

We estimate the over-all uncertainty in our combustion value as less than 0.025%, corresponding to a limit of 370 cal. for the molal heat of combustion. In this connection it is interesting to note that the earlier values of Stohmann,⁵ Roth and Müller,⁵ and Brüll⁶ now appear surprisingly good, as these exceed our present result by only 0.06, 0.05 and 0.03%, respectively. On the other hand, the value reported by Barker⁷ in 1925 is 0.45% higher than our result.

(5) Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, p. 1590, and 1st Ergänzungband, 1927, p. 867.

(6) L. Brüll, *Gazz. chim. ital.*, **65**, 19 (1935).

(7) M. F. Barker, *J. Phys. Chem.*, **29**, 1350 (1925).

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New Mercurials from 2,2-Diphenylpentene-4-ol-1 and Norbornylene

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2-Chloromercurimethyltetrahydrofuran and 2-chloromercurimethyl-5-methyltetrahydrofuran have been prepared by the mercuriation of pentene-4-ol-1 and of hexene-5-ol-2, respectively.¹ We wish to report the preparation of a mercurial, presumed to be of similar structure, by the mercuriation of 2,2-diphenylpentene-4-ol-1. The unsaturated alcohol was prepared by the lithium aluminum hydride reduction of allyldiphenylacetic acid. The same type of reduction to the unsaturated alcohol was observed in the reaction of lithium aluminum hydride with allylacetic acid.

From the mercuriation of norbornylene in methyl alcohol was obtained in good yield a mercurial whose analyses were in agreement with the expected product, 2-chloromercuri-3-methoxybicyclo[2,2,1]-heptane.

2-Chloromercurimethyl-4,4-diphenyltetrahydrofuran was not sufficiently soluble in dilute aqueous alkali to allow pharmacological evaluation. The pharmacological properties of 2-chloromercuri-3-methoxybicyclo[2,2,1]heptane were investigated briefly by Mr. P. A. Nuhfer of these laboratories. The LD₅₀ at 14 days following a single intravenous dose in rats was found to be 0.046 millimole/kg., 0.7 the LD₅₀ of mercurhydrin. The diuretic response in dogs in the six-hour period following the intravenous injection of 0.006 millimole/kg. was ca. 60% that produced by mercurhydrin at the same dose.

Experimental

Pentene-4-ol-1.—Reduction of allylacetic acid was accomplished by the procedure of Nystrom and Brown for ether-soluble acids.² The product obtained in 60% yield, b.p. 141–144°, n_D^{20} 1.4309, gave a positive test for unsaturation with bromine.

2,2-Diphenylpentene-4-ol-1.—The reduction was similar using 1.8 g. (0.05 mole) of lithium aluminum hydride and 5.0 g. (0.02 mole) of allyldiphenylacetic acid.³ The residue from concentration of the ethereal extracts was crystallized from Skelly B. The product weighed 4.6 g. (95%) and

(1) A. N. Nesmeyanov and I. F. Lutsenko, *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 296 (1943); *C. A.*, **38**, 5498 (1944).

(2) R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 2548 (1947).

(3) Generously supplied by General Mills, Inc., Minneapolis, Minn.

melted at 50–51°. *Anal.* Calcd. for C₁₇H₁₈O: C, 85.67; H, 7.61. Found: C, 85.68; H, 7.63.

2-Chloromercurimethyl-4,4-diphenyltetrahydrofuran.—A mixture of 2.4 g. (0.01 mole) of 2,2-diphenylpentene-4-ol-1, 3.2 g. (0.01 mole) of mercuric acetate and 200 ml. of methyl alcohol was allowed to stand at room temperature for 20 days, a length of time undoubtedly greater than necessary. The insoluble material was removed by filtration and a solution of 0.7 g. of sodium chloride in 10 ml. of water was added to the filtrate. The oil which separated was crystallized from methyl alcohol and then from isopropyl alcohol. The crystallized product weighed 2.3 g. (50%) and melted at 113–114°. *Anal.* Calcd. for C₁₇H₁₇OHgCl: Hg, 42.38; Cl, 7.49. Found: Hg, 42.13; Cl, 7.79.

2-Chloromercuri-3-methoxybicyclo[2,2,1]heptane.—To 4.7 g. (0.05 mole) of bicyclo[2,2,1]heptene (norbornylene)⁴ in 50 ml. of methyl alcohol was added a mixture of 15.9 g. (0.05 mole) of mercuric acetate and 50 ml. of methyl alcohol. After the mixture had stood for two days at room temperature, the insoluble material was removed by filtration and a solution of 3.0 g. of sodium chloride in 20 ml. of water was added to the filtrate. After 20 hours, the solid was collected and crystallized from methyl alcohol. The crystallized product weighed 8.8 g. (50%) and melted at 124–125°. Recrystallization from ethyl alcohol raised the melting point to 125–125.5°. *Anal.* Calcd. for C₈H₁₃OHgCl: Hg, 55.52; Cl, 9.81. Found: Hg, 55.32; Cl, 10.12.

(4) Generously supplied by Universal Oil Products Company, Riverside, Ill.

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High Molecular Weight Alkyl Amine Nitrites and Hydrohalides¹

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Diisopropylammonium nitrite has attained some importance as a water-soluble corrosion inhibitor, but it seems to show insignificant lubricating oil solubility. It was considered probable that the higher homologs might also possess corrosion inhibiting properties and significant lubricating oil solubility, and perhaps, greater stability and heat resistance. Several high molecular weight dialkylammonium nitrites were prepared by the addition of concentrated sulfuric acid to a cold mixture consisting of the secondary amine, sodium nitrite, chloroform and/or methanol, and a small amount of water. This method is similar to that of Wachter and Stillman² for preparing lower molecular weight amine nitrites. Other procedures are described in the literature.^{3–5} Several hydrohalides of didodecylamine were also prepared by treating the amine with the appropriate acid.

Didodecylammonium Nitrite.—Didodecylamine⁶ (25 g.), purified according to Hoerr, Harwood and Ralston,⁷ was dissolved in chloroform-methanol (1:1). After cooling to 0°, finely powdered sodium nitrite (15 g.) dissolved in 500 ml. of methanol (containing about 7 ml. of water) was added. Concentrated sulfuric acid was then added dropwise with stirring over a period of 1.5 hours until a pH of 6 was reached. The reaction mixture was filtered at room temperature and the filtrate evaporated under reduced pressure. The residue was purified by dissolving (at 25–30°)

(1) The opinions or assertions contained in this paper are the author's and are not to be construed as official or reflecting the views of the Department of the Navy.

(2) U. S. Patent 2,419,327 of April 22, 1947.

(3) Van der Zande, *Rec. trav. chim.*, **8**, 205 (1889).

(4) Neogi, *J. Chem. Soc.*, **99**, 1252, 1598 (1911).

(5) Wolfe and Temple, *THIS JOURNAL*, **70**, 1414 (1948).

(6) Obtained from Armour and Company.

(7) Hoerr, Harwood and Ralston, *J. Org. Chem.*, **9**, 201 (1944).