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  $\sim 1315$  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  $Fe_2(CO)_9$  resides in the mass spectral (MS) data. As mentioned earlier, our MS data with a parent peak at m/e 326 clearly indicate a *tetra*carbonyl rather than a *tri*carbonyliron 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  $Fe(CO)_3$  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  $\eta^3$ -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-

(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):  $\lambda_{max}$  (hexane) 270 (sh) ( $\epsilon$ 8800), 236 (sh) (14700), 212 nm (23 300). Reported for "1a":  $\lambda_{max}$  (hexane) 270 (sh) ( $\epsilon$  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 coef-ficients, 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:  $\lambda_{max}$  (hexane) 262 (sh) ( $\epsilon$  8000), 215 nm (27 000). (c) The absorbance at 221 nm corresponds to  $\epsilon$  18 600, consistent with the potion that there is a similar absorbing at 221 nm for 29 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.

(19) West, R. J. Organomet. Chem. 1965, 3, 314.

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  $\sim 80$ °C, the  $\eta^2$ -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  $\pi$ and  $\pi^*$  orbitals,<sup>19</sup> would be destabilizing, the resonance effect, involving p-d  $\pi$  bonding and the lowering of the  $\pi^*$  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  $\eta^3$ -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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(20) Murdoch, H. D.; Weiss, E. Helv. Chim. Acta 1963, 46, 1588.

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## Total Synthesis of $(\pm)$ -Hirsutene

Sir:

The recent years have experienced intense activity in the development of synthetic routes to terpenoids possessing tricyclo- $[6.3.0.0^{2,6}]$  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 nonlinearly 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 sequiterpenes.<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.6

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<sup>(14)</sup> Complex 2a:  $n^{16}_{D}$  1.5269,  $n^{20}_{D}$  1.5254. Reported for "1a":  $n^{16}_{D}$ 1.5065 (ref 2b).

<sup>(15)</sup> 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.;

<sup>(17) (</sup>a) Reported for " $\mathbf{la}$ " (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

<sup>(18)</sup> 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.

<sup>(1)</sup> For recent synthetic efforts in this area, see: Paquette, L. A.; Han, Y. K. J. Org. Chem. 1979, 44, 4016. Pirrung, M. C. J. Am. Chem. Soc. 1979, 101, 7130. Oppolzer, W.; Bättig, K.; Hudlicky, T. Helv. Chim. Acta 1979, 62, 1493.

<sup>(2)</sup> For a concise list of references pertaining to the biological activities, see: Little, R. D.; Muller, G. W. J. Am. Chem. Soc. 1979, 101, 7129.
 (3) Lansbury, P. T.; Wang, N. Y.; Rhodes, J. E. Tetrahedron Lett. 1979,

<sup>(4)</sup> Trost, B. M.; Shuey, C. D.; DiNimo, F., Jr.; McElvain, S. S. J. Am. Chem. Soc. 1979, 101, 1284.
 (5) Danishefsky, S.; Zamboni, R.; Kahn, M.; Etheredge, S. J. J. Am.

Chem. Soc. 1980, 102, 2097.

Scheme I



<sup>a</sup> (i)  $CH_2 = CHMgBr/THF/0$  °C, (ii)  $CH_3C(OEt)_3/Hg(OAc)_2/2$ CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H, (iii) KOH/H<sub>2</sub>O, (iv) (COCl)<sub>2</sub>/hexane (v)  $CH_3CHN_2$ , (vi)  $Cu(acac)_2$ /benzene/ $\Delta$ , (vii) 580 °C, PbCO<sub>3</sub> coated glass, (viii) H<sub>2</sub>/PtO<sub>2</sub>, (ix) CH<sub>3</sub>P<sup>+</sup>(Ph)<sub>3</sub>I<sup>-</sup>/n-BuLi/Et<sub>2</sub>O, (x)  $RhCl_3/EtOH/\Delta$ .

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 9.6

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  $3^{12}$  in 91% yield

(8) Hudlicky, T.; Sheth, J. P.; Gee, V.; Barnvos, D. Tetrahedron Lett. 1979, 4889. Hudlicky, T.; Sheth, J. P. Ibid. 1979, 2667. Hudlicky, T.; Kutchan, T. M. Ibid. 1980, 691.

(vinylmagnesium bromide in tetrahydrofuran, 0 °C). The dienvl 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. Omission 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 110-115 °C (0.1 mmHg, Kugelrohr)] proved to be a single isomer as evidenced by <sup>1</sup>H and <sup>13</sup>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 cm<sup>-1</sup>), 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 [Cu(acac)<sub>2</sub>, 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.9,16 Although model studies performed on terminally substituted dienes gave mixtures of isomeric bicyclooctanes,9 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 RhCl<sub>3</sub> in aqueous ethanol<sup>17</sup> (reflux, 30 min) to 8, which was hydrogenated (PtO<sub>2</sub>, 40 psi, 8 h) to a known degradation product of hirsutene, norketone 06

268, 1535

 (14) Marshall, J. A.; Partridge, J. J. J. Org. Chem. 1968, 33, 4094.
 (15) The best results were obtained when 0.513 g of nitrosoethylurea was added to 1.3 mL of 50% KOH and 6 mL of Et<sub>2</sub>O, at 0 °C. After the generation of diazoethane was complete, the ethereal layer was decanted and dried with KOH pellets. An aliquot of 4 mL of Et<sub>2</sub>O was used to wash the aqueous layer. The solution thus obtained was  $\sim 0.3$  M in diazoethane (suitable for 1 mmol of acid chloride).

<sup>(6)</sup> Recent syntheses of hirsutene: Tatsuta, K.; Akimoto, K.; Kinoshita, M. J. Am. Chem. Soc. 1979, 101, 6116. Ohfune, Y.; Shirahama, H.; Matsumoto, T. Tetrahedron Lett. 1976, 2795. Nozoe, S.; Furukawa, J.; Sankawa, U.; Shibata, S. Ibid. 1976, 195

<sup>(7)</sup> For the latest intramolecular cyclopentane annulation procedure and for the literature review, see: Jacobson, R. M.; Lahm, G. P.; Clader, J. W. J. Org. Chem. 1980, 45, 395.

<sup>(9)</sup> Hudlicky, T.; Koszyk, F. J. Tetrahedron Lett. 1980, 2487. Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. J. Org. Chem., submitted for publication (full paper with experimental details for all new compounds)

<sup>(10)</sup> Wilson, S. R.; Turner, R. B. J. Org. Chem. 1973, 38, 2870.

<sup>(12)</sup> 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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian T-60 or HR-220 and Varian CFT-20 spectrometers, respectively, with Varian T-60 or HR-220 and Varian CFT-20 spectrometers, respectively, with  $(CH_3)_4Si$  as internal standard. 3: IR (neat) 3380, 1640 cm<sup>-1</sup>; <sup>1</sup>H NMR  $(CDCl_3) \delta 1.05$  (s, 6 H), 2.1 (br s, 4 H), 3.4 (s, 1 H, hydroxyl), 4.5 (d, 1 H, J = 6 Hz), 5.0–5.9 (m, 4 H); <sup>13</sup>C NMR (CDCl\_3) \delta 2.9.8 (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) 3200–2800, 1705 cm<sup>-1</sup>; <sup>1</sup>H NMR (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 Hz); <sup>13</sup>C NMR (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 cm<sup>-1</sup>; <sup>1</sup>H NMR (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 Hz); <sup>13</sup>C NMR (CDCl\_3)  $\delta$  8.2 (q), 27.8 (t), 30.0 (q), 37.6 (t), 38.2 (s). (a)  $(1, 1)^{12}$ C NMR (CDCl<sub>3</sub>)  $\delta$  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 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.04 (s, 3 H), 1.07 (b, 3 H), 1.10 (s, 3 H), 1.85 (s, 1 H), 2.1 (br s, 5 H), 2.4 (d, 4 H,  $J \simeq 3$  Hz), 5.4 (s, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  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 (M<sup>+</sup>), 189 (62), 147 (39), 133 (29), 106 (50), 104 (85), 95 (43), 91 (B), 77 (42). 7: IR (neat) 1738, 1660 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  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). (13) Bangel, S.; Cresson, P. C. R. Hebd. Seances Acad. Sci., Ser. C 1969, 269, 153.

<sup>(16)</sup> The use of PbCO<sub>3</sub> conditioning minimizes the competing processes A slurry of PbCO<sub>3</sub> in H<sub>2</sub>O is poured through the column, and the column is dried at 300 °C prior to pyrolyses

<sup>(17)</sup> Andrieux, J.; Barton, D. H. R.; Patin, H. J. Chem. Soc., Perkin Trans 7 1977. 359.

Careful medium-pressure liquid chromatography [silica gel, CH<sub>2</sub>Cl<sub>2</sub>, hexane (9:1)], furnished pure analytical samples of 7 and 7a. Their <sup>13</sup>C NMR spectra, as well as the comparison of the IR spectra of their hydrogenation products with those of authentic 9,6 served as final structure proofs. Norketone 9 was converted to hirsutene 1 according to an already published procedure.<sup>6</sup>

The described synthesis proves rewarding in the following ways. First, it marks an easy access to the coriolin class of sesquiterpenes by having served as a model study for the production of the more complicated systems. Several approaches to the oxygenated coriolin nucleus are presently being tested in our laboratory. Second, it ascertains the utility of intramolecular carbenoid addition to 1,3-dienes as a new method for internal cyclopentane annulation. Third, it should be borne in mind that the present approach furnishes hirsutene in 37% overall yield<sup>18</sup> from aldehyde 2 (23% from dimedone), without the use of chromatography, in a single step (except in the preparation of analytical samples); this last criterion makes our approach to the coriolin skeleton attractive from a *practical* point of view.

The synthetic studies of oxygenated coriolins and approaches to the tricyclo[6.3.0.0<sup>4,8</sup>]undecane subunit of retigeranic acid are the points of current interest in our laboratory.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, and the Department of Chemistry at Illinois Institute of Technology for support of this work. Thanks are extended to Professor K. Tatsuta of Keio University, Japan, for providing us with the spectra of hirsutene and norketone. The use of mass spectral facilities and a high-field NMR spectrometer at Indiana University is gratefully appreciated.

Note Added in Proof: After the submission of this manuscript the authors became aware of two very elegant syntheses of hirsutene: one published by A. E. Greene, Tetrahedron Lett. 1980, 3059; the other forthcoming by Little, R. D., et al.

(18) The entire synthesis was repeated three times to ascertain reproducibility and to obtain sufficient materials for <sup>13</sup>C NMR analysis.

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## Synthesis of (±)-Coronafacic Acid. Efficient Intramolecular Diels-Alder Reaction of Latent **Diene-Dienophile Functionality via Thermal Reaction**

Sir:

The structure<sup>1</sup> and stereochemistry<sup>2</sup> of coronatine (1), which induces phytotoxic lesions on the leaves of Italian ryegrass and



(1) Ichihara, A.; Shiraishi, K.; Sato, H.; Sakamura, S.; Nishiyama, K.; Sakai, R.; Furusaki, A.; Matsumoto, T. J. Am. Chem. Soc. 1977, 99, 636.



hypertrophic growth of potato tuber tissue, were reported previously. While the synthesis of  $(\pm)$ -coronafacic acid (2), the acidic component of coronatine, has been completed,<sup>3</sup> no satisfactory results were obtained for the control of its stereochemistry. In order to solve the problem, we utilized an intramolecular Diels-Alder reaction between E,E-diene and enone moieties (a) to produce favorable stereochemistry at  $C_{3a}$  and  $C_6$  in 2 (Scheme I). Though a number of intramolecular Diels-Alder reactions have been applied to the synthesis of natural products,<sup>4</sup> difficulties have always arisen in the construction of the labile diene and dienophile moieties. This communication describes a new stereoselective synthesis of  $(\pm)$ -coronafacic acid through thermal reaction of latent diene-dienophile moieties (b) which are masked as an equally, thermally labile cyclobutene (c) and methyl ketone Diels-Alder product (d), readily derived from trivial compounds as shown by retrosynthesis.

Condensation of the enamine from n-butanal and dimethylamine with diethyl maleate, quaternization with p-TsOMe, and subsequent elimination yielded known diester 35,6 (63% yield from the enamine) (Scheme II). The stereochemistry of diester 3 was

- (2) (a) Ichihara, A.; Shiraishi, K.; Sakamura, S.; Nishiyama, K.; Sakai, R. Tetrahedron Lett. 1977, 269. (b) Ichihara, A.; Shiraishi, K.; Sakamura, S.; Furusaki, A.; Hashiba, N.; Matsumoto, T. Ibid. 1979, 365.
  (3) Ichihara, A.; Kimura, R.; Moriyasu, K.; Sakamura, S. Tetrahedron
- Lett. 1977, 4331.

(4) (a) Oppolzer, W. Angew. Chem., Int. Ed. Engl. 1977, 16, 10; Ibid.
1978, 17, 793. (b) Kametani, T.; Fukumoto, K. Heterocycles 1977, 8, 456.
(c) Wilson, S. R.; Mao, D. T. J. Am. Chem. Soc. 1978, 100, 6289. (d) Taber, D. F.; Gunn, B. P. Ibid. 1979, 101, 3992.

(5) Brannock, K. C.; Bell, A. B.; Burpitt, R. D.; Kelly, C. A. J. Org. Chem. 1964, 29, 801.

(6) Spectral and analytical data for all new compounds are as follows. 3: IR (neat) 1730, 1620 cm<sup>-1</sup>; NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  1.00 (3 H, t, J = 7 Hz), 1.22 (3 H, t, J = 7 Hz), 1.24 (3 H, t, J = 7 Hz), 1.62 (2 H, q, J = 7Hz), 2.20 (1 H, dt, J = 7, 1.5 Hz), 3.20 (1 H, d, J = 1.5 Hz), 4.10 (2 H, q, J = 7 Hz), 4.15 (2 H, q, J = 7 Hz), 6.85 (1 H, s);  $M_w$  calcd for C<sub>12</sub>H<sub>18</sub>O<sub>4</sub> 226.1205, found 226.1242. 4: IR (neat) 3350, 1010 cm<sup>-1</sup>; NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  0.90 (3 H, t, J = 7 Hz), 1.50 (2 H, q, J = 7 Hz), 2.20 (1 H, t, J= 7 Hz), 2.60 (1 H, dd, J = 5, 9 Hz), 3.48 (1 H, t, J = 9 Hz), 3.82 (1 H, dd, J = 5, 9 Hz), 4.05 (2 H, s), 6.00 (1 H, s);  $M_w$  calcd for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub> 142.0992, found 142.0964. Anal. (C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>) C, H; Calcal (67.57; found, 68.04. 5; IR (neat) 3400, 1680 cm<sup>-1</sup>; NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  1.00 (3 H, t, J = 7 Hz), 1.65 (2 H, q, J = 7 Hz), 2.50 (1 H, t, J = 7 Hz), 2.90 (1 H, m), 3.85 (1 H, dd, J = 6, 9 Hz), 7.10 (1 H, dd, J = 2 Hz), 9.00 (1 H, s);  $M_w$  calcd for  $C_{8}H_{12}O_{2}$  140.0836, found 140.0826. 6: IR (neat) 3450, 1080 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  0.95 (3 H, t, J = 7 Hz), 1.55 (2 H, q, J = 7 Hz), 2.25 (1 H, t, J = 7 Hz), 2.60 (2 H, m), 3.55 (2 H, m), 3.95 (4 H, m), 5.15 (1 H, s), H, t, J = 7 H2, 2.60 (2 H, m), 3.55 (2 H, m), 5.55 (4 H, m), 5.15 (1 H, s), 6.20 (1 H, s);  $M_w$  calcd for  $C_{10}H_{16}O_3$  184.1097, found 184.1089. 7: IR (neat) 2750, 1720, 1090 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  1.00 (3 H, t, J = 7 Hz), 1.60 (2 H, q, J = 7 Hz), 2.25 (1 H, t, J = 7 Hz), 3.00 (1 H, d, J = 4.5 Hz);  $M_w$  calcd for  $C_{10}H_{14}O_3$  182.0942, found 182.0941. 8: IR (neat) 1710 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  1.54 (3 H, s), 1.56 (3 H, s), 2.05 (3 H, s), 1.20–2.90 (3 H, m), 3.20 (1 H, m) 3.40 (1 H, m) 6.20 (2 H, m);  $M_w$  calcd for  $C_{14}H_w$  1.20 (3 H, c), 1.20 (2 H, m);  $M_w$  calcd for  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  calcd for  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (2 H, m), 1.20 (2 H, m);  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (1 H, m) 7.20 (1 H, m), 1.20 (2 H, m);  $M_w$  (2 H, m), 1 for  $C_{10}H_1C_3$  182.0942, 100IId 182.0941. 6. 1K (field) 1710 cm<sup>-1</sup>, 1MrK (90 MHz, CCl<sub>4</sub>)  $\delta$  1.54 (3 H, s), 1.56 (3 H, s), 2.05 (3 H, s), 1.20–2.90 (3 H, m), 3.20 (1 H, m), 3.40 (1 H, m), 6.20 (2 H, m);  $M_w$  calcd for  $C_{12}H_{16}O$  176.1201, found 176.1214. 9: IR (neat) 3450, 1700 cm<sup>-1</sup>; NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  0.95 (3 H, t, J = 7 Hz), 1.60 (6 H, s), 1.40–2.00 (3 H, m), 2.20 (1 H, m), 2.20 (1 H, m), 3.00 (1 H, m), 3.30 (1 H, m), 3.60 (1 H, m), 3.90 (5 H, m), 5.20 (1 H, m), 6.30 (1 H, m), 6.40 (2 H, m);  $M_w$  calcd for  $C_{22}H_{30}O_4$  358.2142, found 358.2140. 10: IR (neat) 1690, 1670, 1620 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  1.00 (3 H, t, J = 7 Hz), 1.60 (6 H, s), 1.25–2.10 (3 H, m), 2.50 (1 H, m), 3.15 (1 H, d, J = 8 Hz), 3.35, 3.45 (each 1 H, m), 4.00 (4 H, m), 6.20 (1 H, d, J = 16 Hz), 6.30 (3 H, br s), 6.85 (1 H, dd, J = 8, 16 Hz);  $M_w$  calcd for  $C_{22}H_{28}O_3$  340.2037, found 340.2026. 11: IR (neat) 1710, 1090 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  0.95 (3 H, t, J = 7 Hz), 1.55, 1.60 (each 3 H, s), 1.10–2.60 (11 H, m), 3.40 (2 H, m), 3.50 (each 1 H, m), 3.20 (1 H, s), 6.15 (1 H, s), 6.25 (2 H, m). Anal. ( $C_{22}H_{30}O_3$ ) C, H. 12: IR (KBr) 1740 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  0.95 (3 H, t, J = 7 Hz), 1.15–2.90 (11 H, m), 3.80 (4 H, m), 5.00 (1 H, s), 5.65 (1 H, br s). Anal. ( $C_{14}H_{20}O_3$ ) C, H. 2: IR (KBr) 1740 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  0.95 (3 H, t, J = 7 Hz), 1.15–2.90 (11 H, m), 3.80 (4 H, m), 5.00 (1 H, s), 5.65 (1 H, br s). Anal. ( $C_{14}H_{20}O_3$ ) C, H. 2: IR (KBr) 1740 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  0.95 (3 H, t, J = 7 Hz), 1.10–2.60 (11 H, m), 5.00 (1 H, s), 5.65 (1 H, br s). Anal. ( $C_{14}H_{20}O_3$ ) C, H. 2: IR (KBr) 1740 cm<sup>-1</sup>; NMR (90 MHz, CCl<sub>4</sub>)  $\delta$  0.95 (3 H, t, J = 7 Hz), 1.15–2.90 (11 H, m), 3.80 (4 H, m), 5.00 (1 H, s), 5.65 (1 H, br s). Anal. (C(CHCl<sub>3</sub>) 3100, 1735, 1680, 1630 cm<sup>-1</sup>; NMR  $\delta$  0.95 (3 H, t, J = 7 Hz), 3.00 (1 H, m), 6.95 (1 H, br s). Anal. ( $C_{12}H_{16}O_3$ ) C, H. (1 H, m), 6.95 (1 H, br s). Anal. (C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>) C, H.