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2,2-Dimethylpenta-3,4-dienal Derivatives: Preparation, NMR Spectra, and Crystal Structure#

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Summary. The preparation of some new 2,2-dimethylpenta-3,4-dienal derivatives starting by *Claisen-Cope* rearrangement of the pyrolytic product of the corresponding acetales and followed by condensation reactions is described. The synthesis of homoallenylketone **5** from homoallenylaldehyde **3** by *Grignard* reaction and followed by the oxidation of the formed alcohol using potassium chlorochromate (*KCC*) is reported. All new compounds are characterized by IR, MS, ^{1}H, and ^{13}C NMR spectroscopy. The full assignment of the NMR signals is based on HETCOR and FLOCK pulse sequences. The molecular and crystal structure of 2,2-dimethylhexa-3,4-dienal 2,4-dinitrophenylhydrazone is presented.

Keywords. Allene; 2,2-Dimethylpenta-3,4-dienal; Hydrazones; Spectroscopy; X-ray structure.

2,2-Dimethylpenta-3,4-dienal – Derivate: Herstellung, NMR-Spektroskopie und Kristallstruktur

Zusammenfassung. Die Herstellung einiger neuer 2,2-Dimethylpenta-3,4-dienal – Derivate durch *Claisen-Cope* – Umlagerung der Pyrolyseprodukte der entsprechenden Acetale und anschließende Kondensationsreaktion wird beschrieben. Die Synthese des Homoallenlketons **5** durch *Grignard* – Reaktion und darauffolgende Oxidation des gebildeten Alkohols mit Kaliumchlorochromate (*KCC*) wird vorgestellt. Alle neuen Verbindungen werden mittels IR-, MS-, ^{1}H- und ^{13}C-NMR-Spektroskopie charakterisiert. Die NMR – Signale werden mittels C, H-Korrelationsexperimenten (direkt und long-range) eindeutig zugeordnet. Die Struktur von 2,2-Dimethylhexa-3,4-dienal-2,4-dinitrophenylhydrazon in Lösung und im Kristall wird diskutiert.

Introduction

In this paper, we report on some new 2,2-dimethylpenta-3,4-dienal derivatives. Their preparation was prompted by the idea to follow their transformation in a pyrolytic rearrangement to give new heterocyclic compounds [1, 2]. Some derivatives of homoallenylaldehydes have already been studied and have shown very interesting novel cyclization reactions. Thus, substituted 2,2-dimethylpenta-3,4-dienal azine

Dedicated to Professor *Fritz Sauter* on the occasion of his 65th birthday

underwent a thermally initiated isomerization under formation of a novel tetracyclic heterocyclic structure [3]. Hydrazones of 3-substituted 2,2-dimethylpenta-3,4-dienals cyclized *via* the hydrazone nitrogen atom and the central carbon atom of the allenic structure, followed by an oxidation to 5-substituted 5-hydroxy-4,4,6-trimethyl-2,3,4,5-tetrahydropyridazin-3-ones [4]. Some allene derivatives were found to be physiologically active [5, 6].

Results and Discussion

Homoallenylaldehydes **1**, **2**, and **3** (Fig. 1) were prepared by a one pot synthesis. Isobutyraldehyde acetals with substituted propargyl alcohols underwent a transformation followed by a *Claisen–Cope* rearrangement in the pyrolytic process [7–9]. The alcohol for the preparation of homoallenylaldehyde **3** was prepared from 2-butyn-1,4-diol *via* 4-chloro-2-butynol [10] and 4-phenyl-2-butynol [11].

The derivatives were prepared by the reaction of homoallenylaldehydes **1**–**3** with substituted hydrazines and hydroxyl amine (Fig. 1).

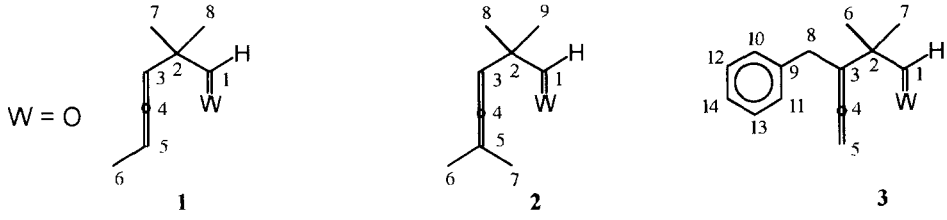
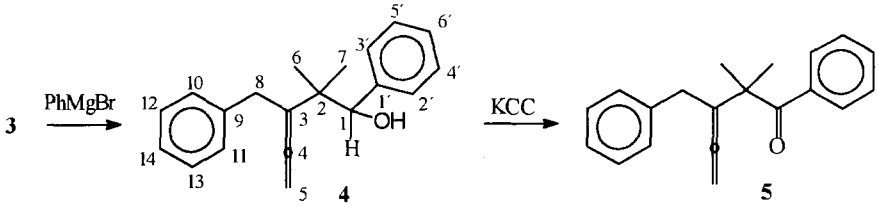


Fig. 1. **a**: W = 2,4-dinitrophenylhydrazono; **b**: W = 4-nitrophenylhydrazono; **c**: W = hydroxyimino; **d**: W = 2-(2-benzothiazolyl)-hydrazono; **e**: W = ethoxycarbonylhydrazono; **f**: W = 4-methyl-2-nitrophenylhydrazono; **g**: W = methylhydrazono

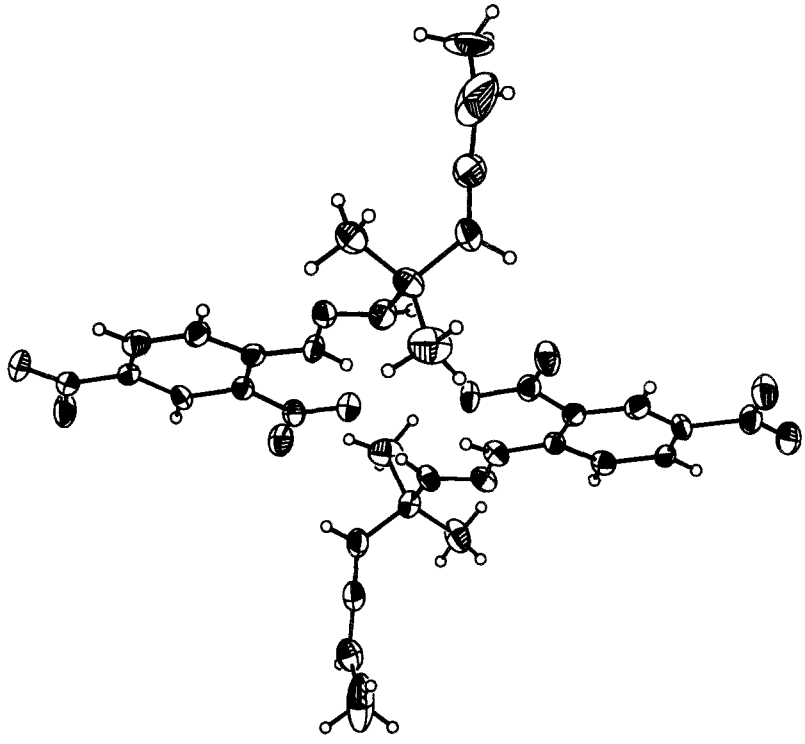
The preparation of 3-benzyl-2,2-dimethyl-1-phenylpenta-3,4-dienon (**5**) is shown in Scheme 1. Alcohol **4** was prepared by a *Grignard* reaction of phenylmagnesium bromide with homoallenylaldehyde **3**. The alcohol thus formed was oxidized to the corresponding ketone **5** using potassium chlorochromate (*KCC*) [12].



Scheme 1

In order to gain information about structure and conformation of compound **1a** in the solid state, an X-ray analysis was performed. There are two independent molecules in the asymmetric unit of the crystal with opposite configuration on the chiral axis. Averaged interatomic distances and bond angles for **1a** are given in the Table 1.

X-ray structural analysis shows a strong intramolecular hydrogen bond between the hydrogen atom of NH and the oxygen atom of the NO_2 group on the same

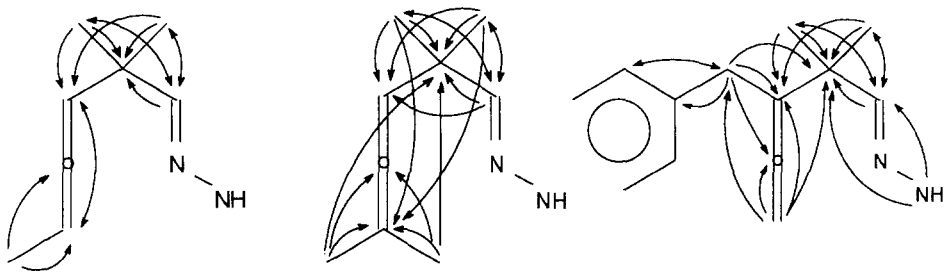


ORTEP plot of both enantiomers of compound **1a** – result of X-ray structural analysis

phenyl moiety under formation of a six-membered ring. The presence of such a type of hydrogen bonding, existing also in solution, is supported by ^{1}H NMR spectroscopy. Thus, the chemical shift of the NH proton of compound **3a** is near 10.5 ppm. In **3b**, where such an interaction is impossible the corresponding value amounts to 7.5 ppm. High long-range coupling constants are characteristic for all allenic systems. Therefore, in the ^{1}H NMR spectra we could observe coupling constants ranging from 3 Hz for $^5J_{H,H}$ to 7 Hz for $^4J_{H,H}$. For full assignment of the signals in ^{1}H- and ^{13}C-NMR spectra COSY, HETCOR, long range HETCOR and FLOCK pulse sequences were used.

Table 1. Selected interatomic distances (Å) and valency angles (°)

Interatomic distances		Valency angles	
N1–N2	1.380	N1–N2–C1	114.9
N2–C1	1.259	N2–C1–C2	123.9
C1–C2	1.489	C1–C2–C3	105.7
C2–C3	1.503	C2–C3–C4	126.4
C3–C4	1.240	C3–C4–C5	171.6
C4–C5	1.375	C4–C5–C6	137.8
C5–C6	1.255	O8′–N7′–O9′	121.8
C2′–N7′	1.435	O11′–N10′–O12′	123.4
C4′–N10′	1.452		



1 **2** **3**

Fig. 2. Long range H–C interactions observed for the allenic part of **1**, **2**, and **3** ($^1J_{CH} = 140$ Hz, $^nJ_{CH} = 7.0$ Hz)

Experimental

The melting points were determined on a Kofler block. IR spectra (ν, cm^{-1}) were measured on a Pye Unicam SP 1000 instrument. Thin-layer chromatography was performed on SiO_2 (Silufol UV 254 Kavalier, Votice) in dichloromethane. Column chromatography was carried out on silicagel 40–100 μm (Merck) and detected by UV light at 254 nm. Mass spectra were obtained using a Finnigan-MAT TSQ70 instrument operated in the electron impact (70 eV) and in the CI mode using a CH_4/N_2O mixture as ionizing gas.

^1H and ^{13}C NMR spectra (δ, ppm) were measured on a Tesla 567 (100 MHz) and a Varian UNITY-400 spectrometer. The chemical shifts were referenced to tetramethylsilane as internal standard or to the solvent signal. Spectral width: 5000 Hz for ^1H and 25000 Hz for ^{13}C; data were collected into 37.5 k and 58.5 k memory, respectively, and zero filled to 64 k data points. COSY spectra: sequence, D1-90 °-t1-45 °-t2; relaxation delay, 1s; sweep width, equal to that of the ^1H spectrum, identical for both ω_1 and ω_2; data table, 2k × 2k; apodization function, sine bell; symmetrized after FT and presented in absolute value mode. HETCOR spectra: sequence, D1-90 °(^{1}H)-$\frac{t1}{2}$-90 °(^{1}H)-τ-90 °-240 °-90 °(^{13}C)/180 °(^{1}H)-τ-90 °(^{1}H)-$\frac{t1}{2}$-D3-90 °(^{13}C)/90 °(^{1}H)-D4-t2; relaxation delay: 1s; $\tau = 3.6$ ms; D3 = 3.6 ms; D4 = 2.4 ms (optimized for a direct coupling of 140 Hz; noise decoupling during acquisition; spectral widths were taken from the corresponding 1D spectra; data table 4 k × 0.5 k, 256 increments, zero filled to 0.5 k; apodization function, sine bell in both dimensions; presented in absolute value mode. FLOCK spectra: sequence, D1-90 °(^{1}H)-$\frac{t1}{2}$-90 °(^{1}H)-τ-BIRD-τ-90 °(^{1}H)-$\frac{t1}{2}$-$\frac{D3}{2}$-90 °(^{1}H)-τ-BIRD-τ-90 °(^{1}H)-$\frac{D3}{2}$-90 °(^{13}C)/90 °(^{1}H)-$\frac{D4}{2}$-90 °(^{1}H)-τ-BIRD-τ-90 °(^{1}H)-$\frac{D4}{2}$-t2; relaxation delay, 1 s; $\tau = 3.6$ ms; D3 = 62.4 ms; D4 = 31.2 ms (optimized for a direct coupling of 140 Hz and long range coupling of 8 Hz; other parameters were identical to that of HETCOR spectra. X-ray data were collected with a KUMA KM-4 kappa four-circles diffractometer. The structure was solved by direct methods using SHELXS-86 [13] and refined on F^2 for all reflections using SHEXL-93 [14]. Crystals suitable for X-ray analysis were obtained by recrystallization from methanol in the form of well-developed yellow-orange plates. The tables of atomic coordinates of all atoms including hydrogens, anisotropic temperature displacement factors, and the full list of interatomic distances and angles were deposited and can be obtained upon request either from one of the authors (*J.M.*) or from the Fachinformationszentrum Karlsruhe [15].

The compound is triclinic with $a = 6.5910(10)$, $b = 8.541(2)$, $c = 14.062(3)$ Å, $\alpha = 98.24(3)$, $\beta = 95.42(3)$, $\gamma = 97.08(33)°$; $V = 772.4(3)$ Å^3; space group P1, $Z = 2$, $D_x = 1.308$ Mg·m^{-3}; $F(000) = 320$, $M_0(K_\alpha) = 0.71073$ Å; 2986 rfl. total, $R = 0.0498$ for obs. rfl. with $I_0 > 2\sigma(I_0)$.

4-Phenyl-2-butynol was prepared from 2-butyn-1,4-diol via 4-chlor-2-butynol [10, 11], 2,2-dimethylhexa-3,4-dienal (**1**) and 2,2,5-trimethylhexa-3,4-dienal (**2**) were prepared according to Ref. [9].

3-Benzyl-2,2-dimethylpenta-3,4-dienal (**3**)

A mixture of 4-phenyl-2-butyn-1-ol, isobutyraldehyde, mesitylene, and a catalytic amount of *p-TSA* was refluxed for 36 h. The mixture was distilled under reduced pressure. Yield, 54%; b.p., 95–105 °C/1.5 mm; $n_D^{20} = 1.5337$; IR (neat): 700 (s), 765 (w), 850 (s), 905 (w), 1025 (m), 1070 (m), 1150 (m), 1355 (m), 1385 (m), 1450 (s), 1490 (s), 1720 (s, C=O), 1935 (s, C=C=C), 2680 (w), 2780 (w), 2950 (s), 3030 (w); ^{1}H NMR: 1.18 (6H, s, CH_3), 3.15 (2H, t, CH_2-Ph, $^5J = 3$ Hz), 4.68 (2 H, t, CH_2=, $^5J = 3$ Hz, 7.10 (5H, s, Ar–H), 9.17 (1H, s, –CH=O); ^{13}C NMR; 21.48 (C6, C7), 35.68 (C8), 48.78 (C2), 78.75 (C5), 106.19 (C3), 126.89 (C14), 128.75 (C12, C13), 129.71 (C10, C11), 139.70 (C9), 201.33 (C1), 208.57 (C4).

General method for the preparation of substituted hydrazones **1–3**

An equimolar mixture of aldehyde and substituted hydrazine in benzene with a catalytic amount of *p-TSA* was refluxed (*Dean-Stark* trap for 4 h). The solvent was evaporated and the remainder was crystallized or purified by column chromatography.

General method for preparation of oximes **2c**, **3c**

An equimolar mixture of aldehyde and hydroxylamin hydrochloride was dissolved in a mixture of ethanol and water (3:1). Half an equivalent of Na_2CO_3, dissolved in a mixture of water and ethanol (4:3), was added dropwise. The mixture was stirred for 1 h and then concentrated and extracted with chloroform. The extract was washed with water, dried, filtered, and the solvent was evaporated.

2,2-Dimethylhexa-3,4-dienal 2,4-dinitrophenylhydrazone (**1a**)

Recrystallization from methanol afforded orange crystals (35%) [16]. M.p., 114–115.5 °C (Ref. [17]: 116 °C); MS (EI, *m/z*): 289 (M^+–CH_3), 243, 228, 197, 167, 122, 106, 53; IR (KBr): 720 (w), 740 (w), 840 (m), 880 (m), 920 (s), 1050 (w), 1070 (s), 1145 (s), 1210 (m), 1270 (s), 1310 (s), 1520 (s, NO_2), 1590 (w), 1620 (s, C=N), 1955 (m, C=C=C), 2890 (w), 2990 (m), 3110 (m), 3360 (s, NH); ^{1}H NMR: 1.31 (6H, s, $(CH_3)_2$C), 1.66 (3H, dd, CH_3–CH=C, $^3J = 6.8$ Hz, $^5J = 3.5$ Hz), 5.15 (1H, dq, CH=C=C, $^4J = 7$ Hz, $^5J = 3.5$ Hz), 5.22 (1H, quint., CH_3–CH=C, $^3J = 6.8$ Hz, $^4J = 7$ Hz), 7.43 (1H, s, HC=N), 7.93(1H, d, H6′, $^3J = 9.5$ Hz), 8.32 (1H, dd, H5′, $^3J = 9.5$ Hz, $^4J = 2.5$ Hz), 9.12 (1H, d, H2′, $^4J = 2.5$ Hz); ^{13}C NMR: 14.49 (C6), 25.6 (C7, 8), 39.8 (C2), 89.1 (C5), 97.31 C3), 116.61 (C6′), 123.43 (C3′), 128.89 (C2′), 129.88 (C5′), 137.77 (C4′), 145.3 (C1′), 157.68 (C1), 203.43 (C4).

2,2-Dimethylhexa-3,4-dienal 4-nitrophenylhydrazone (**1b**)

Recrystallization from methanol afforded yellow crystals (32%). M.p., 68–70 °C; MS (CI, *m/z*); 260 (M + 1), 214, 200, 194, 180, 139, 124, 59; IR (KBr): 700 (w), 730 (w), 750 (m), 840 (m) 880 (w), 930 (w), 1000 (m), 1080 (s), 1110 (s), 1180 (m), 1270 (s), 1300 (m), 1320 (s), 1360 (w), 1470 (m), 1490 (m), 1510 (m), 1550 (w), 1600 (m), 1610 (s), 1620 (m, C=N), 1955 (w, C=C=C), 2890 (w), 2960 (m), 3000 (m), 3260 (s, NH); ^{1}H NMR: 1.27 (6H, s, $(CH_3)_2$C), 1.68 (3H, dd, CH_3–CH=C, $^3J = 6.8$ Hz, $^5J = 3.5$ Hz), 5.14 (1H, dq, CH=C=C, $^4J = 7$ Hz, $^5J = 3.5$ Hz), 5.17 (1H, quint., CH_3–CH=C, $^3J = 6.8$ Hz, $^4J = 7$ Hz), 6.99 (2H, m, *o*-Ar, AA′ part of AA′XX′, $J_{AX} + J_{AX'} = 9.5$ Hz), 7.11 (1H, d, N=CH, z), 7.90(1H, bs,

NH), 8.13 (2H, m, *m*-Ar, XX′ part of AA′XX′); ^{13}C NMR: 14.41 (C6), 25.80 and 25.87 (C7 and C8), 38.46 (C2), 88.53 (C5), 97.98 (C3), 111.18 (C2′, C3′), 126.10 (C4′, C5′), 139.30 (C1′), 150.54 (C6′), 151.11 (C1), 203.07 (C4).

2,2,5-Trimethylhexa-3,4-dienal 2,4-dinitrophenylhydrazone (**2a**)

Recrystallization from petrolether afforded orange crystals (57%). M.p., 99–100 °C (Ref. [17]: 98–99 °C); MS (CI, *m/z*): 347 (M + C_2H_5), 319 (M + 1), 214, 175, 154, 113, 102, 71, 59; IR (KBr): 720 (w), 750 (w), 820 (w), 850 (m), 930 (w), 1050 (w), 1070 (m), 1145 (m), 1220 (m), 1270 (s), 1280 (s), 1310 (s), 1340 (s), 1370 (w), 1430 (m), 1510 (m), 1520 (s), 1590 (s), 1620 (s), 1630 (s), 1950 (vw, C=C=C), 2960 (w), 3000 (m), 3270 (s, NH); ^{1}H NMR: 1.29 (6H, s, CH_3), 1.73 (6H, d, CH_3, $^5J = 2.8$ Hz), 4.99 (1H, sept., =CH, $^5J = 2.8$ Hz), 7.41 (1H, d, N=CH), 7.92 (1H, d, H6′, $^3J = 9.5$ Hz), 8.61 (1H, dd, H5′, $^3J = 9.5$ Hz, $^4J = 2.6$ Hz), 9.11 (1H, d, H3′, $^4J = 2.6$ Hz), 10.95 (1H, bs, NH); ^{13}C NMR: 20.48 (C6, C7), 25.44 (C8, C9), 39.46 (C2), 95.77 (C3), 98.59 (C5), 116.47 (C6′), 123.14 (C3′), 128.70 (C2′), 129.63 (C5′), 137.52 (C4′), 145.19 (C1′), 158.18 (C1), 200.53 (C4).

2,2,5-Trimethylhexa-3,4-dienal 4-nitrophenylhydrazone (**2b**)

Recrystallization from petrolether afforded yellow crystals (48%). M.p., 86–88.5 °C; MS (CI, *m/z*): 302 (M + C_2H_5), 274 (M + H), 234, 222, 194, 177, 139, 71; IR (KBr): 700 (w), 755 (w), 810 (w), 845 (m), 1000 (w), 1080 (m), 1110 (s), 1150 (w), 1180 (m), 1260 (s), 1280 (s), 1310 (s), 1480 (w), 1490 (m), 1500 (w), 1600 (s), 1610 (s), 1950 (vw, C=C=C), 2970 (w), 3000 (m), 3260 (s, NH); ^{1}H NMR: 1.24 (6H, s, CH_3), 1.71 (6H, d, CH_3, $^5J = 2.9$ Hz), 5.01 (1H, sept., =CH, $^5J = 2.9$ Hz), 6.98 (2H, m, *o*-Ar, AA′ part of AA′XX′, $J_{AX} + J_{AX'} = 9.5$ Hz), 7.07 (1H, d, N = CH), 7.68 (1H, bs, NH), 8.13 (2H, m, *m*-Ar, XX′ part of AA′XX′); ^{13}C NMR: 20.48 (C6, C7), 25.76 (C8, C9), 38.82 (C2), 96.52 (C3), 98.02 (C5), 111.08 (C2′, C3′), 126.03 (C4′, C5′), 138.95 (C1′), 150.72 (C6′), 151.65 (C1), 200.14 (C4).

2,2,5-Trimethylhexa-3,4-dienal oxime (**2c**)

Yield, 87% of crude liquid; MS (CI, *m/z*): 182 (M + C_2H_5), 154 (M + 1), 136, 109, 95; IR (neat): 760 (w), 815(m), 950 (s), 1015 (m), 1110 (s), 1150 (w), 1195 (w), 1300 (m), 1360 (m), 1380 (m), 1450 (s), 1610 (w), 1640 (w), 1955 (w, C=C=C), 2280 (m), 2940 (m), 2980 (s), 3300 (s); ^{1}H NMR: 1.18 (6H, s, CH_3), 1.70 (6H, d, CH_3, $^5J = 2.8$ Hz), 4.97 (1H, sept., =CH, $^5J = 2.8$ Hz), 7.33 (1H, s, N=CH), 8.87 (1H, bs, OH); ^{13}C NMR: 20.55 (C6, C7), 25.80 (C8, C9), 37.75 (C2), 96.20 (C3), 98.37 (C5), 157.68 (C1), 200.28 (C4).

2,2,5-Trimethylhexa-3,4-dienal 2-(2-benzothiazolyl) hydrazone (**2d**)

Recrystallization from petrolether afforded 38% of **2d**. M.p., 114–115.5 °C; MS (CI *m/z*): 314 (M + C_2H_5), 286 (M + 1), 175, 151, 136, 123, 113, 89, 59; IR (KBr): 730 (m); 755 (s), 825 (m), 890 (m), 930 (w), 990 (w), 1020 (m), 1105 (m), 1150 (w), 1250 (w), 1275 (m), 1300 (w), 1360 (m), 1450 (s), 1580 (s), 1620 (s), 1630 (s), 1940 (vw), C=C=C), 2900 (m), 2960 (m), 3000 (m); ^{1}H NMR: 1.12 (6H, s, $(CH_3)_2C$), 1.66 (6H, d, $(CH_3)_2C$=, $^5J = 2.9$ Hz), 5.01 (1H, sept., CH=C, $^5J = 2.9$ Hz), 7.06–7.11 (1H, m, H6′), 7.25–7.30 (1H, m, H5′), 7.34 (1H, s, CH=N), 7.45 (1H, d, H4′, $^3J = 7.5$ Hz), 7.60–7.64 (1H, m, H7′); ^{13}C NMR; 20.60 (C6, C7), 25.65 (C8, C9), 39.14 (C2), 96.52 (C3), 98.19 (C5), 117.57 (C4′), 121.30 (C7′), 121.62 (C6′), 125.76 (C5′), 130.19 (C8′), 150.06 (C3′), 153. 56 (C1), 169.83 (C1′), 200.42 (C4).

2,2,5-Trimethylhexa-3,4-dienal 4-methyl-2-nitrophenylhydrazone (**2f**)

Red solid (43%); MS (CI, *m/z*: 316 (M + C_2H_5), 288 (M + 1), 272, 220, 152, 138, 123, 108, 89, 59; IR ($CHBr_3$): 830 (w), 930 (w), 1060 (w), 1220 (m), 1280 (s), 1320 (m), 1520 (s), 1575 (m), 1630 (m), 2940 (w), 2980 (m), 3010 (w), 3290 (w, NH); ^{1}H NMR. 1.26 (6H, s, CH_3), 1.72 (6H, d, CH_3, $^5J = 3.0$ Hz), 2.30 (3H,

s, CH_3–Ar), 4.99 (1H, sept., =CH, $^5J = 3.0$ Hz), 7.24 (1H, d, N=CH), 7.25 (1H, dd, H5′, $^3J = 9$ Hz, $^4J = 2.5$ Hz), 7.74 (1H, d, H6′, $^3J = 9$ Hz), 7.93 (1H, m, H3′), 10.6 (1H, bs, NH); ^{13}C NMR: 20.08 (C7′), 20.66 (C6, C7), 25.87 (C8, C9), 39.21 (C2), 96.55 (C3), 98.27 (C5), 116.07 (C6′), 124.96 (C3′), 127.13 (C2′), 130.27 (C4′), 137.52 (C5′), 140.84 (C1′), 152.97 (C1), 200.36 (C4).

3-Benzyl-2,2-dimethylpenta-3,4-dienal 2,4-dinitrofenylhydrazone (**3a**)

Recrystallization from methanol afforded orange crystals (61%). M.p., 110–112 °C; MS (CI, *m/z*): 381 (M + 1), 253, 214, 175, 89, 59; IR (KBr): 700 (w), 710 (w), 730 (w), 745 (w), 850 (m), 920 (w), 1050 (w), 1070 (m), 1145 (m), 1220 (m), 1270 (s), 1305 (s), 1330 (s), 1370 (w), 1430 (m), 1520 (s, NO_2), 1590 (s), 1615 (s), 1625 (s), 1950 (m, C=C=C), 3000 (m), 3270 (s, NH); ^{1}H NMR: 1.38 (6H, s, CH_3), 3.34 (2H, t, CH_2–Ph, $^5J = 2.7$ Hz), 4.80 (2H, t, $=CH_2$, $^5J = 2.7$ Hz), 7.08–7.23 (5H, m, Ph–H), 7.15 (1H, d N=CH), 7.58 (1H, d, H6′, $^3J = 9$ Hz), 8.29 (1H, dd, H5′, $^3J = 9$ Hz, $^4J = 2.5$ Hz), 9.10 (1H, d, H3′, $^4J = 2.5$ Hz), 10.7 (1H, bs, NH); ^{13}C NMR: 24.73 (C6, C7), 35.57 (C8), 41.10 (C2), 78.02 (C5), 107.99 (C3), 116.53 (C6′), 123.37 (C3′), 126.24 (C14), 128.14 (C12, C13), 129.01 (C10, C11, C2′), 129.81 (C5′), 137.87 (C4′), 139.58 (C9), 145.17 (C1′), 157.28 (C1), 207.39 (C4).

3-Benzyl-2,2-dimethylpenta-3,4-dienal 4-nitrofenylhydrazone (**3b**)

Recrystallization from methanol afforded yellow crystals (45%). M.p., 93–94.5 °C; MS (EI, *m/z*): 335 (M^+), 320, 244, 198, 182, 91; IR ($CHBr_3$): 700, 755, 845, 1080, 1110, 1145, 1270, 1485, 1510 (m, NO_2), 1600 (s), 1940 (C=C=C), 2970, 3015, 3250 (NH); ^{1}H NMR: 1.32 (6H, s, CH_3); 3.31 (2H, t, CH_2–Ph, $^5J = 2.7$ Hz), 4.74 (2H, t, $=CH_2$, $^5J = 2.7$ Hz), 6.82 (1H, d, N=CH), 6.95 (2H, m, *o*-Ar, A,A′ part of A,A′,X,X′, $J_{AX} + J_{AX'} = 9$ Hz), 7.11–7.23 (5H, m, Ph–H), 7.5 (1H, bs, NH), 8.14 (2H, m, m-Ar, X,X′ part of A,A′,X,X′); ^{13}C NMR: 25.01 (C6, C7), 35.33 (C8), 40.58 (C2), 77.84 (C5), 108.81 (C3), 111.32 (C2′, C3′), 125.99 (C14), 126.12 (C4′, C5′), 128.00 (C12, C13), 129.14 (C10, C11), 140.00 (C1′ and C9), 150.20 (C6′), 150.45 (C1), 207.25 (C4).

3-Benzyl-2,2-dimethylpenta-3,4-dienal oxime (**3c**)

Yield of liquid oxime: 82%; IR (neat): 665 (m), 700 (s), 715 (s), 850 (s, (CH) C=C=CH_2), 940, (s, =N–O), 1355, 1380 (m), 1430, 1450 (s), 1500 (m), 1600, 1640 (C=N), 1940 (m, C=C=C), 2910 (m), 2950 (s), 3000 (m), 3040, 3270 (s, O–H); ^{1}H-NMR: 1.25 (6H, s, CH_3), 3.27 (2H, t, $-CH_2$–Ph, $^5J = 3$ Hz), 4.68 (2H, t, $=CH_2$, $^5J = 3$ Hz), 7.18–7.22 (5H, m, Ar–H), 7.20 (1H, s, CH=N), 8.8 (1H, bs, OH); ^{13}C-NMR: 24.98 (C6, C7), 34.93 (C8), 39.39 (C2), 78.36 (C5), 108.73 (C3), 126.07 (C14), 128.07 (C12, C13), 129.14 (C10, C11), 139.77 (C9), 157.08 (C1), 207.07 (C4).

3-Benzyl-2,2-dimethylpenta-3,4-dienal ethoxycarbonylhydrazone (**3e**)

Purification by column chromatography using silica gel (CH_2Cl_2) afforded white crystals (39%). M.p., 50.5–52.5 °C; MS (EI, *m/z*): 286 (M^+), 271, 198, 185, 146, 128, 115, 109, 91; IR (KBr): 700, 840 (m), 1020 (m), 1255 (s), 1335, 1360, 1550 (s), 1690 (s, C=N), 1710 (s, C=O), 1935 (C=C=C), 2900, 2950 (m), 3000, 3030, 3160 (m); ^{1}H NMR: 1.26 (6H, s, CH_3), 1.26 (3H, t, CH_3–CH_2, $^3J = 7$ Hz), 3.25 (2H, t, CH_2–Ph, $^5J = 3$ Hz), 4.20 (2H, q, CH_2–O, $^3J = 7$ Hz), 4.65 (2H, t, $=CH_2$, $^5J = 3$ Hz), 6.98 (1H, s, N=CH), 7.16–7.26 (5H, m, Ar–H), 8.45 (1H, bs, NH); ^{13}C NMR: 14.56 (C3′), 24.75 (C6, C7), 34.99 (C8), 40.47 (C2), 61.39 (C2′), 78.04 (C5), 109.09 (C3), 125.93 (C14), 127.92 (C12, C13), 129.14 (C10, C11), 139.95 (C9), 153.16 (C1), 154.08 (C1′), 207.08 (C4).

3-Benzyl-2,2-dimethylpenta-3,4-dienal 4-methyl-2-nitrophenylhydrazone (**3f**)

Recrystallization from methanol afforded red crystals (50%). M.p., 80–81.5 °C; MS (EI, *m/z*): 349 (M^+), 334, 318, 303, 258, 212, 198, 184, 152, 128, 108, 91; IR (KBr): 690, 765, 825 (m), 840 (m), 920, 1055 (m),

1110, 1145 (s), 1210 (s), 1270 (s), 1320 (s), 1350, 1400 (m), 1430 , 1465, 1520 (s, NO_2), 1565 (s), 1625 (s, C=N), 1940 (C=C=C), 2915 (m), 2960 (m), 3005 (m), 3250 (s, N–H); ^{1}H NMR: 1.33 (6H, s, CH_3), 2.30 (3H, s, CH_3–Ar), 3.31 (2H, t, CH_2–Ph, ^5J = 2.8 Hz), 4.73 (2H, t, =CH_2, ^5J = 2.8 Hz), 7.03 (1H, d, N=CH), 7.10–7.23 (5H, m, Ph–H), 7.31 (1H, dd, H5′, ^3J = 9 Hz, ^4J = 2.2 Hz), 7.70 (1H, d, H6′, ^3J = 9 Hz), 7.93 (1H, m, H3′), 10.42 (1H, bs, NH); ^{13}C NMR: 20.09 (C7′), 25.01 (C6, C7), 35.34 (C8), 40.78 (C2), 77.89 (C5), 108.79 (C3), 116.10 (C6′), 124.98 (C3′), 126.07 (C14), 127.23 (C2′) 128.03 (C12, C13), 129.06 (C10, C11), 130.37 (C4′), 137.44 (C5′), 139.88 (C9), 140.68 (C1′), 152.07 (C1), 207.28 (C4).

3-Benzyl-2,2-dimethylpenta-3,4-dienal methylhydrazone (**3g**)

Aldehyde **3** was dissolved in benzene with a catalytic amount of *p-TSA*; under cooling, an equivalent of methylhydrazine in benzene was added. The mixture was stirred for 2 h and then the solvent was evaporated. Yield: 93%; the hydrazone is highly sensitive to heating.

IR (neat): 700 (s), 840 (m), 1030 (m), 1070 (w), 1110 (m), 1380 (w), 1450 (m), 1470 (m), 1490 (m), 1600 (m), 1675 (m, C=N), 1935 (m, C=C=C), 2840 (m), 2900 (s), 2940 (s), 3000 (m), 3270 (s, N–H); ^{1}H NMR: 1.23 (6H, s, CH_3), 2.69 (3H, s, CH_3–N), 3.27 (2H, t, CH_2–Ph, ^5J = 2.8 Hz), 4.0 (1H, bs, NH), 4.67 (2H, t, =CH_2, ^5J = 2.8 Hz), 6.56 (1H, s, N=CH), 7.14–7.21 (5H, m, Ph); ^{13}C NMR: 25.44 (C6, C7), 34.76 (C1′), 35.01 (C8), 40.00 (C2), 77.54 (C5), 109.94 (C3), 125.78 (C14), 127.89 (C12, C13), 129.06 (C10, C11), 140.41 (C9), 144.62 (C1), 207.02 (C4).

3-Benzyl-2,2-dimethyl-1-phenylpenta-3,4-dienol (**4**)

To a solution of *Grignard* reagent (0.44 g Mg and 2.79 g brombenzene), a solution of aldehyde **3** (2.85 g) in dry diethylether was added dropwise. The mixture was stirred overnight. Then ice (50 g) and HCl were added till the precipitate dissolved. The organic phase was separated, washed with saturated aqueous $NaHCO_3$ solution and then with water and dried over Na_2SO_4. The residue was filtered and evaporated affording 91% of **4**. IR (neat): 705 (s), 750 (s), 770, 850 (m), 1000, 1030 (m), 1040 (m), 1190, 1360, 1385 (m), 1450 (s), 1475 (m), 1500 (s), 1600 (m), 1940 (m, C=C=C), 2870, 2930 (m), 2960 (s), 3015 (s), 3040, 3380 (s, O–H); ^{1}H NMR: 1.00 (6H, s, CH_3), 3.35 (2H, t, CH_2–Ph, ^5J = 3 Hz), 4.59 (2H, t, =CH_2, ^5J = 3 Hz), 4.65 (1H, s, CH–O), 7.17–7.34 (10H, m, Ph, Ph); ^{13}C NMR: 21.70 and 24.16 (C6 and C7), 34.86 (C8), 42.03 (C2), 77.43 (C5), 78.89 (C1), 109.55 (C3), 126.00–129.06 (C14, C6′, C11, C12, C13, C14, C2′, C3′, C4′, C5′), 140.02 (C9), 140.55 (C1′), 207.85 (C4).

3-Benzyl-2,2-dimethyl-1-phenylpenta-3,4-dienon (**5**)

Alcohol **4** (2 g) was dissolved in dry acetone (7 ml), and *KCC* (potassium chlorochromate, 5 g) was added. The mixture was stirred overnight. Then *n*-hexane (120 ml) was added to the mixture. The mixture was stirred for 1 h and the solution was filtered. Solvents were evaporated and the crude product recrystallized from methanol.

Yield, 101 g (51%); M.p., 46–48.5 °C; MS (CI, NH_3, *m/z*): 295 (29), 294 (74, M + NH_4^+), 278 (24), 277 (85, M + 1), 105 (100); IR (KBr): 705 (s), 745, 850, 970 (s), 1070, 1160 (m), 1250 (s), 1380 (m), 1440 (m), 1470 (m), 1500 (m), 1595 (s), 1665 (s, C=O), 1940 (m, C=C=C), 2920, 2970 (s), 3010 (m), 3040; ^{1}H NMR: 1.44 (6H, s, CH_3), 3.17 (2H, t, CH_2–Ph, ^5J = 3.5 Hz), 4.75 (2H, t, =CH_2, ^5J = 3.5 Hz), 6.91–7.58 (8H, m, Ar–H), 8.03 (2H, ArH–C=O, ^3J = 8 Hz, ^4J = 2 Hz); ^{13}C NMR: 26.21 (C6, C7), 35.61 (C8), 49.84 (C2), 79.25 (C5), 110.43 (C3), 126.09 (C14), 127.91 (C12, C13)$^+$ 128.11 (C4′, C5′)$^+$, 128.80 (C2′, C3′), 129.21 (C10, C11), 132.04 (C6′), 136.88 (C1′), 138.95 (C9), 203.84 (C1), 206.52 (C4).

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