Notes

A department for short papers of immediate interest.

Preparation and Properties of Tertiary Alkyl Formates

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Although Cottle[1] has reported the use of ion exchange resins as catalysts in the preparation of alkyl esters, he utilized special dry resins and limited his work to the acetate esters. In this work tertiary alkyl esters of formic acid have been prepared using ion exchange resins containing as much as 53% moisture.

Five tertiary alkyl formates were prepared by Barkenbus.[2] He made *tert*-butyl formate by the reaction of aluminum *tert*-butoxide with *n*-butyl formate and also, using sulfuric acid as the catalyst in the reaction of formic acid with isobutylene. The use of sulfuric acid as a catalyst in the addition of acids other than formic to alkenes has been reported.[3-5]

Earlier workers[6,7] have prepared tertiary alkyl formates but their yields have been poor and the esters impure.

The cationic exchange resins tested in this study were of the polystyrene divinylbenzene sulfonic acid type, the most effective resin being Dowex 50-X8 (200–400 mesh). Reactions were run using the resin as obtained from the supplier, that is, "wet" containing as much as 53% moisture. Other reactions were run using resins which had been dried at 100° for 24 hr. In addition both types of resin were reused several times without losing their effectiveness. The best yields of the ester were obtained when between 1–1.5% wet catalyst (based on the weight of formic acid) was used at a reaction temperature below 65°. Below this catalyst concentration the reaction rate was too slow to be efficient while above this concentration and temperature the formation of polymer by-product became appreciable.

It is of interest to note that no reaction took place when diisobutylene was treated with formic acid in the presence of Dowex 50-X8. This would seem to indicate that, although diisobutylene type material is a by-product in the formation of *tert*-butyl formate, the ion exchange resin is not a catalyst for the addition of acids to the higher polymers of isobutylene.

EXPERIMENTAL

tert-Butyl formate. A typical preparation is given. Formic acid (208 g., 4.5 moles) and "wet" Dowex 50-X8, 200–400 mesh (2.5 g., 1.2% by weight of formic acid) were placed in a gas washing bottle and isobutylene gas was bubbled through the system at the approximate rate of one mole per hour. After 4 hr. the gas flow was discontinued and the resin filtered off. The reaction mixture was washed with eight portions of ice water and then dried over anhydrous magnesium sulfate. Vacuum distillation of the product gave *tert*-butyl formate (43.6% yield): b.p. 83°/760 mm., n_D^{25} 1.3790, d_4^{25} 0.8717 (reported,[2] n_D^{25} 1.3783, d_4^{25} 0.8718, b.p. 82.8/760 mm.).

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.9; H, 9.8. Found: C, 59.2; H, 9.7.

tert-Amyl formate. Anhydrous formic acid (50 g., 1.09 moles) and 2 methyl butene-2 (72 g., 1.03 moles) were agitated occasionally for two days at room temperature in a 4-oz. glass stoppered bottle using "wet" Dowex 50-X8, 200–400 mesh (0.3 g., 0.6% by weight of formic acid) as the catalyst. The resin was filtered off and the filtrate was washed six times with ice water. After drying over anhydrous magnesium sulfate the sample was distilled. There were obtained. 2-methyl-2-butene boiling at 41° and *tert*-amyl formate (23.8%) b.p. 112.1°, n_D^{25} 1.3952, d_4^{25} 0.8821 (reported[2] n_D^{25} 1.3951, d_4^{25} 0.8853, b.p. 112.9°).

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.0; H, 10.7. Found: C, 62.1; H, 10.4.

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(1) D. Cottle, U. S. Patent 2,678,332 (1954).

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(3) G. Timofejev and L. Andreasov, *Chem. Zentr.*, 96, (II), 1652 (1925).

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(5) R. Altschul, *J. Am. Chem. Soc.*, 68, 2605 (1946).

(6) W. Taylor, *J. Chem. Soc.*, 1852 (1937).

(7) E. Sucharda and T. Mazonski, *Brit. Chem. Abstracts*, B 497 (1933).

Reduction of Fluorenonecarboxylic Acids to Fluorenecarboxylic Acids[1]

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Many of the syntheses in the fluorene series are rendered difficult by the inaccessibility of the fluorenecarboxylic acids. The reduction of the fluorenonecarboxylic acids to the corresponding fluorene acids is the step which seems to give the poorest yields. Several processes have been described for this reduction but the Clemmensen and

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