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

Received March 8, 1943

---

[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-

---

[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.