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 Brüll[6] 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 Barker[7] in 1925 is 0.45% higher than our result.

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[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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RECEIVED DECEMBER 1, 1950

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

BY R. L. ROWLAND

2-Chloromercurimethyltetrahydrofuran and 2-chloromercurimethyl - 5 - methyltetrahydrofuran have been prepared by the mercuration 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 mercuration 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 mercuration 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 LD$_{50}$ at 14 days following a single intravenous dose in rats was found to be 0.046 millimole/kg., 0.7 the LD$_{50}$ of mercuhydrin. 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 mercuhydrin 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°, $n^{16}\text{D}$ 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 melted at 50–51°. *Anal.* Calcd. for $C_{17}H_{18}O$: 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 $C_{17}H_{17}OHgCl$: 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]2-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 $C_8H_{13}OHgCl$: Hg, 55.52; Cl, 9.81. Found: Hg, 55.32; Cl, 10.12.

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[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.

[4] Generously supplied by Universal Oil Products Company, Riverside, Ill.

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RECEIVED JANUARY 25, 1951

High Molecular Weight Alkyl Amine Nitrites and Hydrohalides[1]

BY VINCENT C. PETRILLO

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 Stillman[2] 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.—Didodecylamine[6] (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 *p*H 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°)

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[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).

in 2780 ml. of methanol–acetone (1:99). After filtration, the filtrate was cooled to about −60° in order to precipitate the amine nitrite. Further crystallizations from methanol-acetone (1:9; 2300 ml.) were carried out until a constant melting point was reached. Each time the product was washed with cold acetone, and dried in a vacuum desiccator. The final product (19.3 g., 68% yield) melted[8] with decomposition at 125.4–127.2°. Didodecylammonium nitrite is a white solid with a very slight odor, insoluble in water, soluble in methanol, chloroform and slightly soluble in acetone. It was stored in an amber-colored bottle, since discoloration developed on exposure to ordinary light.

Anal.[9] Calcd. for $C_{24}H_{52}N_2O_2$: C, 71.9; H, 13.1; N, 7.0. Found: C, 72.4; H, 12.9; N, 6.8.

Dioctadecylammonium Nitrite.—Prepared in a similar manner and crystallized as white, glistening leaflets from chloroform, yield 83%, m.p.[8] 114.5–114.7°, discoloring at 100°. It is soluble in chloroform and methanol but insoluble in water.

Anal.[9] Calcd. for $C_{36}H_{76}N_2O_2$: C, 76.0; H, 13.5; N, 4.9. Found: C, 76.9; H, 13.6; N, 5.6.

Attempted Synthesis of Di-*n*-hexylammonium Nitrite.—Di-*n*-hexylamine[10] (50 g.), purified by vacuum fractional distillation, was added to 100 ml. of methanol. Finely divided sodium nitrite (28 g.), dissolved in 900 ml. of methanol containing 10 ml. of water, was added. After cooling to about −10°, while stirring, concentrated sulfuric acid (7.46 ml.) was added dropwise. At the end of the reaction, acetone was added and the mixture filtered. The filtrate was evaporated under reduced pressure to a volume of about 300 ml., acetone (100 ml.) added, and the mixture filtered. A saturated aqueous solution of sodium nitrite was added slowly to the filtrate until the top layer separated out as a wax-like solid. The latter was filtered off and the residue pressed between filter papers. Crystallizations were made from pentane–acetone (23:2). The purified substance (30.6 g., 49%) was white and wax-like, soluble in methanol and acetone, insoluble in petroleum ether (b. range 30–60°), and in pentane.

Technical difficulties were encountered in analyzing this substance. It melted[8] with decomposition at 134.8–135.8°.

Didodecylamine Hydrochloride.—Didodecylamine (5 g.) was dissolved in 100 ml. of isopropyl alcohol, and then 1.22 ml. of concentrated hydrochloric acid added slowly, while stirring. The solution was evaporated almost to dryness under reduced pressure, and the residue recrystallized from isopropyl alcohol. The product (82%) showed shiny, white plates, and melted[8] with decomposition at 207.8–210.8° (literature value[11] m. 203–204°).

Anal.[9] Calcd. for $C_{24}H_{52}NCl$: C, 73.9; H, 12.9; N, 3.6. Found: C, 73.7; H, 13.5; N, 3.6.

Didodecylamine Hydroiodide.—To a solution of didodecylamine (5 g.) dissolved in 100 ml. of isopropyl alcohol, 2.68 ml. of hydriodic acid (45%) was added while cooling. The reaction mixture was filtered, and the residue washed with cold methanol until it became white. The hydroiodide (84%), a shiny, white, crystalline powder, melted[8] with decomposition at 232.8–234.0°.

Anal.[9] Calcd. for $C_{24}H_{52}NI$: C, 59.9; H, 10.9; N, 2.9. Found: C, 60.3; H, 11.2; N, 3.0.

Acknowledgment.—The author wishes to express his grateful appreciation for the coöperation of Dr. G. K. Holmes, Messrs. P. A. Gelber and J. H. Bowen, Jr., of the Aeronautical Materials Laboratory, and to the Department of the Navy for permission to publish this material.

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RECEIVED JANUARY 23, 1951

The Action of Sodium Hydride on Certain Aryl Bromides[1]

BY G. E. PHILBROOK, H. F. GOBER[2] AND C. L. HENRY[2]

The chemistry of sodium hydride has been reviewed by Hansley and Carlisle.[3] A re-examination of the literature to December, 1950, failed to disclose any report on the action of sodium hydride on aryl halides. Sodium hydride generally acts as a condensing agent on carbonyl compounds[3] and fails to show marked reducing properties. This paper reports the action of sodium hydride on bromobenzene, *o*-bromotoluene, *m*-bromotoluene, *p*-bromotoluene, 2-bromo-1,4-dimethylbenzene, 4-bromo-1,3-dimethylbenzene and 4-bromo-N,N-dimethylaniline.

The sodium hydride used was the 98% technical grade (Elchem. 704) from E. I. du Pont de Nemours and Co., Inc. The *m*-bromotoluene and 4-bromo-N,N-dimethylaniline were prepared by standard methods. The bromoxylenes were prepared by direct bromination of *p*-and *m*-xylene using iron as a carrier. The xylenes were purified by the method of Mair, *et al.*[4] The bromoxylenes were purified by repeated fractional crystallization from the melt. Physical constants: 2-bromo-1,4-dimethylbenzene, m.p. 9.0–10.0° (cor.), b.p. 205° (cor.) (760 mm.), n^{20}_{D} 1.5481, d^{20}_{20} 1.35026; 4-bromo-1,3-dimethylbenzene, m.p. −17.0 to −16.0° (cor.), b.p. 206° (cor.) (760 mm.), n^{20}_{D} 1.5481, d^{20}_{20} 1.34430.

The reactions were studied at the boiling points of the compounds employed except for bromobenzene which was studied at 180° and 1710 mm. pressure. The apparatus was constructed with ground joints sealed with sealing wax. Blank runs demonstrated the absence of moisture in the apparatus and reagents and the absence of leaks. The reactions were run in a 500-ml. three-necked flask equipped with a mercury-sealed mechanical stirrer and a short helix-packed column. The column prevented spray carry-over. The volatile products were led through a water condenser, a liquid receiver, an ice-cooled trap and a gasometer in that order. One gram mole of halide and hydride were used. The reaction period was 20 hours in all runs.

The hydrogen was collected over water and its volume measured directly. The residue in the flask was filtered with the exclusion of moisture and the solid residue was extracted with ether. The ether extract was combined with the liquid products and filtrate for analysis by fractional distillation in a low hold-up 20-plate column. The solid residue was analyzed for sodium hydride by titration with water and measurement of the volume of hydrogen evolved. The solution resulting from this determination was analyzed for bromide ion by the Volhard method.

These reactions give low conversion yields and low yields of hydrocarbons. For *m*-bromotoluene, *p*-bromotoluene, 2-bromo-1,4-dimethylbenzene and 4-bromo-N,N-dimethylaniline the conversions found were 19.5, 26.8, 6.5 and 32.2% respectively. The hydrocarbon produced in these cases accounts for approximately 50% of the reacting halide. In these cases the sodium bromide found accounts for 90% or more of the bromine in the reacting halide. The tars from these four compounds were found by sodium fusion to be practically free of bromine. *o*-Bromotoluene and 4-bromo-1,3-dimethylbenzene gave conversion yields of 5.8 and 5.9% and very low yields of

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(8) Bath was heated at a rate of about 10° per minute, and sealed melting point tube introduced into the bath when the temperature reached about 10° below that of the expected melting point. Final melting point was corrected.

(9) The author acknowledges the help of Dr. N. L. Drake, Chemistry Department, University of Maryland, for arranging for the analyses on the compounds reported herein.

(10) Obtained from Sharples Chemicals, Incorporated.

(11) Wibaut, Heiermann and Wegtendonk, *Rec. trav. chim.*, **57**, 456 (1938).

(1) This work was supported by a contract (N7-onr-351) with the Office of Naval Research.

(2) This paper is taken in part from theses submitted by H. F. Gober and C. L. Henry in partial fulfillment of the requirements for the degree of Master of Science.

(3) V. L. Hansley and P. J. Carlisle, *Chem. Eng. News*, Aug. 10, 1945, p. 1332.

(4) B. J. Mair, *et al.*, *J. Research Natl. Bur. Standards*, **37**, 229 (1946), RP1744.