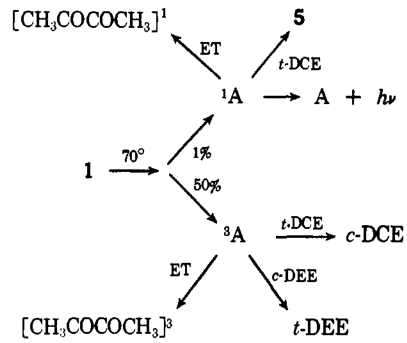
Scheme I



We summarize our findings in Scheme I. In addition to the remarkably efficient and selective[19] formation of ^{3}A relative to ^{1}A, we wish to point out that the blue (acetone fluorescence) chemiluminescence is a "red herring" with respect to the major method for excited state production from **1**. This shows the hazards of making mechanistic conclusions solely on the basis of low-efficiency chemiluminescence. Finally, **1** is a "self-quencher" of chemelectronic production of ^{3}A, while dissolved oxygen is a "promoter" of chemiluminescence. We conclude that low concentrations of **1** in the absence of oxygen (*i.e.*, under conditions that chemiluminescence is *decreased*) are most favorable for efficient production of chemically useful excited states (triplets) from **1**.

Acknowledgments. The authors thank Mr. Mark P. Niemczyk for his assistance in the early phases of this work. Special thanks are extended to Professor Karl Kopecky for kindly providing us with a detailed procedure for the preparation of **1**. We also thank Professor David Kearns for a helpful discussion of the mechanism of dioxetane decomposition.

(19) Although we are not in a position yet to make a distinction between a multistep or concerted production of ^{3}A, we point out that Kearns has calculated that the energy of passing from 1 to ^{3}A might be lower than from 1 to ^{1}A: *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

(20) NATO Postdoctoral Fellow, 1971–1972.

Nicholas J. Turro,* Peter Lechtken[20]
Department of Chemistry, Columbia University
New York, New York 10027
Received January 12, 1972

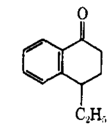
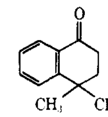
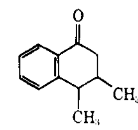
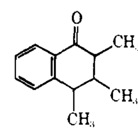
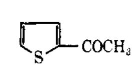
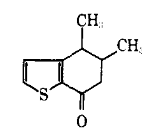
Oxidation by Metal Salts. IX. Formation of Cyclic Ketones

Sir:

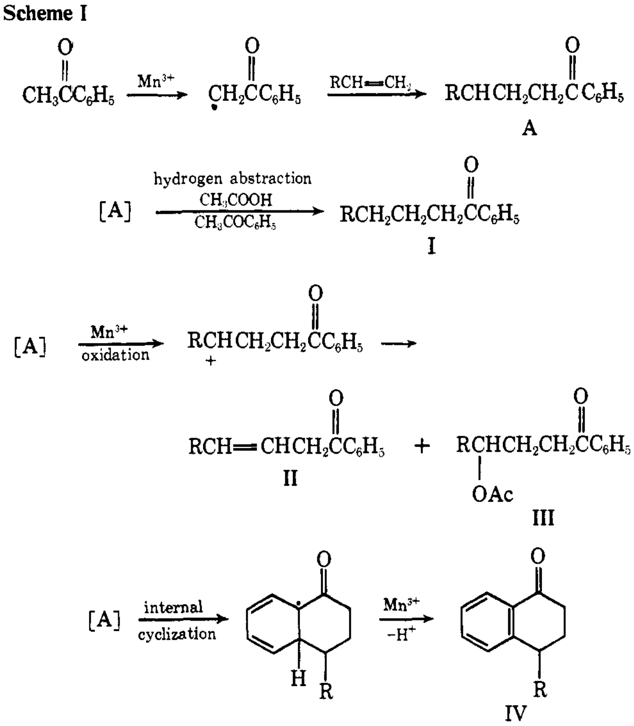
In an earlier communication[1] we described a reaction of olefins with aliphatic ketones in the presence of manganic and ceric acetates, which led to the formation of three major products: saturated ketone I, unsaturated ketone II, and keto acetate III. We have now found that when an aromatic ketone such as acetophenone was used, a new fourth product, α-tetralone IV, was obtained as the predominant product in about 50% yield[2] (Table I).

The formation of these cyclic ketones together with the three noncyclic products can best be explained by the mechanism shown below (Scheme I). As shown, the radical intermediate A undergoes three competing reactions: (1) hydrogen abstraction from the solvent, (2) oxidation by the higher valent metal ion, and (3) internal cyclization. The ratio of tetralone IV (R_1 = C_2H_5; R_2 = H) to saturated ketone I (15, at 1.35 *M* acetophenone) was independent of the nature or concentration of the metal ion used and decreased as the acetophenone concentration increased. The ratio of tetralone IV to the oxidation products II and III, how-

Table I. Yields of Cyclic Ketones

Ketone	Olefin	Cyclic ketone	Yield (based on Mn^{3+}), %
$C_6H_5COCH_3$	Butene-1		49
	Isobutylene		43
	Butene-2		40
	Butene-2		53
	Butene-2		43

Scheme I



(1) E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, **93**, 524 (1971).

(2) Yield is based on the requirement of 2 equiv of metal ion/mol of tetralone.

Table II. Effect of the Metal Oxidant on the Ratio of Oxidation Products to Cyclized Ketone

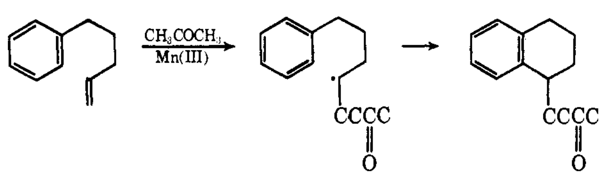
[Oxidant], *M*	(II + III)/IV
Mn(III), 0.11	0.13
Mn(III), 0.23	0.23
Ce(IV), 0.017	0.19
Ce(IV), 0.034	0.35
Cu(II), 0.0039, + Mn(III), 0.10	0.85

ever, decreased linearly as the metal ion concentration increased, as shown in Figure 1 and Table II. These observations are all consistent with the proposed scheme in which products I and IV are produced *via* a free-radical pathway.

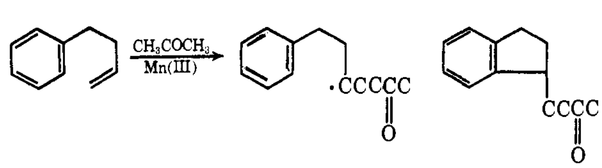
The relative rates of oxidation of the radical A by Mn(III), Ce(IV), and Cu(II) as estimated from Table II indicate that Cu(II) is a stronger oxidant than Ce(IV), which in turn is a stronger oxidant than Mn(III).[1]

From Figure 1 the bimolecular rate of oxidation of radical A by Cu(II) relative to the rate of internal radical cyclization was found to be 240 at 25°. This high rate of oxidation of radical A by cupric acetate relative to internal cyclization is comparable to that reported for the cyclization of the δ-phenylbutyl radical[3] to tetralin (350). The lower value obtained here is most probably due to a more rapid rate of cyclization of the tetralone precursor, due to stabilization of the cyclohexadienyl radical intermediate by the carbonyl group, rather than to differences in radical oxidation rates.[4] Assuming the rate of radical oxidation by cupric acetate to be approximately $7.6 \times 10^7 \ M^{-1}\ sec^{-1}$, which is the value reported[4] for the secondary butyl radical at 57°, the rate of internal cyclization of radical A can be calculated to be about $3 \times 10^5\ sec^{-1}$, which is comparable to other reported rates of radical cyclization.[5]

Another variation of the synthesis of a cyclized product utilizing the reaction of a ketone with an olefin in the presence of Mn(III) or Ce(IV) is exemplified by the reaction of acetone with 5-phenylpentene-1, which gave the tetralin V as the predominant product in 70% yield. 4-Phenylbutene-1, however, gave only minor amounts of the cyclized product VI as shown in Table III. As



V



VI

expected, the two adduct radicals had similar rates of oxidation by Mn(III) and hydrogen abstraction as shown in the last column in Table III. The difference in behavior of these two olefins, therefore, was due to

(3) J. K. Kochi and R. D. Gilliom, *J. Amer. Chem. Soc.*, **86**, 5251 (1964).
(4) J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 4855 (1965).
(5) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

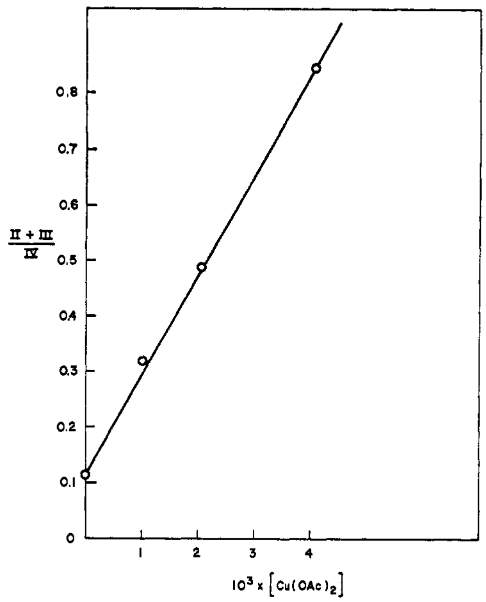


Figure 1. Effect of added cupric acetate on the product ratio.

the difference in the rates of cyclization of the two radical intermediates, which, in the case of the six-membered ring, is some 55–65 times greater than the rate of cyclization to form an indan.[6]

Table III. Product Ratios of the Reactions of Aromatic Olefins with Acetone

Olefin[a]	Ox[b]/(V or VI)	S[c]/(V or VI)	Ox[b]/S[c]
$C_6H_5(CH_2)_3CH{=}CH_2$	0.20	0.12	1.5
$C_6H_5(CH_2)_2CH{=}CH_2$	11.0	7.8	1.4

[a] Identical reaction conditions, 45°, $[Mn(III)]_{av}$ = 0.09 *M*. [b] Ox = unsaturated ketone + keto ester. [c] S = saturated noncyclic ketone.

Acknowledgment. The authors are indebted to Dr. P. G. Rodewald for the synthesis of some cyclic ketones, and to Mr. G. E. Stead for skillful assistance in carrying out the reported experiments.

(6) W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964).

E. I. Heiba,* R. M. Dessau
Mobil Research and Development Corporation
Central Research Division
Princeton, New Jersey 08540
Received January 10, 1972

"Through-Space" Coupling between Bucking Fluorine and Hydrogen Nuclei in *trans*-1,1′-Difluorotetrabenzopentafulvalene[1]

Sir:

Recently, compelling evidence has been put forward in favor of a "through-space" ("direct") mechanism operating in long-range proton–fluorine spin–spin coupling in a series of bridged biphenyls and phenan-

(1) Fulvenes and Thermochromic Ethylenes. 64. For part 63 see E. D. Bergmann and I. Agranat, *J. Chem. Soc. C*, 3532 (1971).