

DECARBOXYLATION OF SODIUM GLYCIDATES: A CONVENIENT METHOD FOR THE SYNTHESIS OF
 α -ACETOXYKETONES, α -DIKETONES, AND α -KETOESTERS

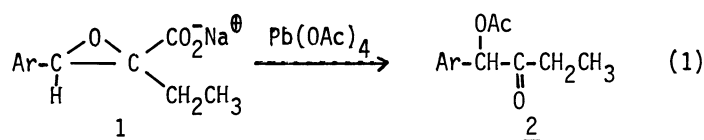
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The decarboxylation of aryl sodium glycidates having substituent at the α -carbon gave the corresponding α -acetoxyketones, α -diketones and α -ketoesters in synthetically useful yields.

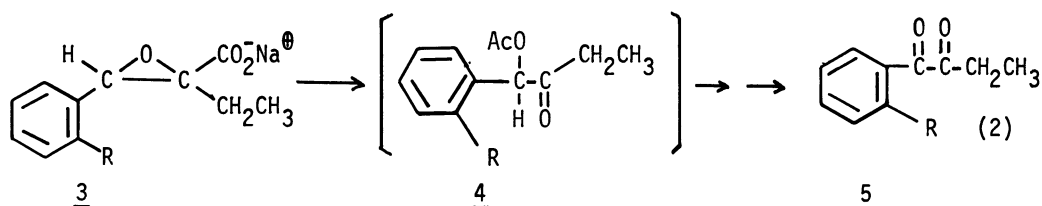
We recently reported the decarboxylative elimination of sodium glycidates derived from cyclic ketones giving α,β -unsaturated ketones in good yields.¹ Further exploratory work in this area employing various aromatic aldehydes led to a novel method for the preparation of α -acetoxyketones², α -diketones³ and α -ketoesters⁴.

The decarboxylation of the sodium glycidates¹ 1a-e with lead tetraacetate-pyridine in refluxing benzene gave the α -acetoxyketones 2a-e in good yields. The following procedure is representative: a mixture of sodium glycidate (1, 0.01 mole), pyridine (0.02 mole), lead tetraacetate (0.02 mole) and dry benzene (100 ml) was stirred under nitrogen for 30 min. at room temperature and then under refluxed for 5 hr. The cooled reaction mixture was treated with ethylene glycol and then washed with dilute hydrochloric acid and water respectively. The benzene layer was evaporated and the crude product was purified by preparative layer chromatography (Merck PF₂₅₄ silica gel; 7:3 chloroform-hexane). Our results are summarized in equation (1).



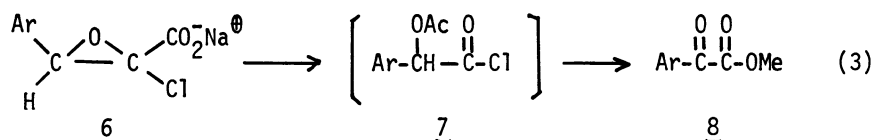
a, Ar = *p*-methoxyphenyl- (100%); b, Ar = 3,4-dimethoxyphenyl- (88%); c, Ar = 2-furyl- (80%); d, Ar = 4-chlorophenyl- (74%); e, Ar = 3,4-methylenedioxyphenyl- (92%)

In the case where the aryl group carries an electronegative substituent (3a and 3b), the final product of the reaction is the corresponding α -diketone (5a and 5b) (equation 2) which is presumably derived from further oxidation of the expected α -acetoxyketone (4a and 4b). The susceptibility of the benzylic position to undergo further oxidation is due to the enhancement of the acidity of the benzylic hydrogen by the inductive effect of the *ortho* substituent. Our postulate seems to be further substantiated by the fact that the activation of the benzylic position with a chloroformyl group also caused further oxidation of the benzylic carbon to the carbonyl group.



a, R = -Cl (72%); b, R = -OCH₃ (99%)

This process involves the decarboxylation of the sodium glycidates ^{4b,5} 6a-c (equation 3) with lead tetraacetate under the same conditions as described above yielding the α -ketoesters 8a-c. These

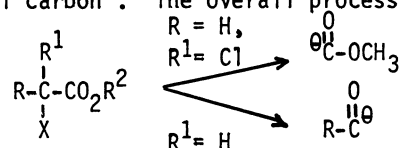


a, Ar = phenyl- (35%); b, Ar = 4-chlorophenyl- (50%);

c, Ar = 3-methoxyphenyl- (25%)

compounds are probably derived from further oxidation of the expected products 7a-c. The sequential work up of the reaction with anhydrous methanol and water gave the α -ketoesters.

The above results further demonstrate the synthetic utility of the α -haloester as a masked nucleophilic acyl carbon¹. The overall process represented by equations (2) and (3) is equivalent



to an oxidative nucleophilic acylation of an aldehyde group.

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