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 γ 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[7] and Borden and Davidson's[9] 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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Sensitized photoreduction of bis(acetylacetonato)copper(II), $Cu(acac)_2$, 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.[1,2] This radical has also been implicated in the oxidation of acetylacetone[3-6] with metal ions; for example, manganese(III) acetate in acetic acid.[3] As the generation of a prima facie acetylacetonyl radical is a key step in the mechanism of the sensitized reduction[1] of $Cu(acac)_2$, it is desirable to demonstrate its presence during the photolysis. We present evidence in this report.

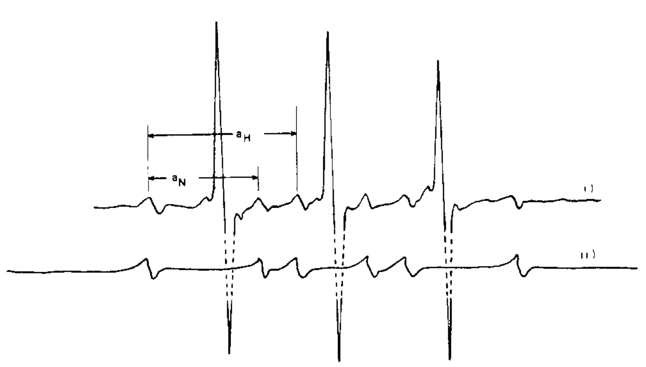


Figure 1. (i) ESR signal from a solution containing 0.006 M $Cu(acac)_2$, 0.011 M benzophenone, and 0.01 M 2-nitroso-2-methylpropane in 9:1 CH_3OH/diethylene glycol after irradiation at 20 °C under nitrogen through a Corning 7-54 filter for 1 h. (ii) Theoretical ESR spectrum of nitroxide **1** for $a_N = 16.00$ G and $a_H = 21.25$ G.

Scheme I

$$Cu(acac)_2 + {}^3Ph_2CO \rightarrow Cu(acac)^+ + acac\cdot + Ph_2CO^{-}\cdot \quad (1)$$

$$XCH_2CH{=}CH_2 + acac\cdot \rightarrow X\dot{C}HCH{=}CH_2 + acacH$$
$$\text{or} \rightarrow XCH_2\dot{C}H{-}CH_2{-}CH(COCH_3)_2 \quad (2)$$

$$PH_2CO^{-}\cdot + AcOH \rightleftharpoons Ph_2\dot{C}OH + AcO^- \quad (3)$$

$$R\cdot + Ph_2\dot{C}OH \rightarrow RH + Ph_2CO \quad (4)$$

$$Cu(acac)^+ + AcO^- \rightarrow Cu(acac)(OAc) \quad (5)$$

$$R\cdot + Cu^{2+} \rightarrow Cu^+ + R^+ \rightarrow \text{carbenium ion reactions} \quad (6)$$

$$Cu(acac)^+ + Ph_2\dot{C}OH \rightarrow Cu(acac) + Ph_2CO + H^+ \quad (7)$$

$$2Cu(acac) \rightarrow Cu + Cu(acac)_2 \quad (8)$$

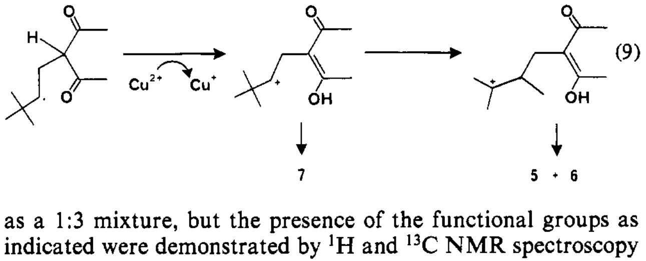
A spin trapping[7,8] experiment during sensitized photoreduction of $Cu(acac)_2$ is restricted to a narrow range of conditions dictated by such factors as the efficiency of the generation, stability of radicals, and nonspecific sensitization. Fortunately, since triplet state benzophenone is quenched by $Cu(acac)_2$ at a nearly diffusion-controlled rate,[2] quenching by 2-nitroso-2-methylpropane[9] ($k_q = 2.8 \times 10^7$ M^{-1} s^{-1}) is not a serious limitation. Irradiation of a solution containing $Cu(acac)_2$, 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[7] ($a_N = 15.5$ G) and a less intense triplet of doublet ($a_H = 22.25$ G, $a_N = 15.00$ G). The latter signal decayed faster than the former. The double triplet signal was not generated when a solution containing $Cu(acac)_2$ 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 β hydrogen has

$$(CH_3)_3C{-}NO + \cdot CH(COCH_3)_2 \longrightarrow (CH_3)_3C{-}N(\dot{O}){-}CH(COCH_3)_2$$

1

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.[7]

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 $Cu(acac)_2$ 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,[2] where R· 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 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 ^1H and ^{13}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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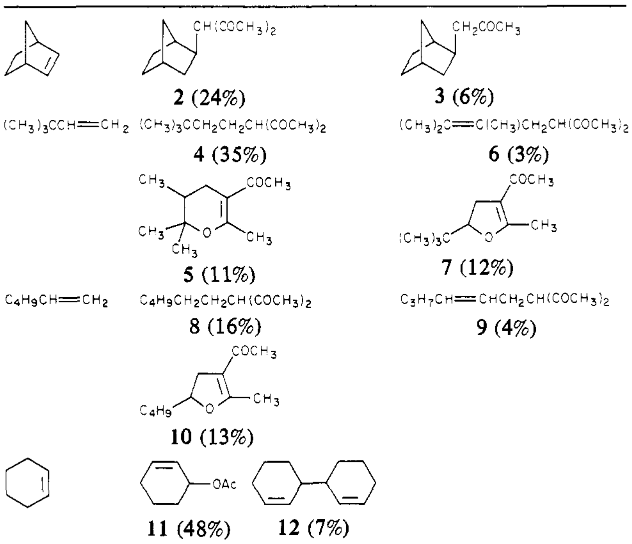
Table I. Benzophenone-Sensitized Photoreduction of $Cu(acac)_2$ in the Presence of Various Olefins



by the triplet signal of the methine proton. The formation of **5** and **6** suggests the intervention of carbenium ion intermediates[10] by electron transfer as shown in eq 10: $Cu(OAc)_2$ is known to be a better oxidizing species[3] than $Cu(acac)_2$.

The product pattern indicates that, besides abstracting a hydrogen, the acetylacetonyl radical also adds to π bonds regiospecifically and exclusively as the C radical. This is in good agreement with the report that 77% of the spin density in the acetylacetonyl radical resides at C_3 and the O-radical structure is unimportant.[6] With poor hydrogen-donating substrates such as norbornene and neohexene the acetylacetonyl radical attacks the double bonds without showing any sign of hydrogen abstraction. The cyclohexenyl radical is much more easily oxidized than the acyclic radical to the corresponding carbenium ion under the reaction conditions, and the 2-norbornyl radical is surprisingly resistant to the oxidation. In view of the ease of solvolytic formation of norbornyl cations,[11] the tendency for radical oxidation must be related to, among other factors, the extent of the s character of the orbital containing the unpaired electron. The oxidative addition, as represented by eq 2 and 6–8, involves reduction to copper(I) and then to copper metal, which would slowly retard the photoreaction. Owing to the reduction process, the addition reaction of the acetylacetonyl radical cannot be schemed into a catalytic cycle at the present stage.

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Registry No. 1, 77350-15-3; *exo*-**2**, 81769-99-5; *exo*-**3**, 25121-32-8; **4**, 81770-00-5; **5**, 81770-01-6; **6**, 81770-02-7; **7**, 81770-03-8; **8**, 64122-32-3; **9**, 81770-04-9; **10**, 81770-05-0; **11**, 14447-34-8; **12**, 1541-20-4; $(CH_3)_3CCH=CH_2$, 558-37-2; $C_4H_9CH=CH_2$, 592-41-6; $Cu(acac)_2$, 46369-53-3; benzophenone, 119-61-9; 2-norbornene, 498-66-8; cyclohexene, 110-83-8; acetylacetonyl radical, 17374-75-3; 2-nitroso-2-methylpropane, 917-95-3.

Supplementary Material Available: Photolysis conditions and isolation of the products and the NMR, IR, and MS data of products **2–11** (5 pages). Ordering information is given on any current masthead page.

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Carbenium-Carbonium Structures, $H_2C^+-CH_4^+$, for the Ethane Dication

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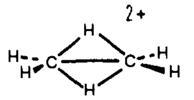
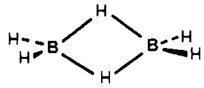
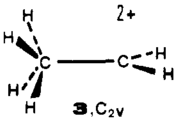
Olah and Simonetta's theoretical reexamination of the ethane dication, $C_2H_6^{2+}$, favored a doubly bridged form, **1** (D_{2h}), similar


1, D_{2h}


2, D_{2h}


3, C_{2v}

to **2**, the structure of the isoelectronic analogue diborane.[1] Despite being highly unstable electrostatically toward dissociation into two methyl cations, **1** was indicated to be a minimum on the potential-energy surface. As part of an extensive theoretical survey of dications,[2] we have also examined a variety of $C_2H_6^{2+}$ structures and states. The results extend the findings of Olah and Simonetta significantly. Surprisingly, the carbenium–carbonium dication geometry, **3**, is significantly more stable than **1**. We also conclude that $C_2H_6^{2+}$ might be observable experimentally, e.g., by charge-stripping mass spectroscopy.[3]

Various fixed points on the $C_2H_6^{2+}$ potential-energy surface were first located and characterized by the number of negative eigenvectors in the force-constant matrix at the 3-21G//3-21G split valence ab initio basis set level (Table I).[4] Some of the geometries were further optimized with a d orbital augmented basis set (6-31G*//6-31G*).[5] Because of the importance of electron correlation in describing the dimerization of borane[6] and the bridging of the ethyl cation,[7] final calculations at the 6-31G* geometries were carried out at the fourth-order Møller–Plesset level (including all single, double, and quadruple excitations) with a larger basis set, including p-type polarization functions on hydrogen (MP4SDQ/6-31G**//6-31G*).[5,8] Correlation does decrease the energy of **1** relative to **3**, but not decisively (Table I). A large number of geometries were explored, but only the lowest energy forms are listed in Table I. In particular, triplet states were found not to be competitive, and singlet structures

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