The methyl and ethyl esters of 2,4-dinitrobenzenesulfenic acid have not so far been recorded, and were here prepared in somewhat unusual manner. On refluxing a solution of 2,4-dinitrobenzenesulfenyl chloride in absolute ethanol, a procedure similar to that by which Fries[4] obtained the methyl and ethyl esters derived from anthraquinone-1-sulfenyl chloride, the main product (*ca.* 80% yield) was the corresponding disulfide, while the ethyl sulfenate was obtained in less than 2% yield. On first warming the reagent in ethylene dibromide solution, however, and then adding excess absolute methanol or ethanol, the corresponding ester crystallized out rapidly and in good yield.

Experimental

2,4-Dinitrobenzenesulfenyl Chloride.—2,4-Dinitrothiophenol was prepared from 3 g. of 2,4-dinitrochlorobenzene according to Willgerodt[5] and the crude, once-precipitated product filtered and washed twice with water. The precipitate was dissolved in warm benzene, separated from any water, and the benzene removed, finally *in vacuo*. Carbon tetrachloride (40 ml.) was added and the suspension boiled gently under reflux while chlorine gas dried over sulfuric acid was bubbled through for two hours. The yellow precipitate formed was filtered off and the filtrate concentrated to 15 ml. to let the product crystallize; yield directly pure product 1.8 to 1.9 g. (52 to 55%, on dinitrochlorobenzene), m.p. 95–96° (cor.). The insoluble by-product was apparently mainly bis-(2,4-dinitrophenyl)-disulfide which was here not split by chlorinolysis.

Methyl 2,4-Dinitrobenzenesulfenate.—2,4-Dinitrobenzenesulfenyl chloride (500 mg.) dissolved in 2 ml. of ethylene dibromide was heated on the boiling water-bath for 30 minutes, taken off from the water-bath and 10 ml. of absolute methanol added with stirring. The product separated as fine canary-yellow needles within a few minutes; yield 310 mg. (63%), m.p. 124.5–125° not appreciably changed by recrystallization from methanol or acetic acid. Decomposition with evolution of gas set in on heating above the melting point. The crystallized product was sublimed at 100–110° and 0.04 mm. for analysis; m.p. 124.8–125.2° (cor.).

Anal. Calcd. for $C_7H_6O_5N_2S$: C, 36.83; H, 2.63; N, 12.17; S, 13.92. Found: C, 36.63; H, 2.50; N, 12.12; S, 13.62.

Ethyl 2,4-Dinitrobenzenesulfenate.—Prepared as above, the product was obtained as coarse orange-yellow needles, m.p. 124.5–125° (cor.) in 67% yield, and sublimed for analysis as before.

Anal. Calcd. for $C_8H_8O_5N_2S$: C, 39.35; H, 3.30; N, 11.47. Found: C, 39.37, 39.26; H, 3.39, 3.32; N, 11.42.

A mixture of the ethyl and methyl 2,4-dinitrobenzenesulfenates melted at 112–114°.

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[4] K. Fries, *Ber.*, **45**, 2966 (1912); K. Fries and G. Schürmann, *ibid.*, **52**, 2173 (1919).

[5] Willgerodt, *ibid.*, **17**, ref., 352 (1884).

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The Heat of Combustion of Biphenyl

BY GEORGE S. PARKS AND LELAND M. VAUGHAN

A new determination of the heat of combustion of biphenyl has seemed desirable in view of its importance in problems of thermodynamics and resonance.

Three samples of this hydrocarbon were burned in the present measurements. The first sample was a high-grade Eastman Kodak Co. material (m.p. 69.1°) which had been dried over anhydrous magnesium perchlorate in an evacuated desiccator for several weeks. For the second sample some of this material was recrystallized from pure benzene and then likewise dried in vacuum. The third sample was prepared with two recrystallizations from benzene, followed by heating for several hours in an electric oven at 100°. It was then cooled from the molten condition in a vacuum desiccator, where the resulting crystals were subsequently kept over the drying agent for at least a week. Four determinations were carried out on Sample 1 and three each on the other two samples.

These combustion measurements were made with the Parr "illium" bomb and the calorimetric procedures which have been fully described in earlier papers[1] from this Laboratory. They are based on Jessup's recent value of 26,419.4 international joules per gram mass for the standard benzoic acid.[2] In particular, it should be noted that the temperature changes in our present study were measured by a calibrated platinum resistance thermometer with a precision of better than 0.005%, whereas all earlier investigators on biphenyl utilized mercury-in-glass thermometers with ensuing uncertainties of 0.05% or more.

Our resulting thermochemical data are summarized in Table I. Under the symbols $-\Delta U/m$ and Δ appear the mean values for the combustions on the three biphenyl samples and the mean deviations of the individual combustions from these mean values. These data are expressed in terms of the defined calorie (4.184 absolute joules) and represent the values for the energy evolved in the isothermal bomb process per gram mass at 25°. The final mean for all three samples was then calculated per mole and corrected to the standard constant-volume process where the reactants and products are each at 1 atmosphere by means of the equations of Washburn.[3] The energy evolved in this hypothetical process is designated in the table of the symbol $-\Delta U_c$. From this quantity $-\Delta H_c$, the heat evolved in the isobaric process at 1 atm., was obtained by addition of the proper work term. Finally, $-\Delta H_f^0$, the heat of formation of biphenyl from gaseous hydrogen and graphitic carbon, was calculated from $-\Delta U_c$ by use of 68.3174 kcal. and 94.0518 kcal.[4] for the heats of formation of water and carbon dioxide, respectively.

TABLE I

THERMOCHEMICAL DATA FOR BIPHENYL AT 25°
(Mol. Wt., 154.200; Density, 1.17)

$-\Delta U/m$ and Δ, calories per gram	
Mean for Sample 1	9687.4 ± 1.5
Mean for Sample 2	9688.4 ± 0.3
Mean for Sample 3	9687.0 ± 0.6
Final mean	9687.6 ± 1.1
$-\Delta U_c$, kcal. per mole for 1 atm.	1491.82
$-\Delta H_c$, kcal. per mole for 1 atm.	1493.30
$-\Delta H_f^0$, kcal. per mole for 1 atm.	−23.10

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[1] J. W. Richardson and G. S. Parks, THIS JOURNAL, **61**, 3543 (1939); G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii and L. A. McClaine, *ibid.*, **68**, 2524 (1946).

[2] R. S. Jessup, *J. Research Natl. Bur. Standards*, **36**, 421 (1946).

[3] E. W. Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

[4] F. D. Rossini and co-workers, "Selected Values of Properties of Hydrocarbons," United States Government Printing Office, Washington, D. C., 1947, p. 156.

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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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°, $n^{16}\mathrm{D}$ 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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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).