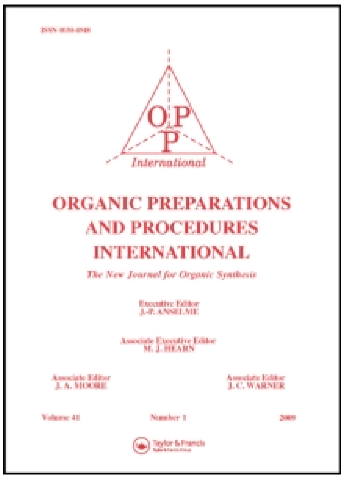

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SYNTHESIS OF β, β-DISUBSTITUTED ACYCLIC α-ENONES WITH AN ASYMMETRIC CARBON

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SYNTHESIS OF β,β-DISUBSTITUTED ACYCLIC α-ENONES WITH AN ASYMMETRIC CARBON

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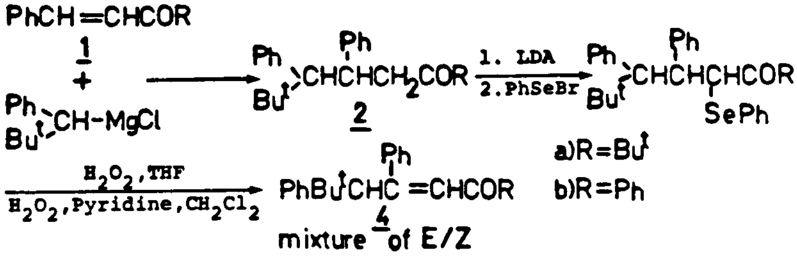
β,β-Disubstituted acyclic α-enones with a chiral center at γ-position are of great interest because the structural unit $C^*-C=C-C=O$ is present in a large number of natural products. Furthermore, these compounds can be employed as models for the study of asymmetric induction in 1,2- and 1,4-nucleophilic addition reactions. This paper describes the synthesis of the racemates (±)(4Z) and (±)(4E) 2,2,7,7-tetramethyl-5,6-diphenyloct-4-en-3-one (4a) and (±)(2Z) and (±)(2E) 5,5-dimethyl-1,3,4-triphenylhex-2-en-1-one (4b)(Scheme 1).

SCHEME 1



The sequence of selenenylation-dehydroselenenylation[1-3] of the corresponding saturated ketones (2) was selected because of the failure of various olefination processes of (±) 3,3-dimethyl-1,2-diphenylbutan-1-one, such as the Wadsworth-Emmons reactions[4-8] with the α-metallated phosphonates (sodium diethyl 3,3-dimethyl-2-oxobutylphosphonate, sodium diethyl ethoxycarbonylmethylphosphonate and sodium diethyl formylmethylphosphonate diethylacetal; base-solvent system: NaH-1,2-dimethoxyethane) and the Peterson olefination[5,9,10] (lithium ethyltrimethylsilylacetate; base-solvent system: lithium diisopropylamide/tetrahydrofuran).

The preparation of 2,2,7,7-tetramethyl-5,6-diphenyloctan-3-one (2a) and of 5,5-dimethyl-1,3,4-triphenylhexan-1-one (2b) was carried out by 1,4-addition of 2,2-dimethyl-1-phenylpropylmagnesium chloride to (E) 4,4-dimethyl-1-phenylpent-1-en-3-one and (E) 1,3-diphenylprop-2-en-1-one respectively. In both cases, a mixture of the two diastereomeric racemates (RR,SS) and (RS,SR)[11] in the ratio 50±3% was obtained. The selenenylation of the ketones was carried out by the addition of benzeneselenenyl bromide to the lithium enolate prepared by treatment with LDA in THF at 0° for 2a and -78° for 2b.[12] The availability of the corresponding enolates is the limiting step of the selenenylation-dehydroselenenylation process.[1-3] The dehydroselenenylation sequence was performed in one step by treatment of the crude α-phenylselenoketone (3) with hydrogen peroxide as oxidant[13] at 30-35°. The process was quantitative and no side-reactions were observed.

The reaction has been accomplished with mixtures of the diastereomeric racemates (RR,SS) and (RS,SR) of the starting ketones (2) and the (RR,SS) isomer of ketone 2a (R=t-Bu). In all cases, a mixture of (Z) and (E) isomers of the α-enones 4 (Table 1) was obtained as in the case of the preparation of trisubstituted olefins.[3] It has been found that the more sterically hindered isomer (RS,SR)[11] of the mixture of the diastereomeric racemates of the starting ketones reacts faster than the (RR,SS) isomer, probably due to greater relief of steric strain in going from the ketone to the corresponding enolate. The overall yields of the selenenylation-dehydroselenenylation sequence are collected in Table 1.

TABLE 1. Yields and Composition of the Acyclic α-Enones 4

Starting ketone	α-Enone	Yield(%)	α-Enone. Composition %(E)/%(Z)
2a[a]	4a	90	61/39[d]
2a[b]	4a	85	51/49[d]
2b[c]	4b	40	60/40[e]

---

[a] 58%(RR,SS)/42%(RS,SR). [b] 100%(RR,SS). [c] 57%(RR,SS)/43%(RS,SR). [d] Determined by g.l.c. (±3%). [e] Evaluated by ^1H-NMR (±3%).

The assignment of (Z), (E) configurations to C=C bond of the two isomers of α-enones 4, previously separated and purified, is based upon the observed values for ^1H and ^{13}C-NMR chemical shifts of the both isomers (Tables 2 and 3). The chemical shifts of the nuclei at γ-position, γ-H and γ-C, are the magnetic parameters of most interest for this study. Thus, the γ-H in (E)-isomer must be more deshielded by the anisotropy of the oxo group[14-16] than in the Z-isomer, whereas the γ-C must absorb at higher field[17-19] owing to cis arrangement of the t-Bu(Ph)CH moiety relative to the oxo group (γ-effect) (Scheme 2). This situation is precisely observed for the α-isomers of the enones 4a and 4b (Tables 2 and 3).

TABLE 2. Proton Chemical Shifts for Isomers of 4a and 4b

4a			4b		
Chemical shifts[a]	α Isomer δ (ppm)	β Isomer δ (ppm)	Chemical shifts[a]	α Isomer δ (ppm)	β Isomer δ (ppm)
6-H(γ-H)[b]	5.37	3.42	4-H(γ-H)	5.29	3.60
4-H[b]	6.33	6.92	2-H[b]	6.71	7.06
t-Bu	0.97	1.14	t-Bu	1.00	1.13
t-Bu-CO	1.19	1.08	p-H[c]	6.87-7.05	6.86-7.02[d]
p-H[e]	6.75-6.90	6.70-6.90	Ar[f]	7.18-7.47	7.10-7.46
Ar[f]	7.05-7.40	7.10-7.20	o-H(1-Ph)	7.89-8.01	7.64-7.80

---

[a] All signals are singlets save those corresponding to aromatic hydrogens. [b] The allylic coupling constants J_{46} and J_{24} could not be obtained; these signals appears slightly broadened singlets. [c] 3-Ph and 4-Ph groups. [d] This signal in the β isomer corresponds to four hydrogens and has been assigned to the p-H of 3-Ph and 4-Ph and o-H of 4-Ph groups. [e] 5-Ph and 6-Ph groups. [f] These signals correspond to the remaining aromatic hydrogens of the molecule.

The differences between the chemical shifts of the γ-H and the γ-C for the (E) and (Z) isomers are $\Delta\delta_{\gamma\text{-H}}$: 1.95 ppm for 4a and 1.69 ppm for 4b; $\Delta\delta_{\gamma\text{-C}}$: -12.18 ppm for 4a and -10.30 ppm for 4b; values of $\Delta\delta_{\gamma\text{-H}}$: 0.1-0.5 ppm[15,17] and $\Delta\delta_{\gamma\text{-C}}$: -6.4 to -8.8 ppm have been reported for related systems.[17,18] Therefore, the (E) configuration can be assigned to α isomers and (Z) configuration to β isomers of enones 4a and 4b (see experimental section). The large value of $\Delta\delta_{\gamma\text{-H}}$ suggets that this hydrogen atom in the (E) isomer must be held close to the oxygen atom and in the plane of the CO group, adopting a preferred conformation close to a planar s-cis disposition with a slight deviation from planarity.[14-16] The interaction between the γ-H and the CO group may be ascribed to an attractive intramolecular interaction between these groups[20] (Scheme 2).

TABLE 3. ^{13}C Chemical Shifts for Isomers of 4a and 4b

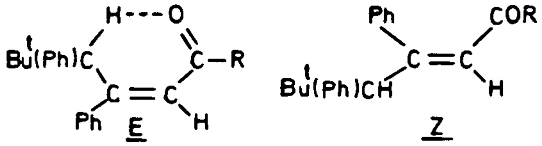
4a			4b		
Chemical Shifts[a]	α Isomer δ (ppm)	β Isomer δ (ppm)	Chemical Shifts[a]	α Isomer δ (ppm)	β Isomer δ (ppm)
Me(t-BuCO)	26.67	26.51	Me	29.72	29.43
Me	29.65	29.40	5-C	35.48	35.65
7-C	35.18	35.44	4-C(γ-C)	55.20	65.50
2-C	44.41	43.71	2-C	-[b]	126.09
6-C(γ-C)	54.10	66.28	Ar[c]	126.40	126.67
4-C	-[b]	123.07		127.37	127.29
Ar[c]	126.31	126.60		127.44	127.65
	127.10	126.81		127.64	127.77
	127.32	127.60		128.50	127.96
	127.59	127.78		128.57	128.17
	129.03	130.44		129.06	128.60
	131.25			131.26	130.39
i-C(5-Ph)	140.41	139.43	p-C(1-Ph)	132.73	132.32
i-C(6-Ph)	143.48	143.66	i-C(1-Ph)	138.93	138.20
5-C	159.73	157.14	i-C(3-Ph)	140.07	139.94
3-C	207.00	205.29	i-C(4-Ph)	143.16	143.25
			3-C	160.17	156.52
			1-C	192.15	194.14

[a] The signals were assigned using the partial decoupled spectra.

[b] The signal corresponding to this carbon atom is concealed by the signals of the aromatic carbon atoms in the α isomers.

[c] These signals correspond to the remaining aromatic carbons of the molecule.

SCHEME 2



EXPERIMENTAL SECTION

Melting points are uncorrected. IR spectra were recorded in CCl_4 solution or on KBr pellet on a Perkin-Elmer spectrophotometer. Glc was carried out on a Perkin-Elmer Sigma-3 instrument provided with a flame ionization detector and a Sigma-10 data collector. The ^1H- and ^{13}C-NMR spectra were recorded on a 80 MHz Varian FT 80A (PFT) spectrometer at 303ºK, using $CDCl_3$ as solvent and TMS as internal reference. The recording conditions were as follow: ^1H-NMR, concentration 13% w/v, acquisition time 2.047 s, spectral width 800 Hz, pulse width 10 μs; ^{13}C-NMR, concentration 25% w/v, acquisition time 1.638 s, delay time 1.64 s, spectral width 5000 Hz, pulse width 6 μs. Mass spectra were recorded on a Varian MAT-711 mass spectrometer. Tetrahydrofuran (THF) was purified in the usual manner by distillation from $LiAlH_4$. Diisopropylamine and pyridine were distilled from potassium hydroxide and stored over molecular sieves. Solutions of lithium diisopropylamine (LDA) in THF were prepared and titrated by the procedure of Vedjes et al.[21]

Preparation of Saturated Ketones 2[22].- To a magnetically stirred solution of 2,2-dimethyl-1-phenylpropylmagnesium chloride in THF (from magnesium (850 mg, 35 mmol) and 1-chloro-2,2-dimethyl-1-phenylpropane[23] (5.84 g, 32 mmol) under nitrogen at 0º was added dropwise a solution of (E) 4,4-dimethyl-1-phenylpent-1-en-3-one[22] or (E) 1,3-diphenylprop-2-en-1-one (30 mmol) in THF (10 ml). Once the addition was completed the mixture was allowed to come to room temperature and stirred for 12 hrs. The reaction mixture was hydrolyzed with a saturated NH_4Cl solution and diluted with Et_2O. The organic layer was washed with water and dried ($MgSO_4$) and the solvent was removed by rotatory evaporation. The residue containing a mixture of the two diastereomeric racemates (RR,SS) and (RS,SR)[11] (50±3% of each) of the corresponding ketones 2a or 2b as a major products were analyzed by ^1H-NMR. The crude products were purified by silica gel chromatography using light petroleum-Et_2O (95:5) as eluent. Pure (RR,SS) diastereomeric racemates in the ratio 58±3% and 42±3% for 2a (69%) and 57±3% and 43±3% for 2b (67%) (by ^1H-NMR) were obtained. The purity was tested by glc (Carbowax-20M 12% on Chromosorb W-AW-DMCS, length 2 m, Φ 1/8 in, column temperature 185º, gas flow (N_2) 35 $ml.min^{-1}$) retention time 63.5 min for 2a (unresolved isomers); (UCC-982 5% on Chromosorb W-AW-DMCS, lenght 2 m, Φ 1/8 in, column temperature 185º, gas flow (N_2) 35 $ml.min^{-1}$) retention time 63.5 min for 2b (unresolved isomers). $\nu_{max}(CCl_4)$: 1.700 cm^{-1} and 1.680 cm^{-1} (CO) for 2a and 2b, respectively.

^{1}H-NMR:

2a: δ(ppm) 0.66(s, t-Bu (RR,SS) isomer), 0.94(s, t-BuCO (RS,SR) isomer), 0.97(s, t-Bu (RS,SR) isomer), 2.06-2.93(m, 4-H and 6-H), 3.75-4.10(m, 5-H), 6.84-7.20(m, Ph).

2b: δ(ppm) 0.70(s, t-Bu (RR,SS) isomer), 0.98(s, t-Bu (RS,SR) isomer), 2.60-3.40(m, 2-H and 4-H), 3.80-4.30(m, 3-H), 6.80-7.80(m, Ph).

Separation of the Diastereomeric Racemates (RR,SS) and (RS,SR) of 2a and 2b.

2,2,7,7-Tetramethyl-5,6-diphenyloctan-3-one (5R6R,5S6S isomer, 2a), mp. 132-134º, was separated by fractional recrystallization from methanol. $\nu_{max}(CCl_4)$ 1.705 cm^{-1} (CO). ^{1}H-NMR: δ (ppm) 0.66(18H, s, t-Bu), 2.06-2.93(3H, m, 4-H and 6-H), 3.75-4.02 (1H, m, 5-H), 7.19(10H, apparent singlet, Ph). MS(m/s) 336 (M^+).

Anal. Calc. fro $C_{24}H_{32}O$: C, 85.71; H, 9.52

Found: C, 85.82; H, 9.46

2,2,7,7-Tetramethyl-5,6-Diphenyloctan-3-one (5R6S,5S6R isomer, 2a), mp. 92-94º, was separated by fractional recrystallization from methanol. $\nu_{max}(CCl_4)$ 1.695 cm^{-1} (CO). ^{1}H-NMR: δ(ppm) 0.94 (9H, s, t-BuCO), 0.97(9H, s, t-Bu), 2.67-2.87 (3H, m, 4-H and 6-H), 3.86-4.10(1H, m, 5-H), 6.84-7.18(10H, m, Ph). MS (m/s): 336 (M^+).

Anal. Calc. for $C_{24}H_{32}O$: C, 85.71; H, 9.52

Found: C, 85.84; H, 9.60

5,5-Dimethyl-1,3,4-triphenylhexan-1-one, (3R4R,3S4S isomer, 2b) mp 156-157º (methanol), was separated by silica gel chromatography (30:1 (w/w) adsorbent-product ratio) using light petroleum-Et_2O (97:3) as eluent. ν_{max}(KBr) 1.675 cm^{-1} (CO). ^1H-NMR δ(ppm): 0.70(9H, s, t-Bu), 2.63-3.31(3H, m, 2-H and 4-H), 3.86-4.16(1H, m, 3-H), 7.09-7.57(15H, m, Ph). MS (m/s): 356 (M^+).

Anal. Calc. for $C_{26}H_{28}O$: C, 87.64; H, 7.86
Found: C, 87.80; H, 8.10

5,5-Dimethyl-1,3,4-triphenylhexan-1-one, (3R4S,3S4R isomer, 2b) mp 140-141º (methanol) was separated by silica gel chromatography (30:1 (w/w) adsorbent-product ratio) using light petroleum-Et_2O (97:3) as eluent. ν_{max}(KBr) 1.670 cm^{-1}(CO). ^1H-NMR δ(ppm): 0.98(9H, s, t-Bu), 2.76-3.33(3H, m, 2-H and 4-H), 4.00-4.24(1H, m, 3-H), 6.86-7.80(15H, m, Ph). MS (m/s): 356 (M^+).

Anal. Calc. for $C_{26}H_{28}O$: C, 87.64; H, 7.86
Found: C, 87.50; H, 8.08

2,2,7,7-Tetramethyl-5,6-diphenyloct-4-en-3-one (4a).- To a solution 0.77M of LDA (4.26 ml, 3.28 mmol) in THF under nitrogen was added dropwise a solution of ketone 2a (mixture of diastereomers: 58±3% (RR,SS)/42±3% (RS,SR) or (RR,SS) isomer (1.0 g, 2.98 mmol) in dry THF (25 ml) with stirring at -10º and the mixture was allowed to come to room temperature and stirred for 1 hr. A solution of benzeneselenenyl bromide (744 mg, 3.28 mmol) in THF (25 ml) was added after cooling to -78º. Once the addition was completed the mixture was hydrolyzed with saturated NH_4Cl solution, water, saturated $NaHCO_3$ solution and saturated NaCl solution and dried ($MgSO_4$). The solvent was removed *in vacuo*.

To a solution of the previous crude product (1.5 g) in THF (15 ml) was added dropwise a solution of 8 mmol of H_2O_2

(906 mg of 30% H_2O_2) in 1 ml of water with stirring at 30-35º. The reaction mixture was vigorously stirred at this temperature for 1 hr and then was diluted with water and worked up. The reaction was monitored by thin layer chromatography (silica gel) using light petroleum-Et_2O (95:5) as eluent. The residue containing a mixture of the two isomers (4Z) and (4E) of the 2,2,7,7-tetramethyl-5,6-diphenyloct-4-en-3-one (4a) and the unchanged ketone 2a was analyzed by glc, IR and ^{1}H-NMR. The overall yield of the process and composition of the mixtures of isomers of the α-enone (4a) were tested by glc (Carbowax-20M 12% on Chromosorb W-AW-DMCS, length 2 m, Φ 1/8 in, column temperature 185º, gas flow (N_2) 35 ml.min^{-1}; retention times: ketone 2a 63.5 min, α isomer 76.0 min, β isomer 93.3 min). The results are collected in Table 1.

The α and β isomers of 4a were separated and purified by silica gel chromatography (30:1 (w/w) adsorbent-product ratio) using light petroleum-Et_2O (97:3) as eluent. The purity was tested by glc and ^{1}H-NMR and the products were analyzed by IR, ^{1}H- and ^{13}C-NMR spectroscopy and mass spectrometry.

α Isomer (4a), mp. 82-84º (methanol). ν_{max}(KBr): 1.680 cm^{-1} (CO), 1.595 and 1.570 cm^{-1} (C=C). MS (m/s): 334 (M^+).

Anal. Calc. for $C_{24}H_{30}O$: C, 86.23; H, 8.98

Found: C, 86.01; H, 9.20

β Isomer (4a), viscous pale yellow liquid. ν_{max}(neat): 1.695 cm^{-1} (CO), 1.620 and 1.600 cm^{-1} (C=C). MS (m/s): 334 (M^+). The ^{1}H- and ^{13}C-NMR data are collected in Tables 2 and 3.

5,5-Dimethyl-1,3,4-triphenylhex-2-en-1-one (4b)[1-3].- The α-phenylselenoketone was obtained as described for 4a except that the intermediate enolate was prepared from ketone 2b (mixture of diastereomers 57±3% (RR,SS)/43±3% (RS,SR) at -78º during 0.5 hr. After addition of benzeneselenenyl bromide the reaction mixture was stirred at -78º during 0.5 hr and hydrolized at this temperature. To a solution of the crude α-phenylselenoketone (1.4 g) and pyridine (400 mg, 2.8 mmol) in dichloromethane (10 ml) was added dropwise a solution of 8 mmol of H_2O_2 (906 mg of 30% of H_2O_2) in 1 ml of water with stirring at 30-35º. The reaction mixture was vigorously stirred at this temperature for 1 hr and then was diluted with water and worked up. The reaction was followed by thin layer chromatography (silica gel) using light petroleum-Et_2O (95:5) as eluent. The residue containing a mixture of the two isomers (2Z) and (2E) of the 5,5-dimethyl-1,3,4-triphenylhex-2-en-1-one (4b) and the unchanged ketone 2b was analyzed by glc, IR and ^{1}H-NMR. The overall yield of the process and the composition of the mixtures of isomers of the α-enone 4b were determined by ^{1}H-NMR spectroscopy. The analysis was based on the differences in the chemical shifts of the 3-H proton of the two isomers of the α-enone 4b. Appropiate signals were expanded and repeatly integrated. The results are collected in Table 1.

The α and β isomers of 4b were separated and purified by silica gel chromatography (30:1 (w/w) adsorbent-product ratio) using light petroleum-Et_2O (97:3) as eluent. The purity was tested by ^{1}H-NMR and the products were analyzed by IR, ^{1}H- and ^{13}C-NMR spectroscopy and mass spectrometry.

α Isomer (4b), mp. 65-67º (methanol). $\nu_{max}(CCl_4)$: 1.660 cm^{-1} (CO) and 1.580 cm^{-1} (C=C). MS (m/s): 354 (M^+).

Anal. Calcd. for $C_{26}H_{26}O$: C, 88.14; H, 7.34.

Found: C, 88.37; H, 7.45.

β Isomer (4b), viscous pale yellow liquid. $\nu_{max}(CCl_4)$: 1.680, 1.660 (CO), 1.620 and 1.600 cm^{-1} (C=C). MS (m/s): 354 (M^+).

The ^1H- and ^{13}C-NMR data are collected in Tables 2 and 3.

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11. Assignment of (RR,SS) and (RS,SR) relative configurations has been carried out through an analysis of the observed values for vicinal coupling constants of both isomers and their conformational distribution. Unpublished results.

12. For 2b the use of other conditions for making the enolate (LDA/THF/0º; sodium amide/THF/0º; sodium methylsulfinylmethide/THF or DME/25º) did not lead to an improvement of the conversion.

13. A two-phase method (dichloromethane-aqueous hydrogen peroxide) in presence of pyridine as buffer has been employed for the attainment of 4b, owing to its greater sensivity to oxidation.

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