through the experimental points. The value for the activity coefficient of potassium chlorate at 0.2 molal of Scatchard and co-workers[1a] from freezing point data is 0.665. Our values at 0.2 molal and 25° are 0.681 and 0.678 from equations (1) and (2), respectively. This difference is of the correct order of magnitude.

The values for the activity coefficients of sodium bromate and potassium chlorate at 0.2 molal from equation (1) are about 0.5% higher than those yielded by equation (2). This agreement is considered satisfactory.

The solubility of sodium bromate at 25° was determined after the method proposed by Scatchard.[1a] A mean value of 2.612 molal was found. The solubility calculated from the work by Ricci[7] is 2.614 molal. The two values are probably within experimental error of the two measurements.

The general trend of the activity coefficients with concentration can be shown by means of a graph of activity coefficients *vs.* molality. Such a graph is shown in Fig. 1.

Summary

The concentrations of isotonic solutions of sodium bromate–sodium chloride and potassium chlorate–sodium chloride were determined from about 0.2 molal to saturation.

The solubility of sodium bromate in water at 25° was measured.

From the observed molalities and ratios of the isotonic solutions the activity coefficients and osmotic coefficients were calculated by comparison with sodium chloride.

BLOOMINGTON, IND. RECEIVED APRIL 21, 1944

---

[7] Ricci, THIS JOURNAL, **56**, 303 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF EMORY UNIVERSITY]

The Addition of 4-Mercaptobiphenyl to a Series of 1-Olefins

BY CHARLES T. LESTER, GEORGE F. RODGERS[1] AND E. EMMET REID

The addition of mercaptans to olefins has been investigated in several different laboratories and its mechanism thoroughly discussed.[2] The additions reported have covered a wide range of both olefins and mercaptans. Most of the resulting sulfides have been low melting solids or liquids.

It seemed to us that, if a mercaptan were used which would give high melting sulfides, the sulfides might be of some interest as a means of identification of the olefins. We have found that 4-mercaptobiphenyl[3] gives high melting solids with styrene and olefins from 1-hexene through 1-heptadecene. All of these products are white crystals, easily purified. The identity of each sulfide has been established by a mixed melting point determination with the sulfide obtained by the reaction of mercaptobiphenyl with the corresponding alkyl bromide. The melting points were taken in duplicate in a Hershberg[4] apparatus[5] with a calibrated Anschütz thermometer. The rate of heating was regulated to produce an increase in temperature of one degree every three minutes. The melting points are recorded in Table I.

TABLE I

MELTING POINTS OF ALKYL BIPHENYL SULFIDES

1 Alkyl group	2 Prepared by addition, °C.	3 Prepared by alkylation, °C.	4 2 and 3 mixed, °C.
Hexyl	75.1–75.7	75.4–76.0	74.8–75.7
Heptyl	83.2–83.9	82.5–83.5	82.4–83.5
Octyl	81.8–82.4	82.3–82.9	81.8–82.6
Nonyl	88.4–88.9	88.2–88.7	87.7–88.7
Decyl	87.2–87.5	86.5–87.2	86.8–87.3
Undecyl	92.1–93.0	91.8–92.8	91.8–92.8
Dodecyl	91.1–91.6	91.2–91.7	91.0–91.5
Tridecyl	95.6–96.3	94.5–95.5	95.4–95.9
Tetradecyl	94.2–94.6	94.5–95.2	94.0–94.6
Pentadecyl	98.4–98.8	98.0–98.7	97.9–98.7
Hexadecyl	97.0–97.7	96.7–97.4	96.6–97.3
Heptadecyl	99.7–100.6	100.1–100.9	99.7–100.7
Phenylethyl	78.1–80.2	77.8–80.0	77.4–79.6

The close proximity of the melting points of the members of the series is disappointing. We had hoped these solids might serve as derivatives for the identification of the olefins.

In Table II are recorded mixed melting points of different members of the series. While a defi-

TABLE II

MIXED MELTING POINTS OF HOMOLOGOUS ALKYL BIPHENYL SULFIDES

	°C.
Hexyl and heptyl	74.6–77.0
Octyl and nonyl	79.3–82.8
Nonyl and decyl	83.0–85.4
Decyl and undecyl	87.0–88.5
Undecyl and dodecyl	87.7–89.0
Dodecyl and tridecyl	90.7–92.0
Tetradecyl and pentadecyl	92.0–94.4
Hexadecyl and heptadecyl	96.0–97.5

---

[1] Taken from the thesis submitted by George F. Rodgers in partial fulfillment of the requirements for a degree of Master of Science.

[2] (a) Posner, *Ber.*, **38**, 649 (1905); (b) Carothers, THIS JOURNAL, **55**, 2008 (1933); (c) Kharasch, Read and Mayo, *Chem. and Industry*, **57**, 752 (1938); (d) Jones and Reid, THIS JOURNAL, **60**, 2452 (1938); (e) Ipatieff, *et al.*, *ibid.*, **60**, 2737 (1938); **61**, 71 (1939).

[3] Gabriel and Deutsch, *Ber.*, **13**, 386–391 (1880).

[4] Hershberg, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 312 (1936).

[5] Loaned to us through the kindness of the Callaway Institute of LaGrange, Georgia.

nite depression is observable it appears that an attempted identification by the use of these solids might lead too frequently to inconclusive results.

All melting points reported are corrected.

Experimental

Preparation of Olefins.—The olefins were prepared by coupling allyl bromide with the Grignard reagent prepared from the appropriate alkyl bromide, following the procedure of Wilkinson.[6] The olefins were ultimately purified by fractionation through a total condensation partial take-off column packed with glass helices.[7] The fraction boiling at the point tabulated by Doss[8] was retained for use. The styrene used was Eastman White Label quality, used without further treatment.

Preparation of 4-Mercaptobiphenyl.—The mercaptobiphenyl was obtained by the reduction of 4-biphenylsulfonyl chloride, prepared from biphenyl by previously recorded procedures.[9] Since we found no adequate description of the preparation of the mercaptan the details follow. In a one-liter Claisen flask were placed 120 g. of mossy zinc, 200 cc. of water, 12 g. of mercuric chloride, and 6 cc. of concentrated hydrochloric acid. The mixture was allowed to stand for a few minutes and the supernatant liquid decanted. To the amalgamated zinc were added 30 g. of biphenylsulfonyl chloride and 200 cc. of concentrated hydrochloric acid. The Claisen flask was attached to a 2-liter flask filled with constant boiling hydrochloric acid, serving as a steam generator, and to a 2-liter distilling flask cooled with a stream of water, serving as a condenser. Both the steam generator and the Claisen flask were heated to vigorous boiling. In this way the mercaptan distilled over as rapidly as it was formed. When the condenser flask became filled the heating was discontinued, the mercaptobiphenyl was filtered from the acid solution, 10 cc. of concentrated hydrochloric acid was added to the filtrate and the latter was used to recharge the steam generator. This reduced greatly the amount of acid used and simplified the purification of the mercaptan. Without any purification save washing free of acid, a pale yellow crystal, m. p. 107–110°, was obtained; yield of crude mercaptan 13.5 g., 61%. We found this product entirely satisfactory for the addition reactions. On recrystallization from alcohol or acetone a white crystal, m. p. 111°, can be obtained.

The Preparation of Alkylbiphenyl Sulfides: (a) Alkylation of 4-Mercaptobiphenyl.—A mixture of 0.5 g. of pure alkyl bromide, a slight excess of theoretical mercaptobiphenyl, and 3 cc. of alcohol were placed in a test-tube. To this was added a slight molar excess of 1 *N* alcoholic potassium hydroxide. The tube was heated in a beaker of water on a steam-bath for six hours. At the end of this time 5 cc. of boiling water was added to the test-tube. This mixture was heated to boiling for a few minutes and then chilled with vigorous shaking in a stream of water. This produced fine crystals which were removed by filtration and recrystallized from aqueous alcohol twice. The melting points are recorded in Table I.

(b) **Addition of 4-Mercaptobiphenyl to Olefins.**—The olefin (0.5–1 cc.) and the mercaptan (0.5 g.) and a few crystals of benzoyl peroxide were sealed in a soft glass semi-micro test-tube. The tube was placed in a flask of nitrobenzene and the nitrobenzene boiled under reflux for ten hours. The tube was removed, cooled, broken, and extracted with ether. The ether solution was washed with 20% sodium hydroxide. The ether was removed under reduced pressure and the residue dissolved in a minimum of acetone. The sulfide was precipitated by the dropwise addition of water. Two crystallizations from acetone usually were sufficient to give white crystals with a sharp melting point.

Summary

1. A satisfactory synthesis of 4-mercaptobiphenyl is described.
2. A series of biphenylalkyl sulfides has been prepared (a) by the addition of the mercaptan to an olefin, (b) by the reaction of the mercaptan with an alkyl bromide.
3. The melting points of these sulfides are given.

EMORY UNIV., GA. RECEIVED JUNE 28, 1944

---

[6] Wilkinson, *J. Chem. Soc.*, 3057 (1931).

[7] Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

[8] Doss, "Physical Constants of the Hydrocarbons," fourth edition, The Texas Co., 1943.

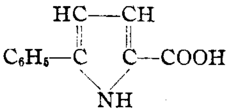
[9] Pollak, Heimberg-Krauss, Katscher and Lustig, *Monatsh.*, **55**, 358–378 (1930).

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

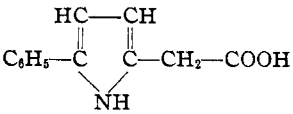
The Preparation of Certain Acids and Esters which Contain Phenylpyrryl Nuclei[1]

BY F. F. BLICKE, R. J. WARZYNSKI, J. A. FAUST AND J. E. GEARIEN

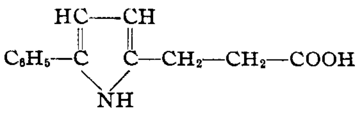
Some time ago we began a study of certain amines and amides which contained phenylpyrryl nuclei because it seemed that these substances might be of pharmacological interest. Among the intermediates required for the preparation of these compounds, which will be described in a later publication, were the following acids and their esters: 5-phenylpyrrole-2-carboxylic acid (I), 2-(5-phenyl)-pyrrylacetic acid (II), β-[2-(5-phenyl)-pyrryl]-propionic acid (III), the 1-methyl and 1-phenyl derivative of compound III, and 2-(4-phenyl)-pyrrylacetic acid (IV); 2-(3-



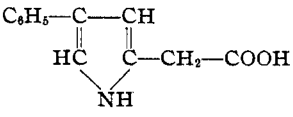
I



II



III



IV

---

[1] We wish to express our indebtedness to the Board of Governors of the Horace H. Rackham School of Graduate Studies, Parke, Davis and Company and Eli Lilly and Company for their joint support of this project. Original manuscript received January 28, 1944.