Total Synthesis of Himachalene Sesquiterpenes of *Aphthona* and *Phyllotreta* Flea Beetles

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Abstract: A total synthesis is presented for himachalene-related norsesquiterpene ketone 1 (racemic), based on the Robinson annulation and other standard reactions. The route involved five steps from cycloheptanone. A favorable result was that the desired diastereomer of 1 was obtained preferentially (97:3) over the unwanted one. Molecular modeling (*ab initio* calculations) aided in confirming the assignment of relative stereochemistry of 1 and in rationalizing the observed ratio of diastereomers. Three related sesquiterpene hydrocarbons and two alcohols were subsequently produced from 1. The six compounds occur naturally in several flea beetle species and likely serve a pheromonal function.

Key words: himachalene, terpenoids, pheromones, annulations, stereoselective synthesis, natural products

Flea beetles of the genera *Aphthona* and *Phyllotreta* (Coleoptera: Chrysomelidae) produce a series of unusual himachalene sesquiterpenes (Figure 1).1 These are released only by one sex (males) and are sensibly detected by the beetle antennae, suggesting a pheromonal function.1 However, confirmation of such activity usually involves field experiments with synthetic compounds. The objective of this research was to synthesize racemic mixtures of compounds 1–6 that would be identical to the natural compounds in spectral and chromatographic properties and in quantities sufficient for field testing (0.1–1 g), preferable without the need for purification by preparative HPLC. Of these compounds, only 6 has been synthesized previously,2 and that synthesis (starting from an aromatic ring) would not provide an easy path to 1–5. Our alternative approach was to prepare ketone 1 first, and then elaborate 2–6 from this. The 7-membered ring of 1 was derived from cycloheptanone, and the 6-membered ring was added with a Robinson annulation.

The relative stereochemistry at the ring junction shown in Figure 1 for 1–5 was based on an NMR and molecular modeling study of natural 4.1 The assignment was not trivial because of the numerous possible conformations of the 7-membered ring. The preparation of both diastereomers of 1 in this study provided an excellent opportunity to check the previous stereochemical assignment.

![Figure 1](image-url) Assigned structures1 for six male-specific compounds in *Aphthona* and *Phyllotreta* flea beetles.

The synthesis of 1 is summarized in Scheme 1. The stereochemical course of the Robinson annulation was particularly favorable, but double bond migration in the 7-membered ring was troublesome in some intermediates. Cycloheptanone (7) was dimethylated to 8 with MeI and t-BuOK in t-BuOH, using the conditions of Ireland and Marshall15 (thermodynamic control). Contrary to expectation, there was no need for a blocking group1 to control the extent of methylation on the 7-membered ring. Three cycles of the reaction were required before 7 and the monomethyl ketone were adequately consumed (Table 1), but there was little tendency to add more than two methyl groups, and the dimethylation was almost entirely (>80%) geminal.

Dimethyl ketone 8 was smoothly brominated to 9 by direct addition of liquid bromine at room temperature using Et2O as solvent.4 The HBr byproduct did not cause undesirable side effects, and it was not removed until workup. Bromo ketone 9 was converted to 10 with LiBr–Li2CO3 in hot dimethylformamide,5 but double-bond positional isomer 15 was also produced. Batches prepared as in the experimental section had as little as 3% 15, while batches using 5× the amount of 9 and 2× the amounts of the lithium salts in the same amount of solvent gave as much as 25% 15. Under the optimal conditions, the yield of 10 from 8 was 79–88%, and from 7 it was 34–38%. Another synthesis of 8 has been reported, based on ring expansion of cyclohexanone with a dimethylated selenium reagent,6,7 and the same reagent was used to prepare 10 di-

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Immediately from 2-cyclohexen-1-one. This approach was not used here because of the high cost, poor availability, and toxicity of the reagents.

Conjugate methylation of 10, followed by Michael addition of the resulting copper enolate to silyl ketone 11 at 78 °C gave silyl diketone 12. Treatment of the product with ethanolic KOH both removed the silyl group (forming diketone 13) and cyclized the diketone to 1. Bicyclic ketone 1 was identical to the beetle-derived compound. Importantly, the ratio of the two possible synthetic diastereomers (1 and 14) was 97:3 in favor of the desired one. Column chromatography on silica afforded 1 in 92% purity, which was deemed acceptable. After column chromatography on silica, the yield of 1 from 10 was 40–44%.

Unconjugated impurity 15 in starting material 10 did not adversely impact the synthesis of 1 as long as both reactions to convert 10 to 12 were run at –78 °C. Impurity 15 did not react with the cuprate reagent, and in the absence of exchange among copper enolates and ketones, 15 rectly from 2-cyclohexen-1-one. This approach was not used here because of the high cost, poor availability, and toxicity of the reagents.

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mained unchanged. The major reaction byproduct at 
−78 °C was trimethyl ketone 18, which resulted from incomplete Michael addition; it was about 35% as abundant as 1 after the cyclization reaction. Fortunately, 15 and 18 were readily separated from 1 on an open column of silica. However, if the Michael addition was run at −20 °C instead of −78 °C, 15 was consumed, and Michael byproduct 16 and, ultimately, 17 were formed. Apparently, the ketones and enolates in the solution were able to exchange/equilibrate at the warmer temperature. The eventual ratio of 17:1 was as high as 0.3:1 when the maximal amount of 15 was present in starting material 10. Importantly, HPLC was needed to purify 1 from 17; thus the production of 17 was to be avoided.

Characterization of intermediate 12 was difficult due to its instability. The initial 13C NMR spectrum indicated good homogeneity (about 90%), but by NMR and GC-MS, the sample changed over time (partial cleavage of the trimethylsilyl group and probable changes in relative configuration at the asymmetric centers). Fortunately, such changes in 12 would not have serious practical consequences. The trimethylsilyl group was to be removed anyway, and enolization/equilibrate under basic conditions in the subsequent step would always lead to the same ratio of product diastereomers.

The availability of both 1 and 14 from the synthesis allowed the assignment of the relative stereochemistry shown in Scheme 1 to be experimentally checked. The NMR data for 1 and 14 and assignments are summarized in Table 2. The coupling constants (J) for the protons at carbons 6 and 7 (Figure 1) were particularly important. These were 9.7 Hz for 1 and 14 Hz for 14. A coupling constant of J = 9.7 Hz could indicate a dihedral angle of about 0° (protons cis) or about 180° (protons trans). Neither possibility could be discounted a priori because of the flexibility of the 7-membered ring. However, ab initio calculation of the lowest-energy conformations of 1 and 14 indicated that the dihedral angle in structure 1 would be 168° (by the Karplus rule, J ~ 10 Hz) and in 14, 74° (J ~ 2 Hz). The Karplus rule only gives approximate J values, but these agree well enough with the data to confirm that the relative configurations were as drawn rather than reversed. Other observable coupling constants and the corresponding predictions of these from molecular modeling and the Karplus rule (Table 2) were reasonably consistent also, giving further credibility to the modeled conformations. The conformations of 1 and 14 were remarkably similar except at carbon 7 (Figure 2). In 1, methyl group 14 was equatorial, while in 14 it was axial. The calculated energies of formation of 1 and 14 differed by 3.0 kcal/mol, with 1 having the lower energy. This difference corresponded to a predicted equilibrium ratio of about 99:1 at

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<th>Table 2 NMR Data for Bicyclic Ketones 1 and 14</th>
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<td>Carbon resonances (δ)</td>
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* Number of attached hydrogens, based on DEPT experiment.

* Predicted J from Karplus rule (J = 7.76 cos2θ − 1.10 cos θ + 1.4).12

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the reflux temperature of EtOH; this was very close to the ratio observed in this study (97:3).

The conversions of 1 to 2–6 were developed from previously reported microchemical tests and isomerizations.1 Ketone 1 was converted to 2 + 3 by methylation with MeLi13 or to 5 by a Wittig condensation14 (Scheme 1). Alcohols 2 and 3 were readily dehydrated to a 50:50 mixture of 4 and 5 by treatment with an acidic ion exchange resin. The ratio could be shifted to about 80:20 in favor of 4 by equilibration in warm formic acid–MeOH.15 (This isomerization was originally reported for the antipodes of 4 and 5, which occur in the European fir tree species, Abies alba and A. nordmanniana).1,15 Alternatively, 2 + 3 could be converted directly to enriched 4 with this reagent. Hydrocarbons 4 and 5 were readily separated on an open column of AgNO3 (20%)–silica. Finally, enriched 4 was cleanly aromatized to 6 with chloranil (2,3,5,6-tetrachloroquinone).16 As with 1, all of the products 2–6 were spectrally and chromatographically identical to the insect derived compounds. With these reactions and separations, any desired mixture of the six components could be readily derived compounds. With these reactions and separations, any desired mixture of the six components can be readily derived compounds. With these reactions and separations, any desired mixture of the six components can be readily derived compounds. With these reactions and separations, any desired mixture of the six components can be readily derived compounds. With these reactions and separations, any desired mixture of the six components can be readily derived compounds.

The above series of reactions does not affect the stereochemistry at the ring junction in 2–5; thus, the previous1 assignment of relative stereochemistry in 4 is consistent with the conclusion based on 1 from this study. The cis-H isomers of 4 and 5 (i.e., 19 and 20) were detected from the syntheses, again with about 3% the abundance of 4 and 5. Byproduct 19 was reported previously as a rearrangement product from α-himachalene under strongly acidic conditions,1,16 and 19 from the present study was identical by GC and MS to 19 prepared by the rearrangement. Thus this study provides a practical source of the racemic compounds for further entomological research and also strengthens the earlier stereochemical conclusions about the compounds.

Starting materials and reagents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were used as received unless otherwise indicated. Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. All reactions were monitored by GC–MS. EI mass spectra were obtained at 70 eV ionization energy on an HP 5973 instrument, which was interfaced to an HP 6890 gas chromatograph. One GC column was EC-5 (30 m × 0.25 mm I.D. × 0.25 μm film); temperature program: 50 °C for 1 min, then increasing at 15 °C per min to 275 °C. The other column was DB-1 (30 m × 0.25 mm I.D. × 0.25 μm film); temperature program: 50 °C for 1 min, then increasing at 10 °C per min to 280 °C. Both columns were from Alltech (Deerfield, IL). The splitless inlet was kept at 250 °C. NMR spectra were obtained on a Bruker Avance 400 MHz instrument. The solvent was either CDCl3 or DMSO-d6, as indicated with spectral data.1 H NMR spectra were acquired at 400 MHz, and 13C NMR spectra, at 100 MHz. Reported shifts are relative to tetramethylsilane. Coupling constants are in Hz. For some samples, DEPT, proton COSY, HMOC, and HMBC experiments were run to aid in assignment of resonances. HPLC was done using a Waters 6000A pump and Waters R401 differential refractometer detector. The column was a 25 cm × 4.6 mm Adsorbosphere Silica 5 μ (Alltech). Multiple batches were run for each reaction, and typical examples are described below.

Molecular modeling was used to study the stereochemistry of compound 1 and its diastereomer 14. Preliminary modeling was carried out using the AMBER17 molecular force field as found in the InsightII/Discover software from Molecular Simulations Inc., San Diego, CA. Subsequently, ab initio calculations were carried out at the 6-31+G** level using software from Parallel Quantum Solutions (PQS Ab Initio Program Package version 2.3) and the Parallel QuantumStation™, PQS1000S. The molecules were geometry-optimized at the above level of theory and also at the 6-311++G** level.

2,2-Dimethylcycloheptanone (8) t-BuOK (42 g, 0.38 mol) and t-BuOH (distilled from CaH2, 300 mL) were introduced into a dry 1000-mL flask under N2 atmosphere and stirred. When the solid had dissolved, cycloheptanone (7) (100 g, 0.089 mol) was added at r.t. After 5 min the flask was set in an ice bath, and Mel (82 g, 0.58 mol) was added in one portion, with stirring. White precipitate began to form after several minutes and

Figure 2 Minimum energy conformations of ketone 1 and its diastereomer, 14, based on ab initio calculations. The key dihedral angle is highlighted.
gradually thickened. After 30 min the ice bath was removed and stirring continued for 2 h. The mixture was vacuum filtered and concentrated by rotary evaporation to about 40 mL. The whole procedure was repeated twice more, using the product from the previous run as the ketone substrate. Then the concentrated product (40 mL) was partitioned between Et₂O (100 mL) and H₂O (50 mL). The Et₂O layer was washed with H₂O (3 × 50 mL), and the combined aq layers were washed with Et₂O (3 × 100 mL). The combined organic layers were dried (MgSO₄). Filtration, rotary evaporation, and then distillation (Kugelrohr, 5 torr; 60–80 °C oven temperature) afforded 6.51 g product, containing 92% of the desired ketone.

Yield: 43% of 8 from 7; tᵣ (GC; EC-5) 6.96 min.

¹H NMR (CDCl₃): δ = 2.45 (2 H, m), 1.60–1.53 (6 H, m), 1.41 (2 H, m), 1.00 (6 H, s).

¹³C NMR (CDCl₃): δ = 218.07, 47.41, 39.96, 39.23, 30.55, 26.42, 25.68 (2 methyl C), 24.75.

EIMS: m/z (%) = 39 (24), 41 (59), 43 (20), 55 (53), 56 (62), 57 (13), 67 (10), 69 (100), 70 (26), 81 (18), 83 (15), 84 (19), 96 (29), 97 (39), 98 (29), 107 (30), 122 (5), 125 (13), 139 (40, M⁺).

3.3-Methylsilyl-3-buten-2-one (11)

Ketone 11 was prepared according to Boeckman et al.¹¹

tᵣ (GC; EC-5) 4.43 min.

¹H NMR (CDCl₃): δ = 6.43 (1 H, d, J = 2.0), 6.10 (1 H, d, J = 2.0), 2.22 (3 H, s), 0.07 (9 H, s).

¹³C NMR (CDCl₃): δ = 203.94, 153.98, 136.75, 26.17, –1.43 (3 methyl C).

EIMS: m/z (%) = 43 (13), 45 (8), 58 (3.4), 73 (32), 75 (37), 97 (22), 127 (100), 141 (1.0), 142 (0.2, M⁺).

7.7-Dimethyl-3-cycloheptene-1-one (15)

Synthetic byproduct of 10, 3% by GC; tᵣ (GC; EC-5) 7.09 min.

¹H NMR (CDCl₃): δ = 5.42 (1 H, m), 5.36 (1 H, m), 3.02 (2 H, m), 1.96 (2 H, m), 1.43 (2 H, m), 1.01 (6 H, s).

¹³C NMR (CDCl₃): δ = 209.99, 130.64, 121.09, 47.64, 39.70, 35.63, 26.43, 24.97 (2 methyl C).

EIMS: m/z (%) = 39 (30), 41 (38), 54 (100), 56 (94), 67 (16), 68 (13), 81 (21), 82 (13), 95 (53), 110 (30), 123 (0.6), 138 (28, M⁺).
EIMS: m/z (%): 41 (63), 43 (22), 55 (56), 56 (66), 69 (100), 83 (20), 84 (23), 95 (28), 98 (19), 111 (33), 112 (34), 121 (37), 136 (3), 139 (20), 154 (38, M*).

2-[3-Oxo-2-(trimethylsilyl)butyl]-7,7-dimethyl-3-cyclohepten-1-one (16)

In one trial reaction, the Michael addition was done at −20 °C rather than −78 °C, giving byproduct 16.

t<sub>k</sub>(GC; EC-5) 12.39 min.

EIMS: m/z (%): 45 (6), 73 (65), 91 (3), 115 (2), 130 (2), 143 (100), 181 (3), 195 (3), 210 (19), 224 (3), 265 (0.6), 280 (0.6, M*).

Bicyclic Ketone 1

Crude silyl diketone 12 (6.0 g, containing 10.5 mmol) was added to KOH (3.5 N) in EtOH (95%) and stirred under an Ar atmosphere at r.t.; the solution became warm due to exothermic cleavage of the silyl group. After the heating had subsided an analytical sample was taken. Then the mixture was refluxed under Ar for 7 h. When the reaction was complete by GC, the mixture was allowed to cool and was shaken with H<sub>2</sub>O (15 mL) and Et<sub>2</sub>O (70 mL). The layers were separated, and the Et<sub>2</sub>O layer was washed with H<sub>2</sub>O (2 × 30 mL). Then the combined aq layers were extracted with Et<sub>2</sub>O (3 × 70 mL).

The combined organic layers were washed with brine (2 × 30 mL), dried (MgSO<sub>4</sub>), and filtered. After removal of solvent by rotary evaporation, the crude product was subjected to column chromatography on an open column (silica (a new 21 × 2.8 cm column was used for each 1 g of crude product); elution was first with Et<sub>2</sub>O (10%), then with Et<sub>2</sub>O (20%) in hexane (four column volumes); compound 1 eluted primarily in the third Et<sub>2</sub>O (20%) fraction.

Overall yield: 1.11 g recovered in 92% purity (5.0 mmol). Calculated yield of 1 from 10 was 40–44%; t<sub>k</sub>(GC; EC-5) 13.26 min; (DB-1) 17.45 min.

1<sup>H</sup>NMR (C<sub>6</sub>D<sub>6</sub>): 4.05 (1 H, d, J = 6.7), 0.87 (3 H, s).

<sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ = 154.35, 143.75, 122.67, 109.33, 40.56, 39.22, 38.77 (11), 79 (7), 91 (27), 93 (21), 105 (51), 106 (7), 107 (6), 115 (7), 117 (8), 119 (67), 120 (13), 121 (6), 133 (100), 134 (14), 145 (4.4), 147 (4.0), 148 (3.8), 161 (9), 175 (1.5), 176 (1.0), 189 (6), 204 (27, M*).

Bicyclic Ketone 17

Synthetic impurity in 1 when 12 was prepared at −20 °C.

t<sub>k</sub>(GC; EC-5) 12.68 min.

EIMS: m/z (%): 41 (24), 55 (14), 65 (17), 77 (27), 79 (21), 91 (67), 105 (56), 119 (63), 133 (65), 147 (100), 148 (42), 161 (13), 162 (16), 175 (31), 190 (100, M*).

Bicyclic Alcohols 2 and 3

To a dry 25-mL flask under an Ar atmosphere was added anhyd Et<sub>2</sub>O (5 mL) and MeLi (1.4 M solution in Et<sub>2</sub>O, 6.5 mmol), and the flask was cooled in a dry ice–EtOH bath and stirred magnetically. Ketone 1 from the previous reaction (1.11 g, containing 5.4 mmol) in Et<sub>2</sub>O (2 mL) was added dropwise to the stirred solution. The flask was allowed to warm gradually to r.t. and then stirred for 30 min more. Hexane (10 mL) was introduced, followed by dropwise addition of H<sub>2</sub>O (2 mL). The layers were separated. The Et<sub>2</sub>O layer and one Et<sub>2</sub>O wash (5 mL) of the aq layer were combined, dried (MgSO<sub>4</sub>), filtered, and the solvent evaporated.

Yield: 1.22 g, containing 2 and 3 in a 19:81 ratio; the main impurity was unexpected 1 (5%). Compounds 2, 3, and 1 were separable, in that order, by HPLC on silica (5% acetone in hexane).

Alcohol 2

t<sub>k</sub>(GC; DB-1) 15.60 min.

1<sup>H</sup>NMR (C<sub>6</sub>D<sub>6</sub>): 0.87 (3 H, s), 1.20 (3 H, s), 0.92 (3 H, d, J = 6.7), 4.05 (1 H, d, J = 6.7).

38.69, 37.12, 36.30, 31.66, 27.68, 26.65, 25.23, 22.45, 19.89.

Bicyclic Hydrocarbons 4 and 5

Crude 2 + 3 (0.80 g) from above was added to Et<sub>2</sub>O (15 mL) and Dowex 50W-X4 (0.25 g) strong cation exchange resin and stirred overnight under an Ar atmosphere. Conversion was complete, by GC; the ratio of 4 to 5 was 0.65–1.2:1. The solution was removed from the Dowex particles and taken to dryness under a stream of Ar. The product was redissolved in hexane and eluted through a column (5 × 1 cm) of silica gel (hexane), to remove unreacted 1 and H<sub>2</sub>O. Quantitation by GC with internal standard indicated that the yield of 4 + 5 was 64%, calculated from 1. Compounds 4 and 5 are quite susceptible to loss when concentrating a hexane solution under a stream of inert gas. Diastereomers 19 and 20 occurred in amounts about 3% those of 4 and 5, respectively, and by GC, each eluted later than the respective main diastereomer.

Hydrocarbon 4

t<sub>k</sub>(GC; DB-1) 13.98 min.

1<sup>H</sup>NMR (C<sub>6</sub>D<sub>6</sub>): 3.98 (1 H, t, J = 5.4), 2.55 (2 H, t, J = 5.4), 1.76 (2 H, dt, J = 5.4, 12.0), 0.91 (3 H, s).

35.76, 35.28, 32.95, 32.90, 30.79, 26.77, 25.14, 22.08, 19.93.

Hydrocarbon 5

t<sub>k</sub>(GC; DB-1) 14.81 min.

1<sup>H</sup>NMR (C<sub>6</sub>D<sub>6</sub>): 3.98 (1 H, t, J = 5.4), 2.55 (2 H, t, J = 5.4), 1.76 (2 H, dt, J = 5.4, 12.0), 0.91 (3 H, s).

35.76, 35.28, 32.95, 32.90, 30.79, 26.77, 25.14, 22.08, 19.93.

Hydrocarbon 19 (Diastereomer of 4)

t<sub>k</sub>(GC; DB-1) 14.22 min.

EIMS: m/z (%): 39 (7), 41 (20), 55 (17), 56 (10), 65 (5), 69 (13), 77 (11), 79 (7), 91 (27), 93 (21), 105 (51), 106 (7), 107 (6), 115 (7), 117 (8), 119 (67), 120 (13), 121 (6), 133 (100), 134 (14), 145 (4.4), 147 (4.0), 148 (3.8), 161 (9), 175 (1.5), 176 (1.0), 189 (6), 204 (27, M*).

Hydrocarbon 20 (Diastereomer of 5)

t<sub>k</sub>(GC; DB-1) 14.97 min.
EIMS: \textit{m/z} (%) = 39 (18), 40 (19), 41 (43), 55 (36), 57 (20), 67 (19), 69 (29), 71 (35), 79 (43), 81 (24), 91 (97), 93 (63), 105 (74), 107 (48), 109 (31), 115 (19), 119 (69), 120 (37), 121 (41), 133 (73), 135 (49), 147 (47), 148 (25), 161 (98), 162 (37), 163 (41), 133 (73), 135 (49), 147 (47), 148 (25), 161 (98), 162 (18), 175 (10), 176 (4.9), 189 (29), 204 (100, M\textsuperscript{+}).

Conversions and Separations of 4 and 5
A mixture of 4 and 5 (approximately 1:1) was isomerized to a >4:1 mixture by stirring at 50 °C for 4 h with formic acid (15% in MeOH; 0.5 g hydrocarbon in 10 mL solvent). Recovery of product was by mixing with hexane (10 mL) and H\textsubscript{2}O (3 mL), followed by separation of layers. The hexane layer was washed with H\textsubscript{2}O (2 mL), dried (MgSO\textsubscript{4}), filtered, and carefully concentrated. The same procedure can be used to convert alcohols 2 + 3 directly to an enriched sample of 4. Compound 4 could be separated from 5 on an open column (20% AgNO\textsubscript{3} on silica; e.g., 0.5 g of a 4:1 mixture on a 5 cm column; hydrocarbon 4 eluted with hexane; then 5 eluted with 5% 1-hexene in hexane).

Wittig Synthesis of 5
Methylenetriphenylphosphorane (0.54 g, 1.5 mmol) was prepared over ice in THF as described previously, and 1 (150 mg, 0.73 mmol) in anhyd THF was introduced dropwise. After warming to r.t. and stirring 30 min, the product was isolated in the usual way. By GC, the reaction was 80% complete. The product did not contain 4.

Aromatic Hydrocarbon 6
A mixture of 4 + 5 (4:1; 30 mg) was added to anhyd benzene (stored over Na, 2 mL) with chloranil (65 mg) and heated to 75 °C overnight in a closed vial. By GC, the conversion of 4 and 5 to 6 was 95% complete. Unreacted chloranil and polar byproducts were removed by passage through a silica column (0.5 × 3 cm; hexane). \( t\textsubscript{R} \) (GC; DB-1) 15.35 min.

\textsuperscript{1}H NMR (\textit{C}_{6}D_{6}) and ElMS as before.\textsuperscript{1}

\textsuperscript{13}C NMR (\textit{C}_{6}D_{6}): \( \delta = 147.52, 141.00, 134.97, 127.65, 126.80, 125.73, 41.19, 39.42, 36.73, 34.48, 33.95, 29.90, 24.10, 21.17, 20.98.\n
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References