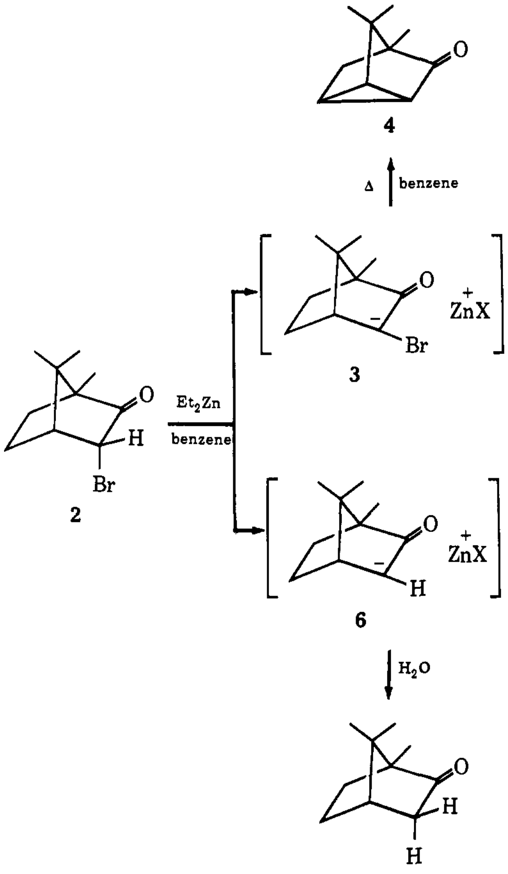
Scheme II



come from **3** or simply represent virgin starting material.

It is for good reasons that the α-elimination route to ketocarbenoids remained unknown for so many years. Generation of the requisite α-haloenolates is often complicated by competing Favorskii rearrangement, Darzens-type condensation, or alkylation of the newly formed enolate by neutral starting material. We have overcome these difficulties with a hindered, nonenolizable dibromo ketone as the substrate and point out here that our method may be confined to systems having these characteristics. Enolates of other α-halo ketones[2] and α-halo esters[12,13] have also been prepared recently by different methods.

The final expulsion of halide represents a more serious problem with this route to ketocarbenoids, for α-haloenolates, once formed, exhibit a relatively high degree of stability.[2,12] No doubt the carbonyl group diminishes greatly the electron density at the site of halogen attachment. Indeed, House has reported[2] that the lithium enolates of several α-chloro ketones survive virtually unchanged after 24 hr at room temperature in dimethoxyethane and fail to give carbenoid products; our own haloenolate **3** loses bromide only slowly at 80° with a half-life of several hours. Certainly the nature of both the halide and the metal should affect the ease of this reaction quite markedly, as with other α eliminations,[1,14] and the search for milder methods of producing carbonyl-conjugated carbenes and carbenoids in this manner continues in our laboratories.

With the feasibility of α elimination adjacent to a ketone now established, the intermolecular trapping of a ketocarbenoid so generated becomes a realistic goal. Not surprisingly, added olefins fail to intercept the camphor carbenoid which possesses an efficient internal trap. We have achieved some success in this regard, however, with another dibromo ketone and shall report on these findings shortly.

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Reinterpretation of "Nonvertical" Triplet–Triplet Energy Transfer and the Photoisomerization of Stilbene

Sir:

The idea of "nonvertical" triplet–triplet energy transfer introduced by Hammond and Slatiel[1] is not a well substantiated concept and deserves further investigation. The mechanism which led these authors[1] to the above concept may be abstracted as follows

$$\begin{aligned} D^* + c &\longrightarrow D + T \quad k_1 \\ D^* + t &\longrightarrow D + T \quad k_2 \\ T &\longrightarrow c \quad k_3 \\ T &\longrightarrow t \quad k_4 \end{aligned}$$

where D and D* are respectively the ground and the triplet states of sensitizer, c and t are respectively *cis*- and *trans*-stilbene, and T is its triplet state. Then, the photostationary ratio of isomers, expressed by

$$[c]_s/[t]_s = (k_2/k_1)(k_3/k_4)$$

reflects the "activation ratio" (k_2/k_1) which is expected to increase as the sensitizer triplet energy is lowered. Experimentally, however, as the triplet excitation energy of the sensitizer decreases below 17 kK, the activation ratio drops.[2,3] This unexpected finding was rationalized by postulating "nonvertical" and "nonspectroscopic" excitation of *cis*-stilbene to triplet state, and the term "nonvertical energy transfer" was introduced. The importance of this concept lies in the nature of the excitation of stilbene. Hammond and Saltiel stressed that *the excitation process is neither spectroscopic nor thermal.* However, it is exactly this excitation mechanism which is not easily understood

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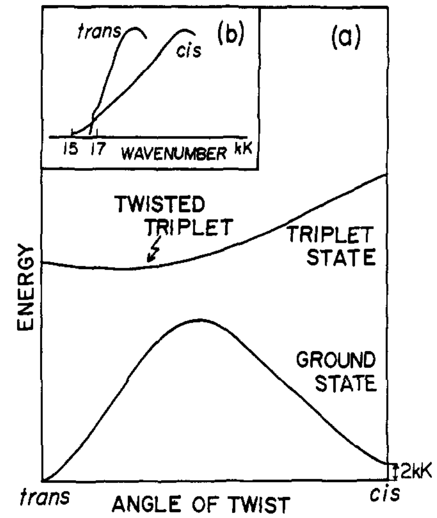

Figure 1. (a) Schematic representation of the potential energy diagrams over the twist angles about the central bond for the ground and triplet excited states of stilbene. (b) The expected ST absorption tails for *trans*- and *cis*-stilbenes.

and which has puzzled us; probably for this reason there have been a number of discussions concerning the validity of the mechanism.

Lamola[4] pointed out that the drop of the activation ratio could also be interpreted on the basis of the contribution of hot bands as well, but no further analyses were given. Bylina[5] showed that the rates of the transfer to stilbene from various sensitizers vary as predicted[6] by the *observed* ST absorption spectra of stilbenes. However, Bylina's contribution has little to do with the validity of "nonvertical" energy transfer. The correlation between the predicted and the observed transfer rates was given only for sensitizers whose triplet energies are *higher* than ~19 kK and which show no unexpected behaviors in the Saltiel plot.[1] "Nonvertical" energy transfer is concerned with sensitizers of much lower energy. Furthermore, even with Bylina's contribution, it is not known *why* the activation ratio should decrease for low-energy sensitizers. Liu[7] proposed a quenching in which energy transfer from the second triplet state of anthracene to stilbene is considered. However, apart from the query of whether the transfer from the second triplet state is generally acceptable for sensitizers other than anthracene, the kinetic scheme does not necessarily eliminate the possibility of transfer from the *first* triplet state. Thus, there seems no unequivocal and clear-cut interpretation which affirms or negates the concept of "nonvertical" energy transfer.

In the present paper, we present a new interpretation which clearly accounts for the drop of activation ratio[1] by an easily understandable and clear-cut mechanism. The importance of the present contribution is that (1) not only the location but also the *spectral distribution* of the ST absorption spectra of stilbenes are considered, and (2) the previous misassignment of the ST absorption is corrected.

The underlying facts which form the bases of the present interpretation are summarized as follows. (1) The ground state of *cis*-stilbene is unstable by 2 kK as compared with *trans*-stilbene.[8] (2) The triplet state of stilbene is stable at an intermediate configuration between the trans and the cis,[9-11] and, as is evident from the existence of the reverse transfer to yield only the trans isomers,[2,3] the configuration of the stable triplet state is close to the trans configuration.[1] (3) The first shoulder in the ST absorption spectrum of *trans*-stilbene appears[12] at 17 kK, and from item (2), the previous assignment[12,13] of this band to the (0,0) transition is probably correct. From these data the potential energy curve as a function of the twist angle may be constructed as shown[14] in Figure 1a. Then, the following features of the ST absorption spectra of stilbene are deduced:[15] (a) the Franck–Condon maximum of *cis*-stilbene lies at higher energy than that of *trans*-stilbene, (b) different from the widely quoted assignment,[18] the (0,0) transition of *cis*-stilbene should be located at ~15 kK, 2 kK lower than that of *trans*-stilbene. Then, the ST absorption spectra of the two isomers *at low temperatures* (ignoring the contribution of hot bands) would tail as schematically and exaggeratedly shown in Figure 1b.

Now, the transfer rate is roughly proportional to the overlap of the ST transition bands in the sensitizer and stilbene. As the triplet energy of the sensitizer decreases, the overlap of course decreases. In view of the absorption tail shown in Figure 1b, these factors dictate that, *the transfer rate decreases more rapidly for the trans isomer than for the cis.* This tendency is more pronounced when the contribution of hot bands is considered. Thus, the expected absorption tail at low temperatures alone would account for the decrease of the activation ratio, and this decrease would be accelerated at higher temperatures. The experimental findings[1,16] are satisfactorily interpreted in this way. For a sensitizer whose triplet energy is lower than ~15 kK, the overlap of the bands is zero at low temperatures, and the excitation of stilbene should entirely be due to the absorption hot bands. This is consistent with the observed relations[16] between the transfer rates and the sensitizer energy.

Finally, we wish to clarify the difference between the present interpretation and that of Hammond and Saltiel.[1] The absorption tails for *cis*-stilbene shown in Figure 1b are due to nonvertical light absorption, and in this sense, the present mechanism still has to involve nonvertical excitation of stilbene. However, the concept of "nonvertical" excitation differs greatly. Hammond and Saltiel claimed that the excitation is "nonspectroscopic," whereas the mechanism proposed here is interpreted within the framework of the "spectroscopic" transitions. The details of the present work with critical evaluation of related works will be presented elsewhere.

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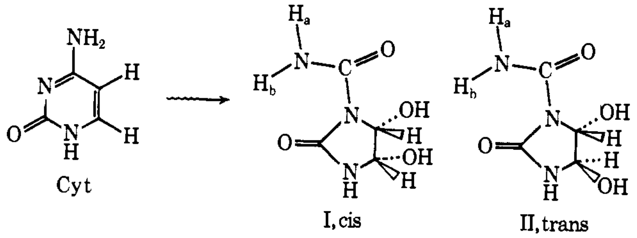
Radiation Chemistry of Nucleic Acids. Isolation and Characterization of Glycols of 1-Carbamylimidazolidone as Products of Cytosine[1]

Sir:

We wish to report the isolation of two major isomeric products (*g* value 0.075) obtained from the radiolysis of cytosine in aerated aqueous solution. These products characterized by spectral and X-ray diffraction analyses are identified as *cis*- (I) and *trans*- (II) 1-carbamylimidazolidone-4,5-diols.



A 1.9×10^{-2} *M* aqueous solution of Cyt[2] (375 ml, pH ~6) was saturated initially and at 2-hr intervals with oxygen and irradiated for 10 hr.[3] The absorbancy decrease was ~5% at λ_{max} 267 nm. The irradiated solution was evaporated (<35°) until dry, and the residue extracted with methanol. The combined extracts were concentrated, applied on Whatman No. 3 paper, and eluted with *n*-propyl alcohol–water (10:3). Material with an R_f value of 0.41 gave a positive Fink's test[4] and was rechromatographed with *sec*-butyl alcohol–water (5:2). Materials with R_f 0.26 (II) and 0.35 (I) were each twice rechromatographed, both fractions remaining somewhat impure. II was purified by washing the residue with a small amount of absolute methanol to eliminate the cis product and was then recrystallized from absolute methanol–chloroform (9:1). The crystals of I were obtained from concentrated methanolic solution after long standing.

The cis isomer melts at 119–122° dec and II at 175–176° dec. Uv spectra of both have only end absorption and show no appreciable changes after refluxing for up to 8 hr at pH ~2 or ~12. The ir (KBr) shows peaks ν_{OH} 3320; ν_{C-OH} 1150, 1115 (1095), 1075, and 1060 (1055); $\nu_{C=O}$ 1667; δ_{NH_2} 1582; and $\nu_{C=O}$ ureide 1739 (1751) cm^{-1} for cis and for trans except where indicated by parentheses.

The nmr ($(CD_3)_2SO$) has peaks of δ 4.94 (s, 1, C_5H), 5.55 (s, 1, C_4H), 6.66 (s, 1, C_5OH), and 6.96 (s, 1, C_4OH) for I; of δ 4.91 (s, 1, C_5H), 5.51 (s, 1, C_4H), 6.60 (s, 1, C_5OH), and 6.90 (s, 1, C_4OH) for II; and of δ 7.39 (s, 1 $CONH_a$), 7.90 (s, 1, $CONH_b$), and 8.70 (s, 1, NH) for both. The addition of D_2O eliminates all signals except C_5H and C_4H. Since NH_2 proton signals have a difference of ~0.5 ppm in chemical shifts, the two are nonequivalent. However, H bonding between $CONH_b$ and C_2O is probably weak (*cf.* X-ray diffraction study), since a strong intramolecular H bonding usually entails a difference of ~2 ppm in chemical shifts.[5]

The mass spectra of both fail to give the parent ions. However, their silyl derivatives, obtained by treatment with $F_3CON[Si(CH_3)_3]_2$ in pyridine (Regisil No. 270001), gave virtually indistinguishable spectra with molecular ions occurring at mass 449, along with abundant M − 15 ions at mass 434. This indicates a tetratrimethylsilyl derivative of $C_4H_7N_3O_4$ which was further confirmed by elemental analysis.

This suggests that both isomers have a glycol moiety and behave like a hCyt.[6] Yet, the NH_2 group, being stable, differs from the expected property of facile deamination observed for hCyt derivatives.[6] Although the nmr spectra also indicate the presence of glycol and an NH_2 group, they do not have the pattern displayed by analogous glycols of Thy,[7] a six-member heterocyclic derivative.

The data being insufficient for an unequivocal structural assignment, analysis by X-ray diffraction was required. Data for a single crystal of the trans isomer were collected on a four-circle fully automated computer-controlled diffractometer. The space group is *Pbca* (orthorhombic) with $a = 13.289$ (8), $b = 13.260$ (8), and $c = 7.139$ (4) Å. There is one molecule per asymmetric unit corresponding to a calculated crystal density of 1.71 g/cm^3. The structure was solved using the symbolic addition procedure for centrosymmetric crystals.[8] The atomic coordinates and thermal parameters were refined by least-squares methods and all seven hydrogen atoms were located in a difference map. The *R* factor (agreement between observed and calculated structure factors) for the full set of 1024 independent reflections is presently 6.5%.

The molecular conformation is illustrated in the stereodiagram in Figure 1 which was drawn by a computer using program ORTEP.[9] The C_4OH and C_5OH are trans to one another. The five-membered ring (excluding C_5) plus the carbonyl oxygen on C_2 are planar to within ±0.05 Å with C_5 being 0.18 Å out of the plane. The plane through the amide group is at an angle of ~13° to the above plane. The molecules are held together by an extensive system of H bonding.

Reviewing the uv, ir, nmr, and mass spectral data and elemental analyses of I and II in light of the assigned structure, we found them logically compatible.

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