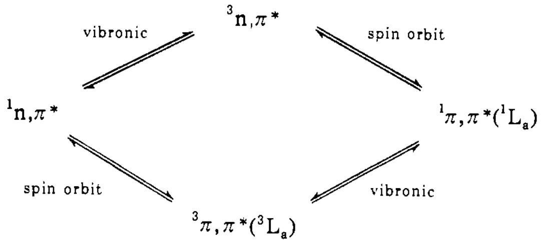
Table II

Aldehyde	Emission (°K)	τ	ϕ	$E_{^1n,\pi^*-^3\pi,\pi^*}$
1a[a]	Phosphorescence (77)	2 msec	0.60 ± 0.05	
1c[a]	Phosphorescence (77)	0.1 sec	0.30 ± 0.03	~3000 cm^{-1}
1d[b]	Phosphorescence (77)	~1 sec		5860 cm^{-1}
1e	Phosphorescence (77)[a]	0.37 sec	0.035 ± 0.005	7700 cm^{-1} [c]
	Fluorescence (298)[d]		0.0003 ± 0.0001[e]	7000 cm^{-1} [d]
1f	Fluorescence (298)[d]		0.0005 ± 0.0002[e]	

[a] S. Murov, Ph.D. Thesis, University of Chicago, 1967. [b] R. Shimida and L. Goodman, *J. Chem. Phys.*, **43**, 2030 (1965). [c] Reference 11. [d] This work. [e] Using acetone as the secondary standard assuming its ϕ to be 0.001, ref 13.

Scheme II



timated to be inversely proportional to the square of the energy gap (ΔE) between the two states. Benzophenone undergoes intersystem crossing at an extremely rapid rate which is several orders of magnitude faster than that of aliphatic carbonyl compounds.[10] Since the ΔE between the ^{1}n,π* and ^{3}n,π* does not vary appreciably for most carbonyl compounds,[11] the higher rate of intersystem crossing of aromatic carbonyl compounds must be attributed to the spin-orbit coupling between the ^{1}n,π* and the $^3\pi,\pi$*.[12] In a series of aromatic aldehydes, the k_{isc} will decrease as the ΔE between the ^{1}n,π* and $^3\pi,\pi$* widens. Our experimental findings are in qualitative agreement with this concept. In the case of **1a–c**, the k_{isc} was so fast such that there was no evidence for the singlet reaction even in neat 2-butenes. However, judging from the stereoselectivity of oxetane formations, the primary reactive species in the case of 2-naphthaldehyde (**1e**) as in the case of acetaldehyde (**1f**) is its ^{1}n,π*. This result may be attributed to two factors: (1) the k_{isc} of **1e** as those of alkanals is relatively slow comparing to the k_a[2-butene] and(or) (2) the $^3\pi,\pi$* of **1e** which may be formed rapidly is comparatively unreactive in the Paterno–Büchi reaction.

In the absence of external perturbation, the major pathway for the decay of a vibrationally relaxed ^{1}n,π* of carbonyl compounds is the intersystem crossing. Aliphatic carbonyl compounds exhibit weak but detectable fluorescence ($\phi_f \sim 0.001$).[13] If the ^{1}n,π* of 2-naphthaldehyde (**1e**) undergoes intersystem crossing at a rate comparable to that of an alkanal, it will exhibit similar fluorescence properties. We found that **1e** exhibits a weak but well defined fluorescence in CCl_4 with maxima at 365, 382, and 404 nm and its uncorrected excitation spectrum corresponds closely to its absorption spectrum (Table II). We also found that the fluorescence of **1e** was readily quenched by *cis*-2-butene with a $k_q\tau_s$ of 7.0 ± 0.7 l. m^{-1}. These observations verified that the photochemical reactions of **1e** with 2-butenes take place mainly from its ^{1}n,π* under our experimental conditions.

If the intersystem crossing of the ^{1}n,π* of aldehydes is the composite of its vibronic coupling with the ^{3}n,π* and its spin-orbit coupling with the $^3\pi,\pi$*, by comparing the photochemical behaviors of **1e** and **1f**, the spin-orbit term does not seem to play an important role in the intersystem crossing ($\Delta E \sim 7000$ cm^{-1}). On the other hand, by comparing the photochemical behaviors of **1c** and **1f**, the spin-orbit term seems to play a predominant role in the same process ($\Delta E \sim 3000$ cm^{-1}). Therefore, the results on the photochemical behaviors of aldehydes cannot be accounted for quantitatively by the simple inverse square relationship between the k_{isc} and ΔE between the states. Either the spin-orbit coupling between ^{1}n,π* and $^3\pi,\pi$* of aromatic carbonyl compounds of very large ΔE between them is less important than predicated by this concept or secondary coupling processes may be important also among the singlet and triplet states in aromatic carbonyl compounds.

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(10) P. M. Rentzepis and C. J. Mitschele, *Anal. Chem.*, **42** (14), 20A (1970).

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

(12) R. M. Hochstrasser, *Accounts Chem. Res.*, 1, 266 (1968); M. A. El-Sayed, *ibid.*, 1, 8 (1968).

(13) A. M. Halpern and W. R. Ware, *J. Chem. Phys.*, **54**, 1271 (1971).

Thallium(III) in One-Electron Oxidation of Arenes by Electron Spin Resonance

Sir:

Thallium exists primarily in oxidation states I and III, and the array of novel organic reactions in which it participates is commonly considered to involve direct two-electron transfer mechanisms.[1,2] The thallation of aromatic compounds with thallium tris(trifluoroacetate) (TTFA) represents a particularly relevant example of the general class of electrophilic aromatic substitution reactions.[1,3]

$$Tl(O_2CCF_3)_3 + ArH \longrightarrow ArTl(O_2CCF_3)_2 + CF_3CO_2H \quad (1)$$

We have found that paramagnetic species, the arene cation radicals, are readily formed in solution under

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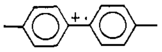
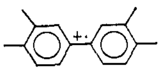
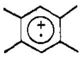
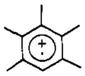
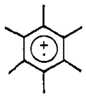
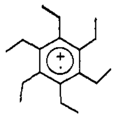
(1) A. McKillop and E. C. Taylor, *Advan. Organometal. Chem.*, 11, 147 (1973).

(2) R. J. Ouellette, *Oxid. Org. Chem.*, **2**, 135 (1973).

(3) (a) A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, and E. C. Taylor, *Tetrahedron Lett.*, 2423 (1969); (b) K. Ichikawa, S. Uemura, T. Nakano, and E. Uegaki, *Bull. Chem. Soc. Jap.*, **44**, 545 (1971); (c) J. M. Broidy and K. A. Moore, *J. Chem. Soc., Perkin Trans. 2*, 179 (1972).

Table I. Hyperfine Coupling Constants of Alkylbenzene Cation Radicals Produced by Oxidation with Thallium(III) Trifluoroacetate in Trifluoroacetic Acid Solution

Arene	Temp, °C	Cation radical[c-f]	Position	Hyperfine coupling constant	⟨g⟩
Toluene	−16		2, 2′, 6, 6′ 3, 3′, 5, 5′ 4, 4′	2.67 0.12 8.61[a]	2.00254
o-Xylene	−16		2, 2′, 6, 6′ 3, 3′ 4, 4′ 5, 5′	3.16, 2.05 <0.02 8.53 <0.02	2.00257
Durene	20		1, 2, 4, 5 3, 6	10.59[a] 0.78	2.00263
Pentamethylbenzene	−16		1, 2, 4, 5 3 6	~10.1[a] Not resolved Not resolved	
Hexamethylbenzene	20		1, 2, 3, 4, 5, 6	6.51[a]	2.00257
Hexaethylbenzene	−16		1, 2, 3, 4, 5, 6 1, 2, 3, 4, 5, 6	2.63[b] 0.37[a]	2.00269

[a] Methyl group coupling constant. [b] Methylene group coupling constant. [c] M. J. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, *J. Amer. Chem. Soc.*, **92**, 5096 (1970). [d] R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, **92**, 412 (1970). [e] M. C. R. Symons and R. Hulme, *J. Chem. Soc.*, 1120 (1965). [f] M. K. Carter and G. Vincow, *J. Chem. Phys.*, **47**, 302 (1967).

thallation conditions. The intense and well-resolved esr spectrum shown in Figure 1a is obtained when a degassed tube containing a frozen solution of TTFA and durene is allowed to warm up in the cavity of the spectrometer. The esr parameters for the durene cation radical obtained in this manner are listed in Table I, together with those derived from other polyalkylated analogs. Toluene also reacts readily with TTFA under these mild conditions to afford the esr spectrum of the *p,p′*-bitolyl cation radical shown in Figure 1b.[4] The same spectrum is obtained when *p,p′*-bitolyl is treated with TTFA.

These results are unique and interesting for several reasons. (a) Heretofore, there has been no direct evidence that Tl(III) can act thermally as a one-electron oxidant due to the instability of Tl(II), although kinetic studies with a few inorganic reductants have indirectly led to suggestions of one-electron transfer.[5] Indeed, photolysis and radiolysis have shown Tl(II) species to be highly metastable, the disproportionation reaction 2 proceeding at close to diffusion-controlled rates

$$2\mathrm{Tl(II)} \rightleftharpoons \mathrm{Tl(III)} + \mathrm{Tl(I)} \qquad (2)$$

in aqueous solution.[6] Thus, the ready participation of Tl(III) in one-electron transfers with arenes sug-

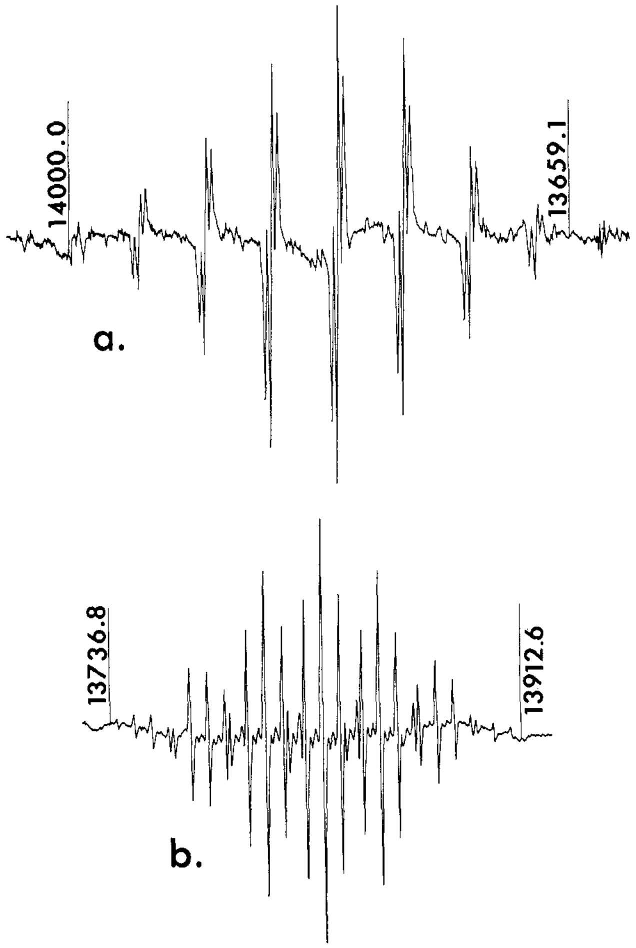


Figure 1. (a) Esr spectrum (central portion) of the durene cation radical from oxidation with Tl(III) in trifluoroacetic acid at 20°. (b) Esr spectrum of *p,p′*-bitolyl cation radical from the oxidation of toluene at −16°. Proton nmr field markers are in kilohertz.

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(4) The very reactive toluene cation radical [T. Komatsu, A. Lund, and P.-O. Kinell, *J. Phys. Chem.*, **76**, 1721 (1972)] is presumably the precursor to bitolyl by coupling with toluene. Bitolyls are formed in low yields during TTFA oxidation (J. W. Powers, unpublished results, and compare ref 3b).

(5) T. A. Turney, "Oxidation Mechanisms," Butterworths, London, 1965, p 26 ff; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 473 ff; B. Warnqvist and R. W. Dodson, *Inorg. Chem.*, **10**, 2624 (1971).

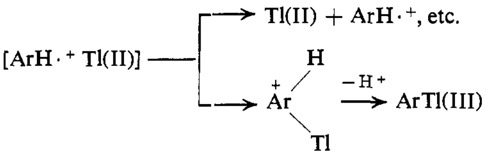
(6) B. Cercek, M. Ebert, and A. J. Shallow, *J. Chem. Soc. A*, 612 (1966); D. M. Brown and F. S. Dainton, *Trans. Faraday Soc.*, **62**, 1139 (1966); D. R. Stranks and J. K. Yandell, *J. Phys. Chem.*, **73**, 840 (1969); J. C. Muller, C. Ferradini, and J. Pucheault, *J. Chim. Phys.*, **63**, 233 (1966); J. K. Kochi and T. W. Bethea, *J. Org. Chem.*, **33**, 75 (1968).

gests that such processes may be more widely operative with other substrates than commonly believed. It represents a viable alternative to the formulation of Tl(III) invariably as a two-electron oxidant, as in the recently described oxidative coupling of phenols.[7]

(b) The formation of arene cation radicals with TTFA may implicate them as common intermediates in the thallation process, *e. g.*

$$\mathrm{Tl(III)} + \mathrm{ArH} \rightleftharpoons [\mathrm{ArH\ Tl(III)}] \tag{3a}$$

$$[\mathrm{ArH\ Tl(III)}] \rightleftharpoons [\mathrm{ArH\cdot^{+}Tl(II)}] \tag{3b}$$



$$[\mathrm{ArH\cdot^{+}\ Tl(II)}] \longrightarrow \mathrm{Tl(II)} + \mathrm{ArH\cdot^{+}},\ \text{etc.} \tag{4}$$

$$[\mathrm{ArH\cdot^{+}\ Tl(II)}] \longrightarrow \overset{+}{\mathrm{Ar}}(\mathrm{H})(\mathrm{Tl}) \xrightarrow{-\mathrm{H}^{+}} \mathrm{ArTl(III)} \tag{5}$$

The transient colors observed on mixing arenes with TTFA suggest the initial formation of charge-transfer complexes (eq 3).[8] Aromatic substitution can then proceed by collapse of the cage species (eq 5), or the arene cation radical can be observed after diffusive separation (eq 4).[9]

(c) Tl(III) allows the generation of a variety of metastable arene cation radicals for esr study under *static* conditions. Herefofore, the one-electron oxidant, cobalt(III) trifluoroacetate, has been employed in a rapid mixing flow method, which is costly and much less convenient.[10] Furthermore, the lines of the spectra are broader due to the concomitant formation of the paramagnetic Co(II) species. Co(III) and Pb(IV)[11] are not suitable oxidants for esr studies of reactive arene cation radical in a static system.

Acknowledgment. We wish to thank the National Science Foundation for financial support and Mr. John Powers for TTFA and helpful discussions.

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[7] M. A. Schwartz, B. F. Rose, and B. Vishnuvajjala, *J. Amer. Chem. Soc.*, **95**, 612 (1973).

[8] Low-temperature studies indicate that the absorption maxima with different arenes vary in the same way as those of the corresponding tetracyanoethylene–arene complexes (J. W. Powers, unpublished results).

[9] (a) The esr studies do not *prove* that these processes are related by a common intermediate, but it is the most economical explanation. (b) We could find no evidence that the disproportionation in eq 2 is reversed in trifluoroacetic acid. Thus, various mixtures of Tl(III) and Tl(I) trifluoroacetates afforded no paramagnetic species whose esr spectrum could be observed at various temperatures.

[10] R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, **92**, 412 (1970); *J. Chem. Phys.*, **57**, 1200 (1972).

[11] *Cf.* R. O. C. Norman, D. Allara, and B. C. Gilbert, *Chem. Commun.*, 319 (1965).

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Stereochemistry of Methoxypalladation of 2-Butenes

Sir:

Unfortunately, the suggestion[1] that the mechanism of the Wacker oxidation of olefins involved cis stereochemistry in the rate-determining hydroxypalladation step has been generally accepted and assumed to apply to all the similar reactions in which nucleophilic attack on olefins coordinated to palladium(II) and platinum(II) take place. The cis hydroxypalladation mechanistic suggestion was based primarily on kinetic results, but the data are also consistent with trans stereochemistry for the addition. Thus, the stereochemical path of the methoxypalladation and methoxyplatination of chelating diolefins, which was demonstrated to take place trans in every case,[2] was regarded as anomalous.

In order to explain this assumed anomaly, it was suggested[3–5] that the reaction of the bicyclic chelating diolefins followed the trans stereochemical path for steric reasons. On the basis of an incorrect structural assignment to the 1,5-cyclooctadiene oxypalladation product,[6] it was also suggested[3] that this addition, contrary to the stereochemical path reported originally,[2] took place to give the cis addition product; X-ray structural determinations have verified the original stereochemical assignments, however.[7] The trans stereochemistry has also been attributed either to the inability of the chelating diolefins to rotate 90° from the position perpendicular to the square plane of the metal complex into a position which would favor cis addition by metal and a ligand attached to it,[8] or to the fact that methanol does not coordinate to the metal prior to addition.[9] There is increasing evidence, however, that when a nucleophile such as acetate,[10] chloride,[11] or amine[12] is not coordinated to palladium prior to attack, the addition stereochemistry is trans, even with simple monoolefins.[13]

In the course of a study designed to explore the synthetic utility of the palladium(II)–copper(II) Wacker-type catalyst for the conversion of methanol solutions of monoolefins to β-methoxy esters in the presence of carbon monoxide, the carbonylation of *cis*- and *trans*-2-butene was carried out. In this way we have been able to determine the stereochemistry of the methoxypalladation reaction since, although the intermediate oxymetallation product is unstable, and cannot be isolated, it can be trapped by carbon monoxide "insertion," a reaction which has been demonstrated to proceed with *100% retention at the carbon bearing the palladium.*[14]

The results of the catalytic carbonylation of *cis*- and *trans*-2-butene (Table I) show that in the initial stages of the reaction, stereospecific trans methoxypalladation is observed, yielding exclusively the *threo*- and *erythro*-β-methoxy esters, respectively. In the later stages of the reaction cis–trans isomerization of both butenes becomes increasingly important such that trans methoxypalladation to the cis–trans mixtures yields both erythro and threo products. The rate of methoxypalladation of *cis*-2-butene is approximately three times faster than that of the trans isomer.

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[1] (a) P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964); (b) *ibid.*, **88**, 1595 (1966).

[2] J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966).

[3] P. M. Henry, *Advan. Chem. Ser.*, No. **70**, 151 (1968); *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 14, F17 (1969).

[4] R. F. Heck, *Fortschr. Chem. Forsch.*, 16, 221 (1971).

[5] M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967).

[6] C. B. Anderson and B. J. Burreson, *Chem. Ind.*, 620 (1967).

[7] (a) W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966); (b) C. Panattoni, G. Bombieri, E. Forsellini, B. Crociani, and V. Belluco, *ibid.*, 187 (1969).

[8] B. L. Shaw, *Chem. Commun.*, 464 (1968); *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, 14, F17 (1969).

[9] F. R. Hartley, *Nature (London)*, **223**, 615 (1969).

[10] P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 7305 (1972).

[11] P. M. Henry, *J. Org. Chem.*, 37, 2443 (1972).

[12] A. Panunzi, A. De Renzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **92**, 3488 (1970).

[13] P. M. Henry, *Accounts Chem. Res.*, **6**, 16 (1973).

[14] L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, **94**, 485 (1972).