(6) Berzelius, J. J., *Ann. chim. phys.* (2), **26**, 43 (1824).
(7) Blumenthal, W. B., IND. ENG. CHEM., **40**, 510–12 (1948).
(8) Blumenthal, W. B., *J. Chem. Educ.*, **26**, 472 (1949).
(9) Blumenthal, W. B., U. S. Patent 2,492,959 (Jan. 3, 1950).
(10) *Ibid.*, 2,525,474 (Oct. 10, 1950).
(11) Blumenthal, W. B., and Leonard, C. S., "Investigation of Physiological and Therapeutic Properties of Zirconium Compounds," report to 12th Intern. Congr. Pure and Appl. Chem., N. Y., Sept. 13, 1951.
(12) Bradley, D. C., and Wardlaw, W. J., *J. Chem. Soc.*, **1951**, pp. 280–5.
(13) Bradt, W. E., and Linford, H. B., *Trans. Electrochem. Soc.*, **70**, 431–40 (1936).
(14) Chauvenet, E., *Ann. chim.*, **13**, 59–86 (1920).
(15) Chauvenet, E., *Compt. rend.*, **164**, 727 (1916).
(16) Clark, D., Powell, H. M., and Wells, A. F., *J. Chem. Soc.*, **1942**, p. 642.
(17) Connick, R. E., and McVey, W. H., *J. Am. Chem. Soc.*, **71**, 3182–92 (1949).
(18) Cronk, G. A., and Naumann, D. E., *J. Lab. Clin. Med.*, **37**, 909–13 (1951).
(19) Cumins, C. A., *Anal. Chem.*, **19**, 376 (1947).
(20) Falinski, Marie, *Ann. chim.*, **16**, 237–325 (1941).
(21) Fitzwilliam, H. J., Kaufman, A. R., and Squire, C. F., *J. Chem. Phys.*, **9**, 678–82 (1941).
(22) Gable, H. S., *J. Am. Chem. Soc.*, **53**, 1276–8 (1931).
(23) Glazebrook, R. T., Rosenhain, W., and Rodd, E. H., Brit. Patent 112,973 (Jan. 29, 1918).
(24) Golden, L. B., Lane, I. R., Jr., and Acherman, W. L., IND. ENG. CHEM., **44**, 1930–9 (1952).
(25) Hauser, O., *Z. anorg. Chem.*, **53**, 73–7 (1907).
(26) Hauser, O., and Herzfeld, H., *Ibid.*, **106**, 1 (1919).
(27) Hevesy, G. von, and Kimura, K., *J. Am. Chem. Soc.*, **47**, 2540 (1925).
(28) Hevesy, G. von, and Lögstrup, M., *Ber.*, **59B**, 1890–3 (1926).
(29) Hodgman, C. D., "Handbook of Chemistry and Physics," pp. 475, 481, 1901–2, Cleveland, Ohio, Chemical Rubber Publishing Co., 1945.
(30) Hückel, W., "Structural Chemistry of Inorganic Compounds," Vol. I, p. 133, New York, Elsevier Publishing Co., Inc., 1950.
(31) Hummers, W. S., Tyree, S. Y., Jr., and Yolles, S., *J. Am. Chem. Soc.*, **74**, 139–41 (1952).
(32) Kita, T., Tokumitsu, T., and Katsumurai, T., *Bull. Inst. Phys. Chem. Research (Tokyo) Chem. Ed.*, **23**, 239–40 (1944).
(33) Kolb, A., *Z. anorg. Chem.*, **83**, 146 (1913).
(34) Kroll, W., *Trans. Electrochem. Soc.*, **89**, 263–76 (1946).
(35) Larsen, E. M., and Gammill, A. M., *J. Am. Chem. Soc.*, **72**, 3615–19 (1950).
(36) Leuchs, K., Ger. Patent 295,246 (1915).
(37) Lilliendahl, W. C., and Rentschler, H. C., *J. Electrochem. Soc.*, **91**, 285–94 (1947).
(38) Maihle, A., and Gordon, F., *Bull. soc. chim.*, **29**, 101–6 (1921).
(39) Mathews, J. M., *J. Am Chem. Soc.*, **20**, 815–39 (1898).
(40) Mathieu, Jean-Paul, *Cahiers phys.*, **22**, 33–6 (1944).
(41) Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, pp. 138, 147, 148, 149, 150–1, 152, 154, 159, 161, 162, 163, New York, Longmans, Green and Co., 1930.
(42) Montignie, E., *Bull. soc. chim.*, **1946**, p. 176.
(43) Moser, L., and Ertl, K., *Z. anorg. allgem. Chem.*, **118**, 269–83 (1921).
(44) Natl. Bur. Standards (U. S.), *Circ.* **500**, 718–20 (1952).
(45) Pascal, P., "Traité de Chimie Minérale," Vol. V, p. 682, Paris, Masson et Cie, 1932.
(46) Peyronel, G., *Gazz. chim. ital.*, **72**, 89–93 (1942).
(47) Plotnikov, V. A., and Gutman, E. B., *J. Appl. Chem. (U.S.S.R.)*, **19**, 826–32 (1946).
(48) Rosenheim, A., and Frank, P., *Ber.*, **38**, 814 (1915).
(49) Ruff, O., and Wallstein, R., *Z. anorg. allgem. Chem.*, **128**, 96–116 (1923).
(50) Schumb, W. C., and Nolan, E. J., IND. ENG. CHEM., *Anal. Ed.*, **9**, 371–3 (1937).
(51) Sidgwick, N. V., "Chemical Elements and Their Compounds," pp. xxix, 628, 634, 654, Oxford, Clarendon Press, 1950.
(52) Sidgwick, N. V., "Electronic Theory of Valence," p. 274, London, Oxford University Press, 1932.
(53) Slotterbeck, O. C., U. S. Patent 2,408,101 (Sept. 24, 1946).
(54) Thomas, A. W., and Owens, H. S., *J. Am. Chem. Soc.*, **57**, 1825–8 (1935).
(55) *Ibid.*, pp. 2131–5.
(56) Troost, L., *Compt. rend.*, **61**, 109 (1865).
(57) Van Mater, H. L., U. S. Patent 2,482,816 (Sept. 27, 1946).
(58) Venable, F. P., and Deitz, R. O., *J. Elisha Mitchell Sci. Soc.*, **38**, 74–5 (1922).
(59) Venable, F. P., and Moehlmann, E. O., *J. Am. Chem. Soc.*, **44**, 1705–7 (1922).
(60) Wainer, E., U. S. Patent 2,507,128 (May 9, 1950).
(61) Wainer, E., and Van Mater, H. L., *Ibid.*, 2,452,616 (Nov. 2, 1948).
(62) Wedekind, E., and Willie, H., *Kolloid-Z.*, **34**, 283–9 (1924).
(63) Weiler, J. F., Titanium Alloy Manufacturing Division, National Lead Co., "Review of Literature on Zirconium and its Compounds as Catalysts" (Dec. 16, 1949).
(64) Weiser, H. B., "Inorganic Colloid Chemistry," Vol. II, pp. 264–6, New York, John Wiley & Sons, Inc., 1935.
(65) Wilhelm, H. A., and Walsh, K. A., U. S. Patent 2,602,725 (July 8, 1952).
(66) Young, Ralph C., *J. Am. Chem. Soc.*, **53**, 2148–53 (1931).
(67) Zabel, H. W., *Chem. Ind.*, **60**, No. 1, 37–9 (1947).

RECEIVED for review April 3, 1953. ACCEPTED December 9, 1953.

Phenylsodium Route to Phenylacetic Acid and Dimethyl Phenylmalonate

JOHN F. NOBIS AND LOUIS F. MOORMEIER

National Distillers Chemical Co.,
Division of National Distillers Products Corp., Cincinnati 37, Ohio

AS A result of an investigation concerned with the use of dispersed sodium in the preparation of organosodium compounds, new industrial routes to phenylacetic acid and dimethyl phenylmalonate have been developed. These syntheses appear to be more economical than existing routes and do not require the isolation of any intermediates. The starting materials for either end product are dispersed sodium and chlorobenzene. Thus, it has been found that the well-known reaction (*1, 2, 4, 5, 7–10*) between sodium and chlorobenzene, leading to phenylsodium, may be made essentially quantitative if freshly dispersed sodium is used. The reaction takes place best in a toluene medium, and when the formation of phenylsodium is complete the reaction mixture is refluxed for 2 hours. This reflux period serves to effect a metalation reaction between the phenylsodium and an equimolar portion of the toluene medium, thus forming benzylsodium. Rapid carbonation of the mixture on dry ice give essentially a theoretical yield of phenylacetic acid. Yields of 90 to 95% may be obtained by controlled addition of benzylsodium to ethyl ether saturated with carbon dioxide at −20° C. If gaseous carbon dioxide is added to the benzylsodium suspension over several hours at 30° to 40° C., there is obtained a 70% yield of phenylmalonic acid along with 25% of phenylacetic acid. Treatment of this reaction mixture with methanol and hydrogen chloride, followed by a 5-hour heating period, gives an easily separable mixture of dimethyl phenylmalonate and methyl phenylacetate. If it is desired, the free acids may be separated before esterification by their solubility differences in benzene and the phenylmalonic acid esterified separately. The yield of dimethyl phenylmalonate, based on phenylmalonic acid, is 94%, while the over-all yield based on chlorobenzene is 65%.

TABLE I. PHENYLSODIUM PREPARATIONS

(Maximum sodium particle size 35 μ, usually 10–15 μ; chlorobenzene diluted with equal weight of reaction medium; 5% of chlorobenzene charge added to initiate reaction)

Expt. No.	Reaction Medium	Sodium, Gram-Atoms	Chlorobenzene, Moles	Initiation Time, Min.	Chlorobenzene Addition Time, Min.	Carbonation Method	Yield of Benzoic Acid, %	Yield of Phenylacetic Acid, %	Special Procedure
1	Toluene	1.17	0.50	6	40	Gas	99.2	...	Carbonated at 0–20° C. for 25 min.
2	Desulfurized, dry toluene	2.30	1.0	1	33	Solid	96.1	...	.....
3	Toluene	1.17	0.60	20	30	Gas	...	42.5	Refluxed 2 hours before carbonation at 5–10° C. for 15 min.
4	Toluene	1.17	0.50	20	35	Gas	...	60.0	Refluxed 2 hours before carbonation at −20° to −30° C.; 23.9% phenylmalonic acid also formed
5	Toluene	1.17	0.50	20	35	Solid	...	99.5	Refluxed 2 hours before carbonation
6	90% Toluene–10% benzene	1.17	0.50	2	15	Solid	...	82.0	Chlorobenzene diluted 1/1 with benzene; refluxed 3 hours at 103° C. before carbonation
7	Toluene	1.15	0.50	2	25	Gas	...	92.0	Carbonated by addition of benzylsodium to ethyl ether saturated with CO_2 gas at −20° C.; gas passed through carbonation mixture during 45-min. addition period
8	*o*-Xylene	0.59	0.25	1	14	Solid	98.7	...	.....
9	Ethylbenzene	1.17	0.50	5	25	Solid	99.0	...	.....
10	*n*-Octane	1.17	0.50	5	70	Solid	100.0	...	Chlorobenzene not diluted
11	Iso-octane	2.30	0.95	5	25	Solid	99.1	...	Chlorobenzene diluted 1/1 with benzene; 2 ml. amyl alcohol in 5 ml. benzene added to initiate reaction
12	Benzene	2.30	1.0	1	33	Gas	99.4	...	50% Sodium dispersion prepared in toluene and transferred under nitrogen into benzene to form 15% dispersion; carbonated at 0–20° C. for 25 min.
13	Benzene	2.30	1.0	1	30	Solid	99.6	...	50% Sodium dispersion prepared in iso-octane and transferred under nitrogen into benzene to form 15% dispersion
14	*n*-Pentane	2.30	1.0	1	60	Gas	97.5	...	50% Sodium dispersion prepared in *n*-octane and transferred under nitrogen into *n*-pentane to form 15% dispersion; carbonated at 0–20° C. for 75 min.

PHENYLSODIUM AND PHENYLACETIC ACID

Although the preparation of phenylacetic acid by carbonation of benzylsodium has been described by a number of investigations (*2, 4, 5, 7–10*), this sodium route to phenylacetic acid has not been attractive commercially because of the difficulty of preparation of the intermediate organosodium compounds, the long reaction periods required, and the relatively low over-all yields. Benzylsodium has been previously prepared in moderate yields by metalation of toluene with either *n*-amylsodium or phenylsodium. Work in the laboratories of the National Distillers Chemical Co., however, has shown that phenylsodium may be rapidly and safely prepared in nearly theoretical yields from chlorobenzene and freshly dispersed sodium in toluene at 25° to 30° C. Benzylsodium may be formed in 95 to 99% yields by refluxing the resulting phenylsodium suspension for 2 hours. The sodium is completely transferred to an equimolar portion of the toluene by a metalation reaction.

$$\underset{\text{chlorobenzene}}{C_6H_5Cl} + 2Na \rightarrow \underset{\text{phenylsodium}}{C_6H_5Na} + NaCl$$

$$\underset{\text{phenylsodium}}{C_6H_5Na} + \underset{\text{toluene}}{C_6H_5CH_3} \rightarrow \underset{\text{benzylsodium}}{C_6H_5CH_2Na} + \underset{\text{benzene}}{C_6H_6}$$

Carbonation of this reaction mixture on solid carbon dioxide gives 95 to 99% yields of phenylacetic acid.

$$C_6H_5CH_2Na + CO_2 \rightarrow \underset{\text{sodium phenylacetate}}{C_6H_5CH_2COONa}$$

$$C_6H_5CH_2COONa + HCl \rightarrow \underset{\text{phenylacetic acid}}{C_6H_5CH_2COOH} + NaCl$$

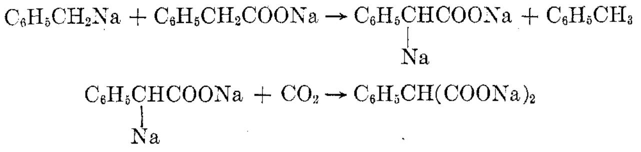
In connection with this study of the phenylacetic acid synthesis, it was necessary to make a thorough examination of the conditions for the preparation of phenylsodium. Although phenylsodium may be prepared in high yields in a variety of aliphatic and aromatic hydrocarbons (Table I), it is best prepared in toluene when the desired end product is phenylacetic acid or phenylmalonic acid. It may be noted from the results of experiment 6 (Table I) that the hydrocarbon to be metalated must be present in considerable excess, since 10% benzene in toluene reduced the yield of benzylsodium and phenylacetic acid. A number of other factors are also of importance. Thus, it is essential to have present a 12 to 17% excess of sodium, an active freshly prepared sodium dispersion containing 15 to 20% sodium by weight, a sodium particle size average below 25 microns, and an inert atmosphere. Although it has been previously reported (*8, 11, 12*) that high speed stirring is essential for maximum yields of organosodium compounds, no particular advantages were noted in this work when high speed stirring was used during the chlorobenzene-sodium reaction.

Preparation of the 15% sodium dispersion may be accomplished in either of two ways, by formation of a 50:50 dispersion of sodium and medium in small equipment, followed by transfer to a large reactor for dilution to the 15% sodium concentration (by weight), or by dispersion of the sodium at the desired 15% sodium concentration in a flask large enough to handle subsequent reactions. When preparations of phenylsodium are to be made in media boiling below the melting point of sodium (97.5° C.), the sodium must be dispersed first in a higher boiling media at the 50% concentration. The dispersion may then be diluted with the desired media in the same reactor or after transfer to the larger reactor, as in the second method. An inert atmosphere must be maintained at all times to avoid deactivation of the sodium or hydrolysis of the phenylsodium. The laboratory equipment used in these studies for the preparation of the sodium dispersion and the phenylsodium has been described (*3*).

The initiation of the reaction between chlorobenzene and dispersed sodium is almost always immediate (1 to 5 minutes), if care is taken in fulfilling the required conditions. The reaction is characterized by an increasingly rapid temperature rise, accompanied by the appearance of black phenylsodium. Preparation of 1 mole of phenylsodium in a benzenoid hydrocarbon medium is usually accomplished in about 1/2 hour. The data listed in Table I show that the reaction between chlorobenzene and sodium is more rapid in benzenoid hydrocarbons than in aliphatic hydrocarbons. However, the addition of a small amount of benzenoid hydrocarbon to preparations of phenylsodium in aliphatic hydrocarbons often increases the rate of reaction between the sodium and chlorobenzene (compare experiment 11, Table I, with experiments 10 and 14).

The yield of phenylsodium may be determined by conversion to benzoic acid. This is accomplished either by pouring the reaction mixture on powdered dry ice or by admitting gaseous carbon dioxide to the reaction flask held at an internal temperature of 0° to 20° C. Gaseous carbonation at higher temperatures gives lower yields of benzoic acid because of the reaction of phenylsodium with the product sodium benzoate, thus forming benzophenone and a trace of triphenyl carbinol by continued reaction. An estimate of the amount of phenylsodium present in the reaction mixture may be obtained by titration of an aliquot portion for sodium chloride. The molar amount of sodium chloride is equal to the phenylsodium.

PHENYLACETIC ACID. In order to obtain maximum yields of phenylacetic acid from the benzylsodium, a large excess of carbon dioxide is essential. Experiments 3, 4, and 5, listed in Table I, show the effect of various carbonation temperatures and carbonation techniques on the yield of this acid. At temperatures above −70° C., metalation of the sodium phenylacetate by the unreacted benzylsodium becomes a serious side reaction if gaseous carbon dioxide is added to benzylsodium. Disodium phenylmalonate is then formed in the presence of excess benzylsodium (*4, 5*).



$$C_6H_5CH_2Na + C_6H_5CH_2COONa \rightarrow C_6H_5\underset{\displaystyle Na}{\underset{|}{C}}HCOONa + C_6H_5CH_3$$

$$C_6H_5\underset{\displaystyle Na}{\underset{|}{C}}HCOONa + CO_2 \rightarrow C_6H_5CH(COONa)_2$$

Although carbonation of benzylsodium on dry ice gives 95 to 99% yields of phenylacetic acid, this method of carbonation is not the most economical and may present certain plant handling problems. As a result, other carbonation techniques were evaluated, and it was found that gaseous carbonation could be used if a reverse addition of reactants was employed.

The equipment illustrated in Figure 1 was arranged so that the benzylsodium suspension could be added dropwise to ethyl ether saturated with gaseous carbon dioxide at −20° C. A slow stream of carbon dioxide was passed through the carbonation mixture during the addition to ensure the presence of an excess of the gas. The benzylsodium had previously been transferred under nitrogen to the top flask, *I*. The use of Dispersator stirring kept the benzylsodium from settling to the bottom and thus allowed a controlled addition rate (45 minutes per mole) through the 6-mm. stopcock. It is essential to pass a slow stream of nitrogen over the dropping tip to prevent carbonation at the end of this tube, *J*. Dispersator stirring in the carbonation vessel served to give excellent mixing of gas, liquid, and solid. The yield of phenylacetic acid prepared in this manner ranged from 90 to 95%.

PHENYLMALONIC ACID

Since phenylmalonic acid was known to be present as a by-product during certain gaseous carbonation experiments designed to produce phenylacetic acid, it seemed to be of considerable interest to investigate a slow carbonation at or above room temperature in order to prepare exclusively phenylmalonic acid. Accordingly, a series of experiments were performed, and it was found that at carbonation temperatures above 30° C. phenylmalonic acid was produced in about 70% yield with an accompanying 25% yield of phenylacetic acid. A previously reported (*9*) attempt to control the benzylsodium carbonation reaction gave a 43% yield of phenylmalonic acid and a 10% yield of phenylacetic acid. The failure of this earlier attempt to produce better yields may have been due to the method used for preparation of the benzylsodium. The phenylsodium was initially prepared from amylsodium and benzene. The benzylsodium was then prepared by the addition of toluene to the benzene suspension of phenylsodium. As indicated earlier in this paper, the presence of even a relatively small amount of benzene reduced the yield of benzylsodium.

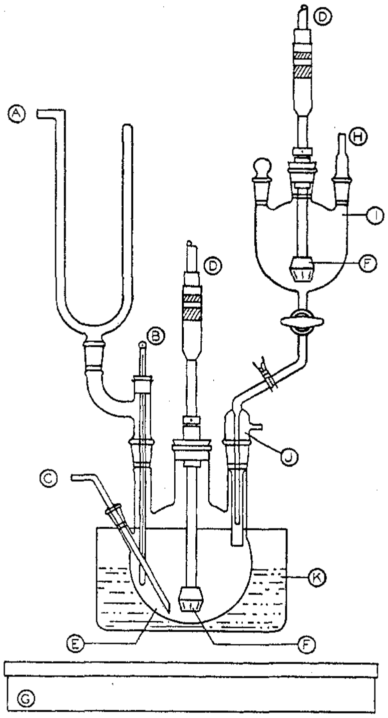


Figure 1. Gaseous Carbonation Unit

A. Condenser, dry ice–methanol with 29/42 joint
B. Low temperature thermometer
C. Carbon dioxide inlet, 10/30 joint
D. Flexible stirrer coupling, attached to Haskins V.B.-2 and operated at low speeds
E. Carbonation flask 3-liter, three-necked with one 29/42 and one 35/40 side neck
F. Dispersator
G. Safety pan
H. Nitrogen inlet, 24/40
I. Benzylsodium flask, 1-liter, three-necked, with 45/50 center neck
J. Addition tube, 35/40 with nitrogen inlet to prevent carbonation at dropping tip
K. Dry ice–methanol bath

Table II illustrates the various effects due to changes in rate and temperature of carbonation of benzylsodium. It is apparent from the phenylacetic acid experiments (Table I) that as the temperature of carbonation of benzylsodium nears −70° C. the rate at which benzylsodium metalates the initially formed sodium phenylacetate approaches zero. Thus, carbonation of benzylsodium on dry ice gives 97% phenylacetic acid; gaseous carbonation at −20° C. gives 60% phenylacetic acid and 40% phenylmalonic acid. Since slow gaseous carbonation of benzylsodium at 30° C. (experiment 1, Table II) gave a 67% yield of phenylmalonic acid, it was hoped that a higher carbonation temperature might increase this yield. However, it was found that the yield of phenylmalonic acid could not be increased much above 70% regardless of carbonation temperature or rate. It was evident, though, that carbonation at high temperatures decreased the yield of phenylacetic acid, and thus all of the sodium and chlorobenzene could not be accounted for in isolated products. This apparent anomaly may be explained if a continued metalation reaction is assumed. Thus, if the alpha carbon is metalated further by unreacted benzylsodium in the presence of carbon dioxide, there would be produced the trisodium salt of phenyltricarboxymethane, $C_6H_5C(COONa)_3$. On neutralization with hydrochloric acid, the phenyltricarboxymethane might be expected to decarboxylate to phenylmalonic acid. Actually, in the experiments where a low accountable yield was obtained, considerable carbon dioxide was evolved during neutralization, even though the temperature was below 5° C.

In experiments 2, 3, and 5, Table II, approximately one half of the theoretical quantity of carbon dioxide was added rapidly to the benzylsodium suspension. After this addition, the reac-

TABLE II. RELATION OF CARBONATION TEMPERATURES TO YIELD OF PHENYLMALONIC ACID

(Reaction of 2.3 gram-atoms sodium with 1.0 mole chlorobenzene)

Expt. No.	Reflux Time, Min.	Carbonation		Benzylacetic Acid Yield, %	Phenylmalonic Acid Yield, %	Total Yield[a]	Special Procedure
		Temp., ° C.	Time, min.				
1	60	30	195	16.3	67.3	83.6[b]	.....
2	120	40	30	16.3	67.6	83.9	Approx. one half theoretical quantity CO_2 added in 20 min.; carbonation completed rapidly in 10 min.
3	60	40	540	13.5	69.9	83.4[b]	.....
4	120	30–60	90	27.5	67.3	94.8	Approx. one half theoretical quantity CO_2 added in 10 min.; stirred 30 min.; carbonation completed slowly in 80 min.
5	190	40–50	80	10.9	71.3	82.2	Approx. one half theoretical quantity CO_2 added in 30 min.; stirred 30 min. at 80–90° C.; carbonation completed slowly in 50 min.
6	120	50–60	240	5.2	72.1	77.3	.....
7	120	70–80	240	3.7	74.0	77.7	.....
8	120	85–110	120	9.0	63.4	72.4	.....
9	120	90–100	240	5.1	69.8	74.9	.....

[a] Based on chlorobenzene.
[b] Attributed to only 1-hour reflux.

tion mixture was allowed to stir for a 30- to 60-minute period. It was hoped that this procedure would serve to convert one half of the benzylsodium to sodium phenylacetate and the stirring period that followed would allow for metalation of the sodium phenylacetate by the remainder of the benzylsodium. Although this technique did not increase the yield of phenylmalonic acid as was expected, carbonation time was reduced and a tendency toward better product balances was noted.

DIMETHYL PHENYLMALONATE

Dimethyl phenylmalonate may be prepared, in yields up to 94%, by heating a benzene-methanolic solution of phenylmalonic acid and hydrogen chloride at 60° C. for 5 hours. The results, listed in Table III, show that a large excess of methanol (at least 10 to 1) is required for maximum yields. The use of concentrated sulfuric acid as an esterification catalyst was also investigated. Yields of ester up to 87% are possible if a 3 to 1 ratio of sulfuric acid to phenylmalonic acid is used. It is also important to allow the reaction mixture (phenylmalonic acid, methanol, sulfuric acid, benzene) to stir at room temperature for several hours before raising the temperature to 65° C. Reaction temperatures below 65° C. give slightly lower yields of ester. It may be possible to reduce the extended reaction time, but this possibility was not investigated.

It is also possible to prepare dimethyl phenylmalonate in a stepwise, one-reactor process, from sodium, chlorobenzene, toluene, carbon dioxide, methanol, and hydrogen chloride. After carbonation of benzylsodium at 30° to 50° C., the reaction mixture containing disodium phenylmalonate, sodium phenylacetate, and a small amount of free sodium is treated with a large excess of methanol (10 parts methanol to 1 part phenylmalonic acid). When this addition is complete, anhydrous hydrogen chloride may be passed through the resulting thick slurry in order to neutralize the sodium salts of the organic acids and the sodium methoxide formed from the free sodium. When neutralization is complete, the reaction mixture is heated at 60° C. for 5 hours. Anhydrous hydrogen chloride is passed through the solution during the entire heating period. At the end of this time, the addition of water will serve to remove the sodium chloride (from original chlorobenzene reaction, from excess sodium, and from esterification). The benzene (present as a result of the phenylsodium metalation reaction) and toluene can be removed by flash distillation. Dimethyl phenylmalonate (boiling point, 148° to 152° C./10 mm. and melting point, 47° to 49° C.) and methyl phenylacetate (boiling point 100° to 110° C./10 mm.) are then separated by vacuum distillation.

The diethyl ester of phenylmalonic acid may be prepared (85% yield) by treatment of the acid with absolute ethyl alcohol and anhydrous hydrogen chloride in benzene solution for 5 hours at 60° C.

EXPERIMENTAL

SODIUM DISPERSIONS. Sodium dispersions are stable suspensions of sodium in inert hydrocarbon media with particles ranging in size from submicron to 25 microns in diameter. Methods of preparation, properties, and uses of 50% sodium dispersions are covered in recent publications (*3*, *13*). A procedure similar to that described in those reports for the preparation of 50% sodium dispersions has been used in this research to prepare the 15% sodium dispersions. The equipment used for this preparation

TABLE III. PREPARATION OF DIMETHYL PHENYLMALONATE

Expt. No.	Phenylmalonic Acid, Moles	Absolute Methanol[a], Moles	Temp., ° C.	Time, Min.	Dimethyl Phenylmalonate Yield, %	Methyl Phenylacetate Yield, %	Total Yield	Special Procedure
1	0.11	1.85	60	330	93.1	...	93.1	Anhydrous HCl bubbled through reaction mixture during heating
2	0.50	4.95	60	270	35.4	52.3	87.7	Anhydrous HCl bubbled through reaction mixture during heating; low yield due to a decrease in the methanol–phenylmalonic acid ratio from the usual 10/1 to 5/1
3	0.28	5.56	60	300	94.4	...	94.4	Anhydrous HCl bubbled through reaction mixture during heating
4	0.33	6.66	60	300	33.1	45.3	78.4	Toluene used with methanol; anhydrous HCl bubbled through reaction mixture during heating
5	0.33	6.66	60	1080[b]	80.0	19.7	99.7	1 Mole H_2SO_4 catalyst
6	0.33	6.66	65	1020[c]	86.6	6.6	93.2	1 Mole H_2SO_4 catalyst
7	0.20	8.0	60	1320[d]	85.9	...	85.9	0.6 Mole H_2SO_4 catalyst; increase in methanol–phenylmalonic acid ratio from the usual 10/1 to 20/1

[a] Reagent grade benzene, twice the volume of methanol, also used.
[b] Includes initial 2-hour stirring at 39° C.
[c] Included initial 1-hour stirring at 31° C.
[d] Includes initial 2-hour stirring at 31° C.

has been described (*3*). Where the dispersion is to be used shortly after preparation, the incorporation of a dispersing agent is usually unnecessary, although small amounts (0.24 to 0.50%) of materials such as oleic acid, Dimer acid (Emery Industries, Cincinnati, Ohio), or higher fatty alcohols (*13*) may be used without interference in subsequent reactions. The 15% dispersions settle much more rapidly than the 50% dispersions, but the sodium particles do not coalesce and easily redisperse on gentle agitation.

When preparations of phenylsodium are to be made in benzene or pentane, it is best to disperse the sodium at the 50% concentration in iso-octane or *n*-octane in a 500-ml. creased flask and then transfer, by means of vacuum, to a larger flask for dilution with the lower boiling media. It is best to use a dispersing aid with the sodium in this case. A small amount of Dimer acid (0.25 to 0.50% by weight of sodium) should be incorporated into the sodium-octane mixture.

PHENYLSODIUM. To 54 grams (2.23 gram-atoms) of finely dispersed sodium (nitrogen atmosphere, less than 25-micron particle size average) suspended in 275 grams of toluene in a three-necked flask at 25° to 30° C. is added, with gentle agitation, only 10 to 15 ml. of a mixture of 112.6 grams (1 mole) of chlorobenzene and 100 grams of toluene. Initiation of reaction usually occurs 1 to 5 minutes after addition of the first 10 to 25 ml. of the chlorobenzene-toluene mixture and is characterized by an increasingly rapid temperature rise, plus the appearance of the black phenylsodium particles. In no case should additional chlorobenzene be added until the initial exothermic reaction has occurred and been brought under control. As the temperature approaches 30° to 40° C., a cooling bath (around −20° C.) should be raised around the reaction flask. The internal temperature should never be allowed to exceed 40° C. In cases where no reaction is observed for 20 minutes, 2 to 4 ml. of amyl alcohol may be added to initiate reaction. Cooling is needed immediately after this addition, since the reaction may start rapidly. If, inadvertently, large amounts of unreacted chlorobenzene and sodium are brought together without reaction, the flask should be cooled rapidly to a low temperature. The reaction mixture may be then rendered comparatively safe by dilution with several volumes of mineral oil or kerosene and the resulting mixture should be taken promptly to a burning area for disposal.

After the reaction has started and has been brought under control, the addition of the chlorobenzene-toluene mixture is resumed. The rate of addition and the position of the cooling bath can now be regulated so that the formation of the phenylsodium will be complete in 20 to 30 minutes. The exothermic reaction usually ceases abruptly with the addition of the last few drops of chlorobenzene, and the internal temperature drops to the bath temperature.

Chlorobenzene and sodium do not react as rapidly at 25° to 30° C. in aliphatic hydrocarbons as in benzenoid hydrocarbons. The chlorobenzene addition time must be longer in these media in order to ensure reaction of the chlorobenzene as added. Thus, if the addition rate is too rapid in aliphatic media, reaction may continue for some time after addition is complete.

ANALYSIS FOR PHENYLSODIUM AS BENZOIC ACID. Gaseous carbon dioxide is introduced into the suspension of phenylsodium, as prepared above, if a check on the yield of phenylsodium is desired. The reaction mixture is held between 0° and 20° C. to avoid side reactions. If the Dispersator is used, the gas may be passed over the surface and carbonation completed in 15 to 30 minutes, depending on the efficiency of cooling used. If a sweep stirrer or other similar type of agitation is used, it is best to admit the carbon dioxide beneath the surface of the reaction mixture. Carbonation may also be effected by slowly pouring the reaction mixture on a large excess of dry ice.

The reaction mixture after carbonation is treated with water in order to decompose the excess sodium. It is recommended that a hydrolysis unit (Figure 2), similar to one previously described (*6*), be used for this purpose. Neutralization of the water layer gives 115 to 121 grams (94 to 99%) of benzoic acid, melting at 120° to 122° C.

BENZYLSODIUM AND PHENYLACETIC ACID. After the toluene suspension of phenylsodium is refluxed for 2 hours, carbonation is effected by carefully pouring the reaction mixture on solid carbon dioxide. The excess sodium in the carbonation mixture is decomposed in the hydrolysis apparatus illustrated in Figure 2.

Approximately 200 ml. of water is placed in flask *I* and heated to boiling with steam passing through the trap, *F*, before entering the flask. The steam flow is adjusted until the whole apparatus is filled with steam, and water is condensing on the copper coil, *A*. The sodium phenylacetate reaction slurry is added cautiously in small portions to the steam-water mixture through the addition funnel, *G*. Any excess sodium may cause tiny sparks to appear in the flask, but this phenomenon constitutes no hazard if the air has been completely displaced by steam. After addition of all the reaction mixture, the addition funnel, reaction flask, stirrer, and thermometer are rinsed with toluene and the mixture added to flask *I*. The Dispersator and reaction flask may be treated with live steam to decompose any sodium particles remaining. After the reaction mixture is cooled, the aqueous layer is drawn off through stopcock *J*, and the phenylacetic acid is precipitated by acidification. The yield is 130 to 135 grams (95 to 99%) of phenylacetic acid, melting at 72° to 74° C.

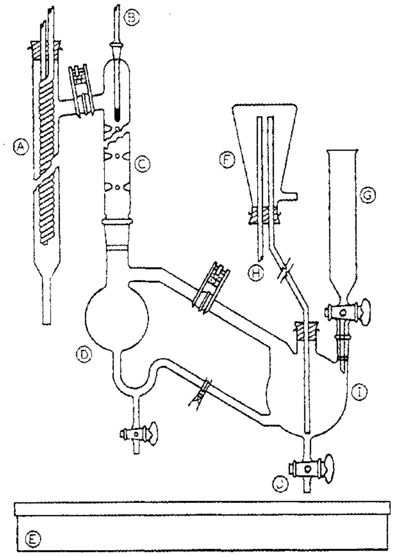


Figure 2. Drowning Unit for Sodium Reaction Mixtures

A. **Vertical copper-coil condenser**
B. **Thermometer**
C. **Vigreux column, 20 inches long × 1.25 inch diameter**
D. **500-Ml., round-bottomed flask with 35/40 joint**
E. **Safety pan**
F. **Water trap for steam, inverted 500-ml. suction flask**
G. **Addition funnel with 6-mm. stopcock**
H. **Steam inlet**
I. **1-Liter, modified round-bottomed flask**
J. **Drainage stopcock, 6 mm.**

PHENYLMALONIC ACID. In all of the experiments listed in Table II, gaseous carbon dioxide was admitted to the suspension of benzylsodium through an addition funnel. The rate of carbonation at the surface of the reaction mixture could then be controlled by the rate of stirring (Dispersator type) and flow of carbon dioxide. When carbonation was complete, the resulting slurry was added to water and steam in the decomposition apparatus illustrated in Figure 1. When the excess sodium had been destroyed, the water layer was separated and treated with decolorizing carbon. The resulting solution of salts was cooled to 0° C. and neutralized with hydrochloric acid. In the presence of phenylacetic acid and sodium chloride, large amounts of phenylmalonic acid are carried down. The phenylacetic acid may be removed by extraction with benzene. Phenylmalonic acid can be separated from the water and salt by extraction with ethyl ether. Evaporation of the ether under vacuum gives fairly pure phenylmalonic acid (melting point, 145° to 148° C.). Since phenylmalonic acid readily decarboxylates to phenylacetic acid, care must be taken in both neutralization and evaporation steps to avoid temperatures above 30° C.

ACKNOWLEDGMENT

The authors wish to express their thanks to V. L. Hansley for his suggestions and assistance during the course of this work.

LITERATURE CITED

(1) Bockmuhl, M., and Erhart, G., U. S. Patent 2,012,372 (1935).

(2) Bryce-Smith, D., and Turner, F., *J. Chem. Soc.*, **1950**, 1975.

(3) Frampton, O., and Nobis, J. F., IND. ENG. CHEM., **45**, 404 (1953).

(4) Gilman, H., and Pacevitz, H. A., *J. Am. Chem. Soc.*, **62**, 1301 (1940).

(5) Gilman, H., Pacevitz, H. A., and Baine, O., *Ibid.*, **62**, 1514 (1940).

(6) Hansley, V. L., IND. ENG. CHEM., **39**, 55 (1947).

(7) *Ibid.*, **43**, 1759 (1951).

(8) Letsinger, R. L., *J. Am. Chem. Soc.*, **70**, 406 (1948).

(9) Morton, A. A., Fallwell, F., and Palmer, L., *Ibid.*, **60**, 1426 (1938).

(10) Morton, A. A., and Heckenbleikner, I., *Ibid.*, **58**, 2599 (1936).

(11) Morton, A. A., and Redman, L. M., IND. ENG. CHEM., **40**, 1190 (1948).

(12) Morton, A. A., and Wohlers, H. C., *J. Am. Chem. Soc.*, **69**, 167 (1947).

(13) U. S. Industrial Chemicals Co., Division of National Distillers Products Corp., New York, N. Y., "Sodium Dispersions" (1953).

RECEIVED for review October 23, 1953. ACCEPTED December 2, 1953.
Presented before the Division of Organic Chemistry at the 124th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill.

Properties of Fluorine-Containing Diesters

CORRELATIVE STUDIES

ROBERT FILLER[1], JOSEPH F. O'BRIEN, JACK V. FENNER, AND J. C. MOSTELLER
Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio

MURRAY HAUPTSCHEIN AND CHARLES S. STOKES
Research Institute of Temple University, Philadelphia, Pa.

THE properties of the fluorocarbons have been studied by several investigators, notably Grosse and Cady (*8*), Fowler and coworkers (*5*), and Haszeldine and Smith (*10*). The relation of structure to physical properties of fluorine-containing compounds other than the fluorocarbons has also been examined to a considerable extent. For example, Kauck and Diesslin (*13*) and more recently Hendricks (*12*) have discussed the properties of the perfluorinated acids and a few of their derivatives, while Nodiff, Grosse, and Hauptschein (*16*) have described the physical properties of perfluoroalkyl halides and dihalides and compared them with analogous hydrogen-containing compounds. Murphy and Zisman (*15*) have discussed some theoretical aspects pertaining to properties of fluorinated compounds.

In the course of studying several series of new fluorinated diesters (*3, 4, 11, 17*), a number of physical properties were determined and some interesting relationships were noted. The types of compounds considered in this paper include dicarboxylic acid esters, glycol esters, and the various analogous compounds derived from fluorine-containing mono- and dicarboxylic acids, alcohols, and glycols.

I. Dicarboxylic Acid Esters
    A. $C_nH_{2n+1}O_2C(CH_2)_xCO_2C_nH_{2n+1}$
    B. $C_nH_{2n+1}O_2C(CF_2)_xCO_2C_nH_{2n+1}$
    C. $C_nF_{2n+1}CH_2O_2C(CH_2)_xCO_2CH_2C_nF_{2n+1}$
    D. $C_nF_{2n+1}CH_2O_2C(CF_2)_xCO_2CH_2C_nF_{2n+1}$

II. Glycol Esters
    A. $C_nH_{2n+1}CO_2(CH_2)_xO_2CC_nH_{2n+1}$
    B. $C_nH_{2n+1}CO_2CH_2(CF_2)_xCH_2O_2CC_nH_{2n+1}$
    C. $C_nF_{2n+1}CO_2(CH_2)_xO_2CC_nF_{2n+1}$
    D. $C_nF_{2n+1}CO_2CH_2(CF_2)_xCH_2O_2CC_nF_{2n+1}$

It was of interest to compare the properties of the fluorinated diesters with those of their hydrogen-containing analogs, to note the effects of structural changes, and to determine the influence of CF_2 groups on these properties. Information concerning methods of preparation and properties of individual compounds may be found in earlier papers (*3, 4, 11, 17*).

BOILING POINT

The fluorinated diesters exhibit boiling points which are lower than those of the corresponding unfluorinated compounds. This may be attributed to the weaker cohesive forces between perfluoromethylene groups as compared with those between the analogous methylene groups. The boiling point generally decreases as the fluorine content of the diester increases. This is illustrated in Table I, using specific examples of the general types listed above. Four sets of isomers are listed.

In the unfluorinated series, the dicarboxylic acid ester (IA) boils at a higher temperature than the isomeric glycol ester (IIA);

TABLE I. COMPARATIVE BOILING POINTS OF FLUORINATED AND UNFLUORINATED DIESTERS

Type	Compound	B.P., ° C.	Pressure, Mm. Hg	Fluorine, %
IA	$C_4H_9O_2C(CH_2)_4CO_2C_4H_9$	130	1.0	0
IB	$C_4H_9O_2C(CF_2)_4CO_2C_4H_9$	105	1.0	37.8
IC	$C_3H_7CH_2O_2C(CH_2)_4CO_2CH_2C_3F_7$	100	1.0	52.2
ID	$C_3F_7CH_2O_2C(CF_2)_4CO_2CH_2C_3F_7$	80	1.0	63.9
IIA	$C_3F_7CO_2(CH_2)_6O_2CC_3H_7$	122	1.0	0
IIB	$C_3H_7CO_2CH_2(CF_2)_4CH_2O_2CC_3H_7$	112	1.0	37.8
IIC	$C_3F_7CO_2(CH_2)_6O_2CC_3H_7$	96	1.0	52.2
IID	$C_3F_7CO_2CH_2(CF_2)_4CH_2O_2CC_3F_7$	85	1.5	63.9

---

[1] Present address, Department of Chemistry, Ohio Wesleyan University, Delaware, Ohio.