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# A NEW METHOD FOR THE PREPARATION OF KETONES BY DECARBONYLATION OF α-HYDROXY-CARBOXYLIC ACID WITH 2-CHLOROBENZOXAZOLIUM SALT

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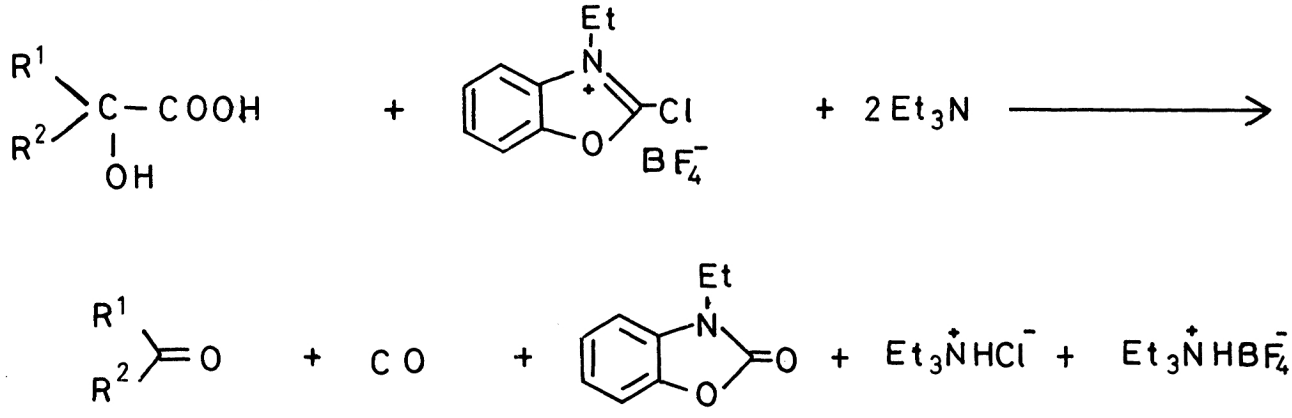
Treatment of α-hydroxycarboxylic acids with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate and triethylamine at room temperature affords ketones in good yields.

In the course of our synthetic investigation utilizing the onium salt of azaaromatics, 2-chloro-3-ethylbenzoxazolium tetrafluoroborate has been shown to be a useful and specific reagent for the replacement by chlorine or the elimination of certain oxygenated functions.[1) 2) 3)]

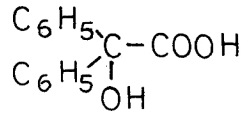
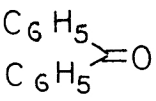
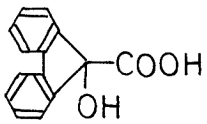
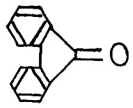
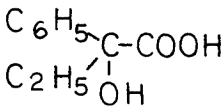
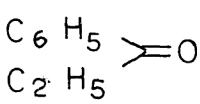
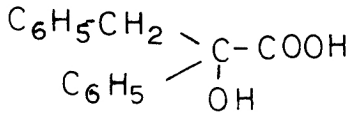
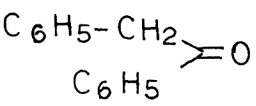
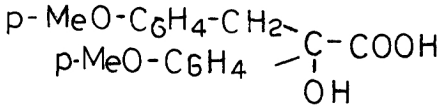
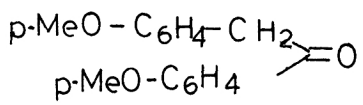
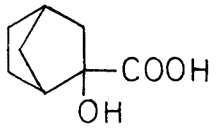
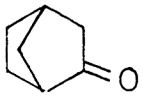
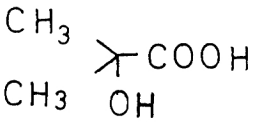
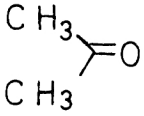
We have now found that α-hydroxycarboxylic acids, readily available from carboxylic acids,[4) 5)] are easily decarbonylated at room temperature to form ketones in good yields on treatment with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate in the presence of two molar amounts of triethylamine as shown in the following equation.



A typical procedure is described for the synthesis of deoxybenzoin by decarbonylation of 2-hydroxy-2,3-diphenylpropionic acid. A solution of triethylamine [243 mg, 2.4 mmol] in dichloromethane [5 ml] was slowly added at room temperature under an argon atmosphere to a mixture of 2-hydroxy-2,3-diphenylpropionic acid [242 mg, 1 mmol] and 2-chloro-3-ethylbenzoxazolium tetrafluoroborate [323 mg, 1.2 mmol]. Carbon monoxide was evolved very rapidly during the addition, and the reaction mixture was stirred for 10 min. After evaporation of the solvent, the residue was chromatographed on silica gel to give deoxybenzoin (85%, 167 mg).

In a similar manner, various α-hydroxycarboxylic acids were decarboxylated to afford ketones in good yields as shown in the Table.

Table Synthesis of Ketones from α-Hydroxycarboxylic Acids

| α-Hydroxycarboxylic Acid | Ketone | Yield(%) |
|---|---|---|
|  |  | 83 |
|  |  | 85 |
|  |  | 84 |
|  |  | 85 |
|  |  | 90 |
|  |  | 66 |
|  |  | 71[6] |

There appeared no reports concerning the direct preparation of ketones from α-hydroxycarboxylic acids without using any oxidizing reagent. The present method opened a new and general route to the synthesis of ketones directly from α-hydroxycarboxylic acids in good yields under mild conditions with the evolution of carbon monoxide by using 2-chloro-3-ethylbenzoxazolium tetrafluoroborate.

REFERENCES AND NOTE

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6) Yield was determined by g.l.c. technique.

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