trast with an increase observed, in the $|\rho_{YZ}|$ values. This can be rationalized with the enhanced contribution of resonance "shunt" by the a-CO as the charge transfer increases, which has a shortening effect on the C_α-C_β bond length due to the double bond character in structure (III); the greater degree of charge transfer (the larger ρ_Y) will bring the greater contribution of resonance shunt, which in turn will result in a shorter C_α-C_β bond. The shorter C_α-C_β bond will naturally mean a larger $|\rho_{YZ}|$ value as observed; hence the parallel increase in the $|\rho_{YZ}|$ with ρ_Y and ρ_Z can be accommodated.

In structure (IV), there is an unpaired electron on C_α so that the substituent Y can interact with the C_d atom, which in turn means the interaction between X and Y; there will be no decrease in the interaction (and hence in ρ_{XY}) between X and Y. Thus our results clearly support involvment of structure III, but not (IV), in the TS of the nucleophilic substitution reaction of a-carbonyl compounds. We can conclude that the involvment of the bridged TS structure is a tenuous one in the light of our results of cross interaction constants.

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$$Y\phi CH_2SO_2Cl \xrightarrow[35.0°C,]{MeOH} \rho_{XY}=-0.69^{12}; \quad Y\phi SO_2Cl$$

$$\xrightarrow[35.0°C,]{MeOH} \rho_{XY}=-0.70^{13}; \; Y\phi CH_2Cl \xrightarrow[50°C]{EtOH} \rho_{XY}=-0.77^{14};$$

$$Y\phi CH_2OS\phi_2 \xrightarrow[35.0°C,]{MeOH} \rho_{XY}=-0.62^{6a}; \quad Y\phi CH_2SO_2F$$

$$\xrightarrow[45.0°C,]{MeOH} \rho_{XY}=-1.24^{6e}.$$

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A Convenient Synthesis of (E)-β-Farnesene

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(E)-β-Farnesene(**1**), (6E)-7,11-dimethyl-3-methylene-1,6,10-dodecatriene (Fig. 1) was known as a constituent of various essential oils[1] and recently used for enhancing the aroma of perfumed materials, e.g. soaps, detergents, and magnolia fragrance[2]. In 1972, W.S. Bowers identified (E)-β-farnesene as an alarm pheromone of several economically important species of aphids[3]. The damage to crops by aphids either by feeding or by transmitting virus disease can be prevented to some extent by insecticides, but aphids are developing increased resistance, particularly to systemic organophosphates[4]. Also, such insecticides do not prevent damage to crops by non-persistent viruses, such as potato virus Y, since these are rapidly acquired and transmitted by aphids. The fast-acting pyrethroids may control infection with non-persistent viruses[5] but are less effective with the more resistant biotypes *Myzus persicae*, so alternative novel approaches appear desirable. Of the chemicals that influence aphid behavior, the most active is the alarm pheromone[6]

which, for most important pest species, is the sesquiterpene hydrocarbon, (E)-β-Farnesene (**1**). Synthetic (E)-β-Farnesene substantially increases the effectiveness of contact pesticides such as permethrin against aphids in the laboratory and this approach is being investigated in field crops[7]. (E)-β-Farnesene was used as an insectide for aphid control. It was reported that (E)-β-Farnesene (10-20μg/nm²) on radish leaves killed Myzus persicae and Neomyzus circumflexus[8].
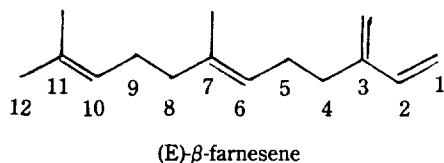

(E)-β-farnesene

Figure 1

Several methods were reported for the dehydration[9] of farnesol and nerolidol with both acidic[2] and basic catalyst to synthesize (E)-β-farnesene. By dehydration, mixtures including α-and β-farnesenes were formed. Even if some improved dehydration reactions[9c,9f] were reported, none are universally applicable and in fact, often give poor yields or unmanageable mixtures. The multistep specific conversion of (E,E)-farnesol into β-farnesene was known[10]. Recently Otera *et al*[11] reported the conversion of farnesol THP ether into the conjugated diene **1**. Several other syntheses[12,13,14,15] have been reported in the literature. Three groups[12] have reported the synthesis of (E)-β-farnesene by the establishment of the (E)-configuration at C-6 position and the β-substituted dienic moiety from C-1 to C-3 position from readily available starting materials..Two syntheses[13] involved the construction of the butadienyl moiety. Stille's synthesis[14] depended on the cross-coupling of geranyl bromide which has (E)-configuration at C-6 position with (2-methylene-3-butenyl) trimethyltin in the presence of zinc chloride. Otsuka *et al*[15] described the synthesis of β-farnesene by isoprene oligomerization.

Here we wish to report a convenient and practical method to synthesize (E)-β-farnesene by regioselective 1,4-elimination reaction of farnesyl chloride, which in turn was readily prepared from farnesol.

Farnesyl chloride(**3**) was easily prepared[16] from farnesol(**2**) by treatment with thionyl chloride and pyridine. Exposure of farnesyl chloride(**3**) to t-BuOK in DMSO(Method A) or in THF in the presence of 18-crown-6(Method B) at 40°C afforded diene **1** in β-form exclusively. No other isomers were detectable. t-BuOK attacks the methylhydrogen preferentially rather than the methylene hydrogen. This explains why the β-isomers are formed exclusively from allylic chloride **3**. The addition of 18-crown-6 accelerated the rate.
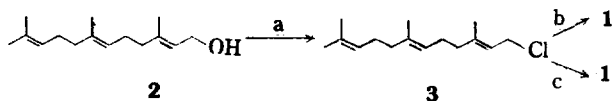
a (a)SOCl₂, pyr., 0°C, 88%; (b)KOtBu, DMSO, 40°C, 62%; (c) KOtBu, THF, 18-crown-6, 40°C, 87%

Scheme 1

Typical procedure is as follows. Method A: To a stirred solution of farnesyl chloride (0.25g, 1.0 mmol) was added

KOtBu (0.30g, 2.7 mmol) in DMSO (5.0 m*l*). The mixture was stirred at 40°C for 14 hr. To the reaction mixture ether (30 m*l*) was added and washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and then concentrated in vacuo. The crude product was separated by preparative thin layer chromatography using n-hexane: ethyl acetate (9:1) (Rf = 0.72) as eluents to afford (E)-β-farnesene[17] (0.13g, 62%). The (E)-β-farnesene thus obtained was identical in all respects (TLC, IR, ¹H-and ¹³C-NMR) with the material reported in the literature.[9-15,18] Method B: To a stirred solution of farnesyl chloride (0.25g, 1.0 mmol) was added 18-crown-6-ether (0.53g, 2.0 mmol) followed by KOtBu (1.1g, 10 mmol) in dry THF (5.0 m*l*). The mixture was stirred at 40°C for 12hr. To the reaction mixture ether (30 m*l*) was added and washed with water and saturated NaCl solution. The organic layer was dried over $MgSO_4$ and then concentrated in vacuo. The crude product was separated by preparative thin layer chromatography using n-hexane: ethyl acetate (9:1) (Rf = 0.72) as eluents to afford β-farnesene (0.18g, 87%).

The above synthetic method described is considered to be convenient and economic to prepare a fair amount of β-farnesene, the alarm pheromone of aphids to conduct field test experiments[19].

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