Anal. Calcd. for $C_{10}H_6O_8 \cdot 2H_2O$: H_2O, 12.42. Found: H_2O, 12.40. Calcd. for $C_{10}H_6O_8$: Neut. eq., 63.5. Found: Neut. eq., 63.8.

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New Synthesis of α-Keto Esters

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The importance of α-keto acids and their derivatives as vital biochemical intermediates[2] makes a direct and efficient synthesis of these compounds particularly desirable. We have accomplished this objective by making use of the remarkable ability of selenium dioxide to oxidize active methylene groups.[3,4]

We have found that the reaction of selenium dioxide with an α-bromo ketone of the type $RCOCH_2Br$ in an anhydrous alcohol as solvent produces the corresponding α-keto ester in high yield. From α-bromoacetophenone in absolute ethanol a 70% yield of ethyl benzoylformate was obtained. When methanol was employed as the solvent, the methyl ester was formed in 80% yield.

The reaction path probably involves conversion of the α-halomethyl group to an acid bromide. This would then react rapidly with the solvent to produce the keto ester. The mechanism of the oxidation step is probably the same as that recently postulated by Corey and Schaefer[5] for the reaction of selenium dioxide with a ketone of the type $RCOCH_2R$ to produce an α-diketone.

EXPERIMENTAL

Ethyl benzoylformate. To 9.0 grams (0.074 mol.) of selenium dioxide dissolved in 75 ml. of boiling absolute ethanol was added 15.0 g. of α-bromoacetophenone; the resulting solution was refluxed for 12 hr. The extracts were then poured into water, extracted with ether, dried over magnesium sulfate, and distilled to give 9.2 g. (70% yield) of the desired ester, b.p.$_2$ 97–98°.[6]

Methyl benzoylformate. The same procedure was used to form the methyl ester with the exception that methanol was used as the solvent. The yield was 80%, b.p.$_{14}$ 137°.[7]

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Simplified Zinc-Copper Couple for Use in Preparing Cyclopropanes from Methylene Iodide and Olefins

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It has been recently found that olefins react with methylene iodide and zinc-copper couple to give cyclopropanes.[1] This elegant reaction is quite general in that it is applicable to olefins which are hindered and are either electronegatively- or electropositively-substituted. The method for preparing the zinc-copper couple is important with respect to its reactivity with methylene iodide and its reproducibility for preparing cyclopropanes. The zinc (90%)-copper (10%) couple which has been used most effectively previously is prepared by reaction of zinc dust, cupric oxide, and hydrogen at 500°[1,2] and is subsequently activated by iodine. For purposes of synthesis, this method of obtaining the couple is inconvenient; the activity of the couple is also affected by the temperature at which it is prepared. Couples derived from granulated zinc and copper powder do give cyclopropanes but in erratic yields; those obtained by thermal decomposition of cupric citrate in the presence of zinc dust react with methylene iodide with difficulty.[1]

We would like to report a simple zinc-copper couple which is satisfactory for effecting reaction of methylene iodide with olefins to give cyclopropanes. The couple is prepared simply and rapidly by successive washing of zinc powder with hydrochloric acid (3%), aqueous copper sulfate (2%), water, ethanol, and ethyl ether, respectively.[3] The results obtained for reaction of methylene iodide and the zinc-copper couple in ethyl ether with 1-octene, cyclohexene, (+)-limonene and dihydropyran are

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