NOTES

A General Method for the Synthesis of *t*-Butyl Esters

By B. Abramovitch, J. C. Shivers, B. E. Hudson and C. R. Hauser

There are several good methods for the preparation of *t*-butyl acetate from *t*-butyl alcohol. The one described in "Organic Syntheses"[1] employs acetyl chloride and magnesium. We prefer the method using acetyl chloride and dimethylaniline.[2] The method has now been developed and extended to the preparation of various *t*-butyl esters. Certain of these esters have been used in recent investigations,[3,4] but the details for their synthesis were not given. The general procedure is described below.

One mole each of dry *t*-butyl alcohol and dry dimethylaniline and 150–200 cc. of dry ether were placed in a flask equipped with a reflux condenser, mercury-sealed mechanical stirrer, and a dropping funnel. One mole of the appropriate acid chloride was added slowly from the dropping funnel. If refluxing became too vigorous the flask was immersed in an ice-bath. The reaction mixture (containing a precipitate of dimethylaniline hydrochloride) was finally heated on the water-bath for one to two hours and allowed to stand for several hours (except in the experiment with bromoacetyl bromide; this was added at 0° and the mixture allowed to stand at room temperature for a few hours). The mixture was stirred with water until the solid material dissolved. The ether layer was separated and extracted with portions of 10% sulfuric acid until the extract did not become cloudy when made alkaline. The ether solution was dried with sodium sulfate followed by Drierite and the solvent distilled. The residue was fractionated. The yields and analytical data for the *t*-butyl esters are given in Table I.

Table I

Yields of *t*-Butyl Esters

Acid chloride used	*t*-Butyl ester obtained	B. p., °C.	Yield, %
Acetyl chloride	Acetate[4]	98.0–98.5	63–76
Propionyl chloride	Propionate[4]	118–118.5	63
i-Butyryl chloride	Isobutyrate[a]	127.0–128.3	71
i-Valeryl chloride	Isovalerate[b]	154.0–156.0	33
Bromoacetyl bromide	α-Bromoacetate[3]	73–74 at 25 mm.	70
Cinnamyl chloride	Cinnamate[c]	144 at 8 mm.	58

[a] *Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.23; H, 11.09. [b] *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.22; H, 11.47. Found: C, 68.05; H, 11.33. [c] *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.04; H, 7.90.

Department of Chemistry
Duke University
Durham, North Carolina

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[1] Spassow, "Organic Syntheses," **20**, 21 (1940).

[2] See Norris and Rigby, This Journal, **54**, 2097 (1932).

[3] Abramovitch and Hauser, *ibid.*, **64**, 2274 (1942).

[4] Hauser, Abramovitch and Adams, *ibid.*, **64**, 2714 (1942).

By-Product 1,3-Butylene Glycol

By J. B. Cloke and R. M. Wolff[1]

The usual method for the preparation of 1,3-butylene glycol consists in the reduction of aldol. Some time ago Dr. Emil R. Stein of the Shawinigan Chemicals, Ltd., informed one of us that he had prepared this glycol by the alkaline saponification of one of their by-products. This by-product, consisting mainly of the acetate of 1,3-butylene glycol, was obtained to the extent of 4 to 6% in the production of ethyl acetate by the Tischtschenko reaction, in particular by the action of aluminum butoxide on acetaldehyde.

In the following procedure, the crude 1,3-butylene ester is alcoholized in the presence of hydrochloric acid and the liberated glycol is then separated by distillation.

Methyl Alcoholysis.—A mixture of 1500 cc. of the by-product ester residue, kindly supplied by Dr. Stein, 2560 cc. of methanol and 9 cc. of concentrated hydrochloric acid was heated in a flask attached to a jacketed twenty-four bulb Snyder column[2] and a stillhead which was regulated to give a high reflux ratio. The distillation was conducted slowly until the methyl alcoholysis was complete and the methyl acetate and methyl alcohol had been removed. The 1,3-butylene glycol (594 cc.) was obtained by the fractionation of the residue under diminished pressure. The compound boiled at 113° at 12 mm. At atmospheric pressure, a fraction was collected of b. p. 206–207°, d^{20}_4 1.005, n^{25}_D 1.435, which values correspond closely with the recorded data for 1,3-butylene glycol.

Ethyl Alcoholysis.—A mixture of 1500 cc. of by-product butylene ester, 2890 cc. of ethyl alcohol and 9 cc. of con-

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[1] This note has been constructed from a thesis submitted by Robert M. Wolff to the Faculty of the Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Bachelor of Chemical Engineering, June 10, 1941.

[2] A smaller and simpler column may be used with equally satisfactory results.

centrated hydrochloric acid was distilled in a 5-liter flask attached to a Vigreux column and stillhead. A high reflux ratio was maintained. The azeotropic mixture (b. p. 71.8°) of 46% of ethyl alcohol and 54% of ethyl acetate was first removed and this was followed by ethyl acetate of b. p. 77.1°. The distillation of the residue under diminished pressure gave 600 cc. of the glycol, which was practically the same yield as in the foregoing run.

Walker Laboratory
Rensselaer Polytechnic Institute
Troy, N. Y.
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The Bromination of 4-Phenylphenyl Bromoacetate

By Lee C. Hensley and Stewart E. Hazlet

This report contains additional experimental data obtained in this Laboratory in connection with substitution reactions in esters containing diphenyl groups.[1] 4-Phenylphenyl bromoacetate was selected because of its similarity to 4-phenylphenyl chloroacetate, the bromination of which was studied recently,[2] and because it contained the larger bromine atom in place of chlorine.

Preparation of the Bromoacetates of the Bromophenylphenols.—These esters were prepared by treating the appropriate phenol, in the presence of 1,4-dioxane as a diluent, with one and one-half molecular proportions of bromoacetyl bromide in an equivalent quantity of dry pyridine. The colorless esters were extracted from the reaction mixtures with boiling benzene and recrystallized from suitable solvents, *cf.* Table I.

Table I

Bromoacetates of the Bromophenylphenols

Phenol used	Yield, %[d]	Solvent	Crystal form	M. p., °C.	Formula	Analyses, % Br Calcd.	Found
2-Bromo-4-phenyl-[a]	15.4	Ligroin (70–90°)	Irregular platelets	55–56	$C_{14}H_{10}O_2Br_2$	43.24	43.69
2,6-Dibromo-4-phenyl-[a]	20	Ligroin (70–90°)	Prisms	78–79	$C_{14}H_9O_2Br_3$	53.45	53.75
2,6-Dibromo-4-(4-bromophenyl)-[b]	45.5	Ligroin (70–90°) or ethanol	Long prisms	148–149	$C_{14}H_8O_2Br_4$	60.60	60.06
4-(4-Bromophenyl)-[c]	34.4	Ethanol	Long prisms	141.5–142	$C_{14}H_{10}O_2Br_2$	43.24	43.20

[a] Ref. 3. [b] Bell and Robinson, *J. Chem. Soc.*, 1127 (1927). [c] Hazlet, This Journal, **59**, 1087 (1937); *cf.* also [b]. [d] Purified products.

Bromination of 4-Phenylphenyl Bromoacetate. (A) In Glacial Acetic Acid ("Analytical Reagent").—To a solution of 15 g. of 4-phenylphenyl bromoacetate[2] in 100 ml. of hot glacial acetic acid ("analytical reagent"), a trace of iron powder was added, 3.4 ml. of bromine dissolved in 30 ml. of glacial acetic acid was introduced dropwise over a period of twenty minutes, and the subsequent steps were much the same as in the procedure described previously.[2]

From what corresponded to *Fraction A-I* in the anaolgous study,[2] 2.1 g. of 4-phenylphenyl acetate (m. p. 84–86°) was obtained. From what corresponded to *Fraction A-II*,[2] approximately 0.1 g. of each of the following was obtained by fractional crystallization: 4-phenylphenol (m. p. 160°), 2,6-dibromo-4-phenylphenol (m. p. 89–93°), and 2,6-dibromo-4-(4-bromophenyl)-phenol (m. p. 154–157°). Identification by means of a mixed melting point determination with an authentic sample was made in each case.

(B) In Specially Treated Glacial Acetic Acid.—The method was similar to that used for the chloroacetate,[2] and separations were effected as in (A) above. From 10 g. of 4-phenylphenyl bromoacetate, 7.5 g. of starting material (m. p. 111.5–112°) and 0.4 g. of 4-phenylphenol (m. p. 160–164°) were obtained and identified by the mixed melting point method.

(C) In Carbon Tetrachloride.—Ten grams of the bromoacetate was treated in carbon tetrachloride in much the same manner as that reported previously for the chloroacetate.[2] After one crystallization from ethanol, 5 g. of product resulted; several recrystallizations gave a product which melted at 140–140.5°, and no depression in melting point was observed when a sample of this product was mixed with a sample of 4-(4-bromophenyl)-phenyl bromoacetate prepared as described above and listed in Table I.

The ester was hydrolyzed; the resulting phenol melted at 163–164°. A mixture of it and 4-(4-bromophenyl)-phenol, obtained by the hydrolysis of 4-(4-bromophenyl)-phenyl benzoate,[3] melted at 163–164°. This further justified the characterization of the substitution product as 4-(4-bromophenyl)-phenyl bromoacetate.

The bromination of 4-phenylphenyl bromoacetate proceeds in a manner which is essentially analogous to the bromination of the chloroacetate studied previously, *viz.*, in glacial acetic acid ("analytical reagent") several products were obtained: 4-phenylphenol, 2,6-dibromo-4-phenylphenol, 2,6-dibromo-4-(4-bromophenyl)-phenol, and 4-phenylphenyl acetate. These results differ from those obtained with 4-phenylphenyl acetate[4]; in that case, 2-bromo-4-phenylphenyl acetate was formed.

In specially treated glacial acetic acid, no substitution was effected, and starting material and some 4-phenylphenol were obtained.

When carbon tetrachloride was the solvent used, bromination of 4-phenylphenyl bromoacetate yielded 4-(4-bromophenyl)-phenyl bromoacetate; under similar condi-

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[1] For the last report *cf.* Hazlet and Van Orden, This Journal, **64**, 2505 (1942).

[2] Hazlet, Hensley and Jass, *ibid.*, **64**, 2449 (1942).

[3] Hazlet, Alliger and Tiede, *ibid.*, **61**, 1447 (1939).

[4] Hazlet and Kornberg, *ibid.*, **61**, 3037 (1939).