

boiled for thirty minutes and then extracted with chloroform. The chloroform extracts, washed thoroughly with water, were concentrated and a low melting solid was obtained which was recrystallized from ethanol (1.5 g., m. p. 38–40°).

2-Methyl-3-*n*-hexadecyl-1,4-naphthoquinone.—The oxidation was accomplished by adding a solution of chromic anhydride to the hydrocarbon in acetic acid at room temperature. After heating for one-half hour at 60°, the product was isolated by diluting with water, extracting with ether, and concentrating the extracts. Purification of the crude quinone was effected by converting it into the hydroquinone, washing the latter thoroughly with petroleum ether and reoxidizing with ferric chloride. The quinone was obtained from ether as pale yellow, fluffy needles melting at 98–98.5°; yield, 35%.

Anal. Calcd. for $C_{27}H_{40}O_2$: C, 81.81; H, 10.10. Found: C, 81.61; H, 10.22.

The dihydrodiacetate from petroleum ether melts at 78–79°.

Anal. Calcd.: C, 77.18; H, 9.54. Found: C, 77.03; H, 9.29.

RESEARCH LABORATORIES

MERCK & CO. INC.

RAHWAY, NEW JERSEY RECEIVED SEPTEMBER 26, 1941

The Densities of Morpholine–Water Solutions¹

BY H. M. TRIMBLE AND ALICE FRANCES BUSE

Morpholine was prepared for this work by the commonly accepted method,² taking special precautions to exclude water and carbon dioxide of the air during its final distillation. The refractive index of several preparations at 20° was 1.4542 ± 0.0002.

TABLE I

DENSITIES OF MORPHOLINE–WATER SOLUTIONS

Morpholine % by weight	25°	Densities 30°	35°
14.17	1.0066	1.0047	1.0026
21.97	1.0128	1.0105	1.0083
26.72	1.0165	1.0140	1.0166
35.55	1.0238	1.0210	1.0180
47.36	1.0325	1.0290	1.0255
53.07	1.0355	1.0317	1.0280
57.05	1.0369	1.0330	1.0291
72.67	1.0352	1.0308	1.0264
84.05	1.0249	1.0204	1.0158
89.65	1.0164	1.0119	1.0073
100.00	0.9947	0.9897	0.9850

Each value of the density given in the table is the mean of four determinations, agreeing to one part in ten thousand or better, made with four different pycnometers.

(1) We wish to express our appreciation to the Carbide and Carbon Chemicals Corp., 30 East 42nd Street, New York, N. Y., who kindly supplied the morpholine used in this study.

(2) Friedman, Barnard, Doe and Fox, *THIS JOURNAL*, **62**, 2366 (1940).

Friedman, Barnard, Doe and Fox² have determined the specific gravities of morpholine–water solutions at 20°. The densities at this temperature, found by interpolation in their data and conversion, fall exactly in line with our own. The variation of density with temperature is nearly exactly rectilinear for all of the solutions. We find that the density of pure morpholine at 20° is 0.9994 as given by Dermer and Dermer,³ not 1.0007 as quoted by Friedman, *et al.*, from Beilstein.

(3) Dermer and Dermer, *THIS JOURNAL*, **59**, 1148 (1937).

CHEMISTRY DEPARTMENT

OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE

STILLWATER, OKLAHOMA RECEIVED AUGUST 20, 1941

NEW COMPOUNDS

Bicyclohexylidene-2,2'-sulfone

Four grams (4.2 cc., 0.025 mole) of dicyclohexenyl (di- $\Delta^{1,1'}$ -cyclohexene)¹ and 10–12 g. (0.16–0.19 mole) of liquid sulfur dioxide plus a few crystals of hydroquinone² were mixed in a glass-lined steel pressure tube. The tube was sealed and heated in a steam jacket for twelve hours. It was then cooled to about 10°, opened, and the excess sulfur dioxide allowed to pass off. The residual liquid was diluted with 6 cc. of petroleum ether (90–100°), the solution cooled in dry-ice and the walls of the tube scratched to induce crystallization. The crystalline mass was kept at 0° for about one hour and then suction filtered. Recrystallization from petroleum ether yielded 2.3 g. of practically colorless crystals, m. p. 76–77°, yield 50%.

Anal. Calcd. for $C_{12}H_{18}S_2$: S, 14.16. Found: S, 14.02.

This procedure for synthesizing a sulfone is substantially that used by Eigenberger³ in preparing the cyclic sulfone from isoprene. Bicyclohexylidene sulfone, like other compounds of this type, decomposes rapidly at 110–120° to form sulfur dioxide and dicyclohexenyl.

(1) Gruber and Adams, *THIS JOURNAL*, **57**, 2555 (1935).

(2) Staudinger, *British Patent* 361,341 (1930).

(3) Eigenberger, *J. prakt. Chem.*, **127**, 307 (1930).

WESTERN RESERVE UNIVERSITY

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RECEIVED SEPTEMBER 18, 1941

Aminobenzene-(4-azo-1')-2'-methyl-4'-N-di-(β -hydroxyethyl)-aminobenzene

To a hydrochloric acid solution of 3-methyl-N-di-(β -hydroxyethyl)-aminobenzene prepared by the quantitative condensation of 1 mole of *m*-toluidine and 2 moles of liquid ethylene oxide under pressure, was added an equimolecular quantity of diazotized *p*-nitroaniline, prepared in the usual manner. A 20% solution of sodium acetate

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 $C_{17}H_{22}O_9N_4$: N, 17.82. Found: N, 17.60.

PFISTER CHEMICAL WORKS
RIDGEFIELD, NEW JERSEY

GEORGE SHULMAN

RECEIVED SEPTEMBER 12, 1941

Dimethylnepentylacetic 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 dimethylnepentylacetic acid was obtained, m. p. 44-45°.

2. **Dimethylnepentylacetic 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_D^{20} 1.4222 (Valentine), d_4^{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. **Dimethylnepentylacetamide** 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. **Dimethylnepentylacetanilide** 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).

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RECEIVED SEPTEMBER 2, 1941

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.

(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 Bigneaud, *ibid.*, **141**, 207 (1941).

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

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