

Unusual Reaction of 6-Nitrobenzotriazolyl Carboxylates with Grignard Reagents

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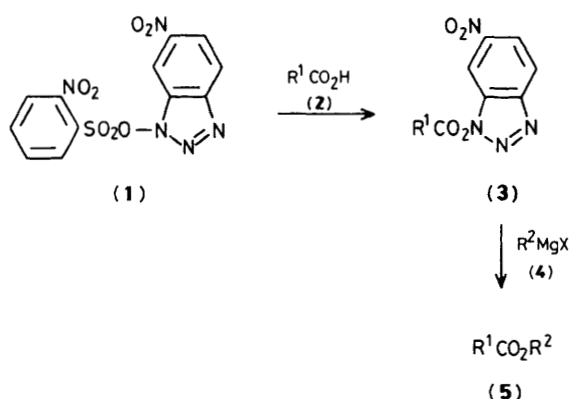
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The reaction of 6-nitrobenzotriazolyl carboxylates with Grignard reagents afforded various carboxylates in fairly good yields.

It is well known that activated esters react with Grignard reagents to give ketones.¹ As a continuation of our study using 1-(2-nitrobenzenesulphonyloxy)-6-nitrobenzotriazole (**1**) as an activating reagent for carboxylic acids,² we examined the reaction of Grignard reagents (**4**) with 6-nitrobenzotriazolyl

carboxylates (**3**), prepared from (**1**) and carboxylic acids (**2**) in tetrahydrofuran (THF). (Scheme 1). The carboxylic esters (**5**) were formed in fairly good yields instead of the anticipated ketones. The results are shown in Table 1.

A typical procedure is as follows. A solution of (**4**) (1.1



Scheme 1

equiv.) in THF was gradually added to a stirred solution of activated ester (3)² in THF at room temperature. Stirring was continued for 8 h. Aqueous 2 M HCl solution was added to the reaction mixture. After removal of THF, the aqueous solution was extracted with Et₂O, the ethereal extract dried over MgSO₄ and evaporated to dryness, and (5) isolated by silica-gel chromatography (benzene: AcOEt 19:1).

The structures of compounds (5) were confirmed by comparison of the i.r. and ¹H n.m.r. spectra with those of

Table 1. Carboxylic esters (5).

(5)	R ¹	R ²	M.p./°C	Yield (%)
a	Ph	Ph	68—69	57
b	Ph	PhCH ₂	oil	64
c	Ph	Et	oil	55
d	Ph	Bu ⁿ	oil	50
e	Ph	Bu ⁱ	oil	45
f	<i>p</i> -NO ₂ Ph	PhCH ₂ CH ₂	60—61	72
g	PhOCH ₂	PhCH ₂ CH ₂	55—56	78
h	<i>c</i> -C ₆ H ₁₁	PhCH ₂ CH ₂	oil	63

authentic esters. This reaction under mild and neutral conditions may be useful for the preparation of carboxylic esters with pH-sensitive substituents.

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