

Base-catalysed Isomerization of Substituted Cyclopropanes to 4,5-Dihydrofurans

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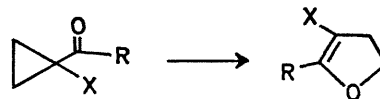
Summary Substituted cyclopropyl phenyl ketones have been found to undergo a base-catalysed isomerization to 4,5-dihydrofurans.

WE report our work on a novel base-catalysed rearrangement of 1-substituted cyclopropyl ketones to 4,5-dihydrofurans. There have been numerous reports of thermolytic¹⁻³ and acid-catalysed⁴⁻⁶ rearrangements of cyclopropyl ketones to 4,5-dihydrofurans.

Treatment of cyclopropyl ketones (**1a**, **1b**) with a catalytic amount of Ph_3P or Et_3N in a sealed tube at 200° gave their isomeric dihydrofurans (**2a**), (**2b**), (**2b'**)† in quantitative yields. Cyclopropyl phenyl ketone (**1c**) gave only 14% of its corresponding dihydrofuran (**2c**) with the isolation of 11% of 1-cyclopropyl-1-phenylethylene (**5**).

† The analytical and spectral data for all new compounds are in agreement with the structures shown.

The rearrangement of the cyclopropanes to dihydrofurans may be visualized as arising from the attack of base at the



(1a) R = Ph, X = CO_2Et

(1b) R = Ph, X = Ac

(1c) R = Ph, X = H

(2a) R = Ph, X = CO_2Et

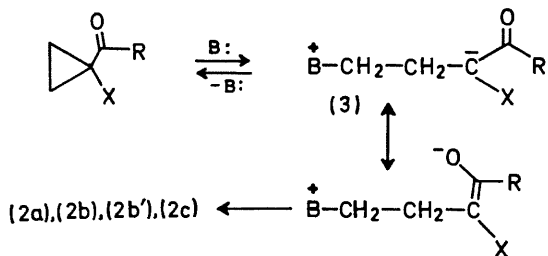
(2b) R = Ph, X = Ac

(2b') R = Me, X = Bz

(2c) R = Ph, X = H

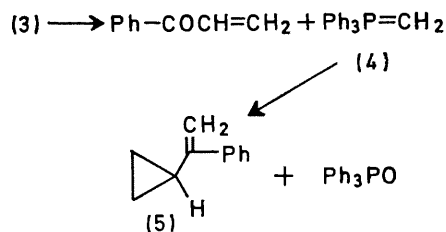
C-2 position of the cyclopropane ring with the formation of a phosphonium (ammonium) betaine intermediate (**3**). Attack by the oxygen of the enolate in a nonreversible

S_N1 displacement of base would lead to the dihydrofurans (2a)—(2c).



In the case of the cyclopropyl phenyl ketone (1c) the phosphonium betaine intermediate (3) undergoes reaction by a second pathway; betaine (3) cleaves in a retro-Michael reaction with the formation of methylenetriphenylphosphorane (4), which undergoes a normal Wittig reaction with starting material to give the substituted ethylene (5) and Ph_3PO .

In order for the base-catalysed isomerization of the cyclopropyl ketones to dihydrofurans to occur in good yields it becomes evident that substituents on the 1-position of the cyclopropane ring must be more electrophilic than hydrogen so that there is stabilization of the incipient carbanion in the betaine, and rearrangement rather than fragmentation, can take place.



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