metalloporphyrin radicals of Cu, V, Cr, and Mn. For example, $[Cu(TPP\cdot)]^+$ is diamagnetic in the solid state, and its structure is highly distorted from D_{4h} symmetry.[19] Antiferromagnetic coupling to give an $S = 0$ state is expected by analogy to **1**. On the other hand, $[Cu(TMP\cdot)]^+$, whose mesityl groups presumably prevent dimer formation and accompanying distortion from D_{4h} symmetry, is an $S = 1$ ferromagnet.[46]

Conclusion

It is apparent from this fairly exhaustive probing of the nature of $[FeCl(TPP\cdot)]^+$ and $Fe(OClO_3)_2(TPP\cdot)$ that these species are oxidized at the porphyrin ring and are not iron(IV) complexes. The UV–vis absorption features are seen now to be characteristic of π-cation radicals, but not dramatically so. The most definitive criteria for making the correct assignment of the site of oxidation have turned out to be Mössbauer spectroscopy, X-ray structure, NMR spectroscopy, and, most simply, IR spectroscopy. Electrochemical and magnetic susceptibility criteria are also useful in favorable circumstances.

The present compounds illustrate a theme in coordination chemistry that is becoming increasingly familiar. We note that axial ligation by chloride or perchlorate leads to iron(III) porphyrins that are oxidized at the porphyrin ring. On the other hand, the presence of terminal oxide[14] or methoxide[12d] ligation leads to authentic iron(IV) porphyrins. Thus, the site of redox is seen to be largely dictated by the nature of the axial ligation. The ex-

cellent $2_{p\pi}$ donor properties of terminal oxo and alkoxo ligands probably provides the best explanation for the ability of these ligands (along with carbido, nitrido,[49] and fluoro[57]) to stabilize high oxidation states of metals.

Perhaps the most unexpected feature of interest to come out of this work has been the clear distinction between antiferromagnetic and ferromagnetic coupling of the metal and ligand spins in $[FeCl(TPP\cdot)]^+$ and $Fe(OClO_3)_2(TPP\cdot)$. The magnetostructural correlation in terms of the symmetries of the magnetic orbitals can be described with heuristically appealing simplicity and may have wide generality.

Supplementary Material Available: Structure factor tables and thermal parameters (Tables A and B) and Figures A and B (4 pages) of proton chemical shifts and an atom numbering scheme (42 pages). Ordering information can be found on any current masthead page.

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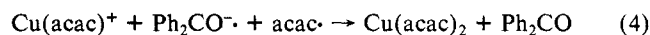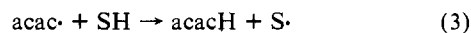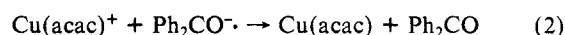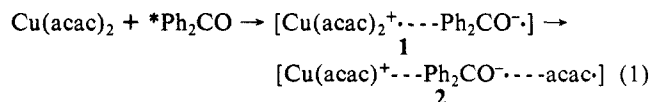
Role of the Acetylacetonyl Radical in the Sensitized Photoreduction of Bis(acetylacetonato)copper(II)

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Contribution from the Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6. Received August 5, 1985

Abstract: Benzophenone-sensitized photoreduction of $Cu(acac)_2$ generated the acetylacetonyl radical ($acac\cdot$) which could be trapped as acetylacetone by hydrogen as well as by a H-atom-donating agent, or as the corresponding nitroxide with 2-nitroso-2-methylpropane, or as addition products with some simple olefins. Observations indicate that the photoreduction to $Cu(acac)$ occurs only if the acetylacetonyl radical is rapidly scavenged so that the reverse electron transfer cannot compete with the trapping process. The acetylacetonyl radical was found to abstract a hydrogen atom as well as to add to the double bond of olefins and behave primarily as a C radical in addition reactions. The relative importance of oxidation of radicals by copper(II) salt was shown to be dependent on their structures.

We have discovered[2–4] that the triplet excited state of aryl ketones sensitized the photoreduction of bis(acetylacetonato)copper(II), $Cu(acac)_2$, to (acetylacetonato)copper(I), $Cu(acac)$, in an H-atom-donating solvent (SH). The solvent was concomitantly oxidized. The fast interaction of a triplet excited ketone with $Cu(acac)_2$ ($k_q = 10^{10} \approx 10^9 \text{ M}^{-1}\text{ s}^{-1}$) was assumed to involve charge transfer as well as spin-exchange processes within complexes leading to the generation of an acetylacetonyl radical from an oxidized species[3] of $Cu(acac)_2$ (eq 1). The association com-

$$Cu(acac)_2 + *Ph_2CO \rightarrow [Cu(acac)_2^+\cdot\cdots\text{-}Ph_2CO^-\cdot] \rightarrow$$
$$\mathbf{1}$$
$$[Cu(acac)^+\text{-}\text{-}\text{-}Ph_2CO^-\cdot\text{-}\text{-}\text{-}\text{-}acac\cdot] \quad (1)$$
$$\mathbf{2}$$

$$Cu(acac)^+ + Ph_2CO^-\cdot \rightarrow Cu(acac) + Ph_2CO \quad (2)$$

$$acac\cdot + SH \rightarrow acacH + S\cdot \quad (3)$$

$$Cu(acac)^+ + Ph_2CO^-\cdot + acac\cdot \rightarrow Cu(acac)_2 + Ph_2CO \quad (4)$$

plexes **1** and **2** have been assumed for the convenience of kinetic analysis. The reactions of each components are formally shown in eq 2–4 without indicating the degree of association. Since the quantum efficiency of the sensitized photoreduction follows the order of the hydrogen-donating power of solvents, e.g., i-PrOH > EtOH > MeOH $\gg$ C_6H_6 (no reaction in benzene),[2,3] eq 3 is the rate-determining step. Therefore, the occurrence of photoreduction depends on a favorable competition of H-abstraction

(1) A part of the results were published as a communication; see: Chow, Y. L.; Buono-Core, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 3770.
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(eq 3) with the reverse electron transfer (eq 4).

The acetylacetonyl radical[5] is an analogue of imidyl radicals[6] which have attracted much attention in recent years. The present study was undertaken to demonstrate the generation of the acetylacetonyl radical in this photoreduction process by trapping experiments.

Results

Spin Trapping of Acetylacetonyl Radicals. Irradiation of a solution of $Cu(acac)_2$, benzophenone, and 2-nitroso-2-methylpropane (NMP) in methylene chloride or benzene under nitrogen with 365-nm light caused steady decreases of the copper(II) ESR signal and showed a doublet of triplet signal within 1 min of irradiation (Figure 1). The hyperfine splitting constants of 13.62 and 3.15 G and a g value of 2.0062 were no doubt caused by nitrogen (triplet) and α-hydrogen (doublet)[7,8] in the adduct. These values are close to those reported[9] for **3**, probably owing to the presence of copper ions. The signal increased to a photostationary

3
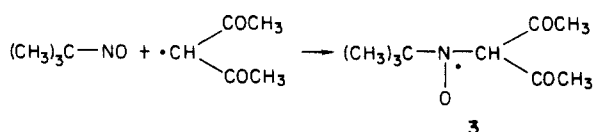
state upon irradiation for several minutes and decayed rapidly in the dark (70% in <30 s). On prolonged irradiation under nitrogen, as the concentration of $Cu(acac)_2$ decreased, a new triplet ($a_N = 15.63$ G, g value 2.0058) presumably due to di-*tert*-butyl nitroxide[8,10,11] appeared which persisted for a long time in the dark. Irradiation in methanol or a mixture of methanol–diethylene glycol (4:1) did not generate any ESR signal within 15 min but gave a weak triplet of doublet with $a_N = 15.50$ and $a_H = 21.25$ G after $20\approx30$ min. This signal must be due to a nitroxide having a N–H bond such as **4** ($a_N = 3.60$, $a_H = 12.36$ G)[10] but not **3**, as we erroneously presumed in the communication.[1]

4   **5**

Irradiation of a similar solution in the presence of toluene (1 M), a good H-atom-donating solvent, gave the triplet of triplet of benzyl *tert*-butyl nitroxide (**5**) ($a_N = 15,30$, $a_H = 7.5$ G, g value 2.0055)[10,11] arising from the trapping of the relatively stable benzyl radical but not acac·. This might indicate that the rate of H-abstraction from toluene by acac· was faster than that of acac· trapping by NMP under these conditions.

Irradiation of a benzene solution of $Cu(acac)_2$ and benzophenone under nitrogen did not cause the photoreduction of $Cu(acac)_2$, but under hydrogen, the ESR signal of $Cu(acac)_2$ decreased regularly, giving a similar pattern to that shown in Figure 1b. Irradiation of a similar solution containing NMP under nitrogen developed a doublet of triplet ($a_N = 13.79$, $a_H = 3.16$ G, g value 2.0057) similar to that assigned above to **3**, but this signal was not obtained under hydrogen. In the latter case, the ESR signal of $Cu(acac)_2$ decreased regularly as in the former case, in spite of the fact that the doublet of triplet did not appear.

The exchangeability of the hydrogen adjacent to the nitroxide group in the radical **3** was examined as follows. A solution
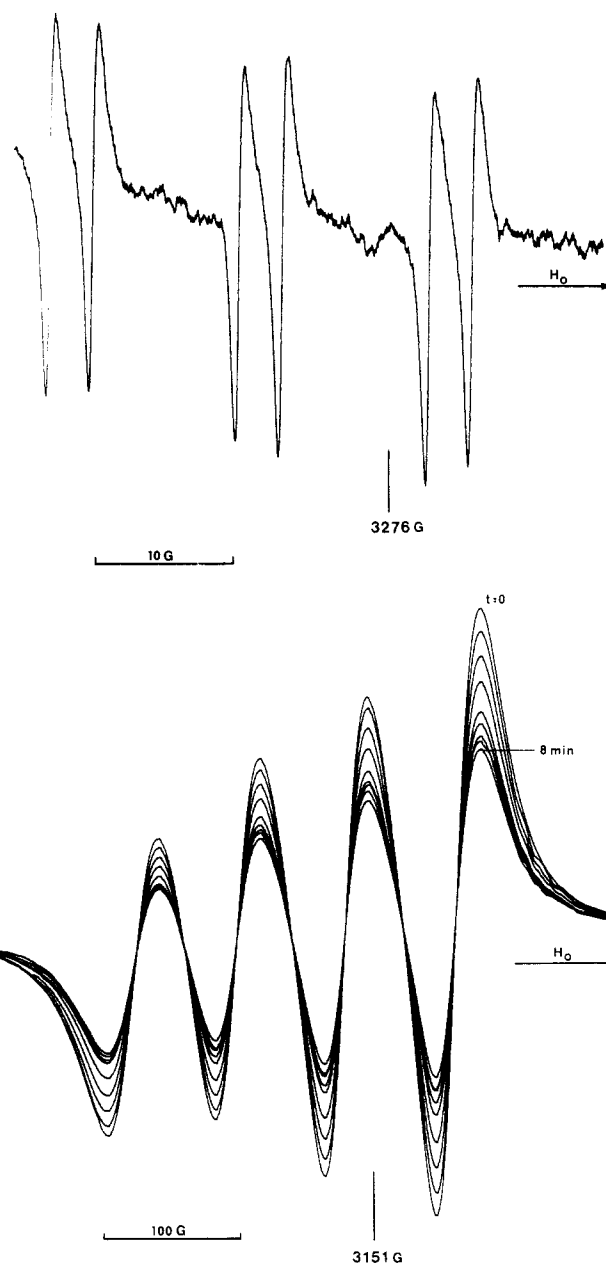
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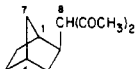(7) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31.
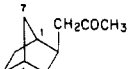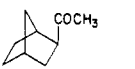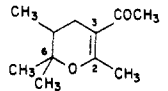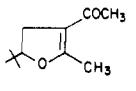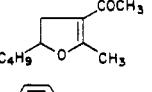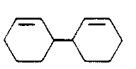
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Figure 1. ESR spectra of the benzophenone-sensitized photoreduction of $Cu(acac)_2$ in the presence of 2-nitroso-2-methylpropane. (a, top) Two-minute irradiation of a methylene chloride solution of $Cu(acac)_2$ (1 mM), NMP (2 mM), and benzophenone (5 mM): $a_N = 13.62$, $a_H = 3.15$ G, g value 2.0062. (b, bottom) Irradiation of the same solution with the monitor of the $Cu(acac)_2$ signal at every minute.

containing $Cu(acac)_2$, benzophenone, and NMP in benzene containing a drop of D_2O was irradiated and the photolysate was shaken to form an emulsion. Not only did the doublet of triplet not collapse to a triplet, the signal decayed much more slowly (in 50–60 min) than it did in pure benzene. Taking advantage of the slow decay, the photolysate showing the doublet of triplet signal developed after irradiation under nitrogen was saturated with hydrogen. The signal of **3** was just as stable under hydrogen as under nitrogen.

Trapping of Acetylacetonyl Radicals with Olefins. As the acetylacetonyl radical consists of two carbonyl groups flanking the C-radical center, it may show reactivity such as addition to double bonds analogous to the succinimidyl radical.[6] The trapping of acac· with some common olefins under the conditions of the sensitized photoreduction of $Cu(acac)_2$ was investigated. For this purpose, acetic acid, a poor H-atom-donating solvent, was used to avoid the competing H-abstraction reaction of acac· (eq 3). In acetic acid, the acid–base equilibrium may cause the formation

Table I. Reaction Products[a] of the Acetylacetonyl Radical with Olefins in the Benzophenone-Sensitized Photoreduction of $Cu(acac)_2$

$(CH_3)_3CCH=CH_2$

6 (30%; 27%)
$(CH_3)_3CCH_2CH_2CH(COCH_3)_2$
9 (35%; 51%)

7 (11%; 0%)

8 (4%; 0%)
$(CH_3)_2C=C(CH_3)CH_2CH(COCH_3)_2$
11 (3%; 0%)[b]

$C_4H_9CH=CH_2$

10 (11%, 6%)
$C_4H_9CH_2CH_2CH(COCH_3)_2$
13 (16%; 57%)[b]

12 (12%; 0%)[b]
$C_3H_7CH=CHCH_2CH(COCH_3)_2$
14 (4%; 0%)[b]

16 (58%; 0%)

17 (7%; 12%)

[a] The percent yields are cited in parentheses, in which the first figures are isolated yields obtained from photolysis in acetic acid solution and the second figures are relative yields obtained by GC analysis from photolysis in acetonitrile.   [b] These two pairs were isolated as mixtures.

Scheme I

18a   **18b**   **19**
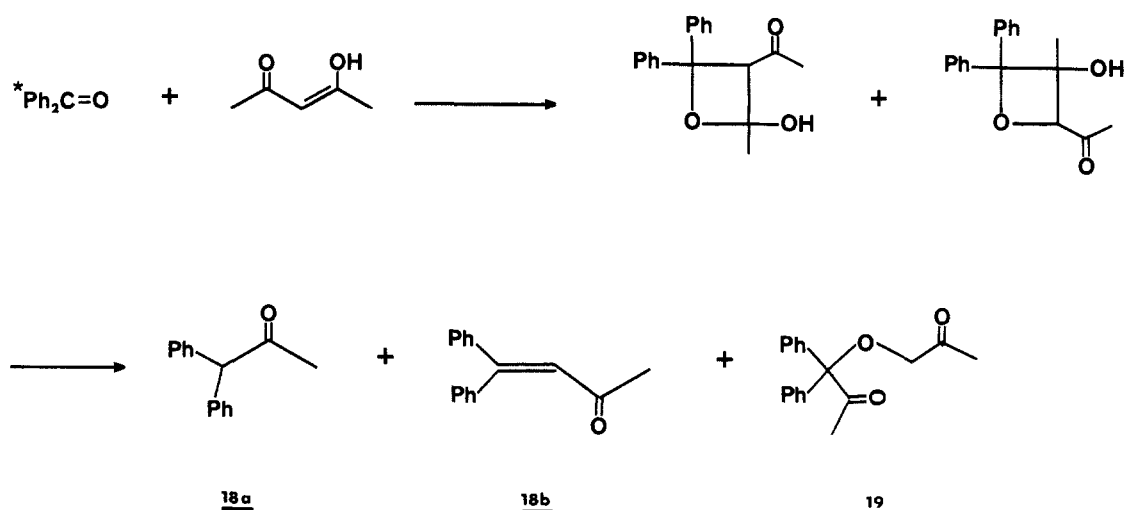
of $Cu(acac)(OAc)$ and $Cu(OAc)_2$, but the former is assumed to react in an analogous manner to eq 1. Benzophenone–sensitized photoreduction of $Cu(acac)_2$ was carried out in the presence of an olefin, and the products were isolated (Table I). In most of these photoreactions, the addition products of the triplet-s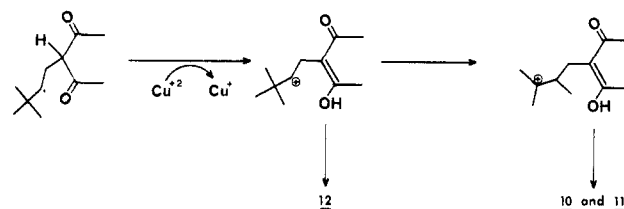tate benzophenone to olefins (oxetanes)[13] and to acetylacetone,[12] such as **18** and **19** (Scheme I), were detected in small amounts that increased rapidly if the photolysates were overirradiated; i.e., continued irradiation after $Cu(acac)_2$ was reduced to a small concentration. This is readily understandable since triple-state benzophenone is quenched by $Cu(acac)_2$ with a near diffusion rate constant,[3] while its addition to olefins is 2–3 orders of magnitude lower (vide infra). Therefore, such side-photoreactions are observable only after $Cu(acac)_2$ diminishes to a small concentration. The formation of byproducts **17–19** has been demonstrated in the thesis presented by GEBC[12] and will not be repeated here. The products shown in Table I were determined by comparison with authentic samples or by spectroscopic data (Table II).

Diketone **9** exists as keto enol tautomers. The enol tautomer constitutes 22% of the mixture in $CDCl_3$ according to the ^{1}H NMR signals of the CH_3CO group at 2.17 (keto) and 2.12 (enol) ppm. In comparison, diketone **6** exists only as the keto form. The methine hydrogens did not exchange upon equilibration with D_2O.

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Scheme II

12   **10 and 11**

Diketone **6** showed two magnetically nonequivalent ^{1}H NMR and ^{13}C NMR signals for the CH_3CO groups that did not collapse to one signal at 100 °C. Presumably, these two CH_3CO groups are diastereotopic. The C_2–H was clearly oriented in the endo configuration because of large coupling constants[14a] of 8.2 and 5.4 Hz. Diketones **13** and **14** were isolated as a mixture, and both existed as keto enol tautomers. Their structures were determined by GC–MS and other spectral data. The triplet of the methine signal at 3.63 ppm for **14** indicated that the neighboring group was a CH_2, and, therefore, the double bond should be at the C_5–C_6 position. Dihydropyran **10** and dihydrofuran **15** showed many similarities in ^{1}H and ^{13}C NMR signals[14b] and IR absorptions that identified the α,β-unsaturated-β-oxy-β-methyl moiety as the common moiety for both compounds. The ^{1}H and ^{13}C NMR spectra of **10** also confirmed that a methyl of the *tert*-butyl group had undergone a 1,2-migration.

Compounds **11** and **12** were isolated as a mixture which showed two different GC–MS spectra. The structures were primarily

Table II. Spectroscopic Data of the Products^a

compd	¹H NMR (J in hertz)	¹³C NMR	MS, m/e (%)	IR and UV
6^b	3.46 (d, 11.0 Hz, H-8), 2.32 (m, 11.0, 8.2, and 5.4 Hz, H-2), 2.17 (s, 3 H), 2.13 (s, 3 H), 1.82 (m, 1 H), 1.51 (m, 4 H), 1.28 (m, 2 H), 1.14 (m, 2 H)	203.8 (s, CO), 203.5 (s, CO), 76.0 (d, C-8), 41.4 (d, C-2), 39.3 (d, C-1), 36.4 (d, C-4), 35.8 (t, C-7), 35.2 (t, C-3), 29.7 (t), 29.4 (t), 28.9 (q), 28.2 (q)	194 (M⁺, 11), 152 (49), 134 (48), 101 (20), 94 (98), 43 (100)	1700 (s), 1360 (m); 282 nm (ε 530), 306 (ε 430), [295 (ε, 950)]^a
7	2.34 (m, 3.5 Hz, H-8), 2.11 (s, 3 H), 1.90 (m, 2 H), 0.9–1.6 (m, 9 H)	208.4 (s, CO), 50.7 (t, C-8), 40.9 (d, C-2), 37.7 (t, C-7), 37.1 (d, C-1), 36.4 (d, C-4), 35.0 (t, C-3), 29.7 (t), 29.6 (t), 28.3 (q)	152 (M⁺,8), 109 (16), 95 (32), 67 (61), 43 (100)	1715 (s), 1355 (m)
9^c	16.47 (s), 3.54 (t, 6.5 Hz), 2.30 (m), 2.17 (s), 2.12 (s), 1.20 (m), 0.96 (s), 0.90 (s)	205.1 (s, keto CO), 191.3 (s, enol CO), 111.0 (s, enol C-3), 70.2 (d, keto C-3), 45.2 (t), 42.1 (t), 30.8 (s), 29.6 (s), 24.2 (q), 23.1 (q)	184 (M⁺, 3), 127 (20), 113 (30), 100 (25), 71 (31), 43 (100)	1730 (m), 1703 (s), 1600, (br, m), 1370 (s), 1250 (s); 275 nm (ε 7200), [287 (ε 5200)]
10	2.20 (s, 3 H), 2.17 (s, 3 H), 2.14 (m, 2 H), 1.30 (s, 3 H), 1.07 (s, 3 H), 0.95 (d, 7 Hz 3 H)	199.5 (s, CO), 164.1 (s, C-2), 109.3 (s, C-3), 79.6 (s, C-6), 1.30 (d, C-5), 30.1 (t, C-4), 29.7 (q), 27.7 (q), 22.1 (q), 20.2 (q), 17.0 (q)	182 (M⁺, 15), 130 (10), 113 (22), 70 (63), 55 (31), 43 (100)	1670 (s), 1580 (s), 1375 (s), 1278 (s), 1150 (s), 1127 (s), 1010 (s), 945 (s); 263 nm (ε 13 500)
11 + 12^d	16.41 (brs), 4.23 (dd, 8 and 10 Hz), 2.75 (m), 2.17 (brs), 1.27 (m), 0.9 (m), 0.90 (s)	195.2 (s), 195.0 (s), 173.5 (s), 168.6 (s), 167.5 (s), 156.7 (s), 113.1 (s), 112.3 (s), 90.7 (d), and others	182 (M⁺, 64), 139 (100), 97 (45), 70 (25), 43 (79) 182 (M⁺, 50), 167 (30), 125 (100), 113 (85), 70 (56), 43 (41)	1720 (s), 1675 (s), 1600 (s, br), 1390 (s), 1240 (s), 940 (s), 630 (m)
13 + 14^d	16.62 (s), 5.43 (m), 3.70 (t, 7.2 Hz), 3.63 (t, 7.5 Hz), 2.5 (m), 2.15 (s), 1.87 (m), 1.27 (m), 0.88 (t br, 7 Hz)	205.1 (s), 134.3 (d), 126.0 (d), 69.5 (d), 69.2 (d), 32.0, 29.8, 29.6, 28.9, 28.1, 23.1, 14.6, 14.4	184 (M⁺, 25), 142 (25), 113 (42), 100 (54), 85 (39), 71 (100), 43 (49); 182 (M⁺, 4), 139 (100), 97 (18), 67 (21), 43 (49)	1729 (s), 1726 (s), 1705 (m), 1680 (s), 1610 (m), 1354 (m), 969 (m)
15	4.62 (m, 1 H), 2.6–3.1 (m, 2 H), 2.18 (s, 6 H), 1.43 (m, 6 H), 0.92 (t, 6.5 Hz, 3 H)	195.1 (s), 168.4 (s), 112.5 (s) 83.3 (d), 36.5, 36.3, 29.8, 27.7, 23.0, 14.5, 14.5	182 (M⁺, 61), 167 (36), 125 (59), 97 (64), 43 (100)	1670 (s), 1602 (s), 1390 (s), 1240 (s), 1017 (m); 260 nm (ε 12 500)
16	1.74 (m, 4 H), 1.95 (s, 3 H), 2.0 (m, 2 H), 5.2 (m, 1 H), 5.8 (m, 1 H)	169.3 (s), 132.1 (d), 127.0 (d), 67.9 (d), 28.9 (t), 25.4 (t), 21.4 (q), 19.5 (t)	140 (M⁺, 8), 98 (66), 80 (44), 79 (100), 43 (35)	1733 (s), 1245 (s)

^{a} Unless specified otherwise, ¹H NMR spectra were taken at 100 MHz. UV spectra were taken in MeOH. The data in square brackets are λ_{max} in MeOH–0.1 N NaOH. ^{b} The ¹H NMR spectra were recorded at 400 MHz, and the coupling patterns of the H-2 and H-8 were obtained by decoupling experiments. ^{c} In solution, the compound exists as a keto enol mixture in a 78:22 ratio. ^{d} The two compounds were isolated as a 3:1 mixture which exhibited the ¹H NMR and IR spectra given. The mass spectra of each compound were obtained by GC–MS.

deduced from mechanistic arguments (see Scheme II) and supported by spectral data. In GC–MS analysis, **11** gave an intense m/e 139 peak which indicates the presence of an acetylacetonyl moiety and **12** gave an intense m/e 125 which indicates the presence of a *tert*-butyl group.

Discussion

In the triplet-state benzophenone-sensitized photoreduction of Cu(acac)₂, acac· is undoubtedly generated, as demonstrated by the formation of nitroxides when trapped by NMP and also by the formation of addition products **6, 7, 9,** and **13** with simple olefins. It is also shown that hydrogen can serve as a H-atom donor in the photoreduction, reacting with acac· as in eq 3 (SH = H₂). This is collaborated by the observation of a copper metal mirror deposited on the ESR tube surface.

The trapping of acac· by NMP to generate nitroxide **3** and the simultaneous decrease of Cu(acac)₂ clearly confirm the generation of the acac· radical as in eq 2 in poor H-atom-donating solvents such as benzene and methylene chloride. These ESR experiments demonstrate that so long as there is an agent to scavenge acac·, be it a SH or NMP, photoreduction occurs as in eq 2. In their absence, the reverse electron transfer (eq 4) occurs, preventing the photoreduction. This essentially confirms our previous mechanistic proposal that the reactions of eq 3 (or eq 6, vide infra) and eq 4 compete with each other to determine the fate of the complex **1** or **2**.

Though the reasons for the stability of nitroxide **3** in the benzene–H₂O emulsion, as opposed to the rapid decay in pure benzene, are not established, nitroxide **3** in photolysates does not react with hydrogen as shown by the comparable decay of the ESR

signal. Therefore, the failure to generate the ESR signal of nitroxide **3** under hydrogen must mean that the reaction rate of acac· with H₂ (eq 3, SH = H₂) is faster than that with NMP. Since the concentrations of H₂ and NMP are about the same, $2 \approx 3 \times 10^{-3}$ M, the rate constant of the former (H₂ + acac·) must be at least an order of magnitude faster than the latter (NMP + acac·). In view of the high bond energy of hydrogen ($D_{H-H} = 104$ kcal/mol), the facile reactions of H₂ with acac· is surprising and may indicate some kind of association of substrates with the copper metal. The degree of association of intermediates in our equations is unknown. It must be emphasized that these equations should be regarded as formal representations.

It will be shown that cyclohexenyl acetate (**16**) and 2,2′-bihexenyl (**17**) are also formed by acac· but by way of H abstraction from cyclohexene. The products **10, 11, 12, 14, 15,** and **16** obtained in the presence of olefins arise from the intervention of carbenium ions that are formed by oxidation of the C-radical intermediates by the Cu(II) species. The rearrangement observed, e.g., 1,2-shift of methyl, is typically that of carbenium ions and not of free radicals. Such oxidation processes are well-documented,[15] and Cu(OAc)₂ is known to be a better oxidizing agent than Cu(acac)₂. This explains the higher percentage of rearrangement products in acetic acid than in acetonitrile. The mechanism of the formation of 2-acetylnorbornane remains un-

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Scheme III

20
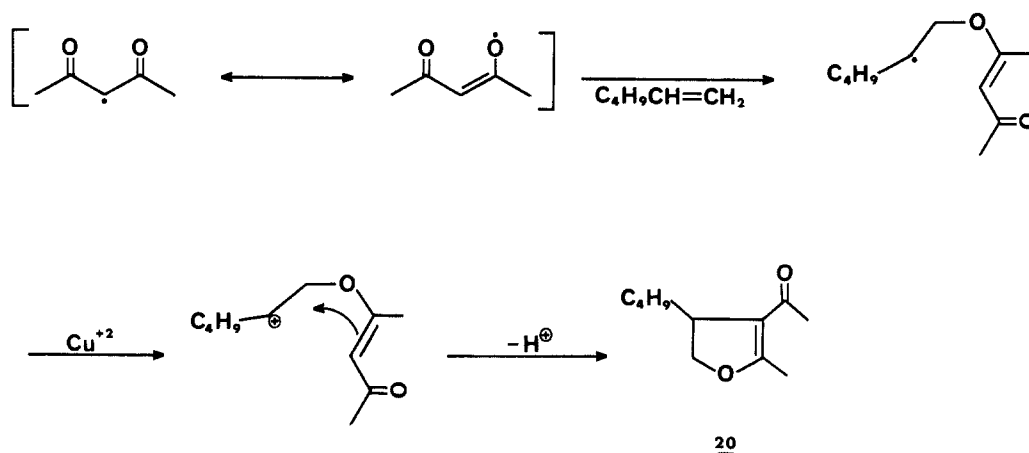
certain. Equations 5–11 are proposed as a possible mechanism for photolysis in acetic acid.

$$Ph_2CO^-\cdot + AcOH \rightleftharpoons Ph_2\overset{\cdot}{C}OH + AcO^- \quad (5)$$

$$RCH_2CH{=}CH_2 + acac\cdot \rightarrow R\overset{\cdot}{C}HCH_2CH(COCH_3)_2 \quad (6)$$

$$Ph_2\overset{\cdot}{C}OH + R\overset{\cdot}{C}HCH_2CH(COCH_3)_2 \rightarrow$$
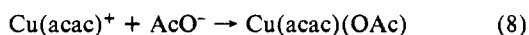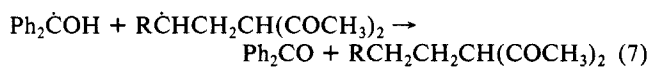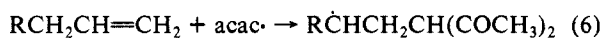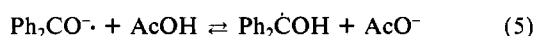$$Ph_2CO + RCH_2CH_2CH(COCH_3)_2 \quad (7)$$

$$Cu(acac)^+ + AcO^- \rightarrow Cu(acac)(OAc) \quad (8)$$

$$R\overset{\cdot}{C}HCH_2CH(COCH_3)_2 + Cu^{2+} \rightarrow$$
$$R^+CHCH_2CH(COCH_3)_2 + Cu^+ \rightarrow \text{carbenium ion reactions} \quad (9)$$

$$Cu(acac)^+ + Ph_2\overset{\cdot}{C}OH \rightarrow Cu(acac) + Ph_2CO + H^+ \quad (10)$$

$$2Cu(acac) \rightarrow Cu + Cu(acac)_2 \quad (11)$$
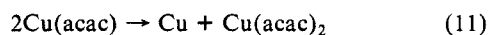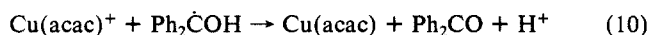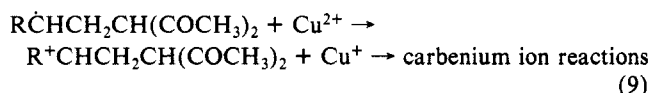
Equations 5–8 represent the simple addition of acetylacetone to a double bond, whereas eq 6 and 9–11 represent an addition process involving the oxidation of intermediate C radicals to carbenium ions. The formation of metallic copper is caused by the latter oxidative addition pattern, while the former nonoxidative addition does not involve a redox step; e.g., no change of the copper oxidation state. As the benzophenone ketyl radical[16] has pK_a 10.7, the acid–base equilibrium (eq 5) in acetic acid is fast and in favor of protonation. As the radical annihilation process (eq 7) should occur as fast as the diffusion allows, the addition step (eq 6) is most likely the rate-determining step. This pattern is analogous to the photoreduction[3] in which the H-abstraction step (eq 3) has been shown to be the rate-determining step. The reactions of eq 9 and 7 compete with each other to determine the fate of the C-radical intermediate. The former is apparently slower in acetonitrile than in acetic acid, reflecting the fact that Cu(OAc)$_2$ is a better oxidizing agent[15] than Cu(acac)$_2$. Using the addition to 3,3-dimethyl-1-butene as the model, the products from carbenium ion rearrangements can be explained by Scheme II. In acetonitrile solution, since eq 5 and 7 cannot operate, the mechanism must be different and more complex. As the photoreaction is slow in this reaction system, triplet-state benzophenone is slowly intercepted by olefins and acetylacetone to accumulate the side products as observed.

It is desirable to provide kinetic evidence that the proposed mechanism is reasonable; i.e., that acac· is generated by eq 1 but not by other reactions, such as a direct interaction of the triplet-state benzophenone with acetylacetone. The rate constants of the interaction of triplet-state benzophenone with various substrates are known, e.g., with[3] Cu(acac)$_2$, as in eq 1, is ≈7 × 10^9 M^{-1} s^{-1}, with NMP in energy transfer[11] is 2.8 × 10^7 M^{-1} s^{-1}, and with H-atom-donating substrates (alcohols, cyclohexane, toluene)[17] is 10^5–10^6 M^{-1} s^{-1}. Hydrogen abstraction by triplet-state

Table III. Elemental Analysis

compound		calculated (%)		found (%)	
		C	H	C	H
6	$C_{12}H_{18}O_2$	74.23	9.28	73.98	9.30
7	$C_{10}H_{16}O$	78.90	10.59	78.82	10.54
9	$C_{11}H_{20}O_2$	71.74	10.87	71.61	10.79
10	$C_{11}H_{18}O_2$	72.53	9.89	72.42	10.02
15	$C_{11}H_{18}O_2$	72.53	9.89	72.46	9.81

benzophenone from acetylacetone is expected to be much slower than those from alkanes. Indeed, there is no evidence for the interaction of triplet-state benzophenone with acetylacetone[18] by any other mode except by the slow addition reaction[12] as shown in Scheme I. These rate constants support the contention that the rate of eq 1 would dominate under ordinary photolysis conditions (i.e., Cu(acac)$_2$ concentration of >0.01 M) and that any triplet-state benzophenone must be exclusively channeled to produce acac· by eq 1. Other radicals, e.g., cyclohexenyl and benzyl radicals, are probably secondary intermediates derived from acac·.

The acetylacetonyl radical may react as the C radical or the O radical owing to conjugation. The ESR studies have shown that the spin density at oxygen is small, and 70% of spin density resides at the C$_3$ atom.[19] Exclusive C-radical reactivity of acac· is supported by the trapping experiments. It should be noted that an O-radical addition (e.g., to 1-hexene) would lead to **20** (see Scheme III), a dihydrofuran isomeric to **15**.

The addition reactivity of acac· is very similar but not quite as exclusive as that of the succinimidyl radical.[6] Thus, acac· primarily abstracts the allylic hydrogens from cyclohexene to give **16** and **17** in significant departure from the reactivity of succinimidyl radicals. However, in this particular case, the product pattern does not indicate the involvement of the C radical or O radical in H abstraction. As the *tert*-butoxy radical primarily abstracts allylic hydrogen, instead of adding to the double bond[20] of cyclohexene, it cannot be completely ruled out that under certain conditions, acac· preferentially assumes O-radical reactivity in which H abstraction prevails over the addition. In the acac· reaction with 1-hexene, if a small amount of allylic H abstraction is involved, it will be difficult to detect and may have escaped detection under the reaction conditions. The possible dichotomous reactivity of acac· with olefins would be related to the electronic configuration of this radical and remains to be more thoroughly elucidated.

The resistance of the 2-norbornyl radical to undergo an electron-transfer reaction (or oxidation by Cu^{2+} as in eq 9) contrasts sharply with the facility with which the cyclohexenyl radical is oxidized. The former resistance is indeed very surprising in view

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of the propensity to form the norbornyl cation by σ-bond-assisted solvolysis.[21] It is surmised that the tendency of radical oxidation by metal ions may be related to the extent of the s character of the orbital containing the unpaired electron. The cyclohexenyl radical, containing the unpaired electron in a purely p orbital, is much more readily oxidized than acyclic secondary radicals from 1-hexene and 3,3-dimethyl-1-butene by Cu^{2+} ions. The 2-norbornyl radical is skeletally strained, forcing the singly occupied orbital to have a large percent of s character. We suspect this is one of the factors that retards oxidation.

Experimental Section

General Conditions. The apparatus and analytical procedures were the same as those used in the previous papers.[3,4]

Photolysis of Benzophenone and $Cu(acac)_2$ in the Presence of Olefins. A solution of $Cu(acac)_2$ (0.5 g, 1.92 mmol), benzophenone (1.0 g, 5.55 mmol), and an olefin (5–6 mmol) in glacial acetic acid (100–200 mL) was irradiated under nitrogen for several hours to give a yellow solution and/or until metallic copper began to form. The photolysate was diluted with water (400 mL) and extracted with ether (3 × 100 mL). The ether extracts were washed with Na_2CO_3 solution and water and dried over $MgSO_4$. GC analysis showed the peaks of the acetylacetone addition products eluting before benzophenone in addition to the minor peaks of oxetanes[13] and the addition products[12] of benzophenone to acetylacetone at higher retention times than benzophenone. The crude products were first chromatographed on alumina. The fractions collected were rechromatographed by column chromatography or preparative HPLC to give the addition products. The GC yields were calculated by taking the sum of acetylacetone and its derivatives as 100%. The photoreduction in acetonitrile was generally slower and gave more byproducts arising from benzophenone addition.

In general, if the photoreduction was stopped before metallic copper formation and the fading of the blue color, the byproduct formations were minimal. The addition product of triplet-state benzophenone to olefins (oxetanes) and acetylacetone rapidly increased after the disappearance of $Cu(acac)_2$. GC was carried out with a 10% SE-30 capillary column (isothermal or temperature programming, 100–240 °C at 10 °C/min).

(1) Norbornene. The GC retention times were 0.8 min (acetylacetone), 9.4 min (**6**), 5.2 min (**7**), 3.8 min (**8**), and 7.9 min; the last peak was tentatively assigned to 2-*endo*-norbornylacetone (2.5%). The GC peak of **8** matched with one of the peaks of a mixture of *exo*- and *endo*-2-acetylnorboranes which were prepared by the hydrogenation of 2-acetyl-5-norbornene (Aldrich, an exo and endo mixture). An authentic sample of **6** was prepared by $Mn(OAc)_2$ oxidation of acetylacetone and norbornene[22] in acetic acid. Diketone **6** was treated with hot NaOH

solution in aqueous MeOH to afford ketone **7**. The semicarbazone of **7** was obtained as colorless needles, mp 192–195 °C (reported 194–195 °C).[23]

(2) 3,3-Dimethyl-1-butene. The GC retention times were 4.1 min (**9**), 6.4 min (**10**), 4.5 min (**11**), and 4.9 min (**12**). The products **11** and **12** were isolated as a mixture, showing two GC peaks (100 °C isothermal) at 4.9 min for **11** and 5.1 min for **12**.

(3) 1-Hexene. The GC retention times were 1.5 min (acetylacetone), 3.03 min (**14**), 3.13 min (**13**), and 4.16 min (**15**). Products **13** and **14** were isolated as a mixture by preparative GC (25% SE-30, 150–240 °C at 15 °C/min).

(4) Cyclohexene. The GC retention times were 5.9 min (**16**) and 8.5 min (**17**). An authentic sample of **15** was prepared by the oxidation of cyclohexene with $Hg(OAc)_2$ in acetic acid.[24]

ESR Experiments. The details of the apparatus and recordings were the same as those described in the previous publication.[4] The light source was an Osram HBO 200-W high-pressure mercury lamp housed in a Wild Leitz illuminator and was filtered through Wild BG-38 and Corning filter No. 7-60 (glass no. 5840, 4.5 mm thickness) to pass the emission centered around 365 nm. Benzene, toluene, and methylene chloride were Fischer Spectrograde, and NMP (Aldrich) was used as supplied. The solution for ESR spectroscopy contained $Cu(acac)_2$ (0.01–0.001 M), benzophenone (0.005 M), and NMP (0.002 M) in the desired solvent. Each experiment was supported by control experiments to ascertain the origin of the spectra. For example, irradiation of a solution containing benzophenone and NMP in CH_2Cl_2 developed only a weak signal (g value 2.0078, a_N = 8.13 G) after 15 min. Irradiation of a similar solution in toluene developed a triplet of triplet (a_N = 15.25, a_H = 7.63 G, g value 2.0058) which is similar to that observed previously.[8,11]

A solution containing $Cu(acac)_2$ (0.001 M) and benzophenone (0.005 M) in benzene was purged with either purified nitrogen or hydrogen. The solution was irradiated in the ESR cavity as described, and the four-line signal of $Cu(acac)_2$ was scanned every 2 min. The intensity of the former remained constant, but that of the latter decreased regularly with concurrent formation of a copper mirror on the tube surface.

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Total Synthesis of Natural Estrone and Estradiol Methyl Ethers in Extremely High Enantiomeric Purity via an Asymmetric Michael Addition to an Unsaturated Sulfoxide

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Abstract: Methoxytetralone enolate ion **1b** underwent an asymmetric Michael addition to enantiomerically pure cyclopentenone sulfoxide (S)-(+)-2 with a diastereoselectivity of 91–94%. A series of eight additional steps led to (+)-estrone methyl ether (**11**) in overall 6.3% yield. Chiral HPLC analysis of (+)-estradiol **12** indicated an enantiomeric purity of at least 97.3%.

Steroidal sex hormones such as estrone and estradiol have attracted the attention of organic chemists because these tetra-

cycles possess important physiological activity and because they represent a clear and severe challenge for total synthesis.[1,2] In