equiv., 190. Found: C, 63.21; H, 3.31; neut. equiv., 188.

The large clusters, m. p. 197° (dec.), 7.0 g., were *o*-phthalic acid.

3-Methylenephthalide.—*o*-Acetobenzoic acid, 3.28 g. (0.02 mole), and 5.0 ml. of acetyl chloride were refluxed gently for one and one-half hours. An external bath temperature of 50° was maintained while the excess acetyl chloride was removed under reduced pressure. The oily residue was treated with 10 ml. of water and enough 10% aqueous ammonia to make the mixture alkaline to litmus. At this point the oil had partially solidified. The mixture was extracted with ether and the ether extracts dried over anhydrous sodium sulfate. The ether was distilled *in vacuo* leaving a semi-solid residue, 2.2 g. This was dissolved in 4.0 ml. of acetone, centrifuged and the clear acetone solution decanted. When diluted with 10 ml. of water an oil separated and soon solidified, 1.5 g., m. p. 50–55°. It was sublimed at 1–2 mm. with a bath at 45–50° and 0.65 g., m. p. 57°, of product was obtained. Gabriel[2] reported a m. p. of 58–60°. The sublimed material could be crystallized from hexane.

Anal. Calcd. for $C_9H_6O_2$: C, 73.97; H, 4.11. Found: C, 73.38; H, 4.21.

The aqueous ammoniacal solution was evaporated to dryness. From the residue there was obtained 0.5 g. of *o*-acetobenzoic acid.

The yield of 3-methylenephthalide was 26.2%.

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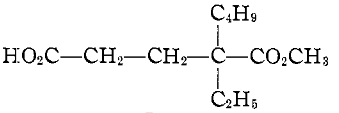
COMMUNICATIONS TO THE EDITOR

REARRANGEMENT IN PREPARATION OF ESTER ACID CHLORIDES

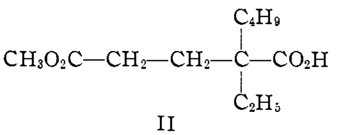
Sir:

In conversion of the half ester of a dibasic acid to the ester acid chloride, it has been assumed that the chlorine becomes attached to the carbon originally present as carboxyl. Thus, Bardhan[1] prepared acid chlorides from the two half esters of trimethylsuccinic acid, and treated each with methylzinc iodide. In each case there was obtained a "similar" mixture of ethyl α,α,β-trimethyllevulinate and ethyl α,β,β-trimethyllevulinate. This was ascribed to the half esters used as starting materials being a similar mixture of isomers, in spite of convincing evidence[2] that half esters so obtained are largely a single isomer.

We have obtained the isomeric half esters, I and II, of α-butyl-α-ethylglutaric acid.[3] Here the hindrance around one carboxyl is so great that the essential homogeneity of the isomers is assured. Esterification of the acid with a large excess of methanol in presence of sulfuric acid gave a high yield of II after one hour under reflux, whereas a 10% yield of II remained after one hundred forty hours under reflux. Each isomer was converted to the acid chloride with thionyl chloride and these heated with tribromoaniline in xylene. From each isomer was obtained a poor yield of a tribromoanilide, m. p. 127–128°, no depression on mixing the two. *Anal.* Calcd. for $C_{18}H_{24}NO_3Br_3$: C, 39.88; H, 4.45. Found: C, 39.94; H, 4.50. Thus, a mixture of ester acid chlorides must have been obtained from each isomer, and there was isolated only the tribromoanilide resulting from reaction with the unhindered acid chloride.

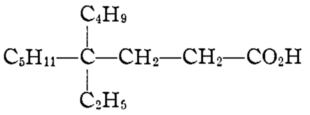

$$HO_2C{-}CH_2{-}CH_2{-}\underset{C_2H_5}{\overset{C_4H_9}{C}}{-}CO_2CH_3$$

I

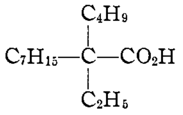

$$CH_3O_2C{-}CH_2{-}CH_2{-}\underset{C_2H_5}{\overset{C_4H_9}{C}}{-}CO_2H$$

II

Further, the acid chloride from each isomeric half ester was treated with dibutylcadmium,[4] and the resulting mixture of keto esters was reduced by the modified Wolff–Kishner procedure.[5] There was obtained in the two cases nearly identical mixtures of acids of the expected equivalent weight and b. p. 148.5–149.5° (1.5 mm.). This mixture was separated into the acids, III (*ca.* 25%) and IV (*ca.* 75%), by virtue of the rapid esterification of III and the very slow esterification of IV. When the esterification procedure used was repeated on the residual IV, no ester was detected. *Anal.* Calcd. for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48; eq. wt., 242.4. Found for III: C, 74.09; H, 12.39; eq. wt., 245.7. Found for IV: C, 74.17; H, 12.01; eq. wt., 241.5; $n^{27}D$ for III, 1.4533; for IV, 1.4472. *p*-Bromoanilide of III, m. p. 88.5–89.0°; of IV, m. p. 121.5–122°. *Anal.* Calcd. for $C_{21}H_{34}NOBr$: C, 63.62; H, 8.65. Found for deriv. of III: C, 64.11; H, 8.42. Found for deriv. of IV: C, 63.51; H, 8.72.


$$C_5H_{11}{-}\underset{C_2H_5}{\overset{C_4H_9}{C}}{-}CH_2{-}CH_2{-}CO_2H$$

III


$$C_7H_{15}{-}\underset{C_2H_5}{\overset{C_4H_9}{C}}{-}CO_2H$$

IV

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[1] Bardhan, *J. Chem. Soc.*, 2604 (1928).

[2] Bone, Sudborough and Sprankling, *ibid.*, **85**, 534 (1904).

[3] Bruson and Riener, THIS JOURNAL, **66**, 56 (1944).

[4] Cason, *ibid.*, **68**, 2078 (1946).

[5] Huang-Minlon, *ibid.*, **68**, 2487 (1946).