129–132° (40 mm.), n^{20}_D 1.4763–1.4769. A higher boiling product, b. p. 185° (5 mm.), n^{20}_D 1.4923–1.4924, proved to be di-(γ-morpholinopropyl)-amine; yield 36 g. (10%).

γ-Diethylaminopropylamine.—In a similar manner 4 moles of β-diethylaminopropionitrile which had been saturated with ammonia at 7 atmospheres pressure (by attaching an ammonia tank to one of the leads of the bomb and shaking it for one-half hour) was reduced to give a 72% yield of γ-diethylaminopropylamine; b. p. 167.5–167.7° (735 mm.), n^{20}_D 1.4419, d^{20} 0.8254, picrate m. p. 193.5–194.0°, phenylurea derivative m. p. 66–67°, and phenylthiourea derivative m. p. 116.5–117.0°. The mixed melting point of this last substance with the phenylthiourea derivative obtained from γ-diethylaminopropylamine made by the phthalimide synthesis according to Shriner and Hickey[7] was 116.0–116.5°. Molecular refraction calculated, 41.89; observed, 41.71. The higher boiling fraction, 150–155° (15 mm.), 25 g. (5% yield), is di-(γ-diethylaminopropyl)-amine, n^{20}_D 1.4541; equivalent weight calculated, 81.3; found, 81.0; picrate m. p. 153.4°.

N^1-(γ-Morpholinopropyl)-sulfanilamide.—To a solution of 28.2 g. (0.2 mole) of γ-morpholinopropylamine in 150 cc. of acetone which was contained in a separatory funnel over a solution of 33 g. of potassium carbonate dissolved in 30 cc. of water was added a total of 50 g. (0.21 mole) of *p*-acetylaminobenzenesulfonyl chloride with intermittent shaking over a period of one and one-half hours. Upon completion of the addition, a white crystalline solid separated which was filtered and washed three times with 50-cc. portions of water to remove potassium carbonate and potassium chloride. The filtrate was concentrated to 100 ml. and on cooling a second crop was collected. These crystals were dried and recrystallized from acetone–water mixture to give 62.5 g. of product which melted sharply at 97°; yield 91.5%. The acetyl derivative was hydrolyzed by heating on the steam-bath with 20% hydrochloric acid for three and one-half hours. The cold hydrolysis mixture was carefully neutralized to the equivalence point with sodium hydroxide and cooled in the refrigerator overnight. The crystallized cake was recrystallized from an acetone–water mixture to give a total of 39.8 g. of N^1-(γ-morpholinopropyl)-sulfanilamide, m. p. 47–50°. On recrystallizing from acetone–ether an anhydrous crystalline product, 33.4 g., was obtained which melted at 94.5–95°; yield 70%.

TABLE III

SULFANILAMIDE DERIVATIVES

-N^1-Sulfanilamide	M. p., °C.	Yield, %	Acetyl derivative, m. p., °C.
γ-Diethylaminopropyl-	109–110	20	[a]
γ-Dipropylaminopropyl-	98–98.5	57	[a]
γ-Dibutylaminopropyl- (as hydrochloride)	110–115	53.5	[a]
γ-Piperidinopropyl-	105.5–106	63.5	109–111
γ-Morpholinopropyl-	94.5–95	79	97–98
Di-(γ-diethylaminopropyl)- (as hydrochloride)	195–197	66.5	83–85
Di-(γ-piperidinopropyl)-	74–76	71	[a]

[a] The acetyl derivatives were obtained only as thick viscous sirups which would not crystallize and were so hydrolyzed without purification.

Summary

The reaction of acrylonitrile with ammonia, primary amines, secondary amines, and amino alcohols and the reduction of the resultant beta-substituted propionitriles to the very useful γ-aminopropylamines has been studied. Twenty of these compounds are described.

γ-Aminobutyronitriles have been prepared from γ-chlorobutyronitrile and reduced to the corresponding δ-aminobutylamines.

The reduction of these basically substituted nitriles not only gives the primary amines but also basically substituted secondary amines in yields of 5 to 30%. Eleven new compounds of this type were isolated.

The procedures described offer a convenient and general method for the synthesis of γ- and δ-basically substituted alkylamines in good yields.

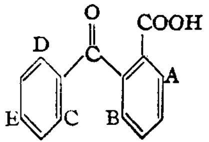
STATE COLLEGE, PA. RECEIVED OCTOBER 18, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Normal and Pseudo Esters of 2-Benzoylbenzoic Acid Types. II

BY MELVIN S. NEWMAN AND BRADLEY T. LORD[1]

A study of the acid catalyzed esterification of substituted 2-benzoylbenzoic acids was undertaken in order to find out more about the structural features which determine whether normal or pseudo esters will form. In a previous publication[2] we outlined a program for the preparation of all of the substituted 2-benzoylbenzoic acids having one or more methyl groups at positions A, B, C, and D of I.



I

We have modified our program to include methyl groups at E because the compounds containing groups at C and/or D are easier to make if they also have a group at E. The presence of a group at E would not be expected to affect any results greatly.

Furthermore, by having groups at E, the preparation of the required compounds becomes more instructive because it is possible to compare the behavior of substituted phthalic anhydrides in the Friedel–Crafts and Grignard condensations. For example, it is possible to compare the behavior of 3-methylphthalic anhydride with benzene in the Friedel–Crafts reaction and with phenylmagnesium bromide since a mixture of the same keto-acids is obtained in each case.[3] It is not possible to compare these reactions using toluene and *o*-tolylmagnesium bromide because toluene

---

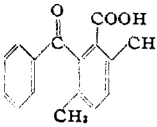
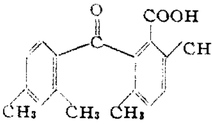
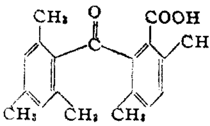
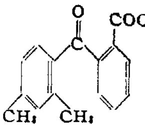
(1) The material in this paper was taken from the Thesis of B. T. L., presented to the Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, August, 1943.

(2) Newman and McCleary, THIS JOURNAL, 63, 1537 (1941).

(3) Newman and McCleary, *ibid.*, 63, 1542 (1941).

TABLE I

PROPERTIES AND YIELDS OF METHYL ESTERS

Compound		II	III	IV	V
Formula					
M. p., °C. (cor.)		182.6–183.2	165.2–165.8	174.8–175.8	141.8–142.2
A (Fischer)	% yield	85	34	78	90
	m. p., °C.	112.0–113.8	61.0–63.0	110.0–111.0	64.0–65.5
B (Normal)	% yield	87	83	92	95
	m. p., °C.	50.4–51.6	62.6–63.6	110.8–111.8	64.6–65.6
C (Pseudo)	% yield	79	75	60	71
	m. p., °C.	113.6–114.4	86.8–87.2	110.0–111.0	62.2–63.2

In all cases the per cent. yield means the yield of crystalline product with the indicated melting point. The total yield of ester in each case was well over 90%. Compound IV: all esters identical. Compound V: ester C different from ester A and B, the mixed melting point being 41–52°

TABLE II

ANALYSIS OF METHYL ESTERS

Compound	Calcd. C	Calcd. H	Found C	Found H
Methyl 2-	76.1	6.0	76.0	6.4^n
(2,4-dimethyl-			76.1	6.1^n
benzoyl)-	$C_{17}H_{16}O_3$		76.2	6.3^p
benzoate			76.0	6.2^p
Methyl	76.1	6.0	76.1	5.8^n
2-benzoyl-3,6-			75.9	5.7^n
dimethyl-	$C_{17}H_{16}O_3$		76.3	6.1^p
benzoate			76.1	6.1^p
Methyl 2-(2,4-	77.0	6.8	77.1	6.7^n
dimethylbenzoyl)-			77.0	6.5^n
3,6-dimethyl	$C_{19}H_{20}O_3$		77.2	6.8^p
benzoate			77.0	6.8^p
Methyl 2-(2,4,6-	77.4	7.1	77.3	6.9^n
trimethylbenzoyl)-	$C_{20}H_{22}O_3$		77.1	7.2^n
3,6-dimethyl-				
benzoate				

n analyses marked ^{n} are for normal esters. *p* analyses marked ^{p} are for pseudo esters. Microanalyses by J. E. Varner and Jean Anderson.

orients para. With *m*-xylene and 2,4-dimethylphenylmagnesium bromide, however, the same products are formed and comparison is possible. The same is true with mesitylene and 2,4-6-trimethylphenylmagnesium bromide.

In this paper we report on the esterification of 3,6-dimethyl-2-benzoylbenzoic acid, II, 3,6-dimethyl-2-(2,4-dimethylbenzoyl)-benzoic acid, III, 3,6 - dimethyl - 2 - (2,4,6 - trimethylbenzoyl) - benzoic acid, IV, and 2-(2,4-dimethylbenzoyl)-benzoic acid, V. Of these acids, II, III, and V could be converted into two different methyl esters. As in the previous cases[2] the esters formed with diazomethane were assumed to be normal esters whereas those formed by treatment of the acid chlorides with methanol and pyridine were assigned the cyclic structure. We have confirmed this assignement of structure by ultraviolet absorption spectra studies.[4] Acid IV gave only the normal ester under all conditions of esterification tried, as was the case previously with 2 - (2,4,6 - trimethylbenzoyl) - benzoic acid.[2] The behavior of the acids II, III, IV, and V on Fischer–Speier esterification and the properties of the various esters are indicated in Table I.

The preparation of acids II, III, and IV is described in the following publication.[5]

Experimental

2-(2,4-Dimethylbenzoyl)-benzoic Acid, V.—This acid was prepared by the condensation of phthalic anhydride with *m*-xylene[6] in sulfur-free benzene. The yield of crude acid, m. p. 139–141°, was 95%. On recrystallization from benzene, the pure acid V, m. p. 141.8–142.2° cor., was obtained.

Preparation of Methyl Esters.—The esters in columns A, B, and C of Table I were made by (A) refluxing the acid in absolute methanol containing dry hydrogen chloride, (B) treatment of the acid with ethereal diazomethane, and (C) treatment of the acid chloride with methanol and pyridine. The esters were isolated as described in detail in previous work.[2] The analyses of the new esters formed are given in Table II.

COLUMBUS, OHIO RECEIVED JANUARY 10, 1944

---

[4] Brode, Newman and Lord, to be reported.

[5] Newman and Lord, THIS JOURNAL, **66**, 733 (1944).

[6] The authors are indebted to Professor C. E. Boord for a gift of purified *m*-xylene from the American Petroleum Institute Project at the Ohio State University.