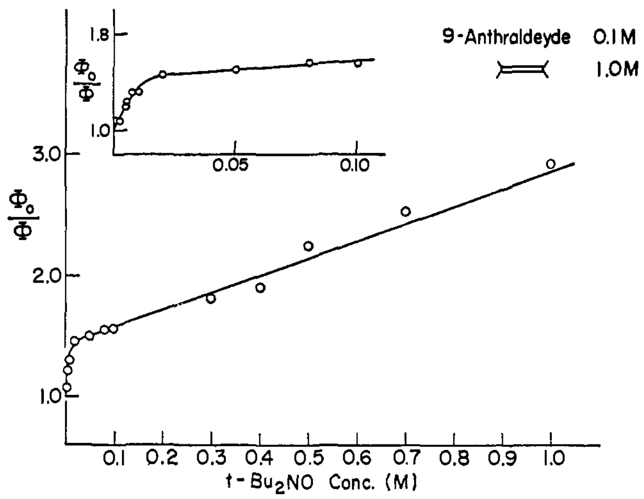

Figure 2.

pendent on the olefin concentration (Table I). However, the quantum yield is lower in neat olefin than in 4 *M* olefin, indicating that the deactivation of excited singlet state by olefin may have occurred.[2e] When the photochemical addition of benzophenone (0.5 *M*) to 2,3-dimethyl-2-butene (1 *M*) was carried out in benzene, benzophenone was found to be considerably less reactive than benzaldehyde (Table I). A linear Stern–Volmer plot was also obtained in the case of benzophenone reaction with a slope of 3 M^{-1}.

Table I

Carbonyl compd	2,3-Dimethyl-2-butene, *M*	$\phi(>C{=}O)$	ϕ(oxetane)
Benzaldehyde	1	0.55 ± 0.02	0.465 ± 0.005
Benzaldehyde	4	0.61 ± 0.02	0.527 ± 0.005
Benzaldehyde	Neat		0.397 ± 0.005
Benzophenone	1	0.09 ± 0.02	
9-Anthraldehyde	1	0.024 ± 0.005	
9-Anthraldehyde	4	0.048 ± 0.005	

When the photochemical addition of 9-anthraldehyde to 2,3-dimethyl-2-butene in benzene was carried out in the presence of various concentrations of di-*t*-butyl nitroxide, quite different results were obtained. The Stern–Volmer plot was nonlinear. The absolute quantum yield of aldehyde consumption decreased sharply at low quencher concentration, followed by a much slower decrease at higher quencher concentration (Figure 2). This result indicated that there are two different reactive species in the photochemical addition of anthraldehyde to 2,3-dimethyl-2-butene. One of them, which accounts for a minor portion of the reaction (23%), is easily quenchable by di-*t*-butyl nitroxide, while the other one, which accounts for the major portion of the reaction (77%), is quenched with difficulty.

The Paterno–Büchi reaction may be expressed by the following steps.

$$\text{ArCOR} \xrightarrow{h\nu} [\text{S}]^* \tag{1}$$

$$[\text{S}]^* + \text{olefin} \xrightarrow{k_s} \text{products} \tag{2}$$

$$[\text{S}]^* \xrightarrow{k_{\text{intersystem crossing}}} [\text{T}]^* \tag{3}$$

$$[\text{T}]^* + \text{olefin} \xrightarrow{k_t} \text{products} \tag{4}$$

$$[\text{T}]^* + \text{quencher} \xrightarrow{k_q} \text{ArCOR} \tag{5}$$

$$[\text{T}]^* \xrightarrow{k_{-t}} \text{ArCOR} \tag{6}$$

where these steps represent excitation, singlet-state reaction, intersystem crossing, triplet-state reaction, quenching, and radiationless decay of the triplet state, respectively.

The rates of these reactions may be estimated from the slope of Stern–Volmer plots. Assuming the quenching rate is diffusion controlled and is 5 × 10^9 l./mole sec, the k_t for benzaldehyde is approximately 1 × 10^9 l./mole sec and k_{-t} is approximately 3 × 10^8 sec^{-1}.

The rates for the radiationless transitions between various electronic states are dependent on the energy gaps between these states. The intersystem crossing efficiency of anthracene is less than that of benzene as measured by fluorescence,[4] and the intersystem crossing efficiency of 2-acetonaphthone is less than that of acetophenone.[5] The energy gap between the n,π^* singlet and the low-lying triplet state of anthraldehyde is considerably larger than that of benzaldehyde, and the rate of radiationless transition between these two states ($k_{\text{intersystem crossing}}$) may become sufficiently slow to be competitive with the rate of singlet-state reaction (k_s). It is conceivable that both states of anthraldehyde are reactive in the Paterno–Büchi reaction. *We wish to emphasize, however, that our experimental data are also consistent with the fact that the short-lived excited state may be an upper triplet state.*

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[4] E. J. Bowen, *Advan. Photochem.*, **1**, 23 (1963).

[5] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[6] NASA Trainee, 1965–1967.

[7] National Science Foundation Undergraduate Research Participant, 1966.

[8] The authors wish to thank the National Science Foundation for its support and Professor L. A. Singer for many stimulating discussions.

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Received July 13, 1967

Photoreduction of Acetophenone and Substituted Acetophenones

Sir:

The correlation of photochemical reactions of organic compounds with the nature of their excited states has been a subject of current interest.[1] In a series of elegant investigations, Hammond and his co-workers demonstrated that the triplet state is the reactive state in the photoreduction of aryl ketones and that the photoreactivity of aryl ketones depends on the nature of their low-lying triplet state.[1a,b] The importance of n,π^* *vs.* π,π^* low-lying triplet states is illustrated by the fact that acetophenone, with a low-lying $^3[\text{n},\pi^*]$ state, is photoreduced with ease, while 2-acetonaph-

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[1] (a) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); (b) G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962); (c) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962); (d) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965); (e) A. Beckett and G. Porter, *ibid.*, **59**, 2051 (1963); (f) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

Table I

Compound	ϕ(ketone) 3130 A	E_T^{a}		τ_{rad},^{b} sec	τ_{phos}, sec	ϕ_{phos}
		cm^{-1} $\times$ 10^4	kcal			
Acetophenone	0.68	2.59	74.1	0.005	0.004	0.74
p-Methylacetophenone	0.66	2.55	72.8	0.14	0.084	0.61
m-Methylacetophenone	0.46	2.54	72.5	0.12	0.074	0.64
3,4-Dimethylacetophenone	0.12	2.50	71.5	0.30	0.17	0.56
p-Methoxyacetophenone	0.04	2.50	71.5	0.38	0.26	0.68
3,5-Dimethylacetophenone	0.018	2.49	71.3	0.20	0.11	0.51
3,4,5-Trimethylacetophenone	0.018	2.46	70.8	0.42	0.20	0.46
m-Methoxyacetophenone	0.006	2.53	72.4	0.71	0.25	0.35
3,4-Methylenedioxyacetophenone	0.002	2.30	65.8	1.20	0.37	0.30

[a] Estimated from the 0–0 transition of the phosphorescence emission. [b] The error is estimated at ±30%.

Table II

Compound	$^3[n,\pi^*]$		$^3[\pi,\pi^*]$	
	Found	Lit.^{a}	Found	Lit.^{a}
Acetophenone	26,900 cm^{-1} 372 mμ	26,500 cm^{-1} 378 mμ		
p-Methylacetophenone	27,200 cm^{-1} 368 mμ		25,900 cm^{-1} 386 mμ	
3,5-Dimethylacetophenone	27,000 cm^{-1} 371 mμ		25,700 cm^{-1} 390 mμ	
p-Methoxyacetophenone	27,800 cm^{-1} 360 mμ	27,400 cm^{-1} 365 mμ	25,600 cm^{-1} 391 mμ	25,300 cm^{-1} 394 mμ

[a] Reference 4.

thone, with a low-lying $^3[\pi,\pi^*]$ state, is photoreduced with difficulty. The low-lying triplet state of benzene derives from the L_a state which is susceptible to substituent effects.[2] It has been shown that substitution in the benzene nucleus with an electron-donating group such as methyl or methoxy will lower the energy of its $^3[\pi,\pi^*]$ state (^3L_a),[3] while it will raise the energy of the $^3[n,\pi^*]$ state of aryl carbonyl compounds.[4] It has been shown by empirical calculation[5] and by the contribution of Lamola[6] that acetophenone has a low-lying $^3[n,\pi^*]$ state and a nearby $^3[\pi,\pi^*]$ state. By successive introduction of methyl groups into acetophenone, it is possible to increase systematically the energy of the $^3[n,\pi^*]$ state and to decrease the energy of the $^3[\pi,\pi^*]$ state so that, in a substituted acetophenone, the low-lying triplet could be π,π^* in nature. The present communication deals with the characterization of the low-lying triplet state of methyl-, polymethyl-, and methoxy-substituted acetophenones and their photoreduction.

Emissions from all methyl- and methoxy-substituted acetophenones are red shifted from acetophenone and have considerably longer radiative lifetimes (τ_{phos}/ϕ_{phos}) (Table I). Although vibrational fine structure is still noticeable in *p*-methyl- and *m*-methylacetophenone, it is more diffused than in acetophenone. These observations suggested that all methyl- and methoxy-substituted acetophenones may have low-lying $^3[\pi,\pi^*]$ states. Recently, an elegant method to measure and characterize S → T transitions of aromatic carbonyl compounds by phosphorescence excitation was developed by Kearns.[4] He demonstrated that *p*-methoxyacetophenone has a low-lying $^3[\pi,\pi^*]$ state and also detected a higher $^3[n,\pi^*]$ state. By applying this method, we found by way of the excitation spectrum that both *p*-methylacetophenone and 3,5-dimethylacetophenone exhibit a $^3[n,\pi^*]$ transition in EPA glass which was blue shifted from acetophenone, as in the case of *p*-methoxyacetophenone[4] (Table II), while the phosphorescence emission from either compound is red shifted from that of acetophenone (Table I). When the excitation spectra were measured in the presence of ethyl iodide, which will intensify the $^3[\pi,\pi^*]$ transition, an additional weaker band was observed at 386 mμ for *p*-methylacetophenone and at 390 mμ for 3,5-dimethylacetophenone, as in the case of *p*-methoxyacetophenone (Table II). These observations verified that the low-lying triplet states of *p*-methylacetophenone and 3,5-dimethylacetophenone are indeed π,π^* in nature.

The photochemical reactivities of these compounds were measured in terms of their quantum yields of photoreduction in 2-propanol (Table I). Although the substituted acetophenones have a low-lying $^3[\pi,\pi^*]$ state, *p*-methyl- and *m*-methylacetophenone still exhibit photoreactivity comparable to that of acetophenone, and polymethyl- and methoxyacetophenones exhibit decreased photoreactivity. It is interesting to note that the triplet-state energies of these ketones are comparable to each other with the exception of 3,4-methylenedioxyacetophenone (Table I), and that the spacings between their $^3[\pi,\pi^*]$ states and $^3[n,\pi^*]$ states do not vary substantially, at least in the few cases we have measured (Table II). However, a qualitative correlation seems to exist between the photoreactivity and the radiative lifetime of these compounds (Table I), *i.e.*, the shorter the radiative lifetime, the higher the reactivity.

By using simple first-order perturbation theory, an approximate ratio of the lifetimes of the $^3[\pi,\pi^*]$ states

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(2) (a) J. Petruska, *J. Chem. Phys.*, **34**, 1120 (1961); (b) L. Goodman and H. Shull, *ibid.*, **27**, 1388 (1957).

(3) H. Sponer and Y. Kanda, *ibid.*, **40**, 778 (1964).

(4) D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966).

(5) S. L. Murov, Ph.D. Thesis, University of Chicago, 1966.

(6) A. A. Lamola, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract R117; A. A. Lamola, *J. Chem. Phys.*, in press.

in substituted acetophenones to the value for the n,π^* state in the unsubstituted molecule can be obtained. It is assumed that the $^3[n,\pi^*]$ state decays with the assistance of the strong charge-transfer singlet state (^1L_a) at 42,000 cm^{-1}, and that the $^3[\pi,\pi^*]$ state decays with the help of the nearest $^1[n,\pi^*]$ state at about 31,000 cm^{-1}.[7] The spin-orbit matrix elements are the same for both processes, and cancel out in the ratio. The result is

$$\frac{\tau_\pi}{\tau_n} = \frac{\Delta E_\pi}{f_\pi}\frac{f_n}{\Delta E_n}$$

where π and n refer to the two kinds of triplets, ΔE is the appropriate energy denominator, and the f_π and f_n are the oscillator strengths of the singlet bands. This ratio is 14 for *p*-methylacetophenone and is to be compared to the observed value of 28. More refined calculations would probably give improved agreement and might explain the dependence on substituent, but we feel that at this stage we can cite the values of the lifetimes as providing additional evidence for the $^3[\pi,\pi^*]$ assignments.

The somewhat rough correlation between decrease of reactivity and increase of lifetime and the near-constancy of the energy of the reacting state suggest that a factor in electronic structure must be responsible for the change in reactivity with substitution. The investigation is being continued to isolate this factor.

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(7) D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952); M. A. El-Sayed, *ibid.*, **38**, 2834, 3032 (1963).

(8) National Science Foundation Predoctoral Fellow, 1962–1965; Esso Fellow, 1965–1966.

(9) The work is abstracted in part from the Ph.D. Thesis of S. L. Murov, submitted to the Department of Chemistry, University of Chicago.

(10) NDEA Fellow, 1966–1967.

(11) The authors wish to thank the National Science Foundation for the support of this work and Dr. A. A. Lamola of the Bell Telephone Laboratories for a copy of his preprint.

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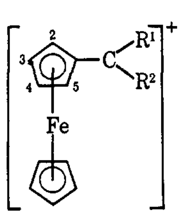
Received July 31, 1967

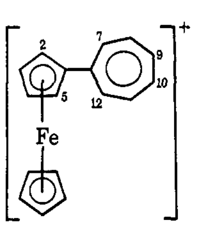
Metal π Complexes of the Sesquifulvalene and Calicene Systems[1]

Sir:

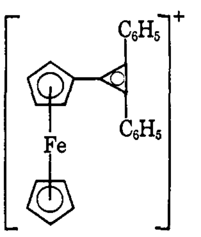
We have made use of the known stability and ready availability of tropylium,[2] diphenylcyclopropenylium,[3] and ferrocenylcarbinyl[4] cations (I) to realize the synthesis and isolation of the stable cations II and III, which are in effect iron π complexes of the sesquifulvalene and calicene systems, IV and V, respectively.



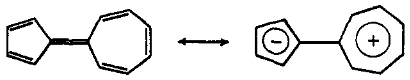
I



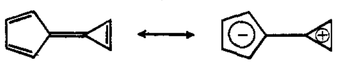
II



III



IV



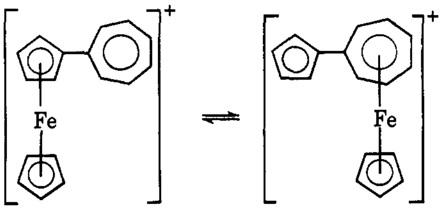
V

The green, crystalline fluoroborate salt of cation II was obtained in one step from the reaction between ferrocene and tropylium fluoroborate in acetonitrile solution. The ultraviolet spectrum (in methylene chloride solution) exhibited λ_{max} (mμ (log ϵ)) 332 (3.6), 404 (4.3), and 700 (3.7).

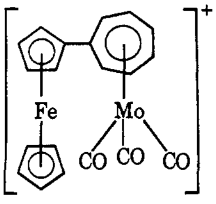
The boron trifluoride etherate catalyzed reaction between ferrocene and 3,3-dichloro-1,2-diphenylcyclopropene[5] in methylene chloride yielded the red crystalline fluoroborate salt of cation III. The ultraviolet spectrum (in methylene chloride) exhibited λ_{max} (mμ (log ϵ)) 250 (4.2), 307 (4.4), and 320 (4.4).

$NaBH_4$ reduction of the salts of either II or III yielded isomeric mixtures (double bond positional isomerism) of ferrocenylcycloheptatriene and ferrocenyldiphenylcyclopropene, respectively.[6]

The reported synthesis of various π-$C_5H_5MC_7H_7$ complexes[7] as well as the suggested valence tautomerism exhibited by metal π complexes of fully conjugated hydrocarbon systems[8] necessitate the consideration of the possible tautomerism IIa $\rightleftharpoons$ IIb (or some intermediate position of the FeC_5H_5 moiety between the extreme forms IIa and IIb).



IIa IIb



VI

The apparent singlets (parts per million downfield from TMS) at δ 5.37 for the four protons[9] H_2–H_5 and at δ 8.30

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(1) (a) Organometallic Studies. XX. (b) For part XIX see M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards *Tetrahedron Letters*, 1695 (1966).

(2) For reviews see (a) M. E. Vol'pin, *Russ. Chem. Rev.*, **29**, 129 (1960); (b) T. Nozoe in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959.

(3) R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2375 (1961).

(4) For a recent review see M. Cais, *Organometal. Rev.*, **1**, 435 (1966).

(5) B. Föhlisch and P. Bürgle, *Ann.*, **701**, 67 (1967).

(6) Structures were confirmed by infrared, nmr, and molecular weight (mass spectrum) measurements, and satisfactory elemental analysis results. Hydride abstraction with trityl fluoroborate from ferrocenylcycloheptatriene and ferrocenyldiphenylcyclopropene gave fluoroborate salts which were identical in every respect (ultraviolet, infrared, nmr) with the cations II and III, respectively, obtained by the direct route.

(7) For example (a) E. O. Fischer and S. Breitschaft, *Angew. Chem.*, **75**, 94 (1963); *Chem. Ber*, **96**, 2451 (1963); (b) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964); (c) R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 129 (1967).

(8) See, for example, R. Ben-Shoshan and R. Pettit, *J. Am. Chem. Soc.*, **89**, 2231 (1967), and leading references therein. See also ref 7c.

(9) The appearance of this singlet is in contrast to other α-ferrocenyl-