloway, THIS JOURNAL, **63**, 2753 (1941).

mixture was refluxed for eight hours. The ether was distilled, leaving a gummy residue which, on recrystallization from nitrobenzene and then from dioxane, yielded a white, crystalline product, m. p. 217.1–217.6°, soluble in carbon disulfide, chloroform, carbon tetrachloride, ether and alcohol. The silicon content was determined gravimetrically as described in the article above referred to.

Anal. Calcd. for $(C_6H_{11}O)_6Si_2O$: C, 64.9; H, 9.91; Si, 8.55. Found: C, 64.8, 64.4; H, 10.0, 9.93; Si, 8.55.

RESEARCH LABORATORY OF INORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
WALTER C. SCHUMB
DONALD F. HOLLOWAY

RECEIVED AUGUST 18, 1941

COMMUNICATIONS TO THE EDITOR

THE FORMATION OF FIBERS FROM NON-FIBROUS NATIVE PROTEINS

Sir:

Proteins have been classified[1] into two structurally distinct groups, namely, the fibrous proteins such as silk, wool, and hair, and the non-fibrous proteins tending toward corpuscular structure and crystallizability.

The non-fibrous native proteins are characteristically susceptible to dissociation and denaturation as a result of environmental effects on intermolecular forces.[2] In several widely different native, non-fibrous proteins dissociation and denaturation have been shown to follow a preliminary unfolding of the molecule characterized by a single, sharp, slower sedimenting boundary in the ultracentrifuge. This unfolded or so-called α-form is labile and is not present long enough to be detected under usual conditions.[3]

Experiments in this Laboratory indicate that the unfolded configuration corresponds with the intermediate fibrous state of non-fibrous proteins which Astbury, *et al.*, have demonstrated with edestin and excelsin using X-ray diffraction patterns.[4] Further confirmation of the fibrous state was found by them in the formation of fibers from urea dispersions of edestin, casein and other proteins.

With the use of detergents it has been found possible to control the transformation of the native forms into the unfolded configuration of all the non-fibrous proteins so far tested in this Laboratory. This change was followed in two ways: by the ability to draw fibers from the precipitated protein; and by the corresponding viscosity changes in the system protein–detergent. Elastic and highly double-refracting fibers were obtained in this manner from the following proteins: crystalline egg albumin, purified preparations of hog thyroglobulin, wheat glutenin, casein, and commercial preparations of zein and blood albumin.

Detergents appear to be superior to other reagents which have been investigated although some, including pyrogallic acid and guanidine hydrochloride, were found to behave somewhat similarly. The conditions favorable for the drawing of fibers appear to vary with the protein, the nature and concentration of the reagent, the temperature and the *p*H of the system. Thirty-nine detergents have been tested so far. The following example illustrates one technique used for the formation of fibers from aqueous solutions of crystalline egg albumin and an alkyl aryl sulfonate: to 4 ml. of a solution of dialyzed egg albumin (4%) at 25° was added 10 ml. of 5%-salt-free "Nacconol N. R. S. F." (trade name for a detergent of the sodium alkyl aryl sulfonate type) at the same temperature and *p*H (7.5). After one-half minute 2 ml. of saturated ammonium sulfate was added to precipitate the protein which then could be drawn into long silky filaments. After three minutes the precipitate became tough and it was no longer possible to form fibers.

Relatively low concentrations of the detergents suffice, and the treatment is not likely to cause as drastic alterations in the protein structure as many of the customary alkaline dispersion procedures now used for the production of artificial protein fibers. The possibility is foreseen that more satisfactory commercial products can be produced from protein molecules which have themselves been permanently transformed into a

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(1) Astbury, *Compt. rend. trav. lab. Carlsberg, Ser. Chim.*, **22**, 45 (1937).

(2) Lundgren, *Nature*, **138**, 122 (1936); **143**, 896 (1939).

(3) Lundgren and Williams, *J. Phys. Chem.*, **43**, 989 (1939).

(4) Astbury, Dickinson and Bailey, *Biochem. J.*, **29**, 2351 (1935).