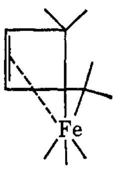
could with some justification be described in terms of σ–π structure **5** rather than the "classical" π-complex interaction **6**. However, it must be emphasized that structure **5** expresses the bonding in terms of the valence-bond approximation, overly emphasizing the presence of Fe–C σ bonds. The structure actually results from the bonding and back-bonding interactions between the butadiene and $Fe(CO)_3$ moieties which must give rise to changes in the bond lengths in the four-carbon chain.[6] Accordingly, the bonding of all carbon atoms to Fe is of an intermediate type which cannot be expressed by one localized VB structure alone. Recognizing the difficulties in formulating a complicated bonding situation, we prefer the less committal structure **6**.[7]


5


6

The interaction of the second $Fe(CO)_3$ group with atoms C_7, C_8, C_9, and C_{10} appears to be the first reported X-ray structural information on an iron tricarbonyl complex of a 1,4-diene system. The $Fe_2\cdots C_9$ and $Fe_2\cdots C_{10}$ distances (2.122 (13) and 2.131 (13) Å) are slightly shorter than the $Fe_2\cdots C_7$ and $Fe_2\cdots C_8$ lengths (2.172 (13) and 2.175 (13) Å), although all the $Fe_2\cdots C$ (olefin) distances are longer than their $Fe_1\cdots C$ counterparts. These longer distances are consistent with a somewhat weaker bonding of an $Fe(CO)_3$ group to a nonconjugated diene than to a 1,3-diene as is suggested by simple Hückel theory.[5,7] In $Fe(CO)_3$ complexes with 1,3-dienes, the projection of one of the carbonyl groups onto the best plane defined by the four carbon atoms of the diene group is almost perpendicular to the central C–C bond. When the $Fe(CO)_3$ group complexes with the 1,4-diene portion of the present structure, the projection of one of the carbonyl groups onto the best plane defined by the C_7, C_8, C_9, and C_{10} atoms is almost perpendicular to the C_7–C_8 bond.

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[6] For compilations of the dimensions in the complexed "butadiene" moiety, see M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **8**, 1941 (1969); S. M. Johnson and I. C. Paul, *J. Chem. Soc. B*, in press.

[7] For a recent review and discussion of the bonding in these complexes, see M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967).

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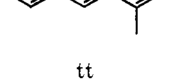
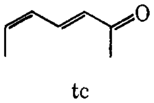
Mechanistic Aspects of 3,5-Heptadien-2-one Photoisomerization

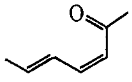
Sir:

Recent reports of the photoisomerization of 2,4-hexadiene have demonstrated the occurrence of a two-bond isomerization in which both double bonds of a hexadiene molecule are isomerized as the result of absorption of one photon.[1,2] The quantum yield data show that a common triplet state or rapidly equilibrating isomeric triplet states are intermediates in the isomerization.[2] We wish to report preliminary results of our closely related study, the photoisomerization of 3,5-heptadien-2-one, which does not proceed *via* one common excited state.

Irradiation of any of the three known geometric isomers of 3,5-heptadien-2-one (tt, tc, and ct)[3,4] as a 10^{-3} *M* solution in ethyl ether results in rapid formation of the same photostationary state of these three isomers. No other products were detected. Glpc analysis of isomer mixtures were carried out using a 20 ft × $^1/_4$ in. 5% FFAP on 60–80 mesh Anakrom AB column at 100°. The photoenol, 6-hydroxy-1,3,5-heptatriene, is not a likely intermediate because its formation would require hydrogen transfer *via* an eight-membered ring and because no conjugated dienones were detected.[5]


tt


tc


ct

Quantum yields (Table I) were determined by irradiation of pure[6] samples of tt, tc, and ct for short periods to ensure low conversion (2–8%) and glpc analysis of the products. A check of the accuracy of the quantum yields was made by using them along with measured

Table I. Quantum Yields for Photoisomerization of 3,5-Heptadien-2-one[a,b]

Wavelength, nm	$\Phi_{tt\to ct}$	$\Phi_{tt\to tc}$	$\Phi_{tc\to tt}$	$\Phi_{tc\to ct}$	$\Phi_{ct\to tt}$	$\Phi_{ct\to tc}$
254	0.28	0.14	0.17	0.25	0.36	0.12
313	0.24	0.15	0.28	0.17	0.23	0.13

[a] Determined for *ca.* 2 × 10^{-2} *M* solutions at room temperature.
[b] Average uncertainty is ±8% at the 90% confidence level.

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[1] H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 2852 (1969).

[2] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

[3] An earlier study of tt as a *ca.* 0.3 *M* solution in ethanol was complicated by polymerization, and only one photoisomer was detected. G. Büchi and N. C. Yang, *Chem. Ind.* (*London*), 357 (1955); *J. Amer. Chem. Soc.*, **79**, 2318 (1957). Our irradiation of a 10^{-2} *M* ether solution of tt led to 88% recovery of heptadienone isomers after the photostationary state had been reached.

[4] The absence of the *cis,cis* isomer in the photoproduct mixtures may be caused by its rapid disappearance *via* a pyran intermediate in a dark reaction. Details of dienone photoisomerizations including this work will be covered in a forthcoming paper.

[5] Unconjugated isomers result from photoenolization of conjugated aliphatic enones; *cf.* N. C. Yang and M. J. Jorgenson, *Tetrahedron Lett.*, 1203 (1964).

[6] Final conversion values were corrected for small amounts of contaminating isomers. Monochromatic 254- and 313-nm light was isolated by the method described by Calvert and Pitts[7] and potassium ferrioxalate actinometry was used.

[7] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 728–747, 783–786.

extinction coefficients to calculate a stationary-state composition. Examination of Table II reveals excellent agreement between calculated and observed stationary-state concentrations.[8]

Table II. Photostationary State Compositions[a]

	% tt	% tc	% ct
	254 nm		
Calcd	25.7	20.8	53.5
Obsd	28.4	20.4	51.2
	313 nm		
Calcd	47.4	28.5	24.1
Obsd	48.0	30.0	22.0

[a] Determined in 10^{-3} *M* ethyl ether solutions.

The direct isomerization was not quenched by added azulene in concentrations of up to 5×10^{-3} *M*, but experiments at higher quencher concentrations were impractical, owing to absorption of light by azulene. The isomerizations could be sensitized by a number of triplet sensitizers to give photostationary states of the same three isomers. Intersystem crossing in molecules which possess both $n\pi^*$ and $\pi\pi^*$ excited states is exceptionally rapid;[9] thus despite the lack of azulene quenching,[10] the direct isomerizations probably proceed *via* triplet states.

Mechanisms which involve a common excited state or rapidly equilibrating excited states can be eliminated. At neither wavelength do the quantum yield data satisfy the conditions (eq 7 in ref 1 and eq 1, 2, and 3 in ref 2) derived for such mechanisms on the assumption that the reactive excited state(s) is reached with unit efficiency from each of the isomeric ground states. Since our reactions involve direct excitation and possible intersystem crossing, this assumption may be invalid. Taking this possibility into account, we have derived eq 1 which is not satisfied by the quantum yields at 254 nm and probably not by those at 313 nm either.[11]

$$\frac{\Phi_{\mathrm{tc}\to\mathrm{tt}}\Phi_{\mathrm{tt}\to\mathrm{ct}}}{\Phi_{\mathrm{ct}\to\mathrm{tt}}\Phi_{\mathrm{tt}\to\mathrm{tc}}} = \frac{\Phi_{\mathrm{tc}\to\mathrm{ct}}}{\Phi_{\mathrm{ct}\to\mathrm{tc}}} \qquad (1)$$

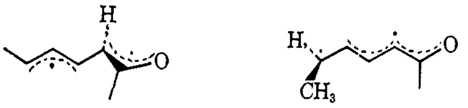
$$(\text{at } 254 \text{ nm } 0.95 \neq 2.1)$$

Having eliminated a mechanism involving rapidly equilibrating excited states, we can consider cases in which rates of equilibration and rates of decay are of the same order. The mechanism in Scheme I involves planar excited states which isomerize one bond at a time. Within the framework of Scheme I, and with the assumption that intersystem crossing is quantitative, the quantum yields for photoisomerization of tt at 313 nm require that tt* partition itself between tt and tc (*via* tc*) in a ratio of 4.1:1. Photoisomerization of ct must proceed *via* tt* and give tt and tc in the same 4.1:1 ratio. However, the observed ratio of $\Phi_{\mathrm{ct}\to\mathrm{tt}}:\Phi_{\mathrm{ct}\to\mathrm{tc}}$ is 1.8:1.[13] A similar scheme involving only the two equilibrating twisted excited states *t and t* can be eliminated on the basis of similar considerations. Our data are consistent with, but do not require, mechanisms which also include excited states which can decay to cc (*e.g.*, inclusion of cc* in Scheme I) and provide a second pathway between ct and tc. Thus, the mechanism may involve equilibrating excited states which decay to ground states more rapidly than hexadiene triplets[14] so that decay competes with isomerization. In addition, a mechanism in which each excited state decays directly to all three ground-state isomers is possible.[15]

Scheme I. Equilibrating Planar Excited States[a]

$$\begin{tikzcd}
\mathrm{ct} \arrow[r, shift left, "h\nu"] & \mathrm{ct}^* \arrow[l, shift left] \arrow[r, shift left] & \mathrm{tt}^* \arrow[l, shift left] \arrow[r, shift right] \arrow[d, shift right] & \mathrm{tc}^* \arrow[l, shift right] \arrow[r, shift right] & \mathrm{tc} \arrow[l, shift right, "h\nu"'] \\
 & & \mathrm{tt} \arrow[u, shift right, "h\nu"'] & &
\end{tikzcd}$$

[a] Starred symbols represent excited states.



*t

t*

Neither our data nor those of the Hammond and Saltiel groups provide the basis for a definitive statement about excited-state geometries. Experimental evidence strongly favors twisted (nonspectroscopic) diene triplets,[16] while our data seem to rule out doubly twisted (common) excited states for dienones. To the extent that this conclusion is generalizable to diene triplets it agrees with Hoffmann's calculations which predict that butadiene in its first excited state is singly twisted.[17] CNDO calculations on propenal predict twisting in the $\pi\pi^*$ triplet but none in the $n\pi^*$ triplet.[18] Thus, the geometry of dienone triplets is likely to be dependent on their electronic configuration.[19]

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(8) Since the quantum yields determined at 2×10^{-2} *M* agree with the stationary-state data at 10^{-3} *M*, quantum yields are not concentration dependent. This rules out a quantum chain mechanism similar to that reported by Hammond, *et al.*,[1] but not found by Saltiel, *et al.*[2]

(9) M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968).

(10) Cases of reactions strongly suspected to proceed *via* triplet states but which are not quenched by triplet quenchers are not unknown. *Cf.* P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(11) We can say that our data at 313 nm do not satisfy eq 1 at the 90% confidence level, but the uncertainty ranges for the two sides of the equation do overlap somewhat at the 95% confidence level.[12]

(12) The fractional uncertainties of individual data are assumed to compound as the square root of the sum of their squares. *Cf.* E. B. Wilson, Jr., "An Introduction to Scientific Research," McGraw-Hill, New York, N. Y., 1952, pp 272–273.

(13) A referee has pointed out that this argument would be weakened considerably if tt* were a mixture of *s-cis* and *s-trans* diene conformers, because they could be produced in different proportion by excitation of tt and ct. Excited states with *s-cis* diene moieties should be of no importance in these direct isomerizations because nmr spectroscopy shows that the ground-state isomers strongly prefer *s-trans* conformations, and uv studies of a series of dienones show that those with *s-cis* diene moieties absorb more weakly in the 254–313 nm region than those with *s-trans* diene moieties. Conformational isomerism of the enone moiety probably occurs, but on detailed examination it does not seem as likely to account for the failure of the mechanism in Scheme I as the explanation offered below. These points will be elaborated in a forthcoming full paper.

(14) Assuming that triplet states are involved, the faster decay rates could be caused by a smaller S_0–T_1 separation in the dienones, the high spin-orbit coupling factor for oxygen $\zeta = 152 \text{ cm}^{-1}$ compared to carbon $\zeta = 28 \text{ cm}^{-1}$, and possible $n\pi^*$ character in the T_1 states of the dienones.[10]

(15) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Amer. Chem. Soc.*, **90**, 4892 (1968).

(16) P. A. Leermakers, J.-P. Montiller, and R. D. Rauh, *Mol. Photochem.*, **1**, 57 (1969), and references therein.

(17) R. Hoffmann, *Tetrahedron*, **22**, 521 (1966).

(18) J. J. McCullough, H. Ohorodynyk, and D. P. Santry, *Chem. Commun.*, 570 (1969).

(19) The most likely T_1 configuration appears to be $\pi\pi^*$ at this time: A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, **91**, 3793 (1969), and A. F. Kluge, unpublished work.

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