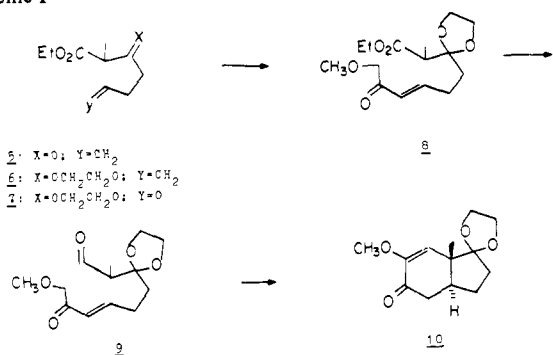
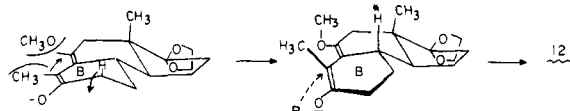


Scheme I



Scheme II

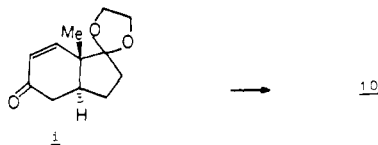


Treatment of the anion corresponding to *trans*-10 (lithium diisopropylamide, tetrahydrofuran, -78 °C) with 3-(trimethylsilyl)-3-penten-2-one,<sup>10</sup> followed by cyclization of the crude reaction product with sodium methoxide in refluxing methanol, afforded **11**,<sup>11</sup> mp 87–88 °C, in 62% yield (found: C, 70.65; H, 7.76).

Previous work from these laboratories<sup>12</sup> suggested that "equatorial alkylation" would occur in our system to provide the correct stereochemistry at C-10. In the case of the dienolate corresponding to **11**, the B ring must be twisted into a half-boat conformation to alleviate the severe interaction between the C-10 methyl and the methoxyl group at C-11. This results in increased accessibility of the  $\alpha$  face. At the same time, the starred hydrogen (Scheme II) would hinder alkylation from the  $\beta$  face.  $\beta$  alkylation would also force the C-10 methyl group to move past the C-11 methoxy through a fully eclipsed position.

Reaction of **11** (Scheme III) with 3 equiv of lithium in tetrahydrofuran/liquid ammonia (1:2) containing 0.9 equiv of water, at -33 °C, followed by treatment of the resulting dienolate with 1-bromo-3-chloro-2-butene<sup>12</sup> and acid hydrolysis (10% aqueous hydrochloric acid, tetrahydrofuran, room temperature) of the crude product afforded a 70% yield of **12**, obtained as a mixture of double-bond isomers.

(8) Authentic samples of *cis*- and *trans*-fused **10** were prepared from the corresponding *cis*- and *trans*-birindenones **1** (reference 1), respectively, by



reduction (DIBAL-H, diethyl ether, -78 °C), epoxidation (*m*-CPBA, dichloromethane, room temperature), oxidation (Collins reagent, dichloromethane, 0 °C), methoxide opening, and dehydration (sodium methoxide, methanol, room temperature). <sup>1</sup>H NMR: CH<sub>3</sub> *trans* 1.06, *cis* 1.12; vinyl H *trans* 5.91, *cis* 5.70. VPC (3%FFAP, 1/8 in. × 10 ft, 200 °C) *cis* 8.9 min, *trans* 11.9 min.

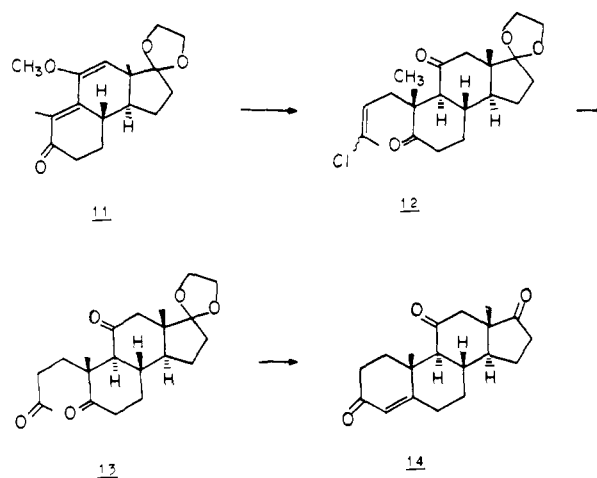
(9) **10**: VPC (3% FFAP/200 °C) *cis* 8.6 min, *trans* 11.9 min. *trans*-**10**: IR (CH<sub>2</sub>Cl<sub>2</sub>) 1690, 1615; <sup>1</sup>H NMR (80 MHz) 1.06 (s, 3 H), 1.5–2.1 (m, 5 H), 2.52 (m, 2 H), 3.58 (s, 3 H), 3.96 (s, 4 H), 5.91 (s, 1 H); <sup>13</sup>C NMR (20.1 MHz) 15.48, 23.31, 33.56, 38.05, 40.84, 46.42, 54.07, 63.53, 64.62, 117.16, 120.68, 151.02, 192.70; MS (CI-ME) 239 (M + 1). *cis*-**10**: IR (CH<sub>2</sub>Cl<sub>2</sub>) 1690, 1630; <sup>1</sup>H NMR (80 MHz) 1.12 (s, 3 H), 1.5–2.1 (m, 5 H), 2.59 (m, 2 H), 3.58 (s, 3 H), 3.95 (s, 4 H), 5.70 (s, 1 H); MS (CI-ME) 239 (M + 1).

(10) Stork, G.; Singh, J. *J. Am. Chem. Soc.* **1974**, *96*, 6181.

(11) **11**: IR (CHCl<sub>3</sub>) 1655, 1600; <sup>1</sup>H NMR (80 MHz) 1.00 (s, 3 H), 2.08 (d, *J* = 2 Hz, 3 H), 1.3–2.9 (m, 10 H), 3.55 (s, 3 H), 3.96 (s, 4 H), 5.36 (s, 1 H); <sup>13</sup>C NMR (20.1 MHz) 13.30, 17.42, 22.09, 26.46, 34.17, 37.56, 46.91, 47.03, 54.19, 64.14, 65.11, 112.79, 117.95, 131.30, 147.80, 154.54, 200.04; MS (CI-ME) 305 (M + 1).

(12) Stork, G.; Logusch, E. *J. Am. Chem. Soc.* **1980**, *102*, 1218, 1219.

Scheme III



Hydrolysis of the vinyl chloride (Hg[OCOCF<sub>3</sub>]<sub>2</sub>, dichloromethane, room temperature, 70% yield)<sup>13</sup> gave **13**,<sup>14</sup> which was cyclized (potassium hydroxide, aqueous methanol, room temperature, 80% yield) to provide ( $\pm$ )-adrenosterone, mp 167–169 °C (ethyl acetate), whose spectral (250-MHz <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, MS) properties were identical with those of an authentic sample.<sup>15,16</sup>

**Acknowledgment.** We thank the National Institutes of Health and the National Science Foundation for their support of this work.

(13) Yoshioka, H.; Takahashi, K.; Kobayashi, M. *Tetrahedron Lett.* **1979**, 3489.

(14) **13**: IR (CHCl<sub>3</sub>) 1740, 1710; <sup>1</sup>H NMR (80 MHz) 0.89 (s, 3 H), 1.32 (s, 3 H), 2.11 (s, 3 H), 1.7–2.9 (m, 17 H); MS (CI-ME) 319 (M + 1). (15) Obtained from the Sigma-Aldrich Chemical Co.

(16) **14**: IR (CHCl<sub>3</sub>) 1740, 1710, 1660, 1620; <sup>1</sup>H NMR (250 MHz) 0.86 (s, 3 H), 1.41 (s, 3 H), 1.0–3.0 (m, 17 H), 5.72 (br s, 1 H); <sup>13</sup>C NMR (62.8 MHz) 14.66, 17.49, 21.61, 31.08, 32.04, 33.73, 34.92, 35.89, 36.48, 38.42, 50.05, 50.31, 50.51, 63.53, 124.83, 167.39, 198.88, 207.12, 216.02; MS (CI-ME) 301 (M + 1).

## On the Structure of the Hypothetical Common Tetramethylene Biradical Intermediate

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1,4-Biradicals are postulated as intermediates in a variety of thermal<sup>1–5</sup> and photochemical<sup>6</sup> reactions. For the parent compound, tetramethylene, Segal<sup>7</sup> reported *two* stable conformers—the *gauche* (**1a**) and the *anti* (**2a**)—in his ab initio configuration interaction study of the singlet potential-energy surface. Data from the thermolyses of 1,2-dimethylcyclobutanes<sup>1</sup> and the cyclic azo compounds **3b**<sup>2a</sup> have been interpreted by assuming<sup>2a</sup> that there

<sup>†</sup> Samuel B. Silbert Fellow, 1981–1982.

(1) Gerberich, H.; Walters, W. *J. Am. Chem. Soc.* **1961**, *83*, 3935, 4884.

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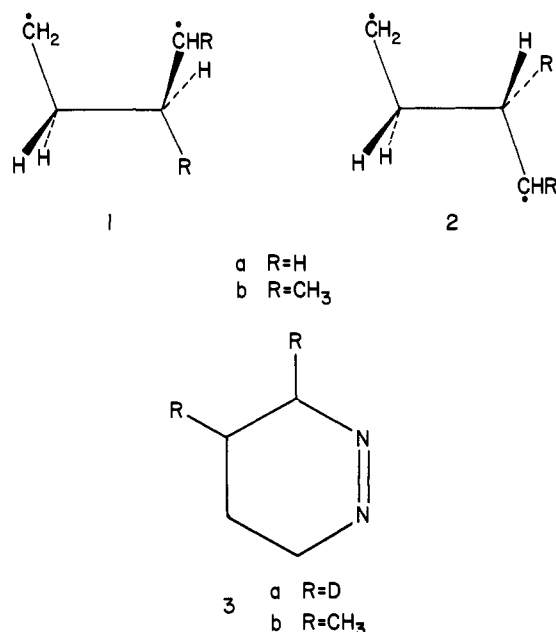
(3) Scacchi, G.; Richard, C.; Back, M. *Int. J. Chem. Kinet.* **1977**, *9*, 513, 525.

(4) Berson, J. In "Rearrangements in Ground and Excited States", de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 311–391.

(5) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 61–67.

(6) (a) Wagner, P. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Jones, G. *Org. Photochem.* **1981**, *5*, 1. (c) Engel, P. *Chem. Rev.* **1980**, *80*, 99–150.

(7) Segal, G. *J. Am. Chem. Soc.* **1974**, *96*, 7892–8.

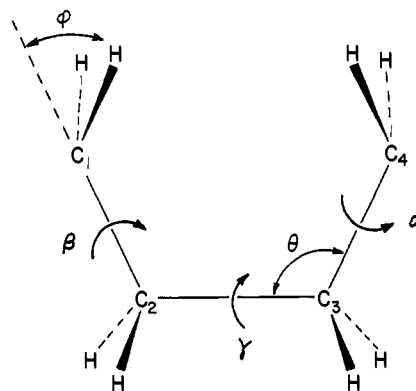


is a *single* biradical intermediate<sup>8</sup> common to both experiments, which exhibits competition among rotation of the terminal methylene groups, fragmentation to olefins, and cyclization to cyclobutanes, with respective rate constants  $k_r$ ,  $k_f$ , and  $k_c$ . The structure of this intermediate has been assumed to be **1b**.<sup>2a</sup> The results of the cycloaddition of ethylene with 2-butene<sup>3</sup> have also been interpreted<sup>2a,3</sup> in terms of the same common intermediate. However, a significant fraction of olefins are expected to form **2b** initially.<sup>4</sup> This creates the need to explain why no additional loss of stereochemistry (by a  $k_r$  process in **2b**) is observed in the cycloaddition products. The response has been to postulate<sup>2a,4</sup> dynamical properties that **2b** must possess either to mimic the behavior of **1b** or to accommodate **1b** as the common intermediate produced in all three experiments.<sup>1,2a,3</sup> One hypothesis<sup>2a</sup> is that loss of stereochemistry of **2** is prevented by an abnormally high barrier for  $k_r$ . However, recent MCSCF calculations by Borden and Davidson<sup>9</sup> predict that **2a** should lose stereochemistry before it cyclizes, and the interpretive discrepancy remains.

In this communication we report the results of ab initio MCSCF calculations that strongly indicate that **1a** does not exist as a local minimum on the singlet potential-energy surface and that the earlier prediction of a *gauche* minimum<sup>7</sup> was an artifact of the minimal basis set used. If a common tetramethylene intermediate exists, we predict it to be **2**.

The two-configuration MCSCF wave function we used is the same as Borden and Davidson's.<sup>9</sup> As they noted, it is variationally superior to Segal's<sup>7</sup> 15-configuration wave function for biradical geometries. With Segal's STO-3G<sup>10</sup> basis set, his reported total energy of **1a** is lowered by 5 kcal/mol when calculated with the MCSCF wave function. This is because the MCSCF orbitals are fully optimized for any given basis set.

Our internal coordinates are defined in Figure 1. In searching for a *gauche* minimum, we used a split-valence 3-21G<sup>11</sup> basis set throughout. We began with  $C_1C_2 = 1.52$  Å,  $C_2C_3 = 1.55$  Å,  $\theta = 113^\circ$ ,  $\phi = 16^\circ$ ,  $HC_1H = 118^\circ$ ,  $HC_2H = 105^\circ$ , and  $\gamma = 60^\circ$ . We performed a grid search in which  $\alpha$  and  $\beta$  were varied independently in  $60^\circ$  increments with other parameters fixed and detected three local minima corresponding to  $(\alpha, \beta, \gamma) = (120^\circ, 120^\circ, 60^\circ)$ ,  $(0^\circ, 120^\circ, 60^\circ)$ , and  $(120^\circ, 240^\circ, 60^\circ)$ . The first of these had the lowest energy, and in fact the other two reverted to  $(120^\circ, 120^\circ, 60^\circ)$  without activation when  $\phi$  was allowed to



**Figure 1.** Internal coordinates of tetramethylene. Fixed values are  $C_1H = C_4H = 1.074$  Å,  $C_2H = C_3H = 1.090$  Å. Other restrictions are  $C_1C_2 = C_3C_4$ ,  $HC_1H = HC_4H$ ,  $HC_2H = HC_3H$ ,  $C_1C_2C_3 = C_2C_3C_4 = \theta$ , and the  $HC_2H$  ( $HC_3H$ ) plane is the perpendicular bisector of the  $C_1C_2C_3$  ( $C_2C_3C_4$ ) angle. The pyramidalization angle  $\phi$ , identical for both methylenes, is the angle between the  $HC_1H$  ( $HC_4H$ ) bisector and a line extending from the  $C_1C_2$  ( $C_3C_4$ ) bond.  $\gamma$  is defined by fixing  $C_2C_3C_4$  and rotating  $C_1$ .  $\alpha = \beta = \gamma = 0^\circ$  in the  $C_{2v}$  geometry shown.

vary as well as  $\alpha$  and  $\beta$ . Independent optimization of  $\theta$ ,  $\phi$ ,  $C_1C_2$ ,  $C_2C_3$ , and  $HC_2H$  lowered the energy of  $(120^\circ, 120^\circ, 60^\circ)$  by 0.9 kcal/mol. A recheck of  $\alpha$  and  $\beta$  showed that  $120 \pm 5^\circ$  was optimum. A 20-point path was then constructed from  $(120^\circ, 120^\circ, 60^\circ)$  to cyclobutane by a simultaneous linear variation of all internal coordinates. The energy decreased monotonically along this path with no evidence of a flat region. In another path starting from  $(120^\circ, 120^\circ, 60^\circ)$ , as  $\gamma$  was increased to  $64^\circ$ ,  $68^\circ$ , and  $72^\circ$  (other parameters fixed), the energy increased with a positive second derivative with respect to  $\gamma$ . Finally a 40-point path was constructed from Segal's<sup>7</sup> reported *gauche* local minimum to cyclobutane by a linear variation of all internal coordinates. Again the energy decreased monotonically along this path. However, when the STO-3G basis set was substituted for 3-21G in our MCSCF wave function, this path exhibited a local minimum corresponding closely to Segal's reported *gauche* geometry,<sup>7</sup> separated from cyclobutane by a barrier of 1.1 kcal/mol. We are therefore convinced that if a *gauche* local minimum deeper than ca. 0.1 kcal/mol existed on our surface, the above procedures would have detected it. *At present there is no theoretical support for the existence of a singlet gauche tetramethylene potential-energy minimum.*

On the other hand, we agree with Segal in predicting an anti minimum at  $\gamma = 180^\circ$  close to his reported optimum geometry. Our preliminary value for the anti  $\rightarrow$  cyclobutane barrier is  $4.7 \pm 1$  kcal/mol,<sup>12</sup> the same as Segal's value of 4.7 for anti to *gauche*.<sup>7</sup> In another preliminary calculation we have approximately located what appears to be the transition state for cis-trans isomerization of cyclobutane (i.e., single methylene rotation). It has a *gauche*-type structure and lies 2.5 kcal/mol below the putative anti  $\rightarrow$  cyclobutane saddle point. If these two transition states retain their present energy ordering once they are rigorously located, this would imply that the path of minimum potential energy for cis-trans isomerization of 1,2-dideuteriocyclobutane does not involve a biradical-like local minimum, in analogy with theoretical predictions for cis-trans isomerization of 1,2-dideuteriocyclopropane.<sup>13</sup>

The fact that 3-21G erases the *gauche* minimum predicted by STO-3G has important consequences for the calculation of biradicals. The most significant difference between the STO-3G and 3-21G basis set is the additional set of diffuse functions in the valence shell of 3-21G. These functions appear to be par-

(8) In this context, a single intermediate is one in which there is no kinetic distinction between **1** and **2**.

(9) Borden, W. T.; Davidson, E. R. *Ibid.* **1980**, *102*, 5409-10.

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(12) The quoted error represents the estimated uncertainty on our surface, since these stationary points were not rigorously located. In fact, the analytical gradient components are very low.

(13) Theoretical calculations have failed to find a local minimum on the trimethylene singlet surface: (a) Horsley, J.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R.; Wright, J. *J. Am. Chem. Soc.* **1972**, *94*, 279. (b) Hay, P.; Hunt, W.; Goddard, W. A., III, *Ibid.* **1972**, *94*, 638.

ticularly important in regions of incipient bonding of the localized orbitals containing the unpaired electrons, i.e., when they are directed toward one another and not too far away. It is possible to view the calculated energy change on going from gauche to cyclobutane as arising from a competition between the stabilizing effect of bond formation and the destabilizing effect of eclipsing interactions as  $\gamma$  is decreased. The barrier with STO-3G arises from its inadequate description of the early stages of bonding. This effect was absent in a comparison of STO-3G and 3-21G in **2a**. Segal's<sup>7</sup> and Borden and Davidson's<sup>9</sup> STO-3G results for **2a** are therefore probably valid. We nevertheless advise great caution in the use of minimal basis sets for biradicals.

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**Registry No.** **1a**, 30967-48-7; **1b**, 70585-69-2.

## Generation and Reactivity of the Acetylacetonyl Radical

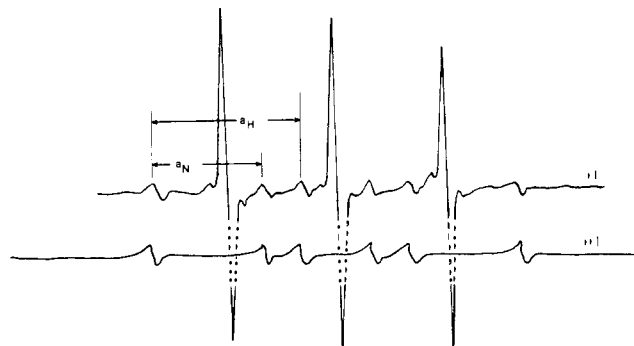
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Received August 31, 1981

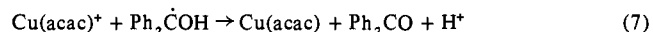
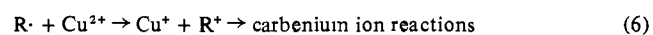
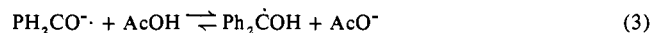
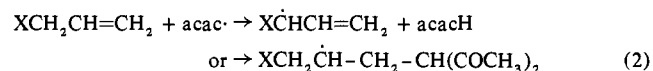
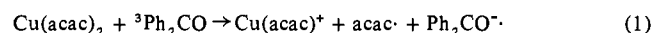
Sensitized photoreduction of bis(acetylacetonato)copper(II),  $\text{Cu}(\text{acac})_2$ , involves the paramagnetic interaction of the triplet excited state of aryl ketones with the complex. It has been proposed that this occurs by a mixture of charge-transfer and spin-exchange processes leading to the intermediacy of the acetylacetonyl radical.<sup>1,2</sup> This radical has also been implicated in the oxidation of acetylacetonone<sup>3-6</sup> with metal ions; for example, manganese(III) acetate in acetic acid.<sup>3</sup> As the generation of a *prima facie* acetylacetonyl radical is a key step in the mechanism of the sensitized reduction<sup>1</sup> of  $\text{Cu}(\text{acac})_2$ , it is desirable to demonstrate its presence during the photolysis. We present evidence in this report.

A spin trapping<sup>7,8</sup> experiment during sensitized photoreduction of  $\text{Cu}(\text{acac})_2$  is restricted to a narrow range of conditions dictated by such factors as the efficiency of the generation, stability of radicals, and nonspecific sensitization. Fortunately, since triplet state benzophenone is quenched by  $\text{Cu}(\text{acac})_2$  at a nearly diffusion-controlled rate,<sup>2</sup> quenching by 2-nitroso-2-methylpropane<sup>9</sup> ( $k_q = 2.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) is not a serious limitation. Irradiation of a solution containing  $\text{Cu}(\text{acac})_2$ , benzophenone, and 2-nitroso-2-methylpropane at 360 nm under the conditions specified in Figure 1 gave an ESR spectrum consisting of the triplet of di-*tert*-butyl nitroxide<sup>7</sup> ( $a_N = 15.5 \text{ G}$ ) and a less intense triplet of doublet ( $a_H = 22.25 \text{ G}$ ,  $a_N = 15.00 \text{ G}$ ). The latter signal decayed faster than the former. The double triplet signal was not

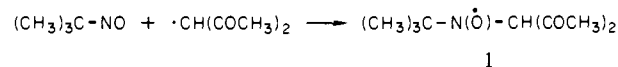


**Figure 1.** (i) ESR signal from a solution containing 0.006 M  $\text{Cu}(\text{acac})_2$ , 0.011 M benzophenone, and 0.01 M 2-nitroso-2-methylpropane in 9:1  $\text{CH}_3\text{OH}/\text{diethylene glycol}$  after irradiation at 20 °C under nitrogen through a Corning 7-54 filter for 1 h. (ii) Theoretical ESR spectrum of nitroxide **1** for  $a_N = 16.00 \text{ G}$  and  $a_H = 21.25 \text{ G}$ .

### Scheme I

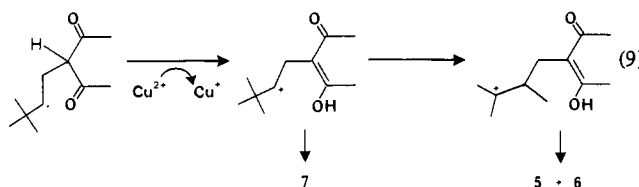


generated when a solution containing  $\text{Cu}(\text{acac})_2$  and the nitrosoalkane was irradiated with a Corex or Pyrex filter or when a solution of benzophenone and the nitrosoalkane was photolyzed at 350 nm under similar conditions. The parameters are consistent with the nitroxide radical **1** and indicate that the  $\beta$  hydrogen has



substantial hyperconjugative interaction with the nitroxide center and/or that it is preferentially oriented perpendicular to the plan defined by the O-N-C bonds.<sup>7</sup>

As we are not certain of possible side reactions of nitrosoalkanes with copper salts, it is essential to confirm the generation of the acetylacetonyl radical by other trapping agents. The results from photolysis of  $\text{Cu}(\text{acac})_2$  and benzophenone in acetic acid in the presence of various olefins are summarized in Table I. Scheme I shows the expected reaction pathways in acetic acid, proposed on the basis of the mechanism studied in methanol,<sup>2</sup> where  $\text{R}\cdot$  is the carbon radical generated from the addition of or abstraction by the acetylacetonyl radical. Compound **3** was shown to be derived from the norbornene addition product **2** by acid- or base-catalyzed retro aldol condensation. The stereochemistry of **2** was deduced from the large coupling constants of the  $\text{C}_2$  proton ( $J_{2,3} = 8$  and 5.5 Hz). Compounds **6** and **7** (eq 9) were isolated



as a 1:3 mixture, but the presence of the functional groups as indicated were demonstrated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and GC-MS techniques. Compounds **8** and **9** were also isolated as a mixture, and the position of the double bond in **9** was indicated

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