did not have the expected exalting effect on diastereomer ratio,[2] and the enantiomeric excess was also reduced slightly by the increased bulk of the alkyl iodide.

Alkylation of the dianion of (*S*)-(−)-prolinol propionamide with 1-iodooctane gave the opposite configuration for **3**, as expected, though the enantiomeric excess was slightly less than that for the comparably alkylated decanamide (66% vs. 72%). A most striking observation was that the opposite configuration was also induced upon alkylating the α anion of prolinol methyl ether. *Thus, methylation of the dianion of 1 at −120 °C in THF gave the S configuration (80% ee), but methylation of the anion of 2 at −100 °C in THF gave the R configuration (82% ee).*[5] It is therefore possible to induce asymmetry equally in either configurational sense with a single chiral auxiliary reagent and the same alkyl iodide. In contrast, alkylation of the dianion of (−)-ephedrine propionamide (LDA as base) reportedly[2] produced an enantiomeric excess of 90% (in the presence of Mg^{2+}), and the alkylation of the methyl ether simply reduced the degree of asymmetry, though inducing an excess of the same configuration, when LDA was employed as the base.[2] For comparison, therefore, we prepared and alkylated the dianion of (−)-ephedrine decanamide and the anion of the corresponding methyl ether. The alkylation product derived from the amide alcohol (*t*-BuLi, THF, CH_3I, −100 °C, 0.5 h) was 81:19 (*S*:*R*); that from the methyl ether was 16:84. The configuration induced by (−)-ephedrine was the same as that induced by (*S*)-(−)-prolinol, though the enantiomeric excess induced in this instance was slightly less when ephedrine was the chiral auxiliary. Clearly, however, the methyl ether again induced asymmetry in the opposite sense, an observation not previously made.[2]

The alkylated products (prolinol and ephedrine amides) were hydrolyzed in a two-phase system (concentrated HCl, hexane, reflux, 8 h) to produce the acids without affecting the configuration. Although the chiral auxiliaries were not recovered, one expects that they could be recycled.

The mechanistic picture for these and related alkylations is not clear. Preliminary work by us with amides of (*S*)-α-methylbenzylamine indicated that alkylation of the corresponding amide anions occurred without any significant configurational preference. The failure of α-methylbenzylamine as a chiral auxiliary strongly suggests chelation as the induction-activating factor for chiral β-hydroxy (methoxy) amides.[6] Further experimental detail, however, is required to define the several species that may be present and to explain the dramatic reversal of induced configuration due to change of functional group.

We have recently described the preparation and some of the column characteristics of capillary columns coated with the liquid crystal, cholesteryl cinnamate.[7] The effective temperature range for such columns is 160–210 °C, which corresponds to the mesophase range of the liquid crystal. In Table II, pertinent details are given of the analyses for the diastereomeric pairs of compounds. Complete resolution was not achieved by using capillary columns coated with either OV-101 (apolar) or SP-2340 (polar); thus, in this instance, the liquid crystal phase uniquely served to analyze the alkylation products.

Table II. Analytical Data for Diastereomeric Pairs of Alkylated Amides

compd	column temp	R^a	$K_{S,S'}{}^a$	$K_{R,S'}{}^a$
3a	200	1.36	9.8	10.2
4a	180	1.50	11.1	11.5
3b	200	3.19	11.8	12.9
4b	180	3.08	12.5	13.4
4c[b]	190	0.75	16.2	16.4
8[c]	185	0.92	11.7	11.9

[a] Ettre, L. S. *J. Gas Chromatogr.* **1963**, *1*, 36. [b] **4c** was obtained by O-methylation of **3c**. [c] **8** is the α-methyl decanamide of (−)-ephedrine methyl ether.

Acknowledgment. We express our gratefulness to Dr. Roy King of the University of Florida, Gainesville, FL, for obtaining the NMR spectral data. We are also indebted to the following individuals in our laboratory: Mr. J. R. Jordan and Ms. B. D. Dueben for technical assistance with GLC and high-performance LC work and Mr. T. Proveaux for obtaining the mass spectral data.

Registry No. 1a, 74036-65-0; **1b**, 74036-66-1; **2**, 74036-67-2; (*R*,*S*)-**3a**, 74036-68-3; (*S*,*S*)-**3a**, 74036-69-4; (*R*,*S*)-**3b**, 74036-70-7; (*S*,*S*)-**3b**, 74036-71-8; (*S*,*S*)-**3c**, 74036-72-9; (*R*,*S*)-**4a**, 74036-73-0; (*S*,*S*)-**4a**, 74036-74-1; (*R*,*S*)-**4b**, 74036-75-2; (*S*,*S*)-**4b**, 74036-76-3; (*R*,*S*)-**4c**, 74036-77-4; (*S*,*S*)-**4c**, 74036-78-5; **5**, 74036-79-6; (*S*)-**6**, 74036-80-9; **7**, 74036-81-0; (*R*)-**8**, 74036-82-1; (*S*)-**8**, 74080-81-2; (−)-ephedrine, 299-42-3; (*S*)-(−)-prolinol, 23356-96-9; (*S*)-(+)-2-methyldecanoic acid, 74036-83-2; *tert*-butyl *n*-nonyl ketone, 74036-84-3; CH_3I, 74-88-4; *n*-$C_8H_{17}I$, 629-27-6; C_2H_5I, 75-03-6; *n*-C_4H_9I, 25267-27-0; *n*-$C_8H_{17}CH_2COCl$, 112-13-0; CH_3CH_2COCl, 79-03-8.

Philip E. Sonnet,* Robert R. Heath

Insect Attractants, Behavior and Basic Biology Research Laboratory Agricultural Research, Science and Education Administration USDA Gainesville, Florida 32604

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(5) An inversion in stereoselectivity involved in asymmetric hydrogenation of *o*-acylcinnamic acid derivatives catalyzed by a chiral aminophosphine–rhodium complex has been recently reported: Onuma, K.; Ito, T.; Nakamura, A. *Chem. Lett.* **1979**, 905.

(6) Since this manuscript was submitted for publication, we have learned of Professor David Evans' (California Institute of Technology, Pasadena, CA) studies of this anion system. We are grateful for information he has related to us, and more definitive data concerning the nature of the anionic species will be forthcoming from his laboratory.

(7) Heath, R. R.; Jordan, J. R.; Sonnet, P. E.; Tumlinson, J. H. *HRC CC, J. High Resolut. Chromatogr. Chromatogr.* **1979**, *12*, 712.

Cyclization of Substituted 5-Hexenyl Radicals as a Model for Photocyclization of 1,5-Hexadien-3-ones

Summary: An examination of substituent effects upon the photochemistry of a number of 1,5-hexadien-3-ones reveals a close parallel with those observed in the cyclization of 5-hexenyl radicals and permits for the first time a rationalization for variations in the regiospecificity of the intramolecular [2 + 2] cycloaddition reactions of these dienones.

Sir: Over a decade ago, in two studies of intramolecular photocyclizations of hydrocarbons, Srinivasan and Carlough[1] and Liu and Hammond[2] noted that when the reacting double bonds were in a 1,5-relationship the photochemistry seemed to be largely controlled by initial C(1)–C(5) bonding, giving a five-membered-ring biradical intermediate which afforded products through disproportionation and closure. Liu and Hammond[2] also sug-

(1) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932.
(2) Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 4936.

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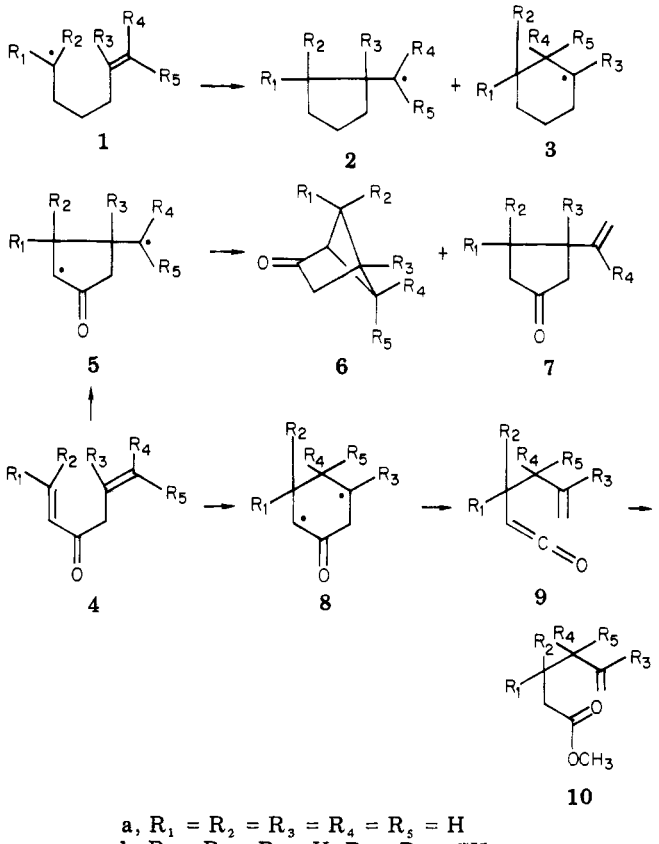
gested that this remarkable selectivity was the result of the well-known kinetic preference for the formation of five-membered rings. In addition, they viewed as "probably a closely related phenomenon"[2] the proclivity of 5-hexenyl radicals to cyclize to cyclopentylmethyl radicals rather than cyclohexyl radicals. In later work, other investigators have proposed that this selectivity observed in the photocyclizations may arise from orbital-symmetry factors[3] or specifically oriented complexes.[4]

Formation of five-membered-ring biradicals in the photocyclization of 1,5-hexadienes, regardless of the nature and position of substituents on the reacting double bonds,[5] has been generally accepted. Bicyclo[2.1.1]hexanes, rather than the isomeric bicyclo[2.2.0]hexanes, are usually obtained.[6] There are, however, exceptions to this behavior.[7] This communication will show that the relationship between the cyclization of 5-hexenyl radicals and the photocyclization of 1,5-hexadienes, in the form of 1,5-hexadien-3-ones, is much closer than originally indicated, and that a rationale for the anomalous behavior of several dienones can be found in this analogy.

Substituent effects on the direction and relative rates of cyclization of 5-hexenyl radical have been extensively studied by Beckwith,[8] who has summarized his major findings as follows:[9] "(i) Substituents at the new radical center [R_4, R_5 in **1**] show remarkably little effect. (ii) Substituents on the attacking radical center [R_1, R_2, in **1**] also show small effects. (iii) Substituents on the olefinic seat of reaction [R_3 in **1**] greatly retard the rate of reaction."

Combining data already in the literature with experimental results obtained in our own laboratory, we note that the effect of substituents on the photochemistry of dienones **4a–f** is virtually identical with that observed for radicals **1a–f**.[8] Just as the unsubstituted 5-hexenyl radical **1a** cyclizes almost exclusively to **2a**,[8] so does parent dienone **4a** undergo 1,5-closure to biradical **5a**, which subsequently yields **6a**.[10] In accord with Beckwith's first generalization, **1b** cyclizes in the same manner as **1a**.[8] The corresponding ketone **4b** analogously gives **5b**; it is insignificant for our purposes here that the eventual product, **7b**, is the result of disproportionation rather than closure.[11a] In extending this relationship, we were suprised to note that **4c**, rather than cyclizing with ease as expected (for corresponding radical **1c** reacts in agreement with Beckwith's second conclusion),[8] had been reported to be photochemically stable.[11] Speculating that this lack of reactivity might be caused by steric hindrance to closure of **5c** and not by its failure to form from **4c**, we irradiated

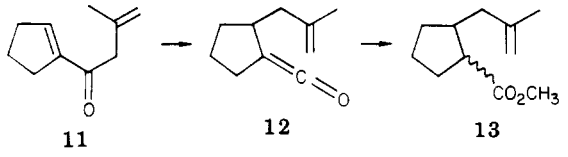


a, $R_1 = R_2 = R_3 = R_4 = R_5 = H$
b, $R_1 = R_2 = R_3 = H$; $R_4 = R_5 = CH_3$
c, $R_1 = R_2 = CH_3$; $R_3 = R_5 = H$
d, $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = CH_3$
e, $R_1 = R_2 = R_3 = CH_3$; $R_4 = R_5 = H$
f, $R_1 = R_2 = R_5 = H$; R_3, $R_4 = (CH_2)_4$
g, $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = Cl$

4c in refluxing *p*-xylene and obtained nearly a quantitative yield of **6c**,[12,13] the desired product.

With a substituent at C(5), as in **1d**, the rate of 1,5-cyclization is lowered to a point where 1,6-cyclization becomes preferred, and hence both **2d** and **3d** are formed (ratio, 43:57).[9] The photochemistry of similarly substituted ketones strikingly parallels this behavior. Upon irradiation **4d** undergoes 1,5-cyclization, giving **5d** and subsequently **6d** (43% yield), and 1,6-cyclization which ultimately yields **10d** (27% yield).[14] Both modes of cyclization are also observed when **4g**, the chlorine analogue of **4d**, is photolyzed.[15]

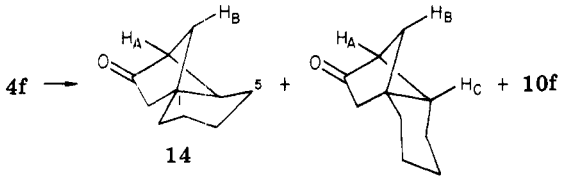
Exclusive 1,6-cyclization is observed when **11** is irradiated[14] (yielding both isomers of **13** from **12**), a result with



(3) Scheffer, J. R.; Wostradowski, R. A. *J. Org. Chem.*, **1972**, *37*, 4317.
(4) White, J. D.; Gupta, D. N. *Tetrahedron* **1969**, *25*, 3331.
(5) Most investigators have recognized that these double bonds can be incorporated in dienes,[1] trienes,[2] tetraenes,[4] enones,[10,11a] α,β-unsaturated esters,[3] and other related systems with little or no effect on the reaction.
(6) Scheffer, J. R.; Boive, B. A. *J. Am. Chem. Soc.* **1971**, *93*, 5490. Wolff, S.; Ayral-Kaloustian, S.; Agosta, W. C. *J. Org. Chem.* **1976**, *41*, 2947, and many references to the work of others contained therein.
(7) In addition to the examples discussed below, two exceptions due to different causes have been reported: Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 522; Yoshioka, H.; Mabry, T. J.; Higo, A. *Ibid.* **1970**, *92*, 923.
(8) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, 2257 and references contained therein.
(9) Beckwith, A. L. J., 2nd International Symposium on Organic Free Radicals, Aix-en-Provence, 1977, in "Radicaux Libres Organiques"; Editions du Centre National de la Recherche Scientifique: Paris, 1978; pp 373–385.
(10) Bond, F. T.; Jones, H. C.; Scerbo, L. *Tetrahedron Lett.* **1965**, 4685.
(11) (a) Gibson, T. W.; Erman, W. F. *J. Org. Chem.* **1972**, *37*, 1148. (b) We confirmed the photochemical stability of **4c** at room temperature.
(12) This product was identified by comparison of its IR spectrum with that of an authentic sample kindly provided by Professor Takayuki Suga (Hirata, T.; Suga, T. *J. Org. Chem.* **1971**, *36*, 412) and preparation of its 2,4-dinitrophenylhydrazone, mp 129–130 °C (lit. mp 130.5–131 °C: Meinwald, J.; Gassmann, P. *J. Am. Chem. Soc.* **1960**, *82*, 2857).
(13) For other examples of biradical reactions which require activation greater than that available at room temperature, see: Barany, F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1946; Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1978**, *43*, 3627; Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2378.
(14) (a) Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 1961. (b) In this and subsequent cases, ester products arise from addition of methanol.
(15) Bond, F. T.; Ho, C.-Y.; McConnell, O. *J. Org. Chem.* **1976**, *41*, 1416.

no exact analogy in Beckwith's data (the appropriate radical has not been studied), but predictable from results that are available. The rate of 1,5-cyclization, already reduced by R_3 in **1d**, is further depressed by substituents on the attacking radical center; hence **1e**, with two methyl groups at C(1), undergoes only 1,6-cyclization to give **3e**.[9,16] Therefore it is not unreasonable to expect the radical that corresponds to **11** by having only one substituent at C(1) also to cyclize in this fashion.

In order to test further the predictive value of this analogy, we examined **4f**[17,18] whose corresponding radical **1f** gives nearly equal amounts of **2f** and **3f**.[8] Photolysis of **4f** gave **14** (= **6f**), **15**, and **10f** in a ratio of 12:66:22.[18,19]



14 15

Thus a satisfactory explanation of the divergent photochemistry of **4d**, **4e**,[16] **4g**, and **11** is provided by the chemistry of 5-hexenyl radicals.

In conclusion, we believe that a simple and effective model for understanding and predicting the regiochemistry of a substantial number of photochemical reactions of hexadienones lies in this analogy. It is noteworthy that this model, which treats the β-carbon atom of the enone system simply as a radical center, is so effective, since the actual mechanism of photocycloaddition is known to be complex.[20] There are indications that this correspondence is also valid in other systems where it is appropriate to consider the α-carbon atom of an enone as the radical center. We are continuing to investigate various aspects of this model and its extension to other systems.[21]

Registry No. 1a, 16183-00-9; **1b**, 54389-00-3; **1c**, 38295-12-4; **1d**, 38295-09-9; **1e**, 38295-11-3; **1f**, 19665-04-4; **2a**, 23907-66-6; **2b**, 73926-43-9; **2c**, 73926-44-0; **2d**, 73926-45-1; **3d**, 3170-58-9; **3e**, 73926-46-2; **3f**, 52692-69-0; **4a**, 6857-93-8; **4b**, 33698-69-0; **4c**, 33698-67-8; **4d**, 998-83-4; **4e**, 5837-45-6; **4f**, 73926-47-3; **4g**, 58208-09-6; **5a**, 73926-48-4; **5b**, 73926-49-5; **5c**, 73926-50-8; **5d**, 73926-51-9; **5g**, 73926-52-0; **6a**, 5164-64-7; **6c**, 72904-15-5; **6c** DNP, 73926-53-1; **6d**, 41414-48-6; **7b**, 33698-76-9; **8d**, 73940-59-7; **8g**, 73940-60-0; **10d**, 32853-30-8; **10f**, 2359-69-5; **11**, 41414-31-7; **12**, 73926-54-2; **13** (isomer 1), 41414-45-3; **13** (isomer 2), 41414-44-2; **14**, 73926-55-3; **15**, 73952-55-3.

(16) No reaction was observed when **4e** was photolyzed at 25 °C. Irradiation at elevated temperature led only to the formation of phorone through hydrogen migration. See also ref 11a and Crowley, K. J.; Schneider, R. A.; Meinwald, J. *J. Chem. Soc. C* **1966**, 571; Kropp, P. J.; Gibson, T. W. *Ibid.* **1967**, 143.

(17) Ketone **4f** was prepared by a Mannich reaction on commercially available 1-cyclohexenylacetone.

(18) Spectroscopic data for **4f**, **14**, **15**, and **10f** follow. All new compounds gave satisfactory high-resolution mass spectra. **4f**: IR 2935 (s), 2850 (m), 2838 (m), 1695 (s), 1613 (m), 1390 (m), 975 (m) 940 (m) cm^{-1}; NMR (60 MHz) δ 6.68–6.00 (m, 2 H), 5.83–5.33 (m, 2 H), 3.10 (s, 2 H), 2.33–1.32 (br m, 8 H). **14**: IR 3000 (w), 2932 (s), 2865 (w), 1762 (s), 1438 (m), 1290 (m), 1113 (m), 1010 (m), 980 (m) cm^{-1}; NMR (220 MHz) δ 2.63 (m, 1 H), 2.52 (d, J = 2.6 Hz, 1 H), 2.12 (d, J = 15.3 Hz, 1 H), 1.89–1.03 (m, 11 H). **15**: IR 2935 (s), 2862 (m), 2850 (m), 1762 (s), 1440 (m), 1085 (m), 1018 (m), 980 (m) cm^{-1}; NMR (220 MHz) δ 2.79 (dd, J = 1.9, 1.9 Hz, 1 H), 2.21 (ddd, J = 16.2, 4.8, 1.0 Hz, 1 H), 1.87–1.70 (m, 6 H), 1.64–1.10 (m, 6 H). **10f**: IR 3070 (w), 2935 (s), 2855 (m), 1741 (s), 1160 (m), 880 (m) cm^{-1}; NMR (60 MHz) δ 4.67 (m, 1 H), 4.58 (m, 1 H), 3.63 (s, 3 H), 2.47–1.00 (br m, 13 H).

(19) The stereochemical assignments for **14** and **15** are based on the chemical shift and multiplicity of the methine protons α to the carbonyl group. In **14**, this proton (H_A) appears as a doublet, coupled only to H_B, and is shielded by the C(5) methylene group. This methylene group also shifts H_B downfield to 2.63 ppm. In **15**, H_A is now observed as a doublet of doublets, being coupled to both H_B and H_C. Neither H_B nor H_C appear below 1.87 ppm. The magnitude of the coupling constants and the variation in the chemical shifts are in accord with expectation. For a further discussion of the NMR spectra of bicyclo[2.1.1]hexanes, see: Meinwald, J.; Lewis, A. *J. Am. Chem. Soc.* **1961**, *83*, 2769; Wiberg, K. B.; Lowry, B. R.; Nist, B. J. *Ibid.* **1962**, *84*, 1594; Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1980**, *45*, 1332.

(20) For a recent mechanistic study on [2 + 2] photocyclizations, see: Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559.

(21) This investigation was supported by grants from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

William C. Agosta, Steven Wolff*

Laboratories of The Rockefeller University
New York, New York 10021

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Use of [3 + 2] Cycloaddition in Elaboration of the ω Chain of Prostaglandins

Summary: The use of 3,5-disubstituted isoxazoles as an aldol or stabilized Wittig condensation equivalent is applied to the construction of the ω chain of prostaglandins.

Sir: Isoxazoles,[1] isoxazolines,[2] and isoxazolidines[3] have enjoyed an increasing use as key intermediates in the synthesis of naturally occurring substances.

We report here a novel approach to the synthesis of the 11-deoxy derivative **9** of a popular prostaglandins synthon,[4,5] featured by the use in a key stage of [3 + 2] regiospecific cycloaddition which allows the arrangement in masked form of the C(13)–C(20) fragment of prostanoids.

Our synthetic strategy, outlined in Scheme I, starts from the known[6] methyl 2-oxocyclopent-5-enyl-1-acetate (**1**), which underwent an easy 1,1,3,3-tetramethylguanidine catalyzed[7] Michael addition of nitromethane to give an 82% yield of the crucial nitro ketone **2**.[8]

(1) Casnati, G.; Quilico, A.; Ricca, A.; Vita Finzi, P. *Gazz. Chim. Ital.* **1966**, *96*, 1064–1072. Stork, G.; McMurry, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 5464–5465. Ohashi, M. *J. Chem. Soc. D* **1969**, 893–894. Scott, J. W.; Saucy, G. *J. Org. Chem.* **1972**, *37*, 1652–1658. Akhren, A. A.; Lakvich, F. A.; Khripach, V. A.; Klebanovich, I. B. *Tetrahedron Lett.* **1976**, 3983–3984. Traverso, G.; Pollini, G. P.; Barco, A.; De Giuli, G. *Gazz. Chim. Ital.* **1972**, *102*, 243–252. Stevens, R. V.; Fitzpatrick, J. M.; Germeraad, P. B.; Harrison, B. L.; Lapalme, R. *J. Am. Chem. Soc.* **1976**, *98*, 6313–6317. Stevens, R. V.; Cherpeck, R. E.; Harrison, B. L.; Lai, J.; Lapalme, R. *Ibid.* **1976**, *98*, 6317–6321. Stork, G.; Hagedorn, A. A., III *J. Am. Chem. Soc.* **1978**, *100*, 3609–3611. Bianchi, G.; De Amici, M. *J. Chem. Soc., Chem. Commun.* **1978**, 962–963.

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(3) Tufariello, J. J. *Acc. Chem. Res.* **1979**, *12*, 396–403, and references cited therein.

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(5) Woodward, R. B.; Gosteli, J.; Ernest, I.; Friary, R. J.; Nestler, G.; Raman, H.; Sitrin, R.; Suter, Ch.; Whitesell, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 6853–6855.

(6) Cassar, L.; Chiusoli, G. P. *Chim. Ind. (Milan)* **1966**, *48*, 323–332.

(7) Pollini, G. P.; Barco, A.; De Giuli, G. *Synthesis* **1972**, 44–45.

(8) This intermediate and all others reported in this communication have the expected spectral and analytical properties. **2**: ^1H NMR ($CDCl_3$) δ 4.4–4.8 (m, 2 H), 3.7 (s, 3 H); IR (film) 1740, 1550 cm^{-1}. **3**: ^1H NMR ($CDCl_3$) δ 5.9 (s, 1 H), 3.7 (s, 3 H), 0.95 (t, 3 H, J = 5 Hz); IR (film) 1740, 1600 cm^{-1}. **4**: ^1H NMR ($CDCl_3$) δ 9.25 (br s, 1 H), 5.95 (s, 1 H), 0.95 (t, 3 H, J = 5 Hz); IR ($CHCl_3$) 1740, 1715, 1600 cm^{-1}. **5**: ^1H NMR ($CDCl_3$) δ 5.9 (s, 1 H), 5.5–6.0 (br s, 2 H), 4.5 (m, 1 H), 0.95 (t, 3 H, J = 5 Hz); IR (Nujol) 1680, 1600 cm^{-1}. **6**: ^1H NMR ($CDCl_3$) δ 5.95 (s, 1 H), 5.1 (m, 1 H), 0.95 (t, 3 H, J = 5 Hz); IR (film) 1770, 1600 cm^{-1}. **7**: ^1H NMR ($CDCl_3$) δ 5.90 (s, 1 H), 5.65 (m, 1 H), 4.90 (m, 1 H), 0.95 (t, 3 H, J = 5 Hz); IR (film) 3500–3000, 1600 cm^{-1}. **8**: ^1H NMR ($CDCl_3$) δ 5.90 (s, 1 H), 5.1 (m, 1 H), 4.75 (m, 1 H), 3.30 (s, 3 H), 0.95 (t, 3 H, J = 5 Hz); IR (film) 1600 cm^{-1}. **9**: ^1H NMR ($CDCl_3$) δ 6.75 (m, 1 H, J = 16 Hz), 6.15 (dd, 1 H, J = 16 and J = 7 Hz), 5.1 (m, 1 H), 4.7 (m, 1 H), 3.3 (s, 3 H), 0.90 (t, 3 H, J = 7 Hz); IR (film) 1670, 1630, 970 cm^{-1}.

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