mediately dissolved in 0.99 ml of isooctane, and 2.0 μl of cyclohexane was added. Vpc analysis on DBTCP revealed a 2:1 ratio of cyclohexane and **13**. The observed rotation of this solution was $-0.010°$. Assuming the density of **13** to be the same as that of cyclohexane, the $[\alpha]^{22}\text{D}$ was $-12.8°$ (isooctane) for **13**.

Acknowledgment. I thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (2754-A1,4), for partial support of this work and Mr. L. T. Burka and Mr. W. A. Black for valuable assistance with some of the experiments and building the vapor-phase kinetics bath. Acknowledgment is also made to the National Science Foundation for funds for the purchase of the mass spectrometer used in this work (Grant No. GP-5234).

The Mechanism of Photoisomerization of 3,5-Heptadienone[1]

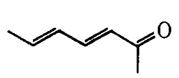
Arthur F. Kluge[2a] **and C. Peter Lillya**[2b]

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002. *Received July 1, 1970*

Abstract: Irradiation of 3,5-heptadienone in dilute diethyl ether solution interconverted the trans,trans, the cis,trans, and the trans,cis isomers in a clean reaction. The products of triplet sensitized isomerization were the same. Variation of sensitizer triplet energy leads to the conclusion that the lowest dienone triplet lies at *ca.* 54 kcal/mol. Azulene did not quench the isomerizations and the quantum yields for direct isomerization do not account for the photostationary state observed in the presence of high-energy sensitizers ($E_T > 58$ kcal/mol). The wavelength dependent quantum yields show that isomerization does not proceed exclusively *via* a common excited state or *via* isomeric excited states which equilibrate faster than they decay.

Photochemical cis–trans isomerization has proved a fertile field for mechanistic organic photochemistry. Simple on the surface, these reactions have proved unusually rich in mechanistic detail and subtlety. Photoisomerization of stilbene is a good example. Hammond and his coworkers invoked the intermediacy of a "phantom triplet" in the sensitized isomerization[3] and also developed a method for examining nonvertical transfer of energy from sensitizers to substrate.[4] Some controversy still exists about whether direct photoisomerization of stilbene proceeds *via* singlet[5] or triplet[6] intermediates. Recently, 2,4-hexadiene, which has two isomerizable double bonds in conjugation, has been studied. Direct irradiation produces the three geometric isomers,[7] and detailed studies show that the excited singlet states derived from geometrically isomeric ground states do not equilibrate with one another.[8] Data for sensitized isomerization of 2,4-hexadiene are consistent with a mechanism involving a common triplet or rapidly interconverting isomeric triplets.[9,10]

Our interest in photoisomerization of conjugated dienones led us to investigate mechanistic details in the case of 3,5-heptadienone. Photoisomerization of this dienone is typical of that of a number of these compounds which we have studied.[11] Irradiation of any of the three known geometric isomers (tt, tc, and ct) as a 10^{-2}–10^{-3} M solution in ethyl ether gives, in high yield, the same photostationary mixture of these three isomers.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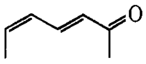
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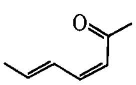
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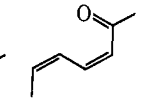
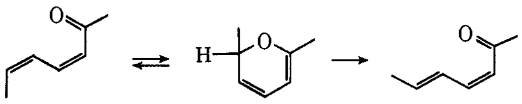

cc

Isomerization is by far the most efficient photoreaction of these dienones. In fact under our conditions no other volatile products can be detected. As is the case for all 14 dienones we have studied, irradiation of 3,5-heptadienones appears to give none of the cis,cis isomer (cc).[12] It seems likely that the absence of cc is caused not by its lack of formation but rather by its subsequent conversion to ct in a dark reaction (eq 1).[11]


(1)

Spectroscopic Studies. The 3,5-heptadienone isomers exhibit both n → π^* and $\pi \rightarrow \pi^*$ absorption maxima in diethyl either solution.[13] The lowest excited singlet state has an $n\pi^*$ configuration and an

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[1] Preliminary communication: A. F. Kluge and C. P. Lillya, *J. Amer. Chem. Soc.*, **92**, 4480 (1970).

[2] (a) N. S. F. trainee, 1965–1969; (b) Alfred P. Sloan Foundation fellow, 1969–1971.

[3] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

[4] W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

[5] (a) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, **88**, 2386 (1966); (b) J. Saltiel, *ibid.*, **89**, 1036 (1967); (c) J. Saltiel, *ibid.*, **90**, 6394 (1968); (d) J. Saltiel, O. C. Zafiriou, E. D. Megarity, and A. A. Lamola, *ibid.*, **90**, 4759 (1968); (e) J. Saltiel and E. D. Megarity, *ibid.*, **91**, 1265 (1969).

[6] (a) K. Muszkat, O. Gegiou, and E. Fischer, *ibid.*, **89**, 4814 (1967); (b) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 12, 3907 (1968).

[7] R. Srinivasan, *ibid.*, **90**, 4498 (1968).

[8] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970). This is also true of the excited singlets from *cis*- and *trans*-1,3-pentadiene: R. Srinivasan, *ibid.*, **92**, 3226 (1970).

[9] H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *ibid.*, **91**, 2852 (1969).

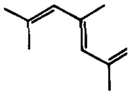
[10] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

[11] A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, **36**, 1988 (1971).

[12] Examination of crude photolysates by ir, nmr, glpc, and tlc has failed to produce any evidence for the existence of *cis,cis*-dienones in these mixtures.

[13] A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, **36**, 1977 (1971).

energy of *ca.* 80 kcal/mol for all three isomers. No fluorescence emission could be detected from 10^{-3} to 10^{-2} *M* cyclohexane solutions of tt at room temperature, nor could any be detected from solutions of dienones **1–5** under similar conditions. A search for phosphorescence emission was made using 10^{-2}–10^{-3} *M* tt, **3**, **4**, and **5** in a methylcyclohexane glass at 77°K. Under conditions which allowed easy detection of acetone phosphorescence ($\tau_p \backsim 6 \times 10^{-4}$ sec)[14] no emission was detected from any of these dienones.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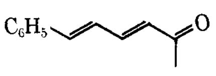
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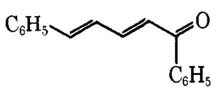
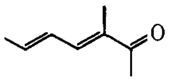

3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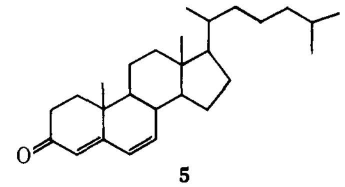
5

Hochstrasser has shown that 10^{-5} *M* napthalene in benzophenone crystals quenches the benzophenone phosphorescence.[15] Since the lowest triplet states of aliphatic dienones are known to lie below the triplet energy of benzophenone (*vide infra*), experiments were performed to determine whether dienone phosphorescence could be sensitized in a benzophenone glass[16] at 77°K. Benzophenone phosphorescence was quenched in a benzophenone glass containing tt, but no new phosphorescence was observed. Similar results were obtained with **3** and **4** as the added dienone. In all cases, concentrations of dienone of approximately 10^{-3} *M* resulted in a quenching of the benzophenone phosphorescence to approximately $^1/_{100}$th of its original intensity. The possibility of quenching by superquencher impurities in the dienones themselves during the direct phosphorescence measurements can be ruled out since such super quenchers should have quenched all of the benzophenone emission.

Quantum Yield Measurements. Quantum yields (see Table I) were determined by irradiation of pure[17] samples of tt, tc, and ct for short periods to ensure low conversion (2–9%) and glpc analysis of the products. Absorption of light by products and back-reaction cause the raw data to be slightly low while product interconversion can cause error in either direction. Corrections for all three sources of error have been made to several sets of data and show that net corrections range from +0.01 to +0.02 unit, usually within the range of uncertainty caused by error in our analytical methods. Final values were obtained by adding an increment of 0.01 to each raw quantum yield. In every case but one, duplicate determinations agreed within 0.02 unit.

Table I. Quantum Yields for Photoisomerization of 3,5-Heptadienone[a–c]

Wavelength, nm	$\Phi_{tt\to ct}$[d]	$\Phi_{tt\to tc}$	$\Phi_{tc\to tt}$	$\Phi_{tc\to ct}$[d]	$\Phi_{ct\to tt}$	$\Phi_{ct\to tc}$
254	0.29	0.15	0.18	0.26	0.36[e]	0.13
313	0.25	0.16	0.29	0.18	0.24	0.14

[a] Solvent diethyl ether. [b] Determined in duplicate or triplicate for *ca.* 2×10^{-2} *M* solutions at room temperature. [c] Average uncertainty is ±8% at the 90% confidence level. [d] These values may be the sum of the quantum yields for ct and cc. [e] Uncertainty ±0.05.

Polymerization and dimerization were checked as causes of quantum inefficiency in the reactions by irradiation of a 10^{-2} *M* solution of tt in ether at 254 nm until a photostationary state was reached. Subsequent vacuum transfer of the products in a glass apparatus at 100° left only 12% nonvolatile material. Thus bimolecular reactions are very inefficient under these conditions. A check of the accuracy of the quantum yield values was made by using them along with extinction coefficients to calculate stationary state compositions using eq 2–4. Examination of Table II reveals excellent

$$\frac{dC_{tt}}{dt} = 0 = C_{ct}\epsilon_{ct}\Phi_{ct\to tt} + C_{tc}\epsilon_{tc}\Phi_{tc\to tt} - C_{tt}\epsilon_{tt}(\Phi_{tt\to ct} + \Phi_{tt\to tc}) \quad (2)$$

$$\frac{dC_{tc}}{dt} = 0 = C_{tt}\epsilon_{tt}\Phi_{tt\to tc} + C_{ct}\epsilon_{ct}\Phi_{ct\to tc} - C_{tc}\epsilon_{tc}(\Phi_{tc\to tt} + \Phi_{tc\to ct}) \quad (3)$$

$$\frac{dC_{ct}}{dt} = 0 = C_{tt}\epsilon_{tt}\Phi_{tt\to ct} + C_{tc}\epsilon_{tc}\Phi_{tc\to ct} - C_{ct}\epsilon_{ct}(\Phi_{ct\to tt} + \Phi_{ct\to tc}) \quad (4)$$

agreement between calculated and observed photostationary state concentrations. Quantum yields for isomerization of 6-methyl-3,5-heptadienone (**6**) were also determined. At 254 nm $\Phi_{t\to c} = 0.19 \pm 0.01$ and $\Phi_{c\to t} = 0.38 \pm 0.02$ while at 313 nm $\Phi_{t\to c} = 0.24 \pm 0.01$.[18,19]

Table II. Photostationary State Compositions for 3,5-Heptadienone[a]

	% tt	% tc	% ct
254 nm			
Calcd[b,c]	25.7	20.8	53.5
Obsd	28.4	20.4	51.2
313 nm			
Calcd[b,d]	47.4	28.5	24.1
Obsd	48.0	30.0	22.0

[a] Determined in 10^{-3} *M* ethyl ether solutions. [b] Based on uncorrected Φ's. [c] ε values in ether at 254 nm (tt = 21,800, tc = 15,900, and ct = 9,300). [d] ε values in ether at 313 nm (tt = 77, tc = 78, and ct = 144).

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(14) D. S. McClure, *J. Chem. Phys.*, 17, 905 (1949).

(15) R. M. Hochstrasser and S. K. Lower, *ibid.*, 40, 1041 (1964).

(16) M. Zander, "Phosphorimetry," Academic Press, New York, N. Y., 1968, pp 122–123.

(17) Final conversion values were corrected for small amounts of contaminating isomers.

(18) These values are corrected for back-reaction and absorption of light by products. $\Phi_{c\to t}$ at 254 nm was calculated using $\Phi_{t\to c}$ and the following photostationary state relationship

$$\frac{C_c}{C_t} = \frac{\epsilon_t\Phi_{t\to c}}{\epsilon_c\Phi_{c\to t}}$$

In ether at 254 nm, ϵ_t = 98[illegible] [illegible] 4310.

(19) Preliminary evidence suggests that the quantum yields for isomerization of tt are temperature dependent. A 10^{-2} *M* solution of tt in ether was frozen in liquid nitrogen and irradiated immediately for 4 min in a Rayonet reactor at 254 nm. The product ratio ct/tc was 5.2, in contrast to the 3.8 observed at room temperature.

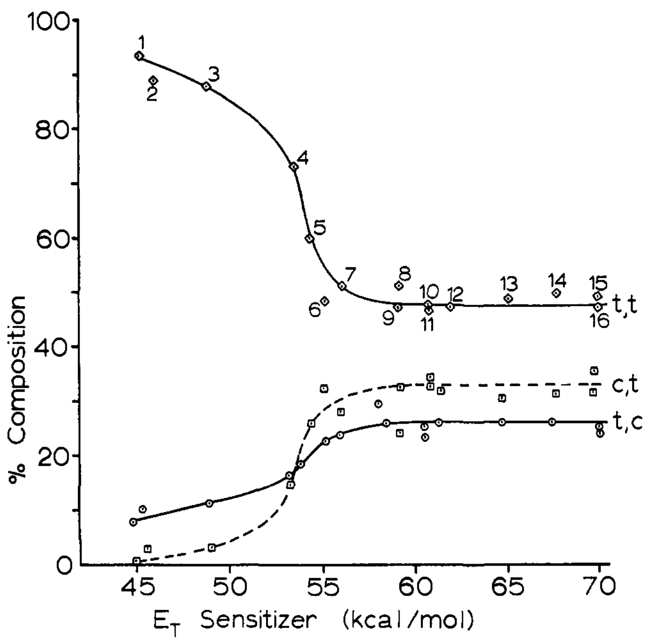

Figure 1. Variation of photostationary state composition with sensitizer triplet energy: ◇, tt; □, ct; ⊙, tc; 1, acridine; 2, benzanthrone; 3, pyrene; 4, fluorenone; 5, benzil; 6, biacetyl; 7, 1-naphthaldehyde; 8, 1-naphthol; 9, 2-acetonaphthone; 10, Michler's ketone; 11, naphthalene; 12, phenanthrene; 13, biphenyl, 14, carbazole; 15, triphenylamine.

Sensitized Photoisomerization. Products from triplet sensitized isomerization of tt in ether solution were the same as those produced by direct irradiation. Photostationary state compositions were determined under conditions in which the sensitizers absorbed 99% of the incident light. A plot of photostationary state composition *vs.* sensitizer triplet energy is shown in Figure 1.

Quenching Experiments. In an early attempt to determine the intersystem crossing efficiency for tt, ether solutions of tt and *trans*-piperylene were irradiated.[20] Under conditions in which tt absorbed all the incident radiation, no isomerization of the piperylene was observed. Lower energy quenchers were also ineffective. Isomerization of tt at 254 nm was not quenched by concentrations of azulene (E_T = 31–39 kcal/mol)[21] up to 4.98×10^{-3} *M*. Absorption of incident radiation by azulene prevented its use at higher concentrations. Isomerization of **6** at 254 nm was also unaffected by azulene in concentrations up to 1.27×10^{-3} *M*.

Discussion

Uv absorption of tt in ether[13] reveals that it possesses spectroscopic $\pi\pi^*$ and $n\pi^*$ singlet states at *ca.* 100–105 and 79–82 kcal/mol, respectively.[22] The change in photostationary state compositions as sensitizer triplet energies are lowered past *ca.* 58 kcal/mol (Figure 2) is strong evidence for existence of the lowest tt triplet at *ca.* 54 kcal/mol. The observed enrichment in tt is attributable to a reduction in the rate of transfer of triplet energy from sensitizer to the tt isomer which occurs when the energy of a donor falls to within 3–4 kcal/mol of that of an acceptor.[23,24] With this information we can construct a partial state diagram for tt consisting of the S_0, S_1, S_2, and T_1 states shown in Figure 2. The S_1–T_1 splitting of 26 kcal/mol is much larger than is typical of $n\pi^*$ splitting.[25] We suggest, therefore, that T_1 is a $\pi\pi^*$ state and that the $n\pi^*$ triplet, T_2, lies between T_1 and S_1 in energy.[26] The $S_2(\pi\pi^*)$–T_1 separation of 46–51 kcal/mol is similar to that of *ca.* 44 kcal/mol reported for *all-trans*-2,4,6-octatrienal (one more C=C than tt) by Evans based on oxygen perturbation of the $S_0 \rightarrow T_1$ absorption intensity.[28]

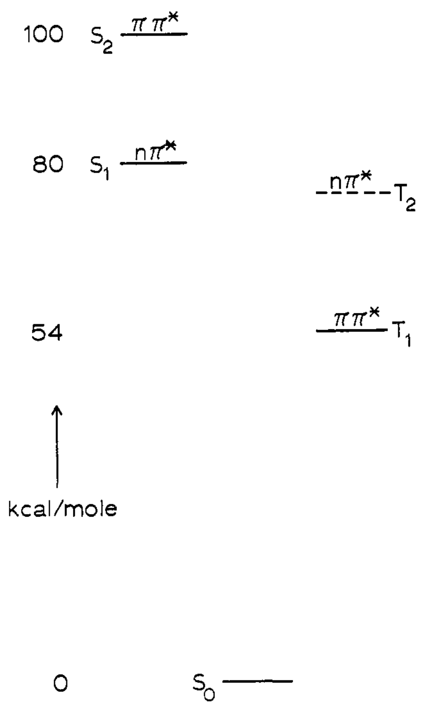

Figure 2. State diagram for *trans,trans*-3,5-heptadienone (tt) in diethyl ether.

No definitive evidence for or against intersystem crossing to dienone triplets can be offered. Failure to find dienone phosphorescence is not significant, since the experiment in benzophenone glass suggests strongly that dienone triplets do not emit. The failure of azulene to quench the isomerization requires that any triplets be quenched at rates less than that of diffusion, or that triplet lifetimes be very short.[29] It is tempting to assume that like cyclopentenone[30] our flexible conju-

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[20] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

[21] A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *ibid.*, 42, 1715 (1965).

[22] No vibrational structure is apparent; thus the mean of each of the given ranges is displaced from the observed λ_{max} to the red to approximate the O–O bands.

[23] (a) K. Sandros and H. L. J. Bäckstrom, *Acta Chem. Scand.*, **16**, 958 (1962); (b) A. A. Lamola in "Energy Transfer and Organic Photochemistry, Technique of Organic Chemistry," Vol. 14, P. A. Leermakers and A. Weisberger, Ed., Wiley, New York, N. Y., 1969, p 47.

[24] This method was first applied to *trans*-piperylene: G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, **83**, 2396 (1961); *J. Phys. Chem.*, **66**, 1144 (1962).

[25] *Cf.* N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 86.

[26] (a) Devaquet and Salem have argued from data on enones in combination with calculations of dienones that T_1 in conjugated dienones should be $\pi\pi^*$.[27] (b) Several steroidal enones have been shown to have just this ordering of states: D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968); *Helv. Chim. Acta*, **51**, 1890 (1968).

[27] A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, **91**, 3793 (1969).

[28] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[29] Assuming a diffusion-controlled quenching rate of 10^{10} l. mol^{-1} sec^{-1} and a maximum of 5% quenching at our highest quencher concentration, we can estimate τ_{max} for triplets as *ca.* 2×10^{-9} sec.

[30] J. L. Ruhlen and P. A. Leermakers, *J. Amer. Chem. Soc.*, **89**,

gated dienones will undergo highly efficient intersystem crossing. Preliminary data on the flexible enone, mesityl oxide, suggest a low Φ_{ISC}, however.[31] Several of our data are difficult to interpret in terms of efficient formation of triplets. First, our quantum yields determined for direct excitation fail to account for the observed photostationary state composition in the presence of high energy sensitizers ($E_t > 58$ kcal/mol). Three equations such as (5) can be derived for the photostationary state assuming that all three dienone isomers quench the sensitizer at equal rates. When used with the observed photostationary state composition, neither the 254 nm quantum yields nor those at 313 nm satisfy these equations within experimental error.[32] Second, wavelength dependence of quantum yields is more easily understood in terms of isomerization occurring during relaxation and internal conversion of vibrationally excited $\pi\pi^*$ singlets[33] than it is in terms of triplets formed after intersystem crossing. Formation of different mixtures of conformationally isomeric excited states, such as those derived from *s-cis-* and *s-trans*-1,3-butadiene,[34] at the different wavelengths offers a less satisfactory explanation of the wavelength dependence.[35] The plot of photostationary state composition *vs.* sensitizer triplet energy (Figure 1) provides no positive evidence for the involvement of conformational isomers.

$$\frac{dC_{tt}}{dt} = 0 = C_{ct}\Phi_{ct\rightarrow tt} + C_{tc}\Phi_{tc\rightarrow tt} - C_{tt}(\Phi_{tt\rightarrow ct} + \Phi_{tt\rightarrow tc}) \qquad (5)$$

Independent of the multiplicity question, the quantum yield data can be used to eliminate several detailed models for the isomerization process. Triplet sensitized isomerization of 2,4-hexadiene proceeds *via* a common excited state or isomeric excited states which equilibrate rapidly with respect to their decay to ground state isomers.[9,10] At neither wavelength do our quantum yield data satisfy the conditions (eq 7 in ref 9 and eq 1, 2, and 3 in ref 10) 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. For example, instead of the sum of all six quantum yields being 2.0 as in the case of 2,4-hexadiene,[10] for 3,5-heptadienone $\Sigma\Phi_{254} = 1.37$ and $\Sigma\Phi_{313} = 1.26$.[36] The photoisomerization is less efficient than that of 2,4-hexadiene triplets.

The assumption of unit excitation efficiency for our unsensitized photoisomerizations may be invalid. Allowing for different excitation efficiencies for the three isomers we have derived eq 6.[37] This equation is

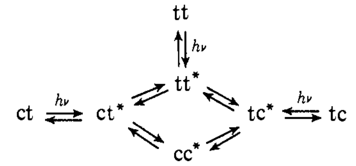
$$\frac{\Phi_{tc\rightarrow tt}}{\Phi_{ct\rightarrow tt}}\frac{\Phi_{tt\rightarrow ct}}{\Phi_{tt\rightarrow tc}} = \frac{\Phi_{tc\rightarrow ct}}{\Phi_{ct\rightarrow tc}} \qquad (6)$$

$$\text{at 254 nm } 0.97 \neq 2.00$$
$$\text{at 313 nm } 1.89 \neq 1.29^{38}$$

clearly not satisfied by the 254-nm quantum yields and probably not by the 313-nm values either.[38] Thus inefficiency cannot be attributed to nonquantitative formation of the reactive excited states alone.

If rates of radiationless decay and rates of equilibration are competitive, a new source of inefficiency caused by incomplete equilibration before decay is introduced. To simplify the discussion we will treat the possible formation of cc and its subsequent dark conversion to ct as part of the "direct" photochemical pathway to ct.[36] Scheme I depicts a mechanism involving planar excited states in which isomerization occurs one bond at a time. If we eliminate cc*, for which there is no positive evidence, ct and tc must be interconverted *via* tt*. Within this framework and with the assumption that the reactive excited states are formed with unit efficiency,[39] we can determine the fate of tt* produced by excitation of tt from quantum yields for isomerization of tt, *e.g.*, at 254 nm. These numbers can then be used to calculate quantum yield ratios such as $\Phi_{ct\rightarrow tt}/\Phi_{ct\rightarrow tc}$. Comparison of calculated and observed ratios in Table III reveals that the scheme lacking cc* predicts

Scheme I. Equilibrating Planar Excited States[a,b]



[a] Starred symbols represent excited states. [b] The symbol *hν* is not intended to imply that the reactive excited states are the spectroscopic singlets.

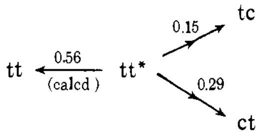


Table III. Quantum Yield Ratios for Mechanism Lacking ce* [a]

Irrad of	λ, nm	Ratio	Calcd[b]	Obsd[c]
ct	254	$\Phi_{ct\rightarrow tt}/\Phi_{ct\rightarrow tc}$	3.73	2.77
ct	313	$\Phi_{ct\rightarrow tt}/\Phi_{ct\rightarrow tc}$	3.69	1.71
tc	254	$\Phi_{tc\rightarrow tt}/\Phi_{tc\rightarrow ct}$	1.93	0.69
tc	313	$\Phi_{tc\rightarrow tt}/\Phi_{tc\rightarrow ct}$	2.36	1.61

[a] Based on the mechanism shown in Scheme I but lacking cc*. [b] From the fate of tt* produced by excitation of tt. [c] From data in Table 11.

4944 (1967); P. deMayo, J.-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); P. J. Wagner and D. J. Bucheck, *ibid.*, **47**, 713 (1969).

(31) Personal communication from Professor J. Saltiel.

(32) Error compounded on the basis that where $y = f(x_1,x_2, \ldots x_n)$ then $\sigma_y{}^2 = \Sigma_i(\partial_y/\partial x_i)\sigma_i{}^2$ where $\sigma_y{}^2$ is variance and σ_y is the standard deviation of y. *Cf.* E. B. Wilson, Jr., "An Introduction to Scientific Research," McGraw-Hill, New York, N. Y., 1952, pp 272–273.

(33) Different behavior of separate vibronic levels within the same electronic state has been proposed: R. S. Becker, E. Dolan, and D. E. Balke, *J Chem. Phys.*, **50**, 239 (1969).

(34) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

(35) Owing to the preference for an *s-trans* diene moiety[13] and the relatively low absorptivity of *s-cis* conformers,[13] production of excited states with *s-cis* diene units by direct excitation should be negligible. Isomerism of the enone unit does occur[13] and its deficiency as an explanation is taken up below.

(36) The fact that cc may be formed and rapidly isomerize to ct in a dark reaction (eq 1) means that our quantum yields for formation of ct may include yields for the formation of cc as well. This does not affect the validity of our analysis.

(37) See Experimental Section for derivation.

(38) The fractional uncertainties of individual data are assumed to compound as the square root of the sum of their squares.[32] For the 313-nm data at a 95% confidence level the uncertainty ranges for the two sides of eq 6 overlap somewhat.

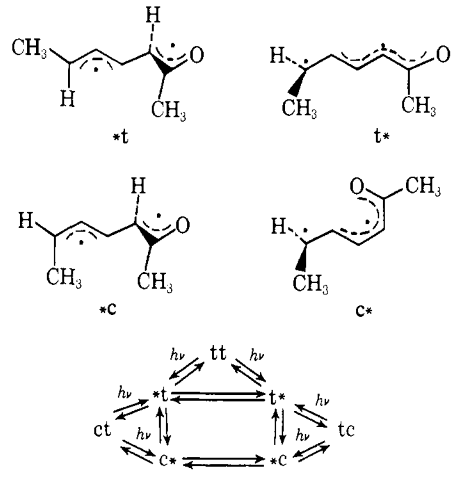
(39) This assumption restricts the generality of our conclusions but is necessary because quantum yields for return to the original isomer are computed as 1.00 − Σ(other quantum yields).

that excitation of ct or tc will produce more tt and less of the third isomer than is actually observed. An obvious way to correct for this is to include cc* which provides a second pathway for interconversion of ct and tc that produces no tt. A second modification which would accomplish the same thing is direct interconversion of ct* and tc* by simultaneous twisting about two bonds.

Alternatively the apparent discrepancy in the behavior of tt* when it is produced in several different ways could be caused by its conformational inhomogeneity. Different ratios of *s-cis-* and *s-trans*-enone units might be produced from the different ground-state isomers. Were this so, we would expect tt* produced from tt and tc to behave similarly since both have comparable amounts of either conformer. However ct, which exists exclusively as the *s-cis* conformer,[13] might produce a very different tt* mixture. The figures in Table III show no such regularity; therefore we feel that conformational inhomogeneity is not the only cause of the differences between the calculated and observed ratios.

Scheme II depicts a mechanism involving singly twisted excited states which are interconverted by simultaneous *ca.* 90° twisting about two bonds. Reasoning similar to that discussed above for the planar excited state mechanism leads to the conclusion that the excited states c* and *c must be included to account for the quantum yield data.

Scheme II. Equilibrating Singly Twisted Excited States[a,b]



[a] See text for explanation of symbols. [b] The symbol *hν* is not intended to imply that the reactive excited states are the spectroscopic singlets.

Even at this intermediate stage this study shows clearly that prudence is called for when using analogy in photochemistry. 3,5-Heptadienone photoisomerization resembles singlet diene isomerization in its inefficiency but resembles triplet diene isomerization in its 2-bond isomerizations. Analogy led us to expect high quantum yields for dienone intersystem crossing,[1] yet our data point to the possibility that they may be relatively small. Several "simple" mechanisms have been eliminated, and we are continuing with experiments directed at the many unsettled questions pointed out here.

Experimental Section

Emission Studies. Fluorescence studies were performed with an Aminco-Bowman spectrofluorimeter using 10^{-2}–10^{-3} solutions of the substrates in purified cyclohexane at room temperature. Compound **4** was also studied at 77°K in methylcyclohexane glass, but no emission was detected. In our phosphorescence studies we employed the same spectrofluorimeter fitted with an Aminco Kiers phosphoroscope attachment. Methylcyclohexane was purified by treatment with fuming sulfuric acid, then with potassium hydroxide, followed by distillation from phosphorus pentoxide. Solutions were prepared at 10^{-2}–10^{-3} *M* in methylcyclohexane or 1:1 ethyl ether–methylcyclohexane and frozen at 77°K to give clear glasses. Observation of phosphorescence from phenanthrene, biphenyl, pyrene, chlorobenzene, and acetone[14] under these conditions eliminates quenching by adventitious impurities in the solvents as the reason for absence of dienone phosphorescence. Benzophenone was recrystallized three times from methanol and then sublimed. A mixture of 2 g of benzophenone and 10 mg of tt was melted at *ca.* 100° and transferred to the sample dewar with a pipet. Immediate cooling to 77°K produced a glass which exhibited benzophenone phosphorescence of *ca.* 1% of the intensity of that produced by similar glasses prepared from pure benzophenone.

Quantum Yields. An optical train consisting of a Hanovia 450-W mercury arc (679A-36) cooled in a Hanovia immersion well, collimating slits and lenses, filter solutions, and Corning color glass filters combined to isolate 254- or 313-nm radiation,[40] and a fused silica reaction cell with a 1-cm path length and 4-ml volume were mounted on an optical bench. Potassium ferrioxalate actinometry[41] was performed in the same cell in which the reaction was run immediately before and after each run. The photon flux during the run was taken as the average of the two determinations; 1 to 2×10^{-2} *M* solutions of dienones in purified diethyl ether were degassed by three freeze-pump-thaw cycles and pipetted into the reaction cell, and the cell was stoppered under an argon stream. After irradiation, 1 ml of the reaction mixture and 1 ml of a standard ethereal solution of naphthalene (internal standard) were pipetted into a screw-cap vial. All transfers were made under argon. Analysis was performed by glpc using an F & M Model 609 flame ionization instrument and a 20 ft × 0.25 in. 5% FFAP on 60–80 mesh Anakrom AB column (44 cc of helium/min) at 100° for the 3,5-heptadienone isomers followed by a 9°/min increase to 150° for naphthalene. Uncorrected quantum yields were, Φ = yield (per cent conversion): at 313 nm, $\Phi_{tt \rightarrow ct}$ = 0.236 (4.3), 0.241 (6.2); $\Phi_{tt \rightarrow tc}$ = 0.146 (4.3), 0.149 (6.2); $\Phi_{tc \rightarrow ct}$ = 0.171 (6.0), 0.162 (4.6); $\Phi_{tc \rightarrow tt}$ = 0.288 (6.0), 0.282 (4.6); $\Phi_{ct \rightarrow tc}$ = 0.129 (7.4), 0.130 (4.8), 0.121 (6.4); $\Phi_{ct \rightarrow tt}$ = 0.249 (7.4), 0.232 (4.8), 0.223 (6.4); at 254 nm, $\Phi_{tt \rightarrow ct}$ = 0.288 (6.5), 0.269 (9.0); $\Phi_{tt \rightarrow tc}$ = 0.152 (6.5), 0.134 (9.0); $\Phi_{tc \rightarrow ct}$ = 0.246 (2.7), 0.261 (4.9); $\Phi_{tc \rightarrow tt}$ = 0.157 (2.7), 0.175 (4.9); $\Phi_{ct \rightarrow tc}$ = 0.112 (1.9), 0.132 (2.0), 0.129 (3.5); $\Phi_{ct \rightarrow tt}$ = 0.304 (1.9), 0.364 (2.0), 0.413 (3.5).

The method used for *trans*-6-methyl-3,5-heptadienone was identical except that glpc analysis was performed at 110° followed by a 9°/min increase to 150°. Uncorrected yields were at 254 nm $\Phi_{t \rightarrow c}$ = 0.196 (2.9% conversion), 0.18 (2.6), 0.198 (3.0), and at 313 nm $\Phi_{t \rightarrow c}$ = 0.255 (2.2), 0.242 (2.0), 0.227 (1.9). Corrections for back-reaction and absorption of light by products were all less than 0.01 unit.

Photostationary State Compositions. Solutions (10^{-3} *M*) of dienones in diethyl ether were irradiated on the optical bench 254 or 313 nm, and reaction progress was followed by glpc as described in the section above with omission of the naphthalene internal standard. The values for 3,5-heptadienone are given in Table II. 6-Methyl-3,5-heptadienone at 254 nm gives a photostationary mixture that is 46.6% trans and 53.4% cis.

Sensitized Isomerizations. Diethyl ether solutions 3.4×10^{-3} *M* in tt (collected by preparative glpc) were prepared with sufficient sensitizer (0.45–0.01 *M*) so that the sensitizer absorbed at least 99.9% of the incident light. These solutions were placed in 1-cm silica uv cuvettes and irradiated by placing them flush with the window of a "black light" hand lamp (λ 300–400 nm).[11] The isomerizations were followed by glpc as described above.

Quenching Experiments. A standard solution of azulene in ether was pipetted into a 1-cm path length uv cuvette and evaporated in a stream of nitrogen. The cell was flushed with argon and 4 ml of an ether solution of dienone, degassed by three freeze-pump-thaw cycles, was pipetted into the cell under argon. The cell was tightly stoppered and irradiated at 254 nm on the optical bench. Quantum yields were determined as described above and were

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(40) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 728–747.

(41) Reference 40, pp 783–786.

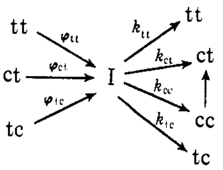
Table IV

Azulene, M	$\Phi_{tt\rightarrow ct}$	$\Phi_{tt\rightarrow tc}$
all-trans-3,5-Heptadienone (tt) (1.6×10^{-2} M)[a,b]		
0.0	0.28 ± 0.02	0.14 ± 0.01
8.3×10^{-4}	0.28 ± 0.02	0.10 ± 0.01
1.66×10^{-3}	0.29 ± 0.02	0.12 ± 0.02[c]
4.98×10^{-3}	0.31 ± 0.03[d]	0.16 ± 0.01
Azulene, M	t	c
trans-6-Methyl-3,5-heptadienone (**6**) (1.02×10^{-2} M)[a,b]		
0.0	0.19 ± 0.01	
1.27×10^{-4}	0.19 ± 0.01	
3.80×10^{-4}	0.19 ± 0.01	
1.27×10^{-3}	0.18 ± 0.01	

[a] Uncorrected for back reaction etc. [b] Uncertaintes are those stemming from analytical error. [c] Precision ±13%. [d] Precision ±11%.

corrected for absorption of light by azulene using the following extinction coefficients: at 254 nm $\epsilon_{azulene} = 12{,}080$, $\epsilon_{tt} = 21{,}800$, $\epsilon_6 = 9830$. Results are listed in Table IV.

Derivation of Equation 5. The scheme below was used where φ's are quantum yields for formation of the common excited state or rapidly equilibrating isomeric states (I) and k's are the rates of decay of the reactive excited state(s) to ground-state isomers. The possible formation of cc and its subsequent conversion to ct are included for the sake of completeness.



Observed quantum yields are defined by eq 7–12

$$\Phi_{tt\rightarrow ct} = [\varphi_{tt}(k_{ct} + k_{cc})]/K \tag{7}$$

$$\Phi_{tc\rightarrow ct} = [\varphi_{tc}(k_{ct} + k_{cc})]/K \tag{8}$$

$$\Phi_{tt\rightarrow tc} = \varphi_{tt}k_{tc}/K \tag{9}$$

$$\Phi_{ct\rightarrow tc} = \varphi_{ct}k_{tc}/K \tag{10}$$

$$\Phi_{tc\rightarrow tt} = \varphi_{tc}k_{tt}/K \tag{11}$$

$$\Phi_{ct\rightarrow tt} = \varphi_{ct}k_{tt}/K \tag{12}$$

where

$$K = k_{tt} + k_{ct} + k_{cc} + k_{tc}$$

Now

$$\frac{(7)}{(9)} = \frac{\Phi_{tt\rightarrow ct}}{\Phi_{tt\rightarrow tc}} = \frac{(k_{ct} + k_{cc})}{k_{tc}}$$

$$\frac{(8)}{(10)} = \frac{\Phi_{tc\rightarrow ct}}{\Phi_{ct\rightarrow tc}} = \frac{\varphi_{tc}}{\varphi_{ct}}\frac{(k_{ct} + k_{cc})}{k_{tc}}$$

$$\frac{(12)}{(11)} = \frac{\Phi_{tc\rightarrow tt}}{\Phi_{ct\rightarrow tt}} = \frac{\varphi_{tc}}{\varphi_{ct}}$$

Looking at the right side of the above three equations it can be seen that

$$\frac{(12)(7)}{(11)(9)} = \frac{(8)}{(10)}$$

or

$$\frac{\Phi_{tc\rightarrow tt}}{\Phi_{ct\rightarrow tt}}\frac{\Phi_{tt\rightarrow ct}}{\Phi_{tt\rightarrow tc}} = \frac{\Phi_{tc\rightarrow ct}}{\Phi_{ct\rightarrow tc}}$$

Acknowledgment. We would like to thank Professors R. A. Caldwell and J. Saltiel for helpful discussions of this work.

Nuclear Magnetic Resonance Spectroscopy. Carbon-13 Spectra of Some Common Oligosaccharides[1]

Douglas E. Dorman[2] and John D. Roberts*

Contribution No. 4141 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.
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Abstract: The applicability of carbon-13 magnetic resonance spectroscopy to the study of oligosaccharides is demonstrated. The spectra of four disaccharides are discussed and interpreted, and the methods used in peak assignments are explained. The dependences of carbon chemical shifts and carbohydrate conformations upon pH are discussed and, contrary to earlier reports, it is shown that no large changes in the anomeric mixture of glucose are observed in strong base. The spectra of four fully acetylated sugars are presented and partially assigned. Finally, a brief investigation of the carbon-13 spectra of amylose and cellulose acetate is presented, and the potential of this method of studying polysaccharide conformations emphasized.

Several investigations of the ^{13}C nuclear magnetic resonance (cmr) spectra of monosaccharides have shown the feasibility and applicability of this method for structural investigations of simple carbohydrates.[3–6] In general, carbon chemical-shift differences have been

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[1] Supported by the Public Health Service, Grant No. 11072, from the Division of General Medical Sciences and by the National Science Foundation.

[2] National Institutes of Health Postdoctoral Fellow, 1967–1970.

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[5] L. D. Hall and L. F. Johnson, *Chem. Commun.*, 509 (1968).

[6] A. S. Perlin and B. Casu, *Tetrahedron Lett.*, 2921 (1969); A. S. Perlin, B. Casu, and H. J. Koch, *Can. J. Chem.*, **48**, 2596 (1970); the demonstration by H. J. Koch and A. S. Perlin, *Carbohyd. Res.*, **15**, 403 (1970), that the proton-decoupled cmr resonance at 119.5 ppm upfield from CS$_2$ of α-D-glucose is absent in α-D-glucose-3-d proves earlier assignments[4,5] of this resonance to the C-2 are incorrect. We have, therefore, throughout this paper taken the C-2 resonances of α anomers to come at somewhat higher field than the C-3 resonances.