Acetone-sensitized *cis–trans* Photoisomerization of Octa-2,6-dienes

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Summary A comparison of the acetone-sensitized *cis–trans* photoisomerization of the octa-2,6-dienes and of the pent-2-enes shows that no two bond isomerization per quantum of excitation occurs, $\phi_{tt\rightarrow cc} = \phi_{cc\rightarrow tt} = 0$, and that with respect to diene interconversion, *cis* and *trans* double bonds in the octa-2,6-dienes behave exactly like *cis* and *trans* double bonds in the pent-2-enes.

The *G* value for the radiation induced *cis* → *trans* isomerization of polybutadiene is 2·25 times the *G* value for pure *cis*-but-2-ene.[1] This observation has prompted the suggestion that triplet excitation can migrate along the polymer chain thereby inducing isomerization in several double bonds. A theoretical model describing this migration of electronic excitation has been suggested.[2] The following comparison of the acetone-sensitized photoisomerization of the octa-2,6-dienes and of the pent-2-enes provides a test of this suggestion.

The octa-2,6-dienes were obtained pure by g.l.p.c. separation.[3] Irradiation conditions and experimental procedures were those reported for the pent-2-enes.[4] Limiting quantum yields for high octa-2,6-diene concentrations are $\phi_{tc\rightarrow tt} = 0{\cdot}16$, $\phi_{tc\rightarrow tt} = 0{\cdot}14$, $\phi_{tc\rightarrow cc} = 0{\cdot}07_0$, $\phi_{cc\rightarrow ct} = 0{\cdot}21$, and $\phi_{tt\rightarrow cc} = \phi_{cc\rightarrow tt} = 0$. After prolonged irradiation a photostationary ratio of the three dienes is established, 36·4% *tt*, 47·7% *tc*, and 15·9% *cc*, which does not represent a true photostationary state since the dienes are consumed in unidentified side reactions (g.l.p.c. analysis indicates a complex product mixture). The quantum yield for diene disappearance for a 0·05 M-diene mixture is *ca.* 0·15.

$$\mathrm{A} \xrightarrow{h\nu} {}^1\mathrm{A} \longrightarrow {}^3\mathrm{A} \qquad (1)$$

$${}^3\mathrm{A} + tt \xrightarrow{2k_t} \mathrm{A} + {}^3tp \qquad (2)$$

$${}^3\mathrm{A} + tc \xrightarrow{k_t} \mathrm{A} + {}^3cp \qquad (3)$$

$${}^3\mathrm{A} + tc \xrightarrow{k_c} \mathrm{A} + {}^3tp \qquad (4)$$

$${}^3\mathrm{A} + cc \xrightarrow{2k_c} \mathrm{A} + {}^3cp \qquad (5)$$

$${}^3tp \xrightarrow{k_6} \alpha\, tt + (1 - \alpha)\, tc \qquad (6)$$

$${}^3cp \xrightarrow{k_7} \alpha\, ct + (1 - \alpha)\, cc \qquad (7)$$

$$\begin{tikzcd} {}^3tp \arrow[dr, "k_8"] & & \\ & \text{diradical} \arrow[r] & \text{products} \qquad (8) \\ {}^3cp \arrow[ur, "k'_8"'] & & \end{tikzcd}$$

$${}^3\mathrm{A} \xrightarrow{k_9} \mathrm{A} \qquad (9)$$

The absence of two bond isomerization rules out intramolecular triplet excitation transfer between octa-2,6-diene double bonds. Equations 1—9, where A refers to acetone, *tt*, *tc*, and *cc* to the octa-2,6-dienes, superscripts 1 and 3 to excited state multiplicity, k_t and k_c are rate constants for excitation of *trans* and *cis* double bonds, respectively, p refers to twisted double bonds, and α is the probability for decay of twisted double bonds to *trans* double bonds, account for the data. Comparison of the octa-2,6-diene quantum yields with those obtained for the pent-2-enes[4] indicates that $k_6/(k_6 + k_8) \simeq k_7/(k_7 + k_8') \simeq 0{\cdot}4$. Assuming

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this equality, stationary state expressions 10 and 11 are obtained. If it is also assumed that octadiene double

$$\left(\frac{[tt]}{[cc]}\right)_{\mathrm{S}} = \left(\frac{k_c}{k_t}\right)^2 \left(\frac{\alpha}{1-\alpha}\right)^2 \qquad (10)$$

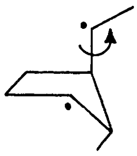
$$\left(\frac{[tc]_{\mathrm{S}}^2}{[tt]_{\mathrm{S}}\,[cc]_{\mathrm{S}}}\right) = 4 \qquad (11)$$

bonds behave exactly like pent-2-ene double bonds, eqn. 10 requires that $([tt]/[cc])_{\mathrm{S}}^{1/2}$ be equal to $([t]/[c])_{\mathrm{S}}$ for the pent-2-enes,[4] in excellent agreement with the observed values of 1·51 and 1·52,[4] respectively. Equation 11 reflects the independent behaviour of the two double bonds predicting closely the observed ratio of $[tc]_{\mathrm{S}}^2/[tt]_{\mathrm{S}}[cc]_{\mathrm{S}} = 3{\cdot}9_3$.

The mechanism gives expressions of type 12 for the

$$\frac{1}{\phi_{tt\rightarrow tc}} = \left(\frac{1}{1-\alpha}\right)\left(\frac{k_6+k_8}{k_6}\right)\left(1+\frac{k_9}{2k_t[tt])}\right) \qquad (12)$$

dependence of the isomerization quantum yields on diene concentration. The observations for *trans,trans*-octa-2,6-diene are in accord with equation 12, giving an intercept to slope ratio, $2k_t/k_9 = 165\ \mathrm{M}^{-1}$, which is double the intercept to slope ratio obtained for *trans*-pent-2-ene isomerization, $k_t/k_9 = 81\ \mathrm{M}^{-1}$.[4]



(I)

The side reactions are no doubt related to the intramolecular cycloadditions observed with hexa-1,5-diene[5] and the dimethyl octa-2,6-diene-1,8-dioates.[6,7] The absence of two bond isomerization in the octadienes suggests that formation of the suggested biradical intermediates, *e.g.* (I), is not revertible.

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