Reaction of *O*-Silylated Enolates of Carboxylic Esters with Benzyne. A Convenient Route to *ortho*-Alkylbenzoic Acids

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The reaction of *O*-silylated enolates of carboxylic esters with benzyne proceeds smoothly to afford *ortho*-alkylbenzoic acids in moderate yields.

A variety of reactions using *O*-silylated enolates (**1**) of carboxylic esters have been documented.[1] In most cases, the nucleophilicity of their α-carbon causes the reactions with numerous electrophiles. Also, in a few cases, the formation of an intermediate radical containing trivalent α-carbon has been proposed.[2] Here we report a novel reaction in which the compounds (**1**) participate. Thus, compounds (**1**) were allowed to react with chloro- or bromo-benzene in the presence of excess $NaNH_2$ at room temperature providing *ortho*-alkylbenzoic acids (**2**) in moderate yields. It is clear that the reaction proceeded *via* a process involving the initial formation of benzyne and its subsequent addition to (**1**) affording intermediate bicyclic compounds which were hydrolysed during the work-up procedure.

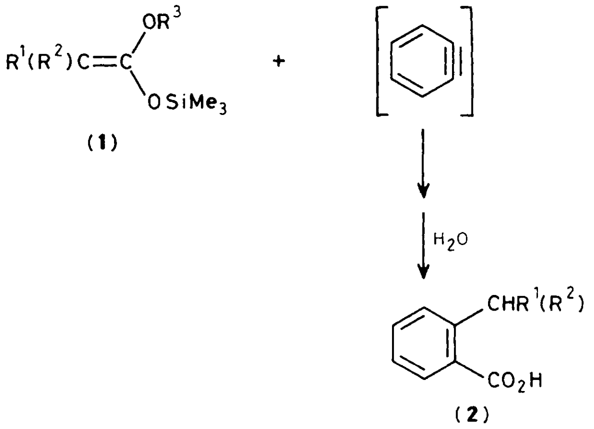
An *O*-silylated enolate (**1**) (10 mM) of carboxylic ester was mixed with chlorobenzene (1.13 g, 10 mM) [or bromobenzene (1.57 g, 10 mM)] and $NaNH_2$ (1.17 g, 30 mM). The mixture was stirred under a nitrogen atmosphere for 24 h at room temperature. It was treated with cold water (30 ml) and extracted with dichloromethane (3 × 50 ml). The organic extract was washed with water, dilute aqueous HCl (10%), and again with water, dried over anhydrous $MgSO_4$, and then the solvent was evaporated under reduced pressure to afford a residue which was subjected to column chromatography on silica gel (50% ethyl acetate–hexane as eluent). The results are summarized in Table 1.

To our knowledge, several synthetic methods of *ortho*-alkylbenzoic acids are now available. Among these, the procedure involving the reaction of 3-alkyl- or 3,3-dialkylphthalides with HI in the presence of phosphorus seems to be the most general method.[6,7] As a result, the former 3-alkylphthalides are easily available and the latter 3,3-dialkylphthalides seem to be prepared using the appropriate Grignard reagents and *ortho*-acylbenzoic acids[8] (or diethyl phtha-

Table 1. Reaction of *O*-silylated enolates (**1**) of carboxylic esters with benzyne.

Substrate	Benzyne source	Product		
			% Yield[a]	M.p. (°C)[b] (lit., m.p.)
(**1a**)	PhCl	(**2a**)	40	62 (64—65)[3]
(**1a**)	PhBr	(**2a**)	42	
(**1b**)	PhCl	(**2b**)	40	150—152 (155—158)[4]
(**1b**)	PhBr	(**2b**)	41	
(**1c**)	PhCl	(**2c**)	42	58—61 (64)[3]
(**1c**)	PhBr	(**2c**)	46	
(**1d**)	PhCl	(**2d**)	51	108
(**1d**)	PhBr	(**2d**)	50	
(**1e**)	PhCl	(**2e**)	39	64—65 (64—65)[5]
(**1e**)	PhBr	(**2e**)	37	
(**1f**)	PhCl	(**2f**)	47	123—124
(**1f**)	PhBr	(**2f**)	50	

[a] Isolated yield by column chromatography. [b] Recrystallized from hexane.



	R^1	R^2	R^3
a;	H	Me	Et
b;	H	Et	Et
c;	Me	Me	Et
d;	Me	Et	Et
e;	H	Pr^i	Et
f;	Et	Et	Et

Scheme 1

late[3]). However, the present method is more easily conductable than the other methods reported. Thus, the reaction of (**1**) with benzyne has been shown to provide an excellent alternative route to (**2**). Detailed study on the mechanism as well as the applicability of the present method to another *O*-silylated enolates and arynes is in progress.

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