

identical but the refractive indices, although not identical, are reasonably close, considering the air sensitivity of the compound and the sensitivity of such indices to impurities.<sup>14</sup>

Examination of the <sup>1</sup>H and <sup>13</sup>C NMR data reveals only small differences between our data and that reported for "1a". These differences, as indicated in Table I, are uniform and represent a shift of the spectrum as a whole, a fact which strongly suggests either concentration, solvent (<sup>13</sup>C NMR), or instrumental differences, rather than gross structural differences, e.g., between 1a and 2a.

The infrared spectra of 2a and "1a" (Table II) are virtually identical, differing in only one respect. An additional metal carbonyl band at 2080 cm<sup>-1</sup> with weak intensity is observed by us, but is not reported by the Sakurai group for their compound. Whether such a band was in fact observed but simply not reported owing to its weak intensity is not clear.

The observation of an infrared absorption of medium to weak intensity at ~1315 cm<sup>-1</sup> in the spectra of all of the (vinylsilane)tetracarbonyliron complexes prepared to date is interesting in view of the suggestion<sup>2a</sup> that this absorption band, observed in the spectrum of "1a", might be assigned to the stretching frequency of a coordinated Si=C bond. Clearly, with the present results, such an assignment is not warranted.<sup>15</sup> The agreement between our UV data and that reported for "1a" is good,<sup>16</sup> although we fail to detect the reported shoulder at 221 nm.<sup>16c</sup>

The key to the assignment of the correct structure to the complex obtained from 3a and Fe<sub>2</sub>(CO)<sub>9</sub> resides in the mass spectral (MS) data. As mentioned earlier, our MS data with a parent peak at *m/e* 326 clearly indicate a tetracarbonyl rather than a tricarbonyliron complex, i.e., structure 2a rather than 1a. Additionally, the high relative intensity of a peak at *m/e* 158, corresponding to the free ligand 3a, is consistent with the preservation of the structural integrity of 3a upon complexation.<sup>17b</sup> Although Sakurai and co-workers observed the same fragmentation peaks,<sup>2,17</sup> they failed to detect the parent mass peak and assumed that the P-28(CO) peak was the parent peak and indicative of a parent Fe(CO)<sub>3</sub> species. Presumably, on the basis of this assumption, in part, and the belief that the cleavage of, or oxidative insertion in, a relatively weak Si-Si bond by a transition metal was quite reasonable,<sup>18</sup> the IR and NMR spectra, as well as the analytical data, were rationalized cogently (but clearly now speciously) in terms of the η<sup>3</sup>-silapropenyl complex 1a. The failure to observe the parent mass peak, however, is not too surprising in view of the propensity of carbonyl-metal complexes to readily fragment in the mass spectrometer. Such fragmentation, characterized by the successive loss of CO molecules, often results in weak, if not absent, parent mass peaks. All of the (vinylsilane)tetracarbonyliron complexes that we have prepared to date are especially sensitive and fragment or decom-

pose extremely easily at elevated probe and ion-source temperatures. As a consequence, great care was necessary in order to obtain meaningful spectra exhibiting parent mass peaks.<sup>11</sup>

Despite their air sensitivity and thermal instability above ~80 °C, the η<sup>2</sup>-vinylsilane complexes 2 are remarkably stable. (Ethylene)tetracarbonyliron, by comparison, is quite unstable and is reported to decompose slowly above -40 °C.<sup>20</sup> Although the inductive effect of the silicon, which raises the energies of the π and π\* orbitals,<sup>19</sup> would be destabilizing, the resonance effect, involving p-d π bonding and the lowering of the π\* orbital, presumably would be stabilizing by virtue of enhanced back-donation by the metal.

Attempts to prepare 1a from 2a thermally as well as photochemically have failed. In view of the evidence for the failure to prepare the η<sup>3</sup>-silapropenyl complex 1a, the validity of the structure 1b immediately becomes suspect. As a consequence, it would appear that the stabilization of a doubly bonded silicon species by a transition metal remains to be conclusively demonstrated.

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P. Radnia, J. S. McKennis\*

Department of Chemistry, Oklahoma State University  
Stillwater, Oklahoma 74074

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## Total Synthesis of (±)-Hirsutene

Sir:

The recent years have experienced intense activity in the development of synthetic routes to terpenoids possessing tricyclo[6.3.0.0<sup>2,6</sup>]undecane ring systems. Hirsutene (1), coriolin, and hirsutic acid present themselves as challenging targets in carbocyclic synthesis as well as an exercise in the efficient introduction of numerous oxygenated centers.

Considerable efforts have also been seen in the area of non-linearly fused tricyclopentanoids such as isocomene and retigeranic acid, both containing the tricyclo[6.3.0.0<sup>4,8</sup>]undecane ring system.<sup>1</sup>

In addition to the synthetic interest elicited by these terpenoids, there exists an array of remarkable physiological properties associated especially with the coriolin-type sesquiterpenes.<sup>2</sup> The antibiotic and antitumor activities of hirsutic acid and coriolin dictate an efficient synthetic approach to these compounds, particularly in view of their uncertain supply from natural sources.<sup>3</sup> Several interesting syntheses have appeared to date, describing the preparation of hirsutic acid,<sup>4</sup> coriolin,<sup>5</sup> and their biogenic precursor, hirsutene.<sup>6</sup>

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(14) Complex 2a: *n*<sub>D</sub><sup>16</sup> 1.5269, *n*<sub>D</sub><sup>20</sup> 1.5254. Reported for "1a": *n*<sub>D</sub><sup>16</sup> 1.5065 (ref 2b).

(15) The infrared spectrum of (ethylene)tetracarbonyliron in the solid state (thin film) also exhibits a weak absorption at 1317 cm<sup>-1</sup>: Andrews, D. C.; Davidson, G. *J. Organomet. Chem.* 1972, 35, 162.

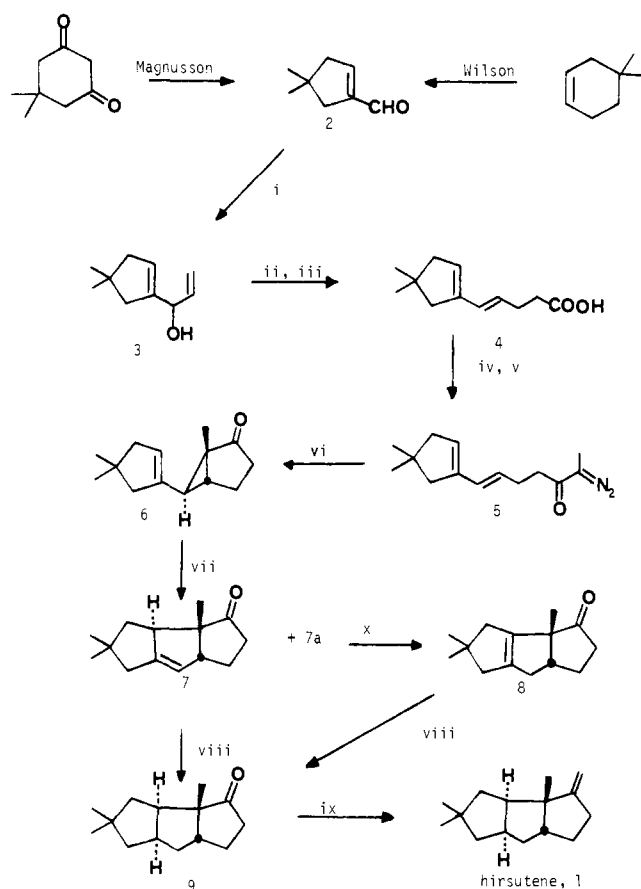
(16) (a) Complex 2a (Beckman Model 25): λ<sub>max</sub> (hexane) 270 (sh) (ε 8800), 236 (sh) (14 700), 212 nm (23 300). Reported for "1a": λ<sub>max</sub> (hexane) 270 (sh) (ε 7000[7700]), 236 (sh) (12 600[13 800]), 221 (sh) (17 400[19 000]), 212 nm (20 500[22 400]). Values in brackets are corrected extinction coefficients, assuming a Fe(CO)<sub>4</sub> rather than a Fe(CO)<sub>3</sub> species; agreement is within 5%. (b) For comparison, complex 2c: λ<sub>max</sub> (hexane) 262 (sh) (ε 8000), 215 nm (27 000). (c) The absorbance at 221 nm corresponds to ε 18 600, consistent with the notion that there is a similar absorption at 221 nm for 2a, but because of poor resolution, it is not observed as a shoulder. On the other hand, first-derivative analysis of the UV spectrum does not reveal a shoulder.

(17) (a) Reported for "1a" (ref 2): MS, *m/e* (rel intensity) 298 (2.9), 270 (4.9), 242 (6.8), 214 (21.6), 158 (23.9), 143 (21.0), 85 (54.4), 73 (100). Complex 2a: MS, *m/e* (rel intensity) 326 (12.8), 298 (9.9), 270 (36.1), 242 (48.9), 214 (73.0), 158 (30.5), 143 (39.7), 85 (87.2), 73 (100). (b) The observation of mass peaks at *m/e* 311 (3.5) and 253 (3.5), corresponding to P-CH<sub>3</sub> and P-Si(CH<sub>3</sub>)<sub>3</sub>, respectively, as well as peaks corresponding to the successive loss of CO from these fragments, also indicates a tetracarbonyliron species.

(18) Sakurai and co-workers had earlier demonstrated the interesting palladium-catalyzed addition of alkynes across a Si-Si bond: Sakurai, H.; Kamiyama, Y.; Nakadiara, Y. *J. Am. Chem. Soc.* 1975, 97, 931.

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Scheme I



<sup>a</sup> (i)  $\text{CH}_2=\text{CHMgBr}/\text{THF}/0^\circ\text{C}$ , (ii)  $\text{CH}_3\text{C}(\text{OEt})_3/\text{Hg}(\text{OAc})_2/\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ , (iii)  $\text{KOH}/\text{H}_2\text{O}$ , (iv)  $(\text{COCl})_2/\text{hexane}$ , (v)  $\text{CH}_3\text{CHN}_2$ , (vi)  $\text{Cu}(\text{acac})_2/\text{benzene}/\Delta$ , (vii)  $580^\circ\text{C}$ ,  $\text{PbCO}_3$  coated glass, (viii)  $\text{H}_2/\text{PtO}_2$ , (ix)  $\text{CH}_3\text{P}^+(\text{Ph})_3/\text{n-BuLi}/\text{Et}_2\text{O}$ , (x)  $\text{RhCl}_3/\text{EtOH}/\Delta$ .

We have been investigating a new method of cyclopentene annulation<sup>7</sup> based on the intramolecular cyclopropanation-rearrangement of dienic diazo ketones.<sup>8,9</sup> We now report a direct application of this methodology to the synthesis of hirsutene (1).

The synthesis is divisible into three major tasks: (a) preparation of dienic acid 4, (b) ring closure and rearrangement to furnish tricyclic ketone 7, and (c) final transformation of 7 to hirsutene via the known norketone 9.<sup>6</sup>

We have chosen as our starting point the cyclopentenylaldehyde 2, a popular compound in the field of coriolin and illudane terpenes (Scheme I). Although the preparation of 2 is not trivial, an overall yield of 64–70% is achieved by using the procedure either of Wilson and Turner<sup>10</sup> or of Magnusson and Thoren.<sup>11</sup>

Aldehyde 2 was converted to vinyl carbinol 3<sup>12</sup> in 91% yield

(vinylmagnesium bromide in tetrahydrofuran,  $0^\circ\text{C}$ ). The dienyl unit in 4 could be introduced via the Claisen rearrangement of an ortho ester, in analogy with the simple case of 1,4-pentadien-3-ol.<sup>8</sup> The inertness of the ring double bond in such rearrangements has been demonstrated by Bangel and Cresson.<sup>13</sup> The use of triethyl orthoacetate as reagent and solvent (25 mL for each g of alcohol, 1:10 ethyl ester), which was not isolated but hydrolyzed, led directly to 4 (20% KOH, reflux, 2 h) in 82% yield from 3. (It proved crucial to wash the crude ester reaction mixture with 3 N HCl to remove excess orthoacetate. Reaction of this wash or attempts to remove orthoacetate by careful distillation resulted in loss of material and yields of 20–40%.) The acid 4 [bp  $110\text{--}115^\circ\text{C}$  (0.1 mmHg, Kugelrohr)] proved to be a single isomer as evidenced by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.<sup>12</sup> Refluxing 4 in a 2:1 hexane/oxalyl chloride mixture for 1 h gave the acid chloride (IR  $1800\text{ cm}^{-1}$ ), which was immediately converted to ethyl diazo ketone 5 (89% from 4) by adding the neat acid chloride to a 0.3 M solution of diazoethane<sup>14</sup> in ether. Any deviation in concentration led to the production of an undesired  $\alpha$ -chloro ketone!<sup>15</sup> In accord with our previous experience regarding the cyclopropanation,<sup>8</sup> 5 gave vinylcyclopropane 6 stereospecifically in 94% yield [ $\text{Cu}(\text{acac})_2$ , refluxing benzene, 8 h]. A detailed spectral analysis failed to show any isomeric material.

The crucial rearrangement of 6 to the cyclopentene 7 was performed by evaporating a sample of 6 through a lead carbonate conditioned, horizontally placed hot tube at 0.1 mmHg.<sup>9,16</sup> Although model studies performed on terminally substituted dienes gave mixtures of isomeric bicyclooctanes,<sup>9</sup> with regard to the substituent at C-8, it was envisioned that the energetics of cis, anti, cis vs. cis, syn, cis ring junctions in 7 will be favorable in the direction of the desired product. Indeed, the crude condensate obtained from the pyrolysis of 6 was shown to contain 68% of 7, 22% of a fragmentation product (shown to be a bicyclic dienone),<sup>9</sup> and 10% of isomeric tricyclic ketone 7a. This compound, as well as the ketone 7, was readily isomerized by  $\text{RhCl}_3$  in aqueous ethanol<sup>17</sup> (reflux, 30 min) to 8, which was hydrogenated ( $\text{PtO}_2$ , 40 psi, 8 h) to a known degradation product of hirsutene, norketone 9.<sup>6</sup>

(12) All new compounds gave spectral and analytical data consistent with their structures. Spectral data of the pertinent intermediates are tabulated below. Infrared spectra were obtained on Pye-Unicam 3-300 and Perkin Elmer Model 257 instruments.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian T-60 or HR-220 and Varian CFT-20 spectrometers, respectively, with  $(\text{CH}_3)_3\text{Si}$  as internal standard. 3: IR (neat)  $3380, 1640\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.05 (s, 6 H), 2.1 (br s, 4 H), 3.4 (s, 1 H, hydroxyl), 4.5 (d, 1 H,  $J = 6\text{ Hz}$ ), 5.0–5.9 (m, 4 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.8 (q, 2 methyl groups), 38.4 (t), 47.5 (t), 48.4 (s), 72.4 (d), 114.7 (t), 124.0 (d), 139.2 (d), 144.2 (s). 4: IR (neat)  $3200\text{--}2800, 1705\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.06 (s, 6 H), 2.1 (br s, 4 H), 2.4 (br s, 4 H), 5.6 (s, 1 H), 5.65 (br s, 1 H), 6.38 (d, 1 H,  $J = 16\text{ Hz}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  27.8 (t), 30.1 (q), 34.0 (t), 38.3 (s), 48.0 (t), 48.6 (t), 127.7 (d), 128.0 (d), 128.7 (d), 140.9 (s), 179.7 (s). 5: IR (neat) 2060, 1640, 1620  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.04 (s, 6 H), 2.08 (s, 3 H), 2.4 (br s, 4 H), 2.7 (br s, 4 H), 5.6 (br s, 1 H), 5.65 (s, 1 H), 6.35 (d, 1 H,  $J = 16\text{ Hz}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.2 (q), 27.8 (t), 30.0 (q), 37.6 (t), 38.2 (s), 46.5 (t), 47.9 (t), 61.9 (s), 127.8 (d), 128.3 (d), 128.5 (d), 140.9 (s), 193.6 (s). 6: IR (neat)  $1716, 1630\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.04 (s, 3 H), 1.07 (s, 3 H), 1.10 (s, 3 H), 1.85 (s, 1 H), 2.1 (br s, 5 H), 2.4 (d, 4 H,  $J \approx 3\text{ Hz}$ ), 5.4 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.7 (q), 21.8 (t), 29.9 (q), 30.8 (d), 31.9 (t), 32.4 (d), 38.4 (s), 39.7 (s), 47.6 (t), 51.2 (t), 126.2 (d), 137.8 (s), 215.9 (s); mass spectrum (70 eV),  $m/e$  (% base peak) 204 ( $\text{M}^+$ ), 189 (62), 147 (39), 133 (29), 106 (50), 104 (85), 95 (43), 91 (B), 77 (42). 7: IR (neat) 1738, 1660  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.01 (s, 3 H), 1.05 (s, 3 H), 1.10 (s, 3 H), 1.4–2.2 (m, 8 H), 2.8–3.4 (m, 2 H), 4.9 (s, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.2 (q), 24.0 (t), 30.1 (q), 30.6 (q), 38.9 (t), 39.9 (t), 41.2 (t), 42.5 (s), 56.9 (s), 60.2 (d), 61.7 (d), 139.8 (d), 153.5 (s), 223.5 (s).

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