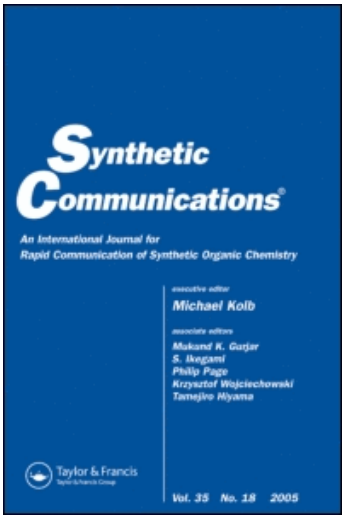

Synthetic Communications
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597304

Allylation of p-ketoaldehydes and functionalized imines by diallyltin dibromide: Formation of skipped and conjugated dienes

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To cite this Article Kumaraswamy, Sudha , Nagabrahmanandachari, S. and Swamy, K. C. Kumara(1996) 'Allylation of p-ketoaldehydes and functionalized imines by diallyltin dibromide: Formation of skipped and conjugated dienes', Synthetic Communications, 26: 4, 729 — 744
To link to this Article: DOI: 10.1080/00397919608086748
URL: http://dx.doi.org/10.1080/00397919608086748

SYNTHETIC COMMUNICATIONS, 26(4), 729-744 (1996)

ALLYLATION OF β-KETOALDEHYDES AND FUNCTIONALIZED IMINES BY DIALLYLTIN DIBROMIDE: FORMATION OF SKIPPED AND CONJUGATED DIENES

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ABSTRACT: Diallyltin dibromide reacts with β-keto-aldehydes possessing no aromatic side groups and with (hydroxy) aryl imines to afford the expected homoallyl alcohols or amines respectively. With β-ketoaldehydes having aromatic side groups, skipped or conjugated dienes are obtained depending on whether or not an aqueous work up procedure is used.

The allylation reaction is a very convenient method for C-C bond formation. Because of their high chemospecificity with respect to the aldehyde group, allyltin compounds are emerging as an important class of

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reagents[1] to effect allylation. In this connection the highly chemoselective allylation of carbonyl compounds using tetraallyltin in acidic aqueous medium reported recently by Yamamoto et al[2] is particularly noteworthy. We have been interested in the utility of diallyltin dibromide (**1**) which is one of the more easily accessible but less exploited reagents.[3] The choice of this reagent is also dictated by the fact that it can form complexes with amines;[4] if allylation could be performed after forming a complex with a chiral diamine, asymmetric induction might be effected. Two classes of substrates interested us. The first type are the β-ketoaldehydes which normally exist in their enolic form,[5] thus possessing a keto as well as an aldehyde (enol) group in effect. The second set of substrates comprises functionalized (mostly phenolic -OH) imines. Although a few allylation reactions using tin powder / allylbromide are known for substrates containing -OH groups,[6] not much is known about their effectiveness in the case of (hydroxy) aryl imines or at carbons having enol functionality. It can also be noted that the reactions of uncharged imines with allyl silanes is sluggish even in the presence of Lewis acids[6] and hence it would be of interest to study the efficacy of **1** since tin reagents are known to be more nucleophilic than their silicon counterparts.[7] Thus we report herein our results on the allylation of β-ketoaldehydes and functionalized imines using diallyltin dibromide (**1**).

Depending on the type of β-ketoaldehyde used, homoallyl alcohols or conjugated dienes or skipped dienes can be obtained by selecting the reaction conditions as outlined in Scheme 1. The substrates **2(a-c)** and the corresponding homoallyl alcohols obtained are shown in Table I. Since all the three compounds have more than one asymmetric carbon centre,

Scheme 1

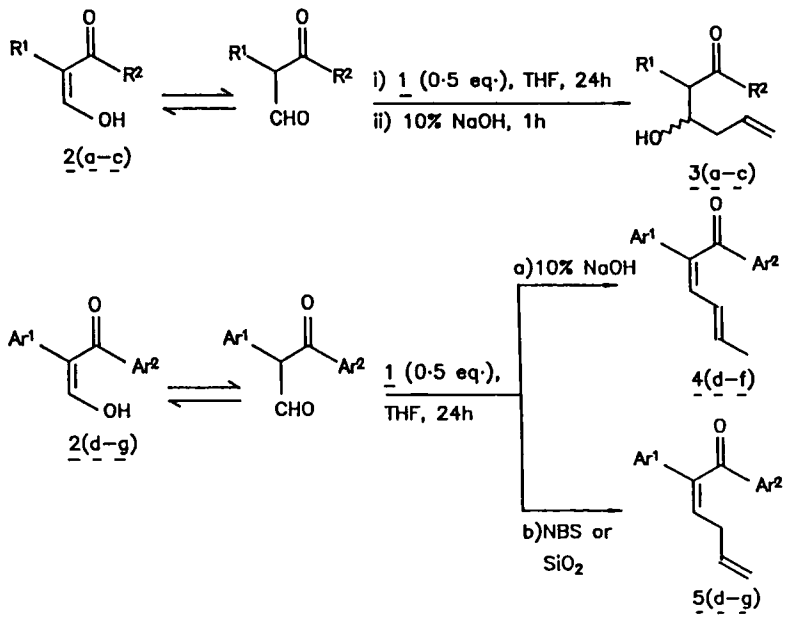
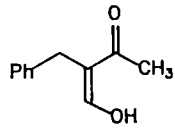
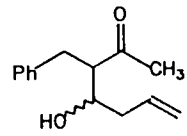
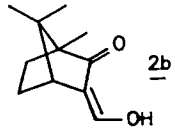
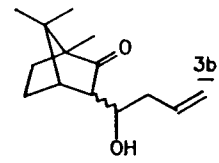
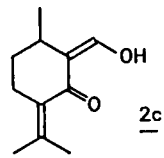
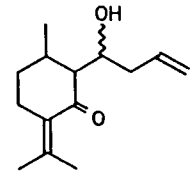


Table I

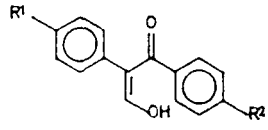
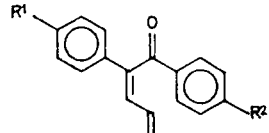
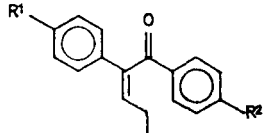
β–Ketoaldehyde (enol form) 2	Homoallyl alcohol 3
 2a	 3a
 2b	 3b
 2c	 3c

diastereomers are obtained. In particular, for **3a** the two diastereomers show well separated signals in both ^{1}H and ^{13}C NMR spectra. Since **3b** and **3c** have three asymmetric carbon centres, we tried to obtain a better resolution for **3c** by using $Eu(hfc)_3$, but it resulted mainly in broadening of the signals. We made an attempt to obtain optically pure compounds by reacting **2b** with diallyltin dibromide (**1**) in the presence of the chiral diamine N, N'- (2-phenyl ethyl) ethylene diamine,[8] but no allylated product could be identified in the reaction mixture. We believe that the formation of the hexacoordinated adduct of the diamine with **1** lowers its reactivity and hence results in this observation.

In contrast to the formation of homoallyl alcohols from **2(a-c)**, the substrates **2(d-f)** with aromatic side groups afforded the conjugated dienes **4(d-f)** under similar conditions of work up (Table II). In the case of **2g** only the skipped diene **5g** is obtained. Compounds **4(d-f)** are not stable over a period of time (> 7 d) and turn reddish brown upon storage even at low temperatures. Both ^{1}H and ^{13}C NMR can be used to identify the products. A doublet at *ca* 1.80 ppm (=CHC$\underline{H}_3$) as well as another doublet at *ca* 7.00 ppm ($\underline{H}$C=CAr, $\underline{J}\approx$10 Hz) in the ^{1}H NMR and a signal at *ca* 19.0 ppm (=CH$\underline{C}H_3$) in the ^{13}C NMR spectrum are characteristic of these compounds. The formation of **4(d-f)** can be explained by first forming the homoallyl alcohol followed by dehydration and [1,3] proton shift. Aromatic groups clearly facilitate the formation of the dienes since otherwise analogous products should have been obtained in the reactions with **2(a-c)** also.

Although we could not isolate the intermediate homoallyl alcohols starting from **2(d-f)**, their dehydrated products, the "skipped dienes" **5(d-g)**

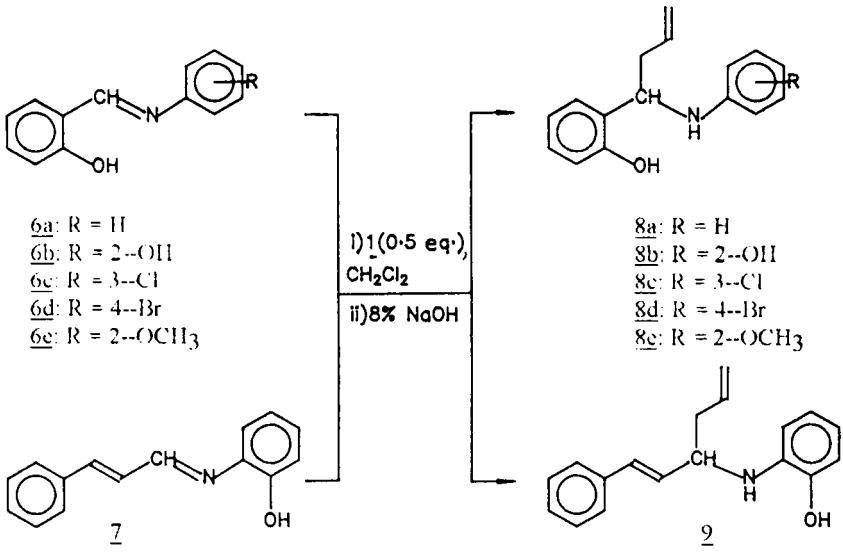
Table II

β-Ketoaldehyde (enol form)	Conjugated diene	Skipped diene
		
2d: $R^1 = R^2 = H$ 2e: $R^1 = H$; $R^2 = OCH_3$ 2f: $R^1 = R^2 = CH_3$ 2g: $R^1 = R^2 = OCH_3$	4d 4e 4f	5d 5e 5f 5g

(Table II) could be isolated if instead of washing with 10% aq. NaOH solution, the reaction mixture was stirred with NBS for 1h and chromatographed. Even though direct chromatography without treatment with NBS gives the same products **5(d-g)** isolation was easier in our hands when NBS was used. Except for **5g** (purity 80%) the other compounds **5(d-f)** were obtained in a pure state. These skipped dienes also decompose [*cf* **4(d-f)**] over a period of several days. The ^1H NMR spectra of these skipped dienes exhibit a characteristic complex triplet at *ca* 2.90 ppm (=CH- $C\underline{H}_2$-CH=) and another triplet at *ca* 6.30 ppm ($\underline{J} \approx 8$ Hz, $C\underline{H}$=CAr); a signal at *ca* 33.0 ppm (=CH-CH_2-$\underline{C}$H=) observed in the ^{13}C NMR also establishes the identity of these products.

We have been able to readily convert the skipped diene **5d** to the conjugated diene **4d** by treating the former with 10% aq. NaOH solution; this gives evidence for the [1,3] proton shift during the formation of the conjugated dienes. Here it is important to note that one cannot predict *a priori* the formation of the skipped or conjugated dienes.

Scheme 2



It can be easily noted that several isomers are possible for the conjugated dienes **4**. However only one is formed preferentially (> 70% of the product mixture, ^{1}H NMR) and hence can be readily isolated. Attempted derivatization in order to know the stereochemistry by reacting **4d** with either maleic anhydride or 2,4-dinitrophenyl hydrazine led to uncharacterizable products. For the skipped dienes also normally one isomer is predominant, although, in two cases [**5d, 5e**] a second minor isomer (< 20%) could be identified (^{1}H NMR, see experimental).[9]

In order to further examine the efficacy of $(allyl)_2SnBr_2$ (**1**), we reacted the (hydroxy) aryl imines **6(a-e)** and **7** with **1**. In all the cases we could isolate the allylated products without using any catalyst and without interference by the -OH group (Scheme 2). We also wanted to check the

reaction of the imine derived from the β-ketoaldehyde **2e** and p-anisidine; however the imine rearranged to the enamine 4-(MeO)C_6H_4-C(O)-C(Ph)=CHNH(C_6H_4-(4'-OMe) (^{1}H, ^{13}C NMR) and therefore no allylation could be effected.

In summary, our reactions add a new and interesting facet to the existing chemistry of allylation reactions. Besides being selective to the aldehyde group (in the enol form) of β-ketoaldehydes, novel water elimination products are obtained where conjugation leads to more stability. Diallyltin dibromide (**1**) is also found to be effective for allylating imines with OH (aryl) groups even in the absence of any catalyst.

EXPERIMENTAL

Chemicals were purchased from Aldrich / Fluka or local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[10] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer (operating at 50 MHz for ^{13}C) in $CDCl_3$ with chemical shifts referenced to $SiMe_4$ (δ=0). IR spectra were recorded on a JASCO FT/IR- 5300 spectrophotometer. Mass spectra were recorded on a VG-70-70H mass spectrometer. Elemental analyses were done on a Perkin-Elmer 240-C CHN analyzer.

Benzyl phenyl ketone was prepared by reduction of benzil with H_2S in the presence of pyridine.[11] Benzyl 4-methoxyphenyl ketone was prepared by the reaction of anisole and phenylacetic acid in the presence of polyphosphoric acid.[12] 4-Methylbenzyl 4-methylphenyl ketone and 4-methoxybenzyl-4-methoxyphenyl ketone were prepared by reduction of the

corresponding benzoin with tin and HCl.[13] The β-ketoaldehydes **2(a-g)** used in the present study were prepared by treating the corresponding ketones with one mole equivalent of sodium and an excess of ethyl formate;[14] use of sodium ethoxide[15-17] in the place of sodium reduced the yields significantly. Most of these ketoaldehydes were not stable at 25°C and hence had to be preserved at 0°C.[18] The (hydroxy) imines **6(a-d)** and **7** were prepared by reacting the corresponding aldehyde with the amine in methanol or toluene; all of them showed the expected ^1H and ^{13}C NMR spectra. The enamine from **2e** and p-anisidine was also prepared similarly [M.p. 162°C. ^1H NMR: 3.77, 3.81 (6H, OCH_3), 6.60-7.60 (m, 14H, H(Ar)+ CH=C), 12.30 (d, J≈20 Hz, NH)]; signals attributable to the imine were not seen.

Reactions of β-ketoaldehydes 2(a-g) with diallyltin dibromide (1):

(a) **Homoallyl alcohols 3(a-c)**. General procedure: The β-ketoaldehyde **2(a-c)** (4 mmol) was stirred with **1** (2 mmol) in dry THF (10 ml) for 24 h at 25°C under nitrogen. The resulting mixture was stirred with 10% aq. NaOH solution (10 ml) for 1 h. The organic layer was extracted with ether, concentrated and chromatographed over silica gel using petroleum ether-ethyl acetate (3:1) to afford **3** as a liquid (**3a-3c** are obtained as a mixture of diastereomers).

3a: Yield 69%. ^1H NMR: 1.89, 1.97 (2s, 3H, CH_3), 2.30 (m, 2H, CH_2-C=C), 2.65 (s, 1H, OH), 2.85-3.10 (m, 3H, $PhCH_2$, CHC=O), 3.77, 3.90 (2m, 1H, CHOH), 5.05-5.37 (m, 2H, $CH=CH_2$), 5.70-5.94 (m, 1H, $CH=CH_2$), 7.02-7.38 (m, 5H, Ph-H). ^{13}C NMR: 32.5, 32.7, 33.4, 35.6, 39.0, 40.3 (CH_3, CH_2Ph, CHC=O), 58.0, 58.4 ($CH_2C=C$), 70.6,

71.7(CHOH), 118.3, 118.6 ($CH=CH_2$), 126.5, 126.6, 128.5, 128.7, 128.9 (C(Ph)), 134.3 ($CH=CH_2$), 138.5, 138.7 (C(Ph)), 213.0, 214.1 (C=O). MS (m/e): 219 (M^+ +1), 105, 91 (100%), 43. Anal. Calc. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found : C, 77.10; H, 8.35.

3b: Yield 70%. ^1H NMR: 0.82-1.02 (complex, 9H, $3CH_3$), 1.27-2.47 (complex, 8H, $3CH_2$, 2CH), 2.74-2.91 (m, 1H, OH), 3.63-3.82 (m, 1H, CHOH), 5.08-5.12 (m, 2H, $CH=CH_2$), 5.71-5.96 (m, 1H, $CH=CH_2$). ^{13}C NMR: 9.4, 9.6, 18.9, 19.5, 20.4, 21.0, 21.5, 29.1, 29.7, 30.8, 40.7, 41.5, 45.2, 45.8, 46.5, 54.8 (CH_3, CH_2, CH), 58.1 (CH_2-C=C), 59.1 (CH-C=O), 60.3 (CH_2-C=C), 68.4, 71.0 (CHOH), 118.7, 119.0 ($CH=CH_2$), 134.7, 134.8 ($CH=CH_2$), 219.1 (C=O). MS (m/e): 222 (M^+), 181, 176, 153, 135, 109, 95, 83, 69, 55, 41 (100%). Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98. Found: C, 75.55; H, 10.01.

3c: Yield 59% . ^1H NMR: 1.03, 1.06 (2d, J= 3.8 Hz, 3H, CH_3), 1.27-1.49 (m, 1H, $CHCH_3$), 1.69-2.79 (complex, 13H, $2CH_3C=C$, $3CH_2$, CH), 3.69-3.91 (br, 1H, CHOH), 5.00-5.18 (m, 2H, $CH=CH_2$), 5.69-5.99 (m, 1H, $CH=CH_2$). ^{13}C NMR: 20.1, 20.7, 21.0, 21.6, 22.3, 22.6, 23.2, 27.9, 29.5, 31.2, 31.4, 32.1, 33.7, 38.2, 40.6 (CH_3, CH_2, CH), 61.3, 62.0 (CH_2-C=C), 71.2, 71.7 (CHOH), 117.1, 117.6 ($CH=CH_2$), 133.3 ($C=CMe_2$), 135.3, 135.8 ($CH=CH_2$), 139.9 ($C=CMe_2$), 208.2, 208.3 (C=O). MS (m/e): 223 (M^+ +1), 222 (M^+), 181, 152, 137, 135, 109, 107, 81, 69, 55, 41, 28 (100%).

(b) **Conjugated dienes 4(d-f)**: General procedure was the same as for **3(a-c)**; petroleum ether - ethyl acetate (95: 5) was used as the eluant for chromatography to afford **4** as a liquid.

4d: Yield 72%. ^1H NMR: 1.81 (d, J=6.6 Hz, 3H, CH_3), 6.05-6.41 (m,

2H, CH=CHMe), 6.97 (d, J= 10.6 Hz, 1H, CH=CPh), 7.25-7.80 (m, 10H, Ph-H). ^{13}C NMR: 18.9 (CH_3), 127.6, 128.2, 128.3, 128.4, 128.7, 129.5, 130.1, 131.7, 136.3, 138.6, 138.9, 139.8, 141.9 (C(Ph)), 197.2 (C=O). MS (m/e): 248 (M^+), 105 (100 %), 77, 51.

4e: Yield 49%. ^{1}H NMR: 1.73 (d, J= 4Hz, 3H, CH_3), 3.76 (s, 3H, OCH_3), 5.92-6.33 (m, 2H, CH=CHMe), 6.76-6.86 (m, 3H, CH=CPh + 2H of Ar-H), 7.16-7.36 (m, 5H, Ph-H), 7.65-7.72 (m, 2H, Ar-H). ^{13}C NMR: 18.7 (CCH_3), 55.3 (OCH_3), 113.3, 113.9, 115.2, 127.4, 128.1, 129.5, 129.8, 131.0, 131.9, 136.6, 138.5, 138.6, 139.6, 162.7 (C(Ar), C=C), 195.9 (C=O). MS (m/e): 378 (M^+), 263, 135 (100%), 105, 94, 77.

4f: Yield 51%. ^{1}H NMR: 1.71 (d, J= 7.6 Hz, 3H, CH-CH_3), 2.28, 2.30 (2s, 6H, 2Ph-CH_3), 5.87-6.35 (m, 2H, CH=CHMe), 6.80 (d, J= 11 Hz, 1H, CH=CAr), 7.09 (s, 6H, Ar-H), 7.56 (d, 2H, Ar-H). ^{13}C NMR (major signals only/ 25 MHz): 18.9 (CH-CH_3), 21.3, 21.6 (Ph-CH_3), 129.0, 129.1, 129.4, 129.9, 130.1, 139.0, 139.1, 140.8 (C(Ar), C=C). MS (m/e): 276 (M^+), 261, 119 (100%), 91, 65, 28.

(c) **Skipped dienes 5(d-g)**: General procedure: The β-ketoaldehyde **2(d-g)** (2.9 mmol) was stirred with **1** (1.5 mmol) in dry THF (10 ml) for 24 h at 25°C under nitrogen. The resulting mixture was treated with NBS (1.5 mmol) for 1 h and the solvent evaporated (silica gel could also be used instead of NBS; however, the use of NBS was found to give a cleaner product). Chromatography of the residue over silica gel using petroleum ether- ethyl acetate (95:5) afforded **5** as a liquid. Since the compounds **5(e-g)** were not very stable when compared to **5d,** we have recorded the MS of **5d** only.

5d: Yield 70%. ^{1}H NMR: 3.01 (t(complex), 2H, =C-CH_2-C=), 5.12 (d(complex), 2H, CH=CH_2), 5.75-5.95 (m, 1H, CH=CH_2), 6.46 (t, J=8 Hz,

1H, CH=CPh), 7.24-7.85 (m, 10H, Ph-H). ^{13}C NMR: 33.9 (=C-CH_2-C=), 116.6 (CH=CH_2), 126.3, 127.9, 128.4, 128.5, 128.9, 129.6, 129.9, 132.3, 133.3, 135.2, 135.9, 140.8, 142.8 (C(Ph), CH=CH_2, CH=CPh). MS (m/e): 248 (M^+), 128, 115, 105 (100%), 77, 51.

Some fractions from the column chromatography showed a second isomer along with **5d** [^{1}H NMR: 2.76 (t(complex), CH_2), 4.86 (d (complex), CH=CH_2), 5.60-5.76 (m, CH=CH_2), 6.17 (t, J= 8 Hz, CH=CPh)].

5e: Yield 52%. ^{1}H NMR: 2.89 (t(complex), 2H, =C-CH_2-C=), 3.68 (s, 3H, OCH_3), 4.93- 5.06 (m, 2H, CH=CH_2), 5.63-5.86 (m, 1H, CH=CH_2), 6.24 (t, J= 5 Hz, 1H, CH=CPh), 6.74-6.83 (m, 2H, Ar-H), 7.12-7.31 (m, 5H, Ph-H), 7.69-7.77 (m, 2H, Ar-H). ^{13}C NMR: 33.4 (=C-CH_2-C=), 55.4 (OCH_3), 113.5, 113.8, 114.0 (C(Ar)), 116.2 (CH=CH_2), 126.0, 127.6, 128.3, 128.7, 129.2, 130.5, 132.1, 135.2, 136.1, 137.8, 142.5, 163.1 (C(Ar), CH=CH_2, CH=CPh), 195.7 (C=O).

A second isomer was also identified in some fractions along with **5e** [^{1}H NMR: 2.73 (t (complex), CH_2), 3.65 (s, OCH_3), 4.85-4.92 (m, CH=CH_2), 5.56-5.63 (m, CH=CH_2), 6.11 (t, J≈8 Hz, CH=CAr)].

5f: Yield 52%. ^{1}H NMR: 2.27, 2.31 (2s, 6H, 2Ph-CH_3), 2.93 (t(complex), 2H, =C-CH_2-C=), 4.93-5.07 (m, 2H, CH=CH_2), 5.64-5.88 (m, 1H, CH=CH_2), 6.29 (t, J= 8 Hz, 1H, CH=CAr), 7.09 (s, 6H, Ar-H), 7.64 (d, 2H, Ar-H). ^{13}C NMR: 21.3, 21.6 (2 Ph-CH_3), 33.7 (=C-CH_2-C=), 116.3, 126.0, 129.0, 129.1, 129.3, 129.5, 129.8, 130.0, 133.0, 135.3, 135.6, 137.4, 139.0, 142.6, 142.9 (C(Ar), CH=CH_2, CH=CAr), 197.1 (C=O).

A second isomer was also identified in some fractions along with **5f** [^{1}H NMR: 2.2 (buried in the signals due to 5f), 2.65 (t (complex), CH_2), 4.89-4.92 (m, CH=CH_2), 5.61-5.80 (m, CH=CH_2), 6.17 (t, J≈ 8 Hz, CH=CAr).

5g: Yield 55%. ^{1}H NMR: 2.75 (t(complex), 2H, =C-C$\underline{H}_2$-C=), 3.69, 3.77 (2s, 6H, 2OC$\underline{H}_3$), 4.90- 5.01 (m, 2H, CH=C$\underline{H}_2$), 5.61-5.91 (m, 1H, C$\underline{H}$=CH$_2$), 6.02 (t, J= 5 Hz, 1H, C$\underline{H}$=CAr), 6.79-6.99 (m, 4H, Ar-$\underline{H}$), 7.15-7.25 (m, 2H, Ar-$\underline{H}$), 7.83-7.93 (m, 2H, Ar-$\underline{H}$). ^{13}C NMR: 34.0 (=C-$\underline{C}$H$_2$-C=), 55.3, 55.6 (2O$\underline{C}$H$_3$), 114.2 (CH=$\underline{C}$H$_2$), 126.6, 127.3, 127.8, 129.6, 130.1, 132.2, 132.4, 134.1, 135.7, 159.4, 164.0 ($\underline{C}$(Ar), $\underline{C}$H=CH$_2$, $\underline{C}$H=$\underline{C}$Ar).

Conversion of 5d to 4d: The skipped diene **5d** (0.100 g) was stirred with 10% aq. NaOH (5 ml) in THF (5ml) for 1 h. Extraction with ether and evaporation of the solvent afforded **4d** (0.08 g, 80 %) [^{1}H and ^{13}C NMR].

Allylation of imines 6(a-e) and 7: General procedure: A mixture of the imine **6(b-e)** or **7** (2-3 mmol) and a stoichiometric amount of diallyltin dibromide (**1**) (1-1.5 mmol) was stirred in dichloromethane (5-8 ml) for 14-20 h under nitrogen [for the reaction of **6a** a solvent mixture of ether and THF (1:1, 5 ml) was used]. The reaction mixture was quenched with 8% aq. NaOH solution and chromatographed using the eluant system hexane / dichloromethane / ethyl acetate to afford products **8** (**a-e**) and **9** respectively.

8a: Yield 68%. ^{1}H NMR: 2.70 (t, 2H, J≈7 Hz, C$\underline{H}_2$-CH=CH$_2$), 4.20 (br s, 1H, N$\underline{H}$), 4.38 (t, 1H, C$\underline{H}$-CH$_2$-CH=CH$_2$), 5.25-5.35 (m, 2H, CH$_2$-CH=C$\underline{H}_2$), 5.70-6.00 (m, 1H, CH$_2$-C$\underline{H}$=CH$_2$), 6.70-7.30 (m, Ar-$\underline{H}$), 9.65 (br s, 1H, Ar-O$\underline{H}$). ^{13}C NMR: 41.4 ($\underline{C}$H$_2$-CH), 59.9 (CH$_2$-$\underline{C}$H), 116.7, 117.2, 119.7, 120.1, 121.3, 126.3, 127.8, 128.6, 129.3, 134.9, 146.8, 156.6, ($\underline{C}$(Ar), $\underline{C}$=$\underline{C}$). Anal. Calc. for $C_{16}H_{18}NO$: C, 80.00; H, 8.75; N, 5.83. Found: C, 79.80; H, 8.25; N, 5.65.

8b: Yield 65%. ^{1}H NMR: 2.62 (dd, 2H, C$\underline{H}_2$-CH=CH$_2$), 4.29 (dd (or t), 1H, C$\underline{H}$-NH), 5.08-5.23 (m, 2H, CH=C$\underline{H}_2$), 5.60-5.89 (m, 1H, C$\underline{H}$=CH$_2$), 6.61-7.30 (m, 8H, Ar-$\underline{H}$). ^{13}C NMR: 41.5 (C$\underline{H}_2$-CH), 60.3 (CH$_2$-C$\underline{H}$), 114.6, 116.2, 117.2, 119.5, 120.2, 121.0, 121.7, 128.6, 134.1, 135.4, 144.9, 156.6 ($\underline{C}$(Ar), $\underline{C}$=$\underline{C}$). Anal. Calc. for $C_{16}H_{18}NO_2$: C, 75.00; H, 7.00; N, 5.47. Found: C, 74.85; H, 6.93; N, 5.35.

8c: Yield: 65%. ^{1}H NMR: 2.67 (t, 2H, C$\underline{H}_2$-CH=CH$_2$), 4.30 (t, 1H, C$\underline{H}$-CH$_2$-CH=CH$_2$), 5.25-5.31 (m, 2H, CH=CH$_2$), 5.70-5.95 (m, 1H, CH=CH$_2$), 6.60-7.20 (m, 8H, Ar-H). ^{13}C NMR: 41.2 (C$\underline{H}_2$-CH), 58.9 (CH$_2$-C$\underline{H}$), 114.3, 116.4, 117.1, 119.7, 120.4, 120.8, 126.0, 127.8, 128.8, 130.3, 134.2, 134.9, 148.1, 159.9 ($\underline{C}$(Ar), $\underline{C}$=$\underline{C}$). Anal. Calc. for $C_{16}H_{16}ClNO$: C, 70.19; H, 5.89; N, 5.12. Found: C, 69.24; H, 5.94; N, 4.92.

8d: Yield 55%. ^{1}H NMR: 2.62 (t, J= 7 Hz, 2H, C$\underline{H}_2$-CH=CH$_2$), 4.15 (s, 1H, N$\underline{H}$), 4.24 (t, J≈8 Hz, 1H, C$\underline{H}$-CH$_2$-CH=CH$_2$), 5.20-5.21 (m, 2H, CH=C$\underline{H}_2$), 5.70-5.95 (m, 1H, C$\underline{H}$=CH$_2$), 6.60-7.27 (m , 8H, Ar-$\underline{H}$), 9.07 (s, 1H, O$\underline{H}$). ^{13}C NMR: 41.3 (C$\underline{H}_2$-CH), 59.4 (CH$_2$-C$\underline{H}$), 117.2, 118.1, 119.8, 120.3, 127.8, 128.8, 132.1, 134.2, 142.0, ($\underline{C}$(Ar), $\underline{C}$=$\underline{C}$). Anal. Calc. for $C_{16}H_{61}BrNO$: C, 61.65; H, 5.07; N, 4.40. Found: C, 61.22; H, 5.33; N, 4.76.

8e: Yield 70%. ^{1}H NMR: 2.67 (t, 2H, C$\underline{H}_2$-CH=CH$_2$), 3.82 (s, 3H, OC$\underline{H}_3$), 4.20 (dd, 1H, C$\underline{H}$-CH$_2$-CH=CH$_2$), 4.80 (s, 1H, N$\underline{H}$), 5.20-5.40 (m, 2H, CH=C$\underline{H}_2$), 5.70-5.90 (m, 1H, C$\underline{H}$=CH$_2$), 6.60-7.30 (m, 8H, Ar-$\underline{H}$), 9.70 (s, 1H, Ar-O$\underline{H}$). ^{13}C NMR: 41.5 (C$\underline{H}_2$-CH), 55.7 (OC$\underline{H}_3$), 60.2 (CH$_2$-C$\underline{H}$), 109.8, 115.1, 117.2, 119.2, 120.0, 120.6, 121.2, 126.6, 127.8, 128.5, 134.3, 136.6, 148.7, 156.8 ($\underline{C}$(Ar), $\underline{C}$=$\underline{C}$). Anal. Calc. for $C_{17}H_{20}NO_2$: C, 75.55; H, 7.41; N, 5.18. Found: C, 75.20; H, 7.31; N, 5.12.

9: Yield: 55%. ^{1}H NMR: 2.42 (t, 2H, $C\underline{H}_2$-CH=CH_2), 3.90 (br m, 1H, $C\underline{H}$-CH_2-CH=CH_2), 5.00-5.20 (m, 2H, CH=$C\underline{H}_2$), 5.70-5.90 (m, 1H, $C\underline{H}$=CH_2), 6.05 (dd, 1H, PhCH=C$\underline{H}$), 6.50 (d,1H, PhC$\underline{H}$), 6.51-6.80, 7.10-7.40 (m, 9H, Ar-$\underline{H}$). ^{13}C NMR: 40.6 ($\underline{C}H_2$-CH), 55.9 (CH_2-$\underline{C}$H), 114.4, 114.5, 118.3, 122.5, 126.5, 127.5, 128.5, 130.6, 131.7, 134.5, 137.1 ($\underline{C}$(Ar) + $\underline{C}$=$\underline{C}$). Residual water could not be removed from the sample. Anal. Calc. (+ H_2O) for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.42; N, 4.95. Found: C, 74.8; H, 7.11; N, 5.14.

Acknowledgements: We thank CSIR (SK) and UGC (SN) for financial support. COSIST and Special Assistance Programme from UGC (India) are also gratefully acknowledged for instrumental facilities. We thank Dr. J. S. Yadav for some mass spectral data.

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9. In the reaction of the β-ketoaldehyde derived from acenapthene-quinone also a skipped diene is formed [^{1}H NMR: 3.45 (t(complex), 2H, =C-C$\underline{H}_2$-C=), 5.10-5.25 (m, 2H, CH=C$\underline{H}_2$), 5.61-6.05 (m, 1H, C$\underline{H}$=CH$_2$), 6.98 (t, 1H, C$\underline{H}$=CAr)]; however we were not able to purify it satisfactorily.

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18. Data for the new β-ketoaldehydes: **2c** (From (R)-(+)-pulegone). Yield 40% (purity 85%). Liquid. ^{1}H NMR: 1.09 (d, $\underline{J}$= 6.8 Hz, 3H, C$\underline{H}_3$),

1.30-1.80 (m, 4H, $2CH_2$), 1.87, 2.24 (2s, 6H, $2CH_3$-C=C), 2.30 (m, 1H, $CHCH_3$), 8.41 (s, 1H, CHOH), 15.58 (br, 1H, OH). ^{13}C NMR (major peaks only): 21.0 (CH_3CH), 24.3, 24.9 (2 CH_2), 29.3, 30.3 ($2CH_3$-C=C), 49.6 ($CHCH_3$), 114.5, 115.6, 126.0 (C=C), 148.2 (CHOH), 181.8 (C=O).

2f (From 4-methylbenzyl 4-methylphenyl ketone). Yield 44%, m.p. 115°C. ^1H NMR: 2.31, 2.34 (2s, 6H, $2CH_3$), 6.95-7.38 (m, 8H, Ar-H), 8.59 (d, J= 5 Hz, 1H, CHOH), 15.97 (d, J= 5 Hz, 1H, OH). ^{13}C NMR: 21.2, 21.6 ($2CH_3$), 115.8, 128.7, 129.4, 129.5, 130.1, 136.9, 142.0 (C(Ar) + C=CHOH), 184.4 (CHOH).

(Received in the UK 08 June 1995)