was added slowly with stirring until the solution was no longer acid to congo red but still acid to litmus. After coupling was complete (two hours), the precipitate was isolated and washed until neutral. The nitro group was then reduced with a 10% solution of sodium sulfide crystals at 90° for three hours. After cooling to 30° the product was isolated and washed until neutral. It was then dissolved in 10% hydrochloric acid, separated by filtration from a small amount of insoluble impurities and reprecipitated at the boil with a 5% sodium hydroxide solution. The product, which separated as maroon-colored granules, was isolated, washed and dried in an oven at 65°; yield 82%. Recrystallized three times from water, the substance formed fine orange-colored rhomboids, m. p. 149°.

The compound is readily soluble in oxygen-containing solvents, slightly soluble in water and aromatic hydrocarbons, and very slightly soluble in aliphatic hydrocarbons. It forms solid solutions with cellulose esters and ethers. Its amino group is diazotizable and it yields an interesting series of insoluble compounds when coupled with phenols, naphthols and aromatic amines. The colors of these products range in general from various shades of blue to black.

Anal. Calcd. for $C_{17}H_{22}O_2N_4$: N, 17.82. Found: N, 17.60.

Pfister Chemical Works
Ridgefield, New Jersey George Shulman

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Dimethylneopentylacetic Acid (2,2,4,4-Tetramethylpentanoic Acid), its Methyl Ester, Amide and Acetanilide

1. Many attempts in the past had been unsuccessful in the preparation of the Grignard reagent of diisobutylene hydrochloride in the usual manner. It was found possible to force the formation of reagents of this type by the presence of ethylmagnesium bromide. Magnesium, 18 g., was placed in the conventional apparatus and a small amount of ethylmagnesium bromide was formed by dropping a 60-cc. aliquot of a solution of 33.3 g. of ethyl bromide in 150 cc. of anhydrous ether into the reaction flask. The remainder of the ethyl bromide solution was added to 180 cc. of anhydrous ether and 74 g. of diisobutylene hydrochloride. This solution was added to the magnesium with vigorous stirring at a rate of one drop per second. Titration indicated a yield of 52% of the Grignard of the tertiary chloride. The flask containing the Grignard reagent was cooled with a salt-ice bath and saturated with carbon dioxide. On decomposition in the usual manner, followed by distillation to remove propionic acid, a yield of 34% of dimethylneopentylacetic acid was obtained, m. p. 44–45°.

2. **Dimethylneopentylacetic acid,** 260 g., b. p. 126–130° at 16 mm, obtained from 2,4,4,6,6-pentamethyl-2-heptene by a large scale oxidation of triisobutylene,[1] was converted to the methyl ester by treating the acid with an excess of methanol saturated with hydrogen chloride. Repeated fractionation gave material b. p. 176.2° at 732 mm. (Cottrell), $n^{20}\text{D}$ 1.4222 (Valentine), d^{20} 0.879. The acid obtained by saponification of the ester, on fractionation gave b. p. 229.6° at 732 mm. (Cottrell), m. p. and mixed m. p. 45°.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.3; H, 11.5. Found: C, 68.7; H, 12.0.

3. **Dimethylneopentylacetamide** was prepared by treatment of an ether solution of the acid chloride with anhydrous ammonia. On recrystallization from petroleum ether the amide gave m. p. and mixed m. p. 71°.

4. **Dimethylneopentylacetanilide** was prepared by treating a benzene solution of the acid chloride with a benzene solution of aniline. On recrystallization from a mixture of benzene and petroleum ether the derivative gave m. p. and mixed m. p. 78°.

[1] Whitmore, *et al.*, This Journal, **63**, 2036 (1941).

School of Chemistry and Physics Frank C. Whitmore
Pennsylvania State College W. R. Wheeler
State College, Pa. J. D. Surmatis

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COMMUNICATIONS TO THE EDITOR

THE FORMATION OF ADIPIC ACID BY THE OXIDATIVE DEGRADATION OF THE DIAMINOCARBOXYLIC ACID DERIVED FROM BIOTIN

Sir:

In recent communications[1,2] we have established the molecular formula as well as the functional groups of biotin ($C_{10}H_{16}O_3N_2S$). Biotin was found to be a monocarboxylic acid containing a cyclic urea structure and sulfur in a thio ether linkage. The basis for the cyclic urea structure was our obtaining a diaminocarboxylic acid ($C_9H_{18}O_2N_2S$) containing 2 primary amino groups by treatment of biotin at 140° with $Ba(OH)_2$. The urea structure was confirmed by the resynthesis of biotin from the diaminocarboxylic acid and phosgene.[3] The resynthesized biotin possessed identical chemical, physical, and biological properties with biotin isolated from natural sources. Evidence for the thio ether structure was based mainly on

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[1] V. du Bigneaud, K. Hofmann, D. B. Melville and J. R. Rachele, *J. Biol. Chem.*, **140**, 763 (1941).

[2] K. Hofmann, D. B. Melville and V. du Vigneaud, *ibid.*, **141**, 207 (1941).

[3] D. B. Melville, K. Hofmann and V. du Vigneaud, *Science*, **94** 308 (1941).