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A NEW METHOD FOR THE SYNTHESIS OF CHLOROINDENES BY VILSMEIER REAGENT

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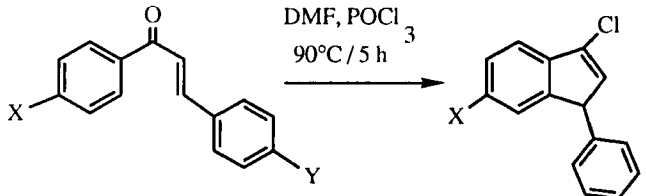
Abstract: Vilsmeier reaction of chalcone (benzalacetophenones) results in cyclization to indene derivatives .

Vilsmeier reagents are normally utilized as formylating agents[1] and their versatility has been acknowledged as an activating agent for halogenation[2]. It has also been used for different synthetic reactions[3]. Earlier studies of Vilsmeier reaction, haloformylation of unsaturated ketones (benzalacetones) have been reported[4]. We found that when the reaction was carried out under drastic conditions, formylation occur in the aromatic ring also[5]. Hence on further investigation of this work, we found that various substituted benzalacetones undergo cyclization of



Y and X = H, Cl, OMe, Me, or NO_2

Scheme -I

chloroindene derivatives under Vilsmeier condition (Scheme 1).It has been reported in the literature[6] that indan-1-ones were prepared by acid catalyzed reaction of chalcones.

In this report, we have described the condition which enable Vilsmeier reagents to afford exclusively chloroindene derivatives in 22 - 31 % yield and the remaining material was polymerized. The results were summerized in Table -I. The reaction was carried out at ambient temperature and 70° C , mostly the starting material was recovered and at 110° C all the compound was polymerized. This method proves to be a worthwhile to synthesis of chloroindenes in one-step. Indene has attracted considerable research activities since it acts as a dienophile in Diels-Alder reaction resulting in fluorene and naphthalene derivatives[7].Indene derivatives has been used as perfumes[8].

Various chalcones we synthesized by Claisen -Schmidt reaction

Table -1: Preparation of chloroindenes;

No	Substrate	Products [a]	Yield (%)
1.	Chalcone	1-Phenyl-3-Chloro-1H-indene	31
2.	4-Chloro chalcone	1-(4-Chlorophenyl)-3-chloro-1H-indene	26
3.	4-Methoxy chalcone	1-(4-Methoxyphenyl)-3-chloro-1H-indene	22
4.	3-Nitro chalcone	1-(3-Nitrophenyl)-3-chloro-1H-indene	27
5.	4'-Methyl chalcone	1-Phenyl-6-methyl-3-chloro-1H-indene	25
6.	4'-Methoxy chalcone	1-Phenyl-6-methoxy-3-chloro-1H-indene	25

a, The products were identified by proton and carbon-13 NMR and Mass spectra. All the compounds gave satisfactory C,H &N analysis.

and had physical properties in accordance with those described in literature[9].

Typical procedure: Preparation of chloroindene from chalcone:- Chalcone 2.08 g (10 mmol) was dissolved in 8 ml of DMF was cooled to 0° C and 6 ml of $POCl_3$ was added dropwise over 30 minutes and stirred for 2 h at room temperature for 5 h and then poured under the stirring onto a mixture of crushed ice (100 g) containing sodium acetate (5 g) and water (30 ml) . The product was extracted with chloroform (3 x 50 ml) and dried over anhydrous sodium sulfate. After removal of the solvent, the crude product was chromatographed through a short column of silica gel using 1:9 ratio of chloroform and petroleum ether as eluent (0.70g, 31% yield). 1H NMR ; δ 4.94 (dd,1H), 6.27 (dd, 1H), 7.29 (m, 9H), 13 C NMR ; δ 51.9, 126.5, 127.2, 127.9,128.3, 128.4, 129.0, 138.0, 141.1 . EIMS; M/z (%) 227 (M+ 90), 228 (M+1, 18), 229 (M+2, 23), 191 (base 100), 165 (23), 149 (60).

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