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).

was washed with dilute sodium carbonate solution, then with dilute sodium sulfate solution, dried over sodium sulfate, and fractionated.

Method B.—Monoisobutyrate, monostearate, diacetate, diisobutyrate, dicaproate, distearate, and dibenzoate: The reaction vessel was a three-necked flask fitted with a thermometer, dropping funnel, and mercury-sealed stirrer. For monoester formation, 0.50 mole of the acid chloride was added dropwise, over a period of one hour at a reaction temperature of 25–35°, to a stirred, cooled mixture of 0.50 mole of 2-methyl-2,4-pentanediol (10% excess for the monoisobutyrate, and 100% excess for the monostearate) and 0.50 mole of pyridine. For diester formation the quantities of reactants, in the same procedure, were 0.50 mole of 2-methyl-2,4-pentanediol and 1.05–1.10 moles of both the acid chloride and pyridine. After the acid chloride addition, the mixture was allowed to react further for either eighteen hours at room-temperature or one hour at 60–70°. The final reaction mixture was treated with 100 ml. of water, and the two layers were separated. The ester layer was washed with dilute sodium carbonate or sodium hydroxide solution, then with dilute sodium sulfate solution, dried over sodium sulfate, and fractionated.

With the mono- and distearate, ether and some alcohol were added to the ester layer to facilitate the difficult phase-separation after washing. The ether was evaporated from the dried solution, and the ester was heated up to 110° at 2 mm. before analysis. In attempted distillations of the mono- and distearate, a portion was heated in a Claisen flask to 200° at 2 mm. Decomposition was evident with both esters; it then was found that the acid no. of the samples had risen to about 54.

Unsuccessful Esterification Reactions with 2-Methyl-2,4-pentanediol.—In several unsuccessful attempts at esterification, evidence was obtained of preferential dehydration of the 2-methyl-2,4-pentanediol, which presumably was catalyzed by the acidic nature of the reaction mixtures. Thus a mixture of 0.75 mole of the diol and 0.50 mole of stearic acid, which was heated for four hours at an increasing temperature of 180–245° under a fractionating column fitted for azeotropic removal of water with benzene, gave 23 ml. of water layer instead of the 9 ml. calculated for esterification. A mixture of 0.50 mole of the diol and 1.00 mole of benzoyl chloride was heated for four hours at an increasing temperature of 30–90°. The crystalline product which separated on cooling the reaction mixture was identified as benzoic acid; the crude acid amounted to an 80% yield. In attempted esterifications with anhydrides of dibasic acids, mixtures of 0.25 mole of the diol and 0.50 mole of either phthalic, succinic, or maleic anhydride were heated at 100–120° for about an hour. The respective dibasic acids were isolated from the reaction mixtures in yields of 30–40%; the other products were not examined.

RESEARCH AND DEVELOPMENT DEPARTMENT
COMMERCIAL SOLVENTS CORPORATION
TERRE HAUTE, INDIANA

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The Preparation of *p*-Amino-tetraphenylmethane

BY BENJAMIN WITTEN AND E. EMMET REID

A systematic investigation of the preparation of *p*-aminotetraphenylmethane by the method of Ullmann and Munzhuber[1] has shown that the best method is to reflux for three hours triphenylcarbinol in two times its weight of glacial acetic acid with two equivalents of aniline hydrochloride. The yield is 70–80%, about the same as was obtained by Ullmann and Munzhuber with four equivalents of aniline hydrochloride and five hours of refluxing. In one hour the yield is only 48%. The aniline hydrochloride must be thoroughly dry. If triphenylmethyl chloride is substituted for the carbinol, the time of reflux can be cut to one hour without detriment to the yield. The product obtained in any case is the hydrochloride, from which the base is liberated by boiling with water containing alkali.

It has been reported[2] that triphenylmethyl chloride and aniline, refluxed in a mixture of alcohol and benzene, give N-triphenylmethylaniline, $(C_6H_5)_3CNHC_6H_5$. We have confirmed this, but have found, however, that, if acetic acid is used as the reaction medium, para substitution takes place and the product is *p*-triphenylmethylacetanilide, $(C_6H_5)_3CC_6H_4NHCOCH_3$. This has been compared with compound obtained from action of acetyl chloride on 4-aminotetraphenylmethane and found to be identical.

Thus three different compounds can be obtained from triphenylmethyl chloride and aniline, depending on the solvent and the presence or absence of hydrochloric acid.

Experimental

***p*-Triphenylmethyl Acetanilide.**—A solution of 2 g. of *p*-aminotetraphenylmethane and 10 g. of acetyl chloride in 100 ml. of benzene was refluxed for one hour. The benzene was boiled off at reduced pressure and the residue recrystallized from benzene. The yield was 2.5 g. (93%) of colorless needles of *p*-triphenylmethylacetanilide melting at 229°.

A mixture of 14 g. of triphenylmethyl chloride, 10 g. of aniline and 50 ml. of acetic acid was refluxed for three hours and poured into 200 ml. of water. The precipitate was filtered off, washed with water, dried at 110°, and recrystallized from toluene. The yield was 16 g. (84%) of colorless crystals melting at 229°.

Anal. Calcd. for $C_{27}H_{27}NO$: C, 85.9; H, 6.1; N, 3.72. Found: C, 86.2; H, 6.1; N, 3.69.

A mixture of this preparation and the former melted at the same temperature.

Acknowledgment.—We wish to thank Mrs. V. Beatrice Jones for her assistance in several of the preparations reported in this paper.

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(1) Ullmann and Munzhuber, *Ber.*, **36**, 407 (1903).

(2) Elbs, *Ber.*, **17**, 704 (1884); Hemilian, *ibid.*, **17**, 746 (1884); Gomberg, *ibid.*, **35**, 1829 (1902); Van Alphen, *Rec. trav. chim.*, **46**, 500 (1927).

CHEMICAL CORPS TECHNICAL COMMAND
EDGEWOOD ARSENAL, MARYLAND

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NEW COMPOUNDS

Esters of *p*-Cyclohexylphenol[1]

***p*-Cyclohexylphenyl propionate** (m. p. 48–50°) was prepared in 53% yield as follows: 20 g. of *p*-cyclohexylphenol, 44 ml. of propionic anhydride and 2 ml. of anhydrous pyridine were refluxed for sixty-five minutes. The volatile portion was distilled off, and the residue was

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(1) Abstracted from the thesis presented by Albert J. Byer to DePaul University in partial fulfillment of the requirements for the M.S. degree in 1943.