With respect to the metalation of benzotrifluoride,[1] the electrophilic interpretation would be that the start of the process is the attraction of the metal component for electrons. If these electrons are found on one of the three fluorine atoms, coördination occurs and the succeeding migrations of proton and metal lead to ortho substitution; if the electrons are found on the aromatic nucleus, direct substitution occurs at the meta position because of the influence of the trifluoromethyl group. These places of high electron density are attacked in the ratio of about five to one. The initial force that operates is the same for either position. The subsequent steps are conditioned to the spatial and other influences present.

With respect to the velocity of the substitution a complete statement is possible only after each reaction has been given much more study than has so far been made. The electrophilic viewpoint would cause the prediction, however, that the position of any phenoxide ion would not be the same when substitution is carried out in aqueous solution as it would be in a non-dissociating solvent because in the former medium, the phenoxide ion would act independently while in the latter it would be under the influence of the strong electron-attracting influence of the adjacent cation and the system would act as an ion-pair. Metalation should be and is retarded. This problem has already been considered in a previous publication[9] from this laboratory. Many of the other systems are also liable to have unusual rates because of coördination which may influence the reaction intermolecularly as well as by the intramolecular process pictured above. Considerable work on the influence of coördination has already been carried out in this Laboratory and will be published in the future. In general, however, the order of reactivity of groups, as far as substitution in the ortho position is concerned, has long been known to be subject to special influences, such as steric effects and the many variations of chelation, under which might be included the pseudo ring systems under discussion.

Finally, attention is called to the fact that the electrophilic viewpoint explains correctly the metalation in the para position of cumene and biphenyl, where cöordination has no influence, and the reaction with cumene is admitted by Roberts and Curtin[1] to be incapable of explanation by the nucleophilic viewpoint. In general, the electrophilic interpretation can be readily used to explain the phenomena so far known without contradicting the nucleophilic viewpoint for reactions of alkali metal salts in aqueous media where the cation influence is removed by solvation.

CHEMICAL LABORATORY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
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[9] Morton and Letsinger, THIS JOURNAL, **67**, 1537 (1945).

Preparation of Ethyl β-Benzylaminopropionate and Benzyl-di-(β-carbethoxyethyl)-amine

BY GILBERT STORK AND S. M. MCELVAIN

In a recent note describing the hydrogenolysis of ethyl β-benzylaminopropionate (I), Mattocks and Hartung[1] used the reaction of benzylamine with ethyl β-bromopropionate to prepare this secondary aminoester; the same reactants had been used earlier in this Laboratory for the preparation of I, which had served as an intermediate in the preparation of benzyl-di-(β-carbethoxyethyl)-amine[2] (II). We now are able to report much simpler methods of preparation of I and II. In connection with a study of certain 4-piperidones,[3] we investigated the preparation of II, the precursor of 1-benzyl-4-piperidone, by the addition of benzylamine to ethyl acrylate and found that this addition could readily be controlled to produce either the secondary aminoester (I), or the tertiary aminoester (II). The former was obtained in 87% yield by the interaction of benzylamine and one equivalent of ethyl acrylate in alcohol solution for twenty-four hours at room temperature. The aminoester II was obtained in 84% yield by allowing benzylamine to react with a 20% excess of two equivalents of ethyl acrylate for four to five days at room temperature. The practically exclusive formation of I from these reactants is in decided contrast to the addition of ammonia[3a] and methylamine to acrylic esters; the latter amine, for example, with an equivalent of methyl acrylate gives a 31% yield of the secondary amine together with a 37% yield of tertiary amine.[4] This peculiar property of benzylamine to give more of the product that results from the reaction of only one of its amino hydrogens also has been used to advantage in the Mannich reaction.[5]

Experimental

Ethyl β-Benzylaminopropionate (I).—Benzylamine was prepared by the method of Winans[6]: the catalytic reduction of benzaldehyde in the presence of alcoholic ammonia with Raney nickel as a catalyst. In the handling of benzylamine it is essential to exclude carbon dioxide as it rapidly forms an addition compound with benzylamine.

To a solution of 58 g. of benzylamine in 400 ml. of absolute alcohol was added 50 g. of commercial ethyl acrylate. There was very little evolution of heat. The resulting alcoholic solution showed a slight pink coloration at first, but after standing for twenty-four hours at room temperature it became orange-red. After this time, the alcohol was removed under reduced pressure and the residue distilled; 90 g. (87%) of ethyl β-benzylaminopropionate[2] (I) was collected as a colorless liquid, b. p. 133–135° (2 mm.); $n^{20}D$ 1.5060. This ester turns brown on long standing.

Benzyl-di-(β-carbethoxyethyl)-amine (II).—In the preparation of this compound, it is necessary to use at least 20% excess of two equivalents of ethyl acrylate

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[1] Mattocks and Hartung, THIS JOURNAL, **68**, 2108 (1946).

[2] Thayer and McElvain, *ibid.*, **49**, 2862 (1927).

[3] (a) McElvain and Stork, *ibid.*, **68**, 1049 (1946); (b) *ibid.*, **68**, 1053 (1946).

[4] Morsch, *Monatsh.*, **63**, 220 (1933).

[5] Mannich and Hieronimus, *Ber.*, **75**, 49 (1942).

[6] Winans, THIS JOURNAL, **61**, 3566 (1939).

to prevent the formation of a considerable amount of the secondary amine (I). For instance, with only a 5% excess of ethyl acrylate 29% of I and 55% of II were obtained.

To a solution of 171 g. of benzylamine in 300 ml. of absolute alcohol was added 384 g. of ethyl acrylate. The flask was cooled in ice water to absorb the heat initially produced. The solution then was allowed to stand at room temperature for four to five days. The color of the solution, which was light yellow at first, gradually became dark red. The alcohol was removed on the steam-bath and the low boiling material was distilled under a water pump vacuum. Fractionation of the remaining material gave 40 g. (12%) of I and 410 g. (84%) of benzyl-di-(β-carbethoxyethyl)-amine[2] (II), b. p. 165-172° (1 mm.); n^{23}D 1.4941.

The hydrobromide of II was prepared by adding the base to an excess of alcoholic hydrogen bromide and removing the solvent. An oily residue, which crystallized on rubbing with ether, was obtained. Recrystallization from an alcohol-ether mixture gave pure benzyl-di-(β-carbethoxyethyl)-amine hydrobromide, m. p. 69-71°.

Anal. Calcd. for $C_{17}H_{26}O_4NBr$: Br, 20.6. Found: Br, 20.9.

LABORATORY OF ORGANIC CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
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Esters of 2-Methyl-2,4-pentanediol[1]

BY PHILIP F. TRYON

2-Methyl-2,4-pentanediol recently has become a cheap commercial compound. The sole ester derivative reported in the literature, though, is the diacetate, prepared from acetic anhydride at reflux.[2] An interest in the esters as solvents and plasticizers led us to the preparation of some aliphatic monoesters and diesters, and a dibenzoate. The data on these compounds are given in Table I. The structures of the monoesters were not determined.

TABLE I

ESTERS OF 2-METHYL-2,4-PENTANEDIOL

Ester	Method	Conversion, %	Boiling range °C.	Mm.	d^{20}_{20}	n^{20}D	Sapn. equiv. Calcd.	Sapn. equiv. Found
Monoacetate	A	43	99-100	20	0.970	1.426	160	164
Monopropionate	A	36	109-112	20	.962	1.429	174	165
Monobutyrate	A	52	119-121	20	.948	1.431	188	180
Monoisobutyrate	B	60	107-110	20	.938	1.428	188	190
Monostearate	B	72	Liquid[b]		.897	1.451	370	390[c]
Diacetate[a]	B	57	104-105	20	.998	1.422	101	104
Dipropionate	A	42	123-124	20	.974	1.426	115	116
Diisobutyrate	B	60	111-114	10	.941	1.424	129	130
Dicaproate	B	38	125-126	3	.930	1.437	157	160
Distearate	B	78	Liquid[b]		.910	1.458	311	318[d]
Dibenzoate	B	50	160-170	3	1.108	1.537	163	158

[a] Literature: b. p. 208-210°, 95° at 12 mm. (reference 2). [b] Not distilled. [c] Corrected for stearic acid content of 0.5%, calculated from acid no. of 1.0. [d] Corrected for stearic acid content of 3.0%, calculated from acid no. of 6.3.

The esterifications of 2-methyl-2,4-pentanediol were accomplished by reaction either with an acid anhydride, or with an acid chloride and pyridine. The esters were all liquids, soluble in organic solvents, and insoluble in water. The lower aliphatic esters, which were mobile, colorless liquids with an ester-like odor, were isolated by fractional distillation under vacuum; the stearates decomposed on attempted distillation under vacuum, at 200°. The sensitivity of 2-methyl-2,4-pentanediol to dehydration under acid conditions was evident from attempted esterifications with stearic acid at 200°, with benzoyl chloride in the absence of pyridine, and with phthalic, succinic, and maleic anhydrides at 100°. In all of these attempts considerable amounts of water-of-dehydration were split out in the reaction mixtures. It is already known that 2-methyl-2,4-pentanediol is readily dehydrated with such catalysts as hydrobromic acid, aniline hydrobromide, and aqueous solutions of inorganic salts.[3]

Experimental

The glass columns used in all of the fractionations were of the total reflux, variable take-off type, operated adiabatically at a reflux ratio of 10:1. The 120 × 1.2 cm. packed sections were filled with single-turn glass helices.

Commercial 2-methyl-2,4-pentanediol was purified by fractionation; the fraction of b. p. 101° at 20 mm. was used.

The propionic anhydride, butyric anhydride, succinic anhydride, isobutyryl chloride, and benzoyl chloride were used as received from Eastman Kodak Co. Caproyl chloride, as received from Eastman Kodak Co., gave poor yields of the diester; it was purified of low-boilers by fractionation, and the 148-150° fraction was used. The acetic anhydride and acetyl chloride were 95% reagent-grade, the phthalic anhydride and maleic anhydride were commercial-grade, and the pyridine was U. S. P. The stearic acid was Armour and Co. Neo-Fat No. 1-65, neutralization equivalent 282; the stearoyl chloride was from Emery Industries, molecular weight about 288.

Method A.—Monoacetate, monopropionate, monobutyrate, and dipropionate: A mixture of 0.50 mole of 2-methyl-2,4-pentanediol and the equivalent quantity of acid anhydride for mono- or diester formation was heated under a reflux condenser, over a period of three hours, from 120-140°. The entire reaction mixture then was fractionated.

With the monoacetate, however, the reaction mixture first was neutralized with a solution of 0.50 equivalent of potassium carbonate in 50 ml. of water. The ester layer

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[1] Prepared for the 1945 Meeting-in-Print of the Division of Organic Chemistry, and presented before the Wabash Valley Section, American Chemical Society.

[2] Franke, *Monatsh.*, **22**, 1071 (1901).

[3] Kyriakides, THIS JOURNAL, **36**, 994 (1914); Bachman and Goebel, *ibid.*, **64**, 787 (1942); Ipatieff and Pines, *ibid.*, **67**, 1200 (1945).