SHORT COMMUNICATIONS

IMPROVED SYNTHESIS OF CHALCONES USING PULVERIZED POTASSIUM HYDROXIDE AND DIMETHYLFORMAMIDE

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THE chalcones which are important intermediates in the synthesis of flavanones[1], dihydroflavanols[2], flavanols[3], aurones[4], flavones[5], dihydrochalcones[6], etc are obtained by the acid or base-catalyzed aldol condensation of 2-hydroxyacetophenones with substituted benzaldehydes[7,8]. Recently Pinkey *et al*[9] suggested the use of triethylbenzylammonium chloride for condensation. However, these methods show a large number of variations[1,7]. The higher concentration of alkali results in the formation of dypnone by self-condensation of acetophenone as well as Cannizzaro reaction of benzaldehydes and the lower concentration of alkali requires longer time for condensation. We have also observed that the isolation of chalcones from reaction mixture necessitates fractional crystallization from appropriate solvents resulting in unsatisfactory yields of the required chalcone.

Dimethylformamide (DMF) is a powerful and versatile solvent[9,10] in which a wide range of organic and inorganic compounds are soluble making it an excellent reaction medium[8,11]. This observation prompted us to study the condensation of acetophenones and benzaldehydes in DMF.

Substituted acetophenones (Ia–f) and substituted benzaldehydes (IIa–d) were dissolved in DMF and pulverized potassium hydroxide was added in boiling solution. The products on separation and purification were found to be chalcones (IIIa–m) as given in table 1. The structures of chalcones were established on the basis of m.p., m.m.p. with authentic samples, elemental analyses and superimposable IR.

It was observed that the reaction time was considerably reduced from 6–24 hr to 10 min and the yields were also improved. This improvement can be attributed to the excellent solvent power and high dielectric constant which while dissolving ionic compounds, solvates the cations more strongly and leaves the anions relatively unencumbered and highly reactive. Due to such behaviour bases are tremendously basic and nucleophiles are tremendously more nucleophilic[12]. Thus the condensation is facilitated.

Experimental Section

All melting points were determined in open capillaries in sulphuric acid bath and are uncorrected. The elemental analyses were carried out at USIC, Nagpur University, Nagpur. The PMR and IR spectra were recorded at the Regional Sophisticated Instrumentation Centre of IIT, Bombay. The substituted acetophenones were prepared and purified by known[8] methods.

Condensation of acetophenones (I) with benzaldehydes (II):

The acetophenone (Ia–f) (10 mmol) and benzaldehyde (IIa–d) (12 mmol) were dissolved in DMF (20 ml). The solution was heated to near boiling and pulverized potassium hydroxide (30 mmol, 1.7 g) was carefully added with constant vigorous stirring. The reaction mixture was boiled with continuous stirring till it became dark red (10 min). The solution was cooled, diluted with water and neutralized with hydrochloride acid. The orange-yellow pasty mass was separated, triturated with ethanol and crystallized from ethanol-acetic acid mixture to get corresponding chalcone (IIIa–m). The yields and melting points are given in table 1. PMR of IIIf($CDCl_3$): 2.40(s, 3H, $ArCH_3$), 3.96(s, 3H, OCH_3), 6.90–7.70(m, 7H, ArH), 7.57(d, 1H, =CH–, J = 16Hz), 7.91(d, 1H, =CH–, J = 16Hz), 12.78(s, 1H, –OH). IR of IIIf (nujol): 3020 (O–H), 1640 (C=O), 980 cm^{-1} (trans CH=CH wagging).

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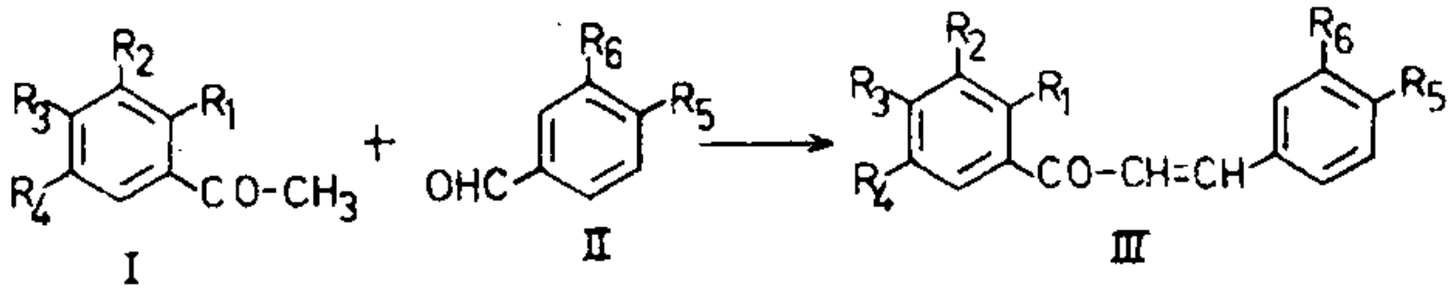

Table 1

Product No.	R_1	R_2	R_3	R_4	R_5	R_6	% yield with KOH/DMF.	Observed m.p.	Literature m.p.
IIIa	H	H	H	H	H	H	85	52°	52°[8]
IIIb	H	H	H	H	OCH_3	H	84	78°	78°[8]
IIIc	OH	H	H	H	OCH_3	H	84	95°	95°[14]
IIId	OH	H	Me	H	OCH_3	H	80	99°	98°[13]
IIIe	OH	H	H	Me	H	H	78	99°	99°[13]
IIIf	OH	H	H	Me	OCH_3	H	81	97°	98°[13]
IIIg	OH	H	H	Me	H	NO_2	60	187°	187°[8]
IIIh	OH	H	H	Me	NO_2	H	67	204°	204°[8]
IIIi	OH	NO_2	H	Me	H	H	72	158°	158°[8]
IIIj	OH	NO_2	H	Me	OCH_3	H	65	210°	210°[8]
IIIk	OH	Br	H	Me	H	H	78	108°	108°[13]
IIIl	OH	Br	H	Me	OCH_3	H	82	148°	149°[13]
IIIm	OH	H	H	H	H	H	80	89–90°	89–90°[15]

Satisfactory elemental analysis was found for all chalcones.

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A NEW ROUTE TO THE SYNTHESIS OF SOME SUBSTITUTED 3,4-BENZFLUORENES

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THE $AlCl_3$-catalyzed condensation of aromatic hydrocarbons with suitably substituted alicyclic lactones having a cyclohexane or a cyclopentane moiety, followed by cyclization, reduction and aromatization of the resulting alkylates, has a limited application in the synthesis of polycyclic compounds, due to extensive rearrangement of the resulting carbocation and polyalkylation[1]. In this laboratory, we have developed a method for the synthesis of some substituted 3,4-benzfluorenes by utilizing the catalyzed alkylation of aromatic hydrocarbons with a substituted indanol derivative which will generate a stable benzylic carbocation in the presence of Lewis acid and thereby promote normal alkylation.

The indanol derivative investigated by us for the alkylation study has been 5-methyl-1-hydroxy-trans-2-indanylacetic acid (I) which has been prepared from 5-methylindan-1-one-2-acetic acid, m.p. 125°, semicarbazone, m.p. 236°, methyl ester, m.p. 53°, synthesized from *β-p*-toluoylpropionic acid by an adaptation of the method of Roy[2]. Sodium borohydride reduction of the keto-acid in alkaline solution according to House *et al*[3] furnished the trans-acid (I) (80%), m.p. 138°, P.M.R.: δ, 4.21 (benzylic H, d, J = 8.8 Hz,