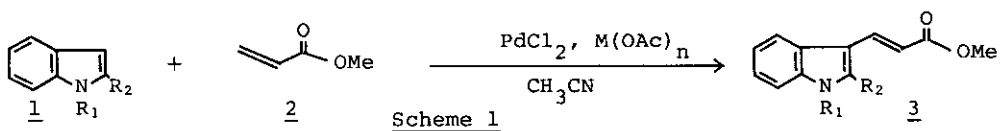
REGIOSELECTIVE VINYLATION OF INDOLES WITH OLEFINS AND $PdCl_2$

Yasuoki Murakami, Yuusaku Yokoyama, and Tsuyoshi Aoki.
School of Pharmaceutical Science, Toho University
2-2-1, Miyama, Funabashi, Chiba, 274, Japan

Direct regioselective vinylations on the C_3-position of ethyl indole-2-carboxylate(1b), N-benzyl derivative(1c) of 1b and N-benzylindole(1d) with methyl acrylate(2) were accomplished in the presence of $PdCl_2$ in good to moderate yields (Scheme 1). Vinylation on the C_3-position was determined by the alternative synthesis. The acetate salts, $Cu(OAc)_2$ or NaOAc, were essential to carry out this reaction, for the starting material was recovered quantitatively without these salts. The results are summarized in Table I. In contrast with 1b, indole itself (1a) was unstable under the reaction condition to give unidentified tarry products. Some results obtained from the reaction of 1c with the conjugated olefins are also shown in Table II.

We believe that this reaction provides a useful method for the preparation of 3-substituted indole derivatives.



1 (R_1) 2 3

Scheme 1

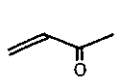
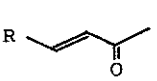
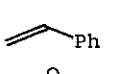
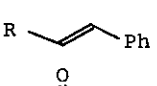
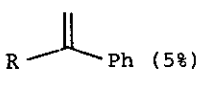
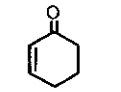
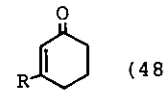
a: $R_1 = R_2 = H$
b: $R_1 = H$, $R_2 = CO_2Et$
c: $R_1 = CH_2Ph$, $R_2 = CO_2Et$
d: $R_1 = CH_2Ph$, $R_2 = H$

Table I

Indole	$M(OAc)_n$	Yield of 3(%)
1b	$Cu(OAc)_2$	49
1c	———	2*
	$Cu(OAc)_2$	81
	NaOAc	61
1d	$Cu(OAc)_2$	49

*94% recovery of starting material

Table II

Olefin	Products
	 (69%)
	 (69%),  (5%)
	 (48%)

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