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INDIUM-INDUCED ALLYLATION OF ACID ANHYDRIDES. A FACILE SYNTHESIS OF ALLYLATED BUTENOLIDES AND PHTHALIDES

Shuki ARAKI, Nobuhito KATSUMURA, Hirokazu ITO, and Yasuo BUTSUGAN*
Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan

Abstract. Indium-mediated allylation of acid anhydrides gave *gem*-diallyl esters, whereas with γ-substituted allylic halides monoallylated hydroxy esters were formed exclusively.

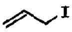
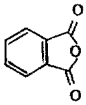
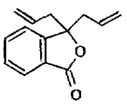
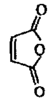
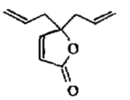
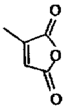
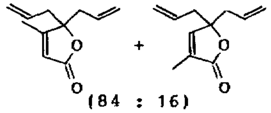
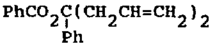
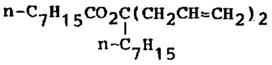
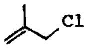
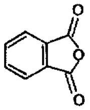
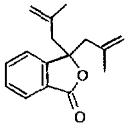
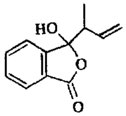
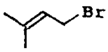
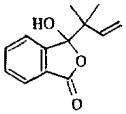
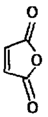
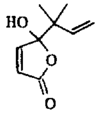
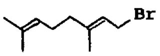
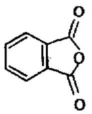
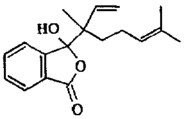
The reaction of organometallics and carbonyl compounds provides a fundamental methodology in synthetic organic chemistry. Aldehydes, ketones, esters, and acid halides are widely used as convenient starting materials for such transformations. Carboxylic acid anhydrides, however, are of diminished synthetic value owing to their complex reaction behavior toward organometallic reagents.1) Recently we have reported that metallic indium markedly facilitates the allylation of aldehydes and ketones.2) Now we describe indium-mediated allylation of acid anhydrides which gives a novel example of *gem*-diallylation of the carbonyl group of acid anhydrides yielding esters. In particular, cyclic anhydrides such as phthalic and maleic anhydrides gave high yields of the corresponding phthalides and butenolides, respectively.

Allyl iodide (504 mg, 3 mmol) in N,N-dimethylformamide (DMF) (1 ml) was added to a mixture of phthalic anhydride (148 mg, 1 mmol) and an indium powder (230 mg, 2 mmol) in DMF (1 ml), and the mixture was stirred at room temperature for 1 h. Saturated aqueous ammonium chloride was added and the product extracted with ether (30 ml x 3). Purification by column chromatography on silica gel afforded 3,3-diallylphthalide (174 mg, 81% yield). Results for various acid anhydrides and allylic halides are summarized in Table.

Phthalic, maleic, and citraconic anhydrides gave the corresponding *gem*-diallylation products in good yields, whereas acyclic anhydrides such as benzoic and octanoic anhydrides gave low yields of the esters. Interestingly, the reaction of γ-substituted allylic halides with cyclic anhydrides stopped at the monoallylation stage, presumably owing to the steric hindrance, yielding the hydroxy lactones as the sole products. The coupling occurred at the γ-position of the allylic halides regioselectively.

Only few works have hitherto been reported on ester formation by the reaction of acid anhydrides with organometallics such as magnesium3) and cadmium reagents.4) Our indium-induced allylation is unique because of its generality, high regio- and chemoselectivity, and good yields. Full scope on the mechanism and synthetic application of this reaction will be reported elsewhere.

Table. Indium-induced Allylation of Acid Anhydrides[a)]

Allylic Halide	Acid Anhydride	Conditions	Product[b)]	Yield/%
		RT, 1 h		81
"		"		57
"		"		86
"	$(PhCO)_2O$	"	$PhCO_2C(Ph)(CH_2CH=CH_2)_2$	33[c)]
"	$(n\text{-}C_7H_{15}CO)_2O$	"	$n\text{-}C_7H_{15}CO_2C(n\text{-}C_7H_{15})(CH_2CH=CH_2)_2$	21
		RT, 1 h[d)]		74
	"	RT, 1 h		90
	"	"		83
"		0°C, 1 h		67
		RT, 2.5 h		72

a) All the reactions were carried out under the ratio of allylic halide : acid anhydride : indium = 3 : 1 : 2. b) All new compounds gave satisfactory spectral and analytical data. c) 4-Phenyl-1,6-heptadien-4-ol was obtained in addition (14% yield). d) With sodium iodide (3 equiv.) under ultrasonication.

References and Notes

1) For example, "Methoden der Organische Chemie" ed by E. Müller, Georg Thieme Verlag, Stuttgart (1970), Band 13/1.
2) S. Araki, H. Ito, and Y. Butsugan, J. Org. Chem., **53**, 1831 (1988).
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