matographic analysis performed after addition of Ce(IV), which in duplicates showed 1.82 ± 0.11 and 1.77 ± 0.07 moles of N_2 for each osmium. In blank experiments using $(NH_3)_5OsN_2^{2+}$, it was shown that 95% of the theoretical yield of N_2 is obtained and that excess Ce(IV) does not produce N_2 from coordinated NH_3.

The analytical results constitute a strong case for the formulation of the cation as $(NH_3)_4Os(N_2)_2^{2+}$. Splitting of the carbon monoxide stretching mode is observed when these are located in the *cis* position.[11–13] By analogy we are inclined to ascribe the splitting observed in the N≡N stretch to the same kind of effect, and on this basis suggest that the N_2 molecules in the new complex $Os(NH_3)_4(N_2)_2^{2+}$ are located *cis* to each other.

The ion $Os(NH_3)_4(N_2)_2^{2+}$ which we have prepared is probably the trace component reported by Borod'ko, *et al.*,[10] as present in the preparation[9] of $Os(NH_3)_5N_2^{2+}$ by the hydrazine method. In one preparation of $Os(NH_3)_5N_2I_2$ we also observed two weak lines at somewhat higher frequency than 2035 cm^{-1}, which is characteristic of the mononitrogen complex. Borod'ko, *et al.*, suggest three states of combination on the basis of the infrared spectra of the unpurified material; in view of our work, two suffice since the *cis*-dinitrogen complex shows two lines in the infrared spectra.[14]

The thermal stability of the dinitrogen complex is much less than that of $Os(NH_3)_5N_2^{2+}$. On heating a solution of the former complex over *ca.* 50°, the solution turns dark.

It is interesting that when $Ru(NH_3)_5N_2^{2+}$ is treated with nitrous acid under conditions similar to those described, the reaction does not follow the course as outlined for $Os(NH_3)_5N_2^{2+}$. Nitrogen is released essentially quantitatively, and a nitrosyl complex is the major ruthenium-containing product. This kind of reaction may explain why Jordan, *et al.*,[15] failed in their attempt to prepare a nitrogen-containing complex by the reaction of a Ru(II) azide complex with nitrous acid.

The rapid diazotization of NH_3 in $Os(NH_3)_5N_2^{2+}$ is remarkable in itself. From the observation that the pentaammine is consumed completely within 1 min, we calculate a lower limit for the specific rate of reaction of HONO with H_3NOs^{II} to be 1 M^{-1} sec^{-1}, a value which can be compared with 2.8×10^{-4} M^{-1} sec^{-1} as reported[16] for HONO reacting with NH_4^+. The rapid diazotization of coordinated NH_3 is by no means a general phenomenon. Thus, when an excess of nitrous acid is added to $Ru(NH_3)_5N_2^{2+}$ and the mixture is left for an extended period of time, the amount of N_2 formed is not materially greater than that observed with an equivalent amount of nitrous acid. On this basis we estimate the specific rate for the reaction of HONO with NH_3 in $Ru(NH_3)_5NO^{3+}$ (this is, the major product of the N_2 elimination reaction) to be less than 2×10^{-3} M^{-1} sec^{-1}.

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On the Mechanism of Energy Transfer from n,π* Triplet State of Carbonyl Compounds to Simple Olefins

Sir:

Electronic energy transfer is a rapidly expanding subject of current interest.[1] The process involves the transfer of electronic excitation energy from a donor to an acceptor which leads to the electronic excitation of the acceptor. Energy transfer from a triplet donor to an acceptor occurs readily when the triplet energy level of the donor is higher than that of the acceptor.[2] The accepted mechanism for such transfer is that of a collisional interaction between the donor and the acceptor with a rate approaching that of the diffusion-controlled process.[3] Although energy transfer from the triplet states of carbonyl compounds to simple olefins has been noted in several isolated instances, the detailed mechanism of such processes has not been investigated.[4] *One specific interesting aspect of these transfers is that there may be insufficient energy in the triplet state of carbonyl compounds to be transferred into the planar triplet state of simple olefins.*

The lowest planar triplet energy level of ethylene was measured by Evans to be 82 kcal/mol (28,700 cm^{-1}), and he reported that alkyl substituents had little effect on the triplet energy levels of conjugated unsaturated compounds.[5] Substitutions of hydrogens by alkyl groups on ethylene may lower the triplet energy level, but the exact magnitude of this decrease is not known. The n,π* triplet energy levels of phenyl carbonyl compounds have been well characterized and range from 66 to 73 kcal/mol (24,000–25,800 cm^{-1}),[6] values substantially below that of ethylene. The triplet energy level of an olefin depends on the angle of twist around the axis connecting the two carbon atoms, and the minimum energy level is reached when the angle of twist is 90° from the planar configuration.[7] A distinct possibility exists that, after the energy transfer, the olefinic acceptor has a geometry different from its ground state, an apparent deviation from the Franck–Condon princi-

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Table I

Donor (M)	E_T, kcal/mol, in hydrocarbon	Olefin (M)	ϕ –>C=O	ϕ_{oxetane}	$\phi_{t \to c}$	$\phi_{c \to t}$	$\phi_{\text{en tr}}$[a]
Benzaldehyde (0.5)	71.5	Ia (1)[b]	0.60 ± 0.02[d]	0.45 ± 0.02	0.12 ± 0.01		0.30 ± 0.03
Benzaldehyde (0.5)	71.5	Ib (1)[c]	0.60 ± 0.03[d]	0.45 ± 0.02		0.18 ± 0.02	
Benzophenone (0.3)	68.0	Ia (1)[b]	0.20 ± 0.02[e]	0.16 ± 0.01	0.24 ± 0.02		0.60 ± 0.04
Benzophenone (0.3)	68.0	Ib (1)[c]	0.20 ± 0.02[e]	0.16 ± 0.01		0.36 ± 0.02	
Triphenylene (0.05)	66.5	Ia (1)[b]			<0.004		<0.004

[a] The quantum yield of energy transfer is taken as the sum of quantum yields of olefin isomerization, $\phi_{t \to c}$ and $\phi_{c \to t}$. [b] The starting olefin was analyzed by vpc to be better than 99.5% pure. [c] The starting olefin was analyzed by vpc to be better than 98.5% pure. [d] The quantum yield of benzaldehyde consumption was measured with 0.5 M n-undecane as an internal standard. [e] The quantum yield of benzophenone consumption was measured with 0.3 M n-octadecane as an internal standard.

ple. Such a possibility has been suggested by Hammond and Saltiel in the energy transfers from various triplet donors to stilbene.[8]

In our recent work on the Paterno–Büchi reaction, there were indications that the triplet state of carbonyl compounds may have transferred their excitation energy to the olefin. In order to ascertain whether bimolecular energy transfer may occur competitively with the Paterno–Büchi reaction, the photochemical reactions of benzaldehyde and of benzophenone with isomeric 3-methyl-2-pentenes (Ia and Ib) were investigated. In these systems, energy transfer will result in the isomerization of the starting olefins. In a parallel experiment for comparison we used triphenylene as the photosensitizer for the isomerization of 3-methyl-2-pentene. The irradiations were carried out in benzene solution with monochromatic light of 3130 Å in an apparatus previously described.[9] The reactions are zero order in carbonyl compound concentration even after 20% of the compound was consumed. The results are summarized in Table I.

The results clearly indicated that in the systems investigated the Paterno–Büchi reaction occurs competitively with bimolecular energy transfer to the olefin, resulting in the isomerization of the olefin. Benzophenone, in spite of a lower triplet energy than that of benzaldehyde, transfers its triplet energy more efficiently to the olefins than benzaldehyde. Triphenylene, although it has a triplet energy only slightly below that of benzophenone, is completely ineffective as a sensitizer.

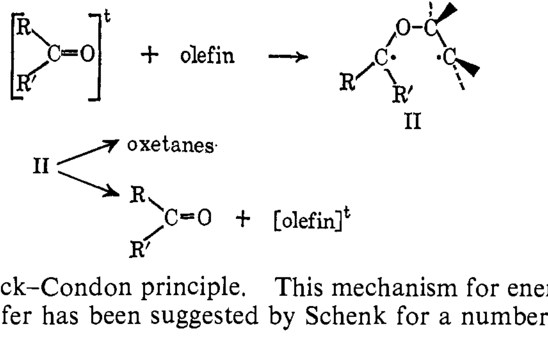
In order to investigate the nature of the intermediate in the oxetane formation and in the olefin isomerization, the quenching of three systems with various concentrations of 2,3-dimethyl-1,3-butadiene was carried out: benzaldehyde and Ia, benzaldehyde and Ib, and benzophenone and Ia. If the triplet state of the carbonyl compound is the common intermediate in both the oxetane formation and the olefin isomerization, a plot of ϕ_0/ϕ against [Q] for either of these two processes will lead to identical Stern–Volmer plots. The plots will have a slope of $k_q\tau$ and an intercept of 1; ϕ_0/ϕ is the ratio of the quantum yield at zero quencher concentration to the quantum yield at various quencher concentrations, [Q] is the quencher concentration, k_q is the bimolecular quenching constant, and τ is the lifetime of the triplet state. We found the slopes for these

$$\frac{\phi_0}{\phi} = 1 + k_q[\text{Q}]\tau$$

two processes to be 6.3 ± 0.3 M^{-1} for benzaldehyde and Ia, 6.0 ± 0.5 M^{-1} for benzaldehyde and Ib, and 25.0 ± 4.0 M^{-1} for benzophenone and Ia. These results indicate that (1) the triplet state of the carbonyl compound is the common intermediate for both the oxetane formation and the olefin isomerization, and (2) the bimolecular rate constants for olefin isomerization or energy transfer in these systems are substantially less than that for collisional transfer or diffusion-controlled rate processes.

If collisional energy transfer were the only mechanism for energy transfer from the triplet state of carbonyl compounds to simple olefins, one would expect benzaldehyde to be a more efficient donor than benzophenone, due to the higher triplet energy level of the former, and triphenylene to sensitize the isomerization of Ia in measurable quantum efficiency. Our results suggest that at least a part of the energy transfer from the triplet state of carbonyl compounds to simple olefins occurs to the nonplanar triplet level of the olefin, and that such transfer occurs efficiently only from compounds with low-lying n,π^* triplet states.

In Paterno–Büchi reactions, the oxetane formation may occur *via* attack on the π system of the olefin by the electron-deficient oxygen of the excited carbonyl function to give a biradical intermediate (II) in the initial step (reaction 1). Energy transfer may proceed *via* the same intermediate. Schematically, the biradical intermediate may cyclize to give the oxetanes (reaction 2) or dissociate to give back the carbonyl compound and the triplet state of the olefin in a nonplanar configuration (reaction 3). In this scheme, the energy transfer involves two steps, and there is no violation of the Franck–Condon principle. This mechanism for energy transfer has been suggested by Schenk for a number of



(1)

(2)

(3)

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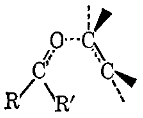
photosensitized reactions,[10] but our results define the scope and the limitation of such a mechanism in energy transfer to olefins; *i.e.*, this mechanism operates efficiently only with donors possessing a low-lying n,π^* triplet state.

Alternatively, the partially vacant n orbital of the n,π^* triplet state of the donor may polarize the π system of the olefin sufficiently during the energy transfer so that the olefin moiety in the transition state (III) is no longer planar. The dissociation follows to give back the carbonyl compound and the olefin triplet state in a nonplanar configuration. This point of view, which is favored by Hammond,[8] will also account for all of our current results. Our work suggests that such an energy transfer may occur efficiently only with a highly polarizing donor and a polarizable acceptor. Work is being continued with the hope of clarifying these points.



III

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Conformational Changes of the Ribose Group in Dinucleoside Mono- and Diphosphates. Temperature Dependence[1]

Sir:

A knowledge of the structure and interactions of simple, model oligo- and polyribonucleotides is essential if an understanding is to be achieved of the factors governing the conformational stability of nucleic acids in solution. Recent studies,[2-15] employing a variety of spectroscopic techniques, have shown that adjacent bases of purine oligo- and polyribonucleotides are capable of forming intramolecular stacks in aqueous solution under appropriate conditions of temperature and pH. Although it is reasonable to expect that the base-stacking interaction will be accompanied by a conformational change of the ribose phosphate backbone, evidence for such a change is lacking at present. In order to obtain information regarding this point we have studied the temperature dependence of the ribose proton spectra for a variety of mono- and dinucleotides. Since the magnitude of a vicinal proton-proton coupling constant is closely related to the dihedral angle between the protons,[16] a study of the temperature dependence of the ribose proton spectra should provide direct evidence for any conformational change of the ribose ring in the stacking process.

The ribose spectra[17] of the dimers[18] consist of two doublets in the range 365-410 cps (downfield from external TMS) and a complex group of signals located in the region of the residual HDO signal. The doublets can be assigned to the $H_{1'}$ protons of the nonequivalent ribose groups and are due to spin coupling with the respective $H_{2'}$ protons.

A summary of the $J_{H_{1'}H_{2'}}$ values for a number of mono- and dinucleotides, over a range of temperatures, is given in Table I. For mononucleotides the magnitudes of $J_{H_{1'}H_{2'}}$ lie between 5.0 and 5.5 cps and are in agreement with values reported in the literature.[19-21] No significant temperature dependence is noted for these couplings in the range studied. In contrast the $J_{H_{1'}H_{2'}}$ couplings for the dimers are all less than the values for corresponding 3′ and 5′ monomeric nucleotides. Furthermore, all dimer coupling constants, except that of the pA-c-p moiety of ApA-c-p, are markedly temperature dependent. In ApA, for example, there is approximately a twofold decrease in

Table I. $J_{H_{1'}H_{2'}}$,[a] of Several Mononucleotides and Dinucleoside Mono- and Diphosphates

Temp, °C	ApA[b] Ap	pA	ApA-c-p Ap	pA-c-p	GpA Gp	pA	AMP-3′	AMP-5′
4	2.3	2.1			2.1	3.0	6.1	5.5
7			2.8	2.9				
15	2.5	2.2	3.7	3.0				
20								5.1
28	3.1	2.8	4.0	3.2			5.6	
35					4.0	4.0		5.2
55			4.6	3.2	4.5	4.2	5.2	5.1
62	4.5	4.1						
67				3.1			5.3	
71	4.7	4.5			5.4	4.3		5.3
80							5.1	

[a] Errors in the *J* values are ±0.10 cps. [b] AMP-3′ = adenosine 3′-monophosphate, ApA = adenylyl-(3′→5′)-adenosine; ApA-c-p = adenylyl-(3′→5′)-adenosine cyclic 2′,3′-monophosphate, etc.

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