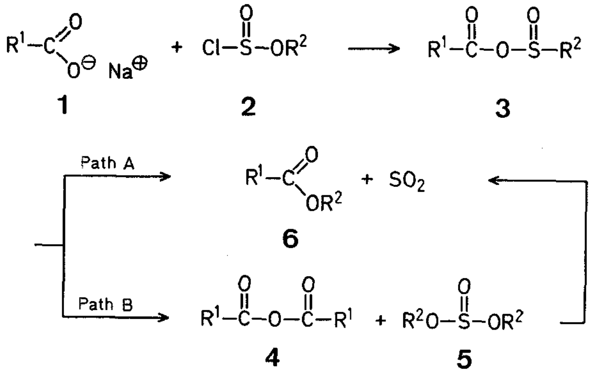
An Ester Preparation Reinvestigated

Josef G. Krause and Ashvin Shah

Chemistry Department, Niagara University, N. Y. 14109, U.S.A.

For years it has been assumed[1] that the Newman and Fones procedure[2] for the preparation of esters (**6**) from alkyl chlorosulfites (**2**) and sodium carboxylates (**1**) proceeds via an intramolecular decomposition of the intermediate mixed anhydride **3** (Path A). During an attempt to verify this mechanism, we have discovered that the mixed anhydride (**3**) decomposes intermolecularly to produce a mixture of the dialkyl sulfite (**5**) and carboxylic acid anhydride (**4**) (Path B). This mixture reacts further to produce ester (**6**) and sulfur dioxide via a mechanism similar to that already established for the decomposition of dialkyl carbonates and anhydrides[3].



We could detect no ester being produced via Path A. Typically, if a mixture of an alkyl chlorosulfite (**2**) and a sodium carboxylate (**1**) is heated for 1 h at 170° in an oil bath, a mixture of the dialkyl sulfite (**5**) and carboxylic acid anhydride (**4**) is produced as shown by G.L.C. If this mixture is heated for an additional 2–3 h at 200–220°, a good yield of ester is obtained. For all practical purposes, it is experimentally simpler to start out with a dialkyl sulfite (**5**) and an anhydride (**4**). The dialkyl sulfites are easier to prepare and are more stable for long periods of time than are the alkyl chlorosulfites.

This method for making esters of primary and secondary alcohols is unusual in that it occurs under neutral conditions, is not subject to equilibrium control, and the product is easily isolated by vacuum distillation following the heating period.

Following are some yields for esters of benzoic acid: *n*-butyl, 95%; *i*-butyl, 85%; and *sec*-butyl, 80%.

Preparation of Alkyl Carboxylates; General Procedure:

Dialkyl Sulfites (**5**): Thionyl chloride (1 equiv) is added dropwise with stirring and cooling to the primary or secondary alcohol (4–6 equiv). The solution is heated on a steam bath for 1 h following addition to complete the reaction. The mixture is vacuum-distilled to obtain the dialkyl sulfite which distils after the excess alcohol has been removed.

Alkyl Carboxylates (**6**): A mixture of the dialkyl sulfite (1 equiv) and the carboxylic acid anhydride (1 equiv) is heated in an oil bath at 210° for 3–5 h, and the ester, which is the only compound to distil, is isolated by vacuum distillation of the crude reaction product.

This work was supported by the Niagara University Research Council.

Received: March 13, 1974

---

[1] Private communication from Professor Newman.

[2] M. S. Newman, W. S. Fones, *J. Amer. Chem. Soc.* **69**, 1046 (1947)

[3] C. J. Michejda, D. S. Tarbell, W. H. Saunders, *J. Amer. Chem. Soc.* **84**, 4113 (1962), and references cited therein.