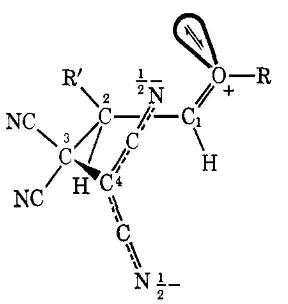

1

(point charges on oxygen and in the center of the line connecting the two anionic nitrogens) and the moments of the cyano groups at C-3 of **1**. The transition state moments, $\mu_{\pm}$, come out as two-thirds of the μ(zwitterion) in Table I. This seems reasonable because (a) the charge separation is not yet complete in the transition state of zwitterion formation and (b) optimal solvation (Kirkwood's concept[4]) is probably not achieved in the transition state.

Though the results are consistent with zwitterionic intermediates in the [2 + 2] cycloadditions of TCNE, the precision of $\mu_{\pm}$ should not be overestimated because the concept[4] is based on many simplifications.

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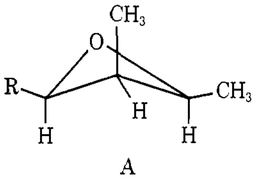
Paterno–Büchi Reactions of Aromatic Aldehydes with 2-Butenes and Their Implication on the Rate of Intersystem Crossing of Aromatic Aldehydes

Sir:

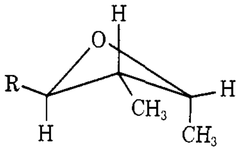
Arnold reported that benzophenone reacted with isomeric 2-butenes to give the same mixture of oxetanes suggesting that the Paterno–Büchi reaction of aromatic carbonyl compounds proceeded *via* the $^3n,\pi^*$.[1] We found that alkanals reacted photochemically with isomeric 2-butenes in a highly stereoselective manner suggesting that the Paterno–Büchi reaction of alkanals proceeded *via* predominantly the $^1n,\pi^*$.[2] This result indicated that the $^1n,\pi^*$ of aldehydes may react with olefins at a rate faster than that of intersystem crossing. The degree of stereoselectivity in the photochemical additions of aldehydes to isomeric 2-butenes may be thus used as a qualitative probe for the rates of intersystem crossing of their $^1n,\pi^*$. This communication deals with the reactions of benzaldehyde and its derivatives with isomeric 2-butenes and their implication on the rate of intersystem crossing in aromatic aldehydes.

Photochemical additions of benzaldehyde (**1a**), *p*-methoxybenzaldehyde (**1b**), *m*-methoxybenzaldehyde (**1c**), 3,4-methylenedioxybenzaldehyde (**1d**), and 2-naphthaldehyde (**1e**) to isomeric 2-butenes were investigated. The reactions were carried out with a Hanovia 450-W Hg arc with a Pyrex filter, and the quantum yield determinations were carried out with an apparatus previously described.[3] The oxetane fractions were isolated by chromatography over alumina. The by-products were alcohols and glycols.[4] Photochemical addition of an aldehyde to 2-butenes may yield four isomeric oxetanes (A–D). *cis*-2-Butene would give oxetanes A and B while *trans*-2-butene would give oxetanes C and D if the additions proceeded stereospecifically. The relative proportions of isomeric oxetanes were analyzed by the areas of low field aliphatic protons in the nmr spectra for **1a–c**. The assignment of isomeric structures was based upon (1) the cis vicinal C–H signals occur at a lower field than the isomeric trans vicinal C–H signals and (2) the cis vicinal C–H signals have higher coupling constants than those of the trans isomers.[2,5,6] The relative amounts of some of the oxetanes formed from **1e** (A and B from *trans*-2-butene and C and D from *cis*-2-butene) were so small such that the low field aliphatic proton signals in the nmr were no longer useful for their quantitative analysis, and they were determined from the integrated areas of the methyl signals in the nmr using 100-Hz scans. Due to the low solubility of **1d** in nonpolar solvents at low temperatures and the poor quantum efficiency of its reactions with 2-butenes, the reactions of **1d** with 2-butenes could not be investigated with the same degree of reliability as the reactions of other aldehydes. The relative amounts of oxetanes formed from **1d** were also estimated from the methyl signals in the nmr. The major source of experimental errors or uncertainties in this work is from the integration of the nmr signals. In all reactions carried out in neat 2-butenes, the unreacted 2-butene was recovered and analyzed for its isomeric composition. It was found that the starting 2-butene had not been appreciably isomerized (<5%). The results are summarized in Table I.

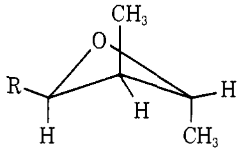
RCHO
1a, R = phenyl
b, R = *p*-methoxyphenyl
c, R = *m*-methoxyphenyl
d, R = 3,4-methylenedioxyphenyl
e, R = 2-naphthyl
f, R = methyl



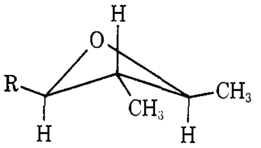
A



B



C



D

The nmr and ir spectra of the oxetane fractions isolated from the irradiations of **1a**, **1b**, or **1c** in neat *cis*- and *trans*-2-butenes were indistinguishable from each other. The results clearly indicated that the reactions proceeded *via* a long-lived biradical inter-

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[1] D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964).

[2] N. C. Yang and W. Eisenhardt, *J. Amer. Chem. Soc.*, **93**, 1277 (1971).

[3] D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

[4] N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Lett.*, 3657 (1964).

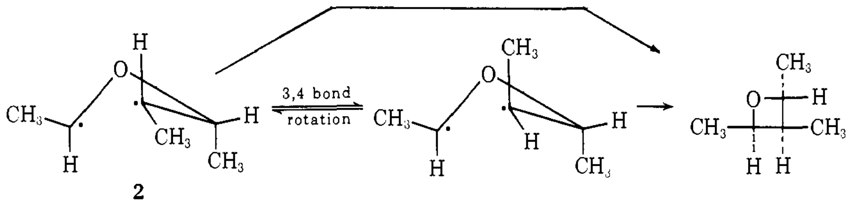
[5] Satisfactory elemental analyses and ir spectra for the oxetane fractions were obtained.

[6] J. J. Beereboom and M. S. von Wittenau, *J. Org. Chem.*, 30, 1231 (1965).

Table I

Aldehyde (concn, M)	Olefin (concn, M)	Oxetanes yield, %	$\phi_{-\mathrm{RCHO}}$[a]	% isomer A	B	C	D	Selectivity[f] ratio
1a (0.5)	*cis*-2-Butene (1.25)[b]	64	0.58 ± 0.02					
	cis-2-Butene (neat)	65		32.5 ± 1.2	5.0 ± 0.4	18.5 ± 2.2	44.0 ± 3.6	
	trans-2-butene (1.20)[b]	66	0.53 ± 0.03					
	trans-2-Butene (neat)	68						
1b (0.18)	*cis*-2-Butene (neat)	53		28.2 ± 0.4	4.9 ± 0.5	17.2 ± 0.4	49.7 ± 0.9	
1b (0.15)	*trans*-2-butene (neat)	43						
1c (0.15)	*cis*-2-Butene (neat)	63	0.14 ± 0.01	30.0 ± 1.7	3.6 ± 1.0	19.1 ± 1.3	47.3 ± 2.1	
1c (0.15)	*trans*-2-Butene (neat)	59	0.13 ± 0.01					
1d (0.03)	*cis*-2-Butene (neat)	42	<0.005	41.0 ± 7.5	22.8 ± 8.1	10.7 ± 1.9	25.5 ± 1.8	1.76:1
1d (0.07)	*cis*-2-Butene (4)[c]	50		36.6 ± 3.9	24.1 ± 0.9	7.9 ± 3.9	31.4 ± 0.1	1.54:1
1d (0.04)	*trans*-2-Butene (neat)	..[d]	<0.005	13.7 ± 1.3	3.6 ± 2.1	30.5 ± 3.5	52.2 ± 4.3	4.78:1
1d (0.08)	*trans*-2-Butene (4)[c]	55		15.1 ± 0.1	5.5 ± 2.0	28.2 ± 1.2	51.2 ± 1.0	3.85:1
1e (0.08)	*cis*-2-Butene (4)[c]	44	0.04 ± 0.01	42.2 ± 0.2	37.8 ± 1.9	3.4 ± 0.1	16.6 ± 1.5	4.00:1
1e (0.03)	*cis*-2-Butene (neat)	57		42.3 ± 1.9	36.6 ± 1.8	2.9 ± 0.7	18.2 ± 2.9	3.75:1
1e (0.11)	*trans*-2-Butene (4)[c]	39	0.02 ± 0.002	3.2 ± 0.7	3.2 ± 0.4	36.2 ± 0.4	57.4 ± 1.3	14.6:1
1e (0.05)	*trans*-2-Butene (neat)	64		3.1 ± 0.3	3.2 ± 0.4	35.3 ± 0.7	58.4 ± 1.4	14.8:1
1f (0.55)	*cis*-2-Butene (5)[c]	..	0.16 ± 0.005[e]	48.1 ± 0.7	40.6 ± 0.6		11.3 ± 1.9	9:1
1f (0.58)	*trans*-2-Butene (5)[c]	..	0.13 ± 0.008[e]	4.6 ± 0.8	42.0 ± 2.3		53.4 ± 3.0	21:1

[a] Measured in 4 M solutions of 2-butene in *n*-hexane. [b] In cyclohexane as the solvent. [c] In *n*-hexane as the solvent. [d] Spoiled experiment. [e] Reference 2. [f] Isomer ratio, (A + B)/(C + D) for *cis*-2-butene and (C + D)/(A + B) for *trans*-2-butene. In the case of **1f**, (A + B)/D for *cis*-2-butene and (B + D)/A for *trans*-2-butene.



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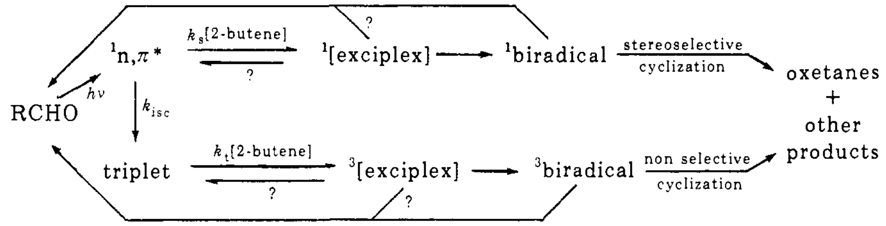
(1)

Scheme I



mediate which had attained all four conformations in equilibrated proportions before their cyclizations to form oxetanes. The formations of A and D were favored over those of B and C approximately by a 3:1 ratio. This preference may be attributed to the favorable conformations of biradicals in the transition states during the cyclization as they contain both the R and the 4-methyl groups in the pseudoequatorial conformations (e′).

The photochemical additions of 2-naphthaldehyde (**1e**) to butenes, like those of acetaldehyde (**1f**), are clearly stereoselective. There was no detectable variation in stereoselectivity in oxetane formation from **1e** when the concentrations of 2-butenes were increased from 4 to *ca.* 11 M (neat). At the first glance, the **1f**–2-butene reactions appear to be more stereoselective than those of **1e**. This actually may not be the case. The loss of stereoselectivity during the addition may be attributed to the rotation around the 3,4 bond in the biradical intermediate. Among the three major conformations at C-2 and C-4 of the biradical intermediate (e′e′, e′a′, and a′e′) formed in the addition of **1f** to 2-butenes, two of them (e′a′ and a′e′) will yield the same adduct whether or not the cyclization occurs before or after the 3,4 bond has rotated; for example, the biradical in conformation **2** (R = CH_3, e′a′) formed from **1f** and *cis*-2-butene will give only the oxetane B (or C) (reaction 1), while those formed from aromatic aldehydes will give a mixture of B and C. The additions of **1d** to 2-butenes appear to be an intermediate case between those of **1e** and benzaldehydes **1a–c**.

Based upon the contributions from various laboratories,[1,2,7,8] the Paterno–Büchi reaction of aldehydes and 2-butenes may be formulated as in Scheme I. The stereoselectivity of oxetane formation will depend on the relative rates of ^{1}[exciplex] formation (k_s[2-butene]) and intersystem crossing (k_{isc}). It has been suggested that the first-order coupling among various excited states of carbonyl compounds may be represented as in Scheme II.[9] The ^{1}n,π* of a carbonyl compound is coupled vibronically with the ^{3}n,π* and spin orbitally with the ^{3}π,π*. The degree of first-order coupling between a singlet and a triplet state and thus the rate of intersystem crossing may be es-

[7] R. A. Caldwell and S. P. James, *J. Amer. Chem. Soc.*, **91**, 5184 (1969).

[8] I. H. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970).

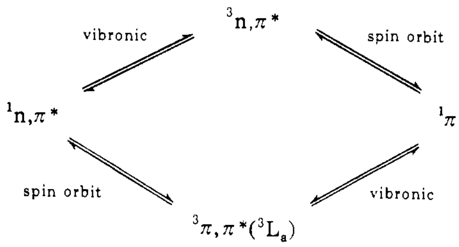
[9] A. A. Lamola, *J. Chem. Phys.*, 47, 4810 (1967).

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 $^1n,\pi^*$ and $^3n,\pi^*$ 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 $^1n,\pi^*$ and the $^3\pi,\pi^*$.[12] In a series of aromatic aldehydes, the k_{isc} will decrease as the ΔE between the $^1n,\pi^*$ 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 $^1n,\pi^*$. 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_8[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 $^1n,\pi^*$ of carbonyl compounds is the intersystem crossing. Aliphatic carbonyl compounds exhibit weak but detectable fluorescence ($\phi_f \sim 0.001$).[13] If the $^1n,\pi^*$ 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 $^1n,\pi^*$ under our experimental conditions.

If the intersystem crossing of the $^1n,\pi^*$ of aldehydes is the composite of its vibronic coupling with the $^3n,\pi^*$ 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 $^1n,\pi^*$ 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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(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).

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