# Nonstereospecific Formation of Olefins in the Norrish Type II Photochemical Cleavage of Ketones from the Singlet Excited State. Evidence for a Singlet Diradical Intermediate

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**Abstract:** Photolysis of *threo*- and *erythro*-4-methyl-2-hexanone-5-$d_1$ in the presence of high concentrations of triplet quencher results in nonstereospecific formation of butenes from the singlet excited state. Olefin formation by transfer of hydrogen from erythro and from threo ketone is calculated to be, respectively, 95 and 90% stereospecific. These results are interpreted in terms of a short-lived singlet diradical intermediate. Olefin formation from the triplet states of the erythro and threo ketone was much less stereospecific. The differences between the singlet and triplet state reactions are discussed in terms of spin effects.

Both the excited singlet state and the triplet state of dialkyl ketones containing a γ-hydrogen atom undergo Norrish type II cleavage to olefin and enol.[1] A 1,4 diradical has been shown to be an intermediate in reactions from the triplet state. Wagner has demonstrated that hydrogen transfer to the oxygen atom of triplet butyrophenone to give a 1,4-diradical intermediate is reversible in nonpolar solvents but that it is irreversible in polar solvents where the quantum yield of the cleavage reaction rises to unity.[2] Yang has shown that photoracemization of (*S*)-(+)-5-methyl-2-heptanone occurs only from the triplet state by formation of a 1,4 diradical capable of rotation and reversal to racemic ketone.[3] Lewis has observed deuterium exchange in the photochemically produced triplet state of the β,γ-dideuterio derivative of γ-hydroxy-γ-phenylbutyrophenone which must occur *via* a 1,4-diradical intermediate.[4] Recently, Stephenson reported that the triplet photochemical cleavage of methyl *erythro*- (**7**) and *threo*-3,4-dimethyl-6-ketoheptanoate (**8**) produced olefins with little or no stereoselectivity.[5]

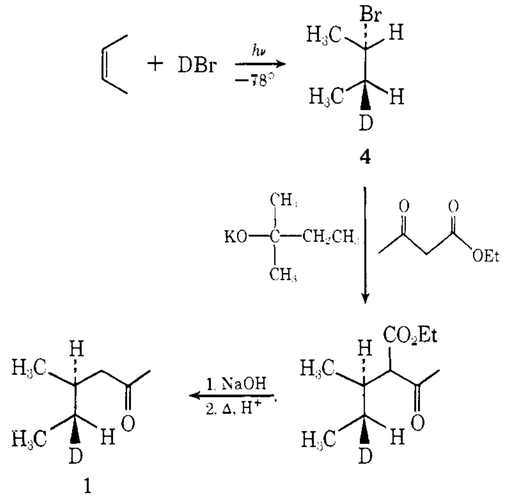
When we began this study there was no comparable body of evidence to support the suggestion of a 1,4-diradical intermediate in the type II cleavage from the excited singlet state. While concerted cleavage of a triplet ketone is strongly disfavored since spin conservation would require formation of either olefin or enol in its triplet state, no such restriction is placed upon reaction of the excited singlet state of ketones. In this connection, Hoffmann's recent calculations indicating that 1,4 diradicals can cleave to olefins with no activation barrier are of interest.[6]

To test for the intervention of a 1,4-diradical intermediate in the type II cleavage of ketones from the singlet excited state, we have examined the stereochemistry of the olefins produced by photolysis of *erythro*- (**1**) and *threo*-4-methyl-2-hexanone-5-$d_1$ (**2**) in the presence of high concentrations of the triplet quencher piperylene. The intervention of a 1,4-diradical intermediate would lead to a nonstereospecific reaction. Here we report that the singlet cleavage of the ketones **1** and **2** is not stereospecific[7] and interpret this result as direct evidence for a short-lived singlet 1,4-diradical intermediate. Similarly, Stephenson has recently reported the nonstereospecific formation of olefins in the type II cleavage of excited singlets **7** and **8**. In our study, rotation about a carbon–carbon bond of a secondary radical led to 5–10% loss of stereochemistry, whereas in Stephenson's case, rotation about a carbon–carbon bond of a tertiary radical led to only a 1.1% loss of stereochemistry.

## Results

**Synthesis.** The synthesis of stereospecifically labeled 4-methyl-2-hexanone-5-$d_1$ was achieved *via* an acetoacetic ester synthetic scheme using *erythro*- (**3**) and *threo*-2-bromobutane-3-$d_1$ (**4**) (Scheme I). Irradiation of a mixture of *cis*-2-butene and DBr at −78° gave **4** in 95% yield;[8] **3** was prepared similarly from DBr and *trans*-2-butene in 84% yield. The isomeric purities of

Scheme I. Synthesis of *erythro*-4-Methyl-2-hexanone-5-$d_1$



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[1] (a) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4009 (1965); (b) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

[2] P. J. Wagner and A. E. Kemppainen, *ibid.*, **89**, 5898 (1967); P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

[3] (a) N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **91**, 7550 (1969); (b) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969).

[4] F. D. Lewis, *ibid.*, **92**, 5602 (1970).

[5] L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *ibid.*, **93**, 1984 (1971).

[6] R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7091 (1970).

[7] In related work, Gano has shown that the photoelimination of *threo*- and *erythro*-1,2-dimethylbutyl acetate is nonstereospecific. Quenching studies were not done to determine whether it was a reaction of singlet excited states or of the triplet state; J. Gano, *Tetrahedron Lett.*, 2549 (1969).

[8] P. S. Skell and R. G. Allen, *J. Amer. Chem. Soc.*, **81**, 5383 (1959).

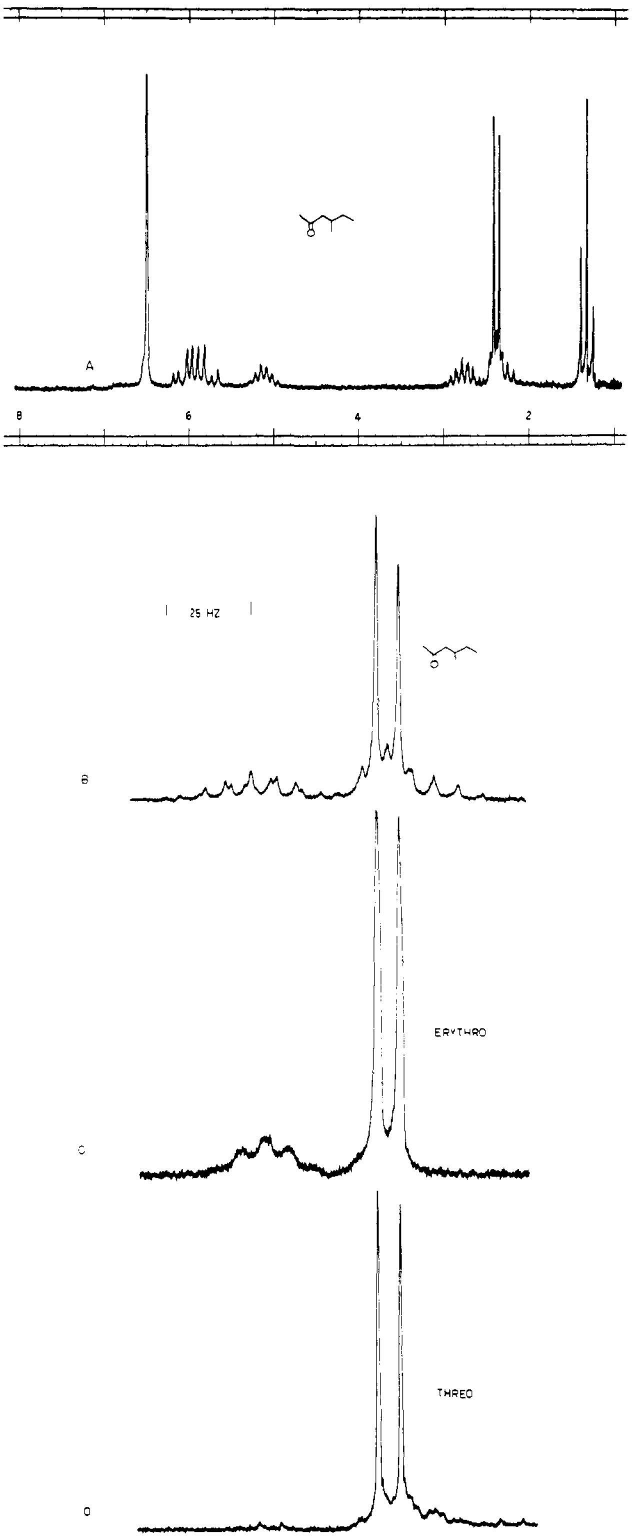

Figure 1. Nmr spectra at 100 MHz of 4-methyl-2-hexanone in $CCl_4$ containing 40 mol % $Eu(fod)_3$: (a) complete spectrum of 4-methyl-2-hexanone; scale expansion of the resonances between $\delta$ 2 and 3 due to the diastereotopic protons in the 5 position and to the 4-$CH_3$ protons in (b) 4-methyl-2-hexanone, (c) *erythro*-4-methyl-2-hexanone-5-$d_1$ (**1**), and (d) *threo*-4-methyl-2-hexanone-5-$d_1$ (**2**).

**3** and **4** were determined by dehydrobromination with potassium ethoxide in ethanol at 70°.[9,10] The resulting butenes were separated by vpc and analyzed for deuterium content by mass spectrometry. The results are summarized in Table I. These data indicated that **3** was 95.0% erythro, 2.1% threo, and 2.9% $d_0$, while **4** was 92.6% threo, 4.2% erythro, and 3.2% $d_0$.

**Table I.** Deuterium Content of Butenes from Dehydrobromination of **3** and **4**

| | 1-Butene | | *trans*-2-Butene | | *cis*-2-Butene | |
|---|---|---|---|---|---|---|
| | % yield[a] | % $d_1$[b] | % yield[a] | % $d_1$[b] | % yield[a] | % $d_1$[b] |
| *erythro*-**3** | 35.2 | 97.1 | 31.0 | 5.6 | 33.8 | 95.2 |
| *threo*-**4** | 24.2 | 96.8 | 65.2 | 94.9 | 10.6 | 13.3 |
| 2-Bromobutane | 20.4 | | 58.5 | | 21.1 | |

[a] Average of three determinations; probable error of the mean was typically ±0.3. [b] Average of six determinations; probable error of the mean was typically ±0.2.

Reaction of *erythro*-bromide **3** with ethyl acetoacetate and potassium *tert*-amyloxide in *tert*-amyl alcohol followed by hydrolysis and decarboxylation of the resulting keto ester gave the *threo*-ketone **2** (97.1% $d_1$) in 21% yield from *trans*-2-butene. Similar treatment of *threo*-bromide **4** gave the *erythro*-ketone **1** (96.8% $d_1$).

**Stereochemistry of the Ketones.** The stereochemistry of the ketones **1** and **2** was initially assigned on the basis of the expected inversion of stereochemistry in the reaction of 2-bromobutane with the enolate anion of ethyl acetoacetate. However, an independent check of the stereochemistry of the ketones was desirable since nucleophilic attack by bromide ion could interconvert the erythro and threo bromides. This possibility was minimized experimentally by employing *tert*-amyl alcohol as the solvent in which potassium bromide has a very low solubility.[11]

The 100-MHz nmr spectra of the isomeric ketones **1** and **2** in the presence of tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato)europium(III), $Eu(fod)_3$,[12] provides a measure of the stereochemical purity of the ketones. In the presence of 40 mol % $Eu(fod)_3$, the chemical shifts of the diastereotopic protons in the 5 position of 4-methyl-2-hexanone occur at $\delta$ 2.31 and 2.78 and differ by 0.47 ppm (see Figure 1). The resonance of the proton in the 5 position of the *threo*-ketone **2** is not obscured by other resonances, but the resonance of the proton in the 5 position of the *erythro*-ketone **1** falls under the doublet due to the 4-methyl group. A comparison of the integral for the erythro proton with the combined integral for the threo proton and the methyl group was used to estimate the isomeric purity of the ketones (Table II). This nmr analysis demonstrates that the alkylation of ethyl acetoacetate with 2-bromobutane in *tert*-amyl alcohol proceeds with complete inversion of stereochemistry within our experimental error of ±1.0%.[11] The nmr analysis of the stereochemistry of the ketones was used in the calculations of the stereospecificity of olefin formation from the ketones **1** and **2**.

**Irradiations.** The photochemical cleavage of the ketones **1** and **2** from the excited singlet state was ex-

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[9] P. S. Skell, R. G. Allen, and G. K. Helmkamp, *J. Amer. Chem. Soc.*, 82, 410 (1960).

[10] R. A. Bartsch, *Tetrahedron Lett.*, 297 (1970).

[11] When the alkylation was carried out with sodium ethoxide in ethanol, the ketones obtained were found to have undergone ~15% isomerization as measured by nmr. This is probably due to the high solubility of NaBr (0.117 *M*) in ethanol. Full details of these isomerizations will be reported later.

[12] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93, 1522 (1971).

**Table II.** Stereochemistry of *Erythro-* and *Threo*-4-Methyl-2-hexanone-5-$d_1$

| | Ketone[a] | | 2-Bromobutane[a] | |
|---|---|---|---|---|
| | % diastereomeric impurity,[b] nmr integration | % $d_0$, mass spectrum | % diastereomeric impurity, dehydrobromination | % $d_0$, mass spectrum |
| *erythro*-**1** | 3.3 ± 1.0 | 3.2 ± 0.2 | 4.2 ± 1.0 | 3.2 ± 0.2 |
| *threo*-**2** | 3.5 ± 1.0 | 2.9 ± 0.2 | 2.1 ± 1.0 | 2.9 ± 0.2 |
| Ketones recovered from photolysis in presence of 3.0 *M* piperylene | | | | |
| *erythro*-**1**[c] | 2.5 ± 1.0 | | | |
| *threo*-**2**[c] | 4.5 ± 1.0 | | | |
| Ketones recovered from photolyses in absence of piperylene | | | | |
| *erythro*-**1**[d] | 9.7 ± 1.0 | | | |
| *threo*-**2**[d] | 12.0 ± 1.0 | | | |

[a] Mean ± probable error of mean. [b] Includes estimates for possible systematic errors. [c] 2–3% conversion of ketone. [d] ~5% conversion of ketone.

**Table III.** Stereochemistry and Deuterium Content of Butenes Formed in the Photolysis of *erythro-* and *threo*-4-Methyl-2-hexanone-5-$d_1$

| Ketone | [Piperylene], *M* | 1-Butene %[a] | 1-Butene % $d_1$[b] | *trans*-2-Butene %[a] | *trans*-2-Butene % $d_1$[b] | *cis*-2-Butene %[a] | *cis*-2-Butene % $d_1$[b] |
|---|---|---|---|---|---|---|---|
| 4-Methyl-2-hexanone | 0.0 | 5.0 | | 75.5 | | 19.5 | |
| 4-Methyl-2-hexanone | 3.0 | 8.8 | | 71.8 | | 19.3 | |
| *threo*-**2** | 0.0 | 12.8 | | 65.0 | 45.1 | 22.2 | 58.9 |
| *threo*-**2** | 3.0 | 16.8 | 97.0 | 53.7 | 9.9 | 29.5 | 88.4 |
| *erythro*-**1** | 0.0 | 11.4 | 97.0 | 71.9 | 91.2 | 16.7 | 70.5 |
| *erythro*-**1** | 1.5 | 13.9 | | 71.9 | 93.0 | 14.1 | 28.9 |
| *erythro*-**1** | 3.0 | 13.8 | 97.0 | 71.6 | 92.8 | 14.6 | 30.1 |
| *erythro*-**1** | 8.4 | 14.1 | | 71.9 | 91.6 | 14.0 | 27.2 |
| Recovered *erythro*-**1** | 8.4 | 14.3 | | 71.2 | 93.4 | 14.5 | 28.4 |

[a] Average of three determinations; the probable error of the mean of these determinations was typically ±0.3. [b] Average of six determinations; the probable error of the mean of these determinations was typically ±0.2.

amined by quenching all triplet reactions with piperylene.[13] Degassed heptane solutions 1.0 *M* in ketones **1** or **2** and 3.0 *M* in piperylene[1] were sealed in Pyrex tubes. The ketones were photolyzed to low conversion (<5%) using a 450-W Hanovia medium pressure mercury lamp surrounded by a Pyrex filter sleeve. Relative yields of 1-butene and *cis-* and *trans*-2-butene were determined by analytical gas chromatography. The deuterium content of the individual butenes was determined by mass spectrometry on samples obtained by preparative gas chromatography (Table III).

To ensure that all triplet reaction was quenched at 3.0 *M* piperylene concentrations, samples of *erythro*-ketone **1** were irradiated in the presence of 1.5 *M* piperylene and in 8.4 *M* piperylene. If triplet quenching were incomplete at 3.0 *M* piperylene, the deuterium content of the butenes produced from ketone reaction in 8.4 *M* piperylene should differ from those found in the photolysis in the presence of 3.0 *M* piperylene. The results (Table III) obtained in the presence of these varying concentrations of piperylene are identical within experimental error.

In order to demonstrate that reversible proton abstraction was not scrambling the stereochemistry of the starting ketone, samples of **1** and **2** were recovered from photolyses in the presence of 3.0 *M* piperylene. Analysis of the recovered ketones (Table II) indicated that within experimental error no isomerizations of the ketones had occurred during photolysis in the presence of 3.0 *M* piperylene. In agreement with this experiment, photolysis of the recovered *erythro*-ketone **1** in 8.4 *M* piperylene gave products identical within experimental error with those from "once photolyzed" **1**.

Photolyses were also carried out in the absence of quencher. The results are reported in Tables III and IV. Nmr analysis of ketones **1** and **2** recovered from photolyses in the absence of quencher had undergone substantial isomerization (Table II).

**Table IV.** Stereospecificity of Olefin Formation of Photolysis of *erythro-* and *threo*-4-Methyl-2-hexanone-5-$d_1$

| Ketone | [Piperylene], *M* | Stereospecificity[a–c] Olefin formed by transfer of H | Stereospecificity[a–c] Olefin formed by transfer of D |
|---|---|---|---|
| **2** | 0.0 | 31.9 ± 0.8 | 79.8 ± 0.8 |
| **2** | 3.0 | 89.6 ± 2.4 | 94.8 ± 0.9 |
| **1** | 0.0 | 85.1 ± 0.8 | 59.8 ± 4.3[d] |
| **1** | 1.5 | 95.4 ± 0.7 | 89.0 ± 5.2[d] |
| **1** | 3.0 | 94.9 ± 0.7 | 88.1 ± 5.0[d] |
| **1** | 8.4 | 95.7 ± 0.8 | 81.4 ± 4.4[d] |
| Recovered **1** | 8.4 | 95.3 ± 0.8 | 92.2 ± 5.3[d] |

[a] Stereospecificity of olefin formed from *erythro*-**1** by transfer of H is given by *trans*-2-butene-$d_1$/(*cis*-2-butene-$d_1$ + *trans*-2-butene-$d_1$) × 100. [b] Corrected for butenes formed from diastereomeric and undeuterated ketone present in starting materials by subtracting the products found in photolysis of these materials. [c] The major source of error in these determinations arises from the ±1.0% uncertainty in the stereochemical purity of the ketones **1** and **2**. The probable error given for these results was determined by propagation of error methods. [d] There are large errors in this measurement due to the small amount of products formed by transfer of deuterium from **1** and due to proportionately large corrections for diastereomeric and undeuterated ketone.

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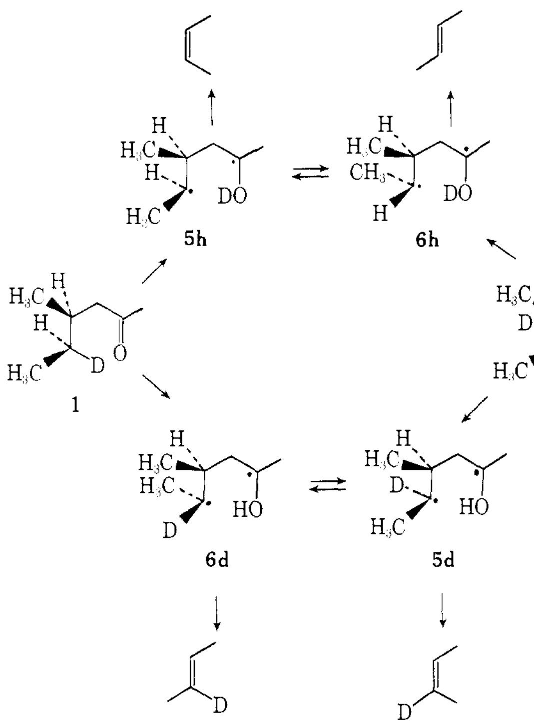
[13] The photolysis of undeuterated 4-methyl-2-hexanone has previously been investigated; P. Ausloos, *J. Phys. Chem.*, 65, 1616 (1961).

**Stereospecificity.** The type II cleavage of ketones **1** and **2** from the singlet excited state is clearly not stereospecific. For example (see Scheme II), a stereospecific concerted cleavage of the *threo*-ketone **2** would be expected to give only *trans*-2-butene-$d_0$, *cis*-2-butene-$d_1$, and 1-butene-$d_1$, but the observed products also included 3.4% *cis*-2-butene-$d_0$ (6.6% of the 2-butene-$d_0$) and 5.3% *trans*-2-butene-$d_1$ (17% of the 2-butene-$d_1$). The amount of olefins formed by nonstereospecific cleavage is much too large to be accounted for by the small amounts of **1** (3.5%) and of undeuterated ketone (2.9%). When the data are corrected by subtracting the products attributable to the small amounts of unlabeled and diastereomeric ketone, the stereospecificity of the formation of olefins by transfer of hydrogen or deuterium from **1** and **2** can be calculated (Table IV).

**Scheme II**



The irradiation of **1** and **2** in the absence of quenchers includes reactions from both the singlet excited state and the triplet state.[14] The data in Table IV clearly indicate that the triplet reaction is much less stereospecific than the singlet reaction.

**Conformational and Isotope Effects on Hydrogen Transfer.** The Norrish type II cleavage of 4-methyl-2-hexanone to give 2-butenes can occur by transfer of either of the two diastereotopic protons in the 5 position. Since we have established that the cleavage from the singlet excited state is largely stereospecific, the yields of *cis*- and *trans*-2-butene can be used as a rough estimate of the amount of hydrogen transfer from a cis conformation to give the cis diradical **5** and from a trans conformation to give the trans diradical **6**. The ratio of *trans*- to *cis*-2-butene (71.8:19.3) found in the photolysis of 4-methyl-2-hexanone is 3.7 and indicates a preference for transfer from a trans conformation.

An estimate of the conformational preference which does not depend on the stereospecificity of the type II elimination can be obtained from observations of the deuterated ketones **1** and **2**. Transfer of hydrogen from **1** can occur only from a trans conformation and will give only deuterated 2-butenes, while transfer of deuterium must occur from a cis conformation and will give only undeuterated 2-butenes. However, in the case of the deuterated ketones, a primary deuterium isotope effect on hydrogen transfer will also have a role in determining which hydrogen atom is transferred. The isotope and conformational effects can nevertheless be separated, since the reactions of both **1** and **2** to give 2-butene are in competition with transfer of hydrogen from the 4-methyl group to give 1-butene. The ratio of the rate of transfer of hydrogen from the trans conformation of **1** to the rate of transfer of a hydrogen from the cis conformation of **2** can be calculated from eq 1. Similarly the ratio for deuterium transfer is given by eq 2.

$$\left(\frac{k_{\text{trans}}}{k_{\text{cis}}}\right)_{\text{H}} = \frac{(\text{2-butene-}d_1/\text{1-butene-}d_1)_1}{(\text{2-butene-}d_1/\text{1-butene-}d_1)_2} = 2.97 \pm 0.12 \quad (1)$$

$$\left(\frac{k_{\text{trans}}}{k_{\text{cis}}}\right)_{\text{D}} = \frac{(\text{2-butene-}d_0/\text{1-butene-}d_1)_2}{(\text{2-butene-}d_0/\text{1-butene-}d_1)_1} = 3.66 \pm 0.23 \quad (2)$$

The isotope effect on hydrogen transfer from the cis and trans conformations can be calculated by the analogous eq 3 and 4. The initial hydrogen transfer in the type II cleavage of **1** and **2** is therefore determined by a combination of a conformational effect favoring transfer from a trans conformation by a factor of 3.0–3.7 and of a deuterium isotope effect favoring hydrogen transfer by a factor of 1.8–2.2. A deuterium isotope effect of 2.7 had previously been found in the type II cleavage of 2-hexanone-5-$d_1$ from the singlet excited state.[16]

$$\left(\frac{k_{\text{H}}}{k_{\text{D}}}\right)_{\text{cis}} = \frac{(\text{2-butene-}d_1/\text{1-butene-}d_1)_1}{(\text{2-butene-}d_0/\text{1-butene-}d_1)_2} = 1.76 \pm 0.06 \quad (3)$$

$$\left(\frac{k_{\text{H}}}{k_{\text{D}}}\right)_{\text{trans}} = \frac{(\text{2-butene-}d_1/\text{1-butene-}d_1)_2}{(\text{2-butene-}d_0/\text{1-butene-}d_1)_1} = 2.18 \pm 0.14 \quad (4)$$

## Discussion

The partial loss of stereochemistry in the olefins formed in the singlet state Norrish type II cleavage of the diastereomeric ketones **1** and **2** provides convincing evidence for a singlet 1,4-diradical intermediate. The intermediate singlet diradical can either cleave to enol and olefin of "retained" stereochemistry or undergo bond rotation to give a different conformation of the radical which subsequently cleaves to give an olefin of opposite stereochemistry (Scheme II). It should be noted that greater loss of stereochemistry is observed when the conformation of the initially generated radical has cis methyl groups (**5**) than when the initial radical has trans methyl groups (6). Thus initial formation of **5d** results in only 90% stereospecificity of olefin forma-

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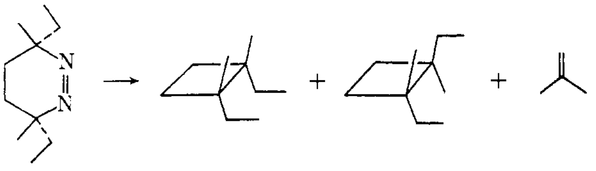
(14) The quantum yields from singlet and triplet reaction of **1** and **2** were not determined. The ratio of type II cleavage from the singlet state to cleavage from the triplet state is 40:60 for 2-hexanone,[1a], 20:80 for 2-octanone,[1b] 62:38 for 5-decanone,[15] and 52:48 for 5-methyl-2-heptanone.[3]

(15) A. Padwa and W. Bergmark, *Tetrahedron Lett.*, 5795 (1968).

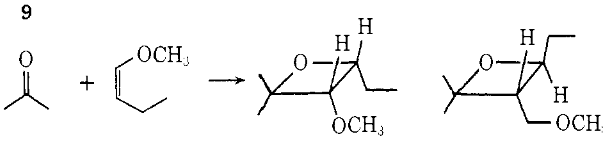
(16) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, 88, 4511 (1966).

tion, whereas initial formation of **6d** or **6h** leads to 95% stereospecificity. Such a result is completely consistent with a singlet 1,4-diradical intermediate. Our stereospecificities are consistent with the formation of a singlet 1,4 diradical which undergoes cleavage to olefin and enol between 10 and 20 times faster than rotation about the carbon–carbon bond. Stephenson's recent report of 1.1% loss of stereochemistry in the formation of olefins from the singlet reaction of the diastereomeric ketones **7** and **8** also provides strong evidence for a 1,4-diradical intermediate.[5] The reasons for the much lower loss of stereochemistry in Stephenson's case will be discussed below.

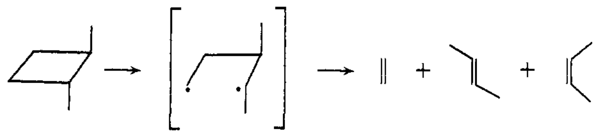
A spin correlation effect was also found by Yang in the photoracemization of (*S*)-(+)-5-methyl-2-heptanone, which occurs from the triplet state but not from the excited singlet state. Similarly, we have found that photoisomerization of **1** and **2** occurs from the triplet state but not from the excited singlet state. Other reactions involving 1,4-diradical intermediates also show large spin correlation effects. Bartlett and Porter found that the excited singlet state of *meso-* and *dl*-**9** produced by direct irradiation gave cyclobutanes with 95–97% retention of stereochemistry; in contrast the triplet state of *meso-* and *dl*-**9** produced by sensitization with triplet thioxanthone gave cyclobutanes with only 61–65% retention of stereochemistry.[17] Turro and Wriede found large differences in stereospecificity between the addition of excited singlet and triplet acetone to 1-methoxybutene.[18]



**9**



Two explanations of spin correlation effects in diradical reactions have been put forth. Bartlett and Porter[17] believe that the triplet diradical has a longer lifetime than the singlet diradical, since it must undergo spin inversion to the singlet diradical prior to formation of ground-state singlet products. The longer lifetime of the triplet diradical allows rotation about carbon–carbon bonds and consequent loss of stereochemistry. Stephenson and Brauman have proposed an alternate hypothesis concerning spin correlation effects.[19] They compared the high stereospecificities (95–99%) found for the photochemically generated singlet diradicals of Stephenson,[5] Bartlett,[17] and Yang[3] with the lower stereospecificity (64–90%) found by Walters for the singlet diradicals generated by thermal decomposition of *cis-* and *trans*-1,2-dimethylcyclobutane at 425 ± 50°.[20] Taking Walters' case as a model for the behavior of a thermally equilibrated diradical, Stephenson and Brauman contended that the diradicals produced from the photolysis of azo compounds and from Norrish type II photoreactions showed stereospecificities too high to be those due to a thermally equilibrated singlet diradical. The high stereospecificities of the photochemically generated singlet diradicals were attributed to the initial formation of a vibrationally "hot" 1,4 diradical which undergoes rapid deactivation directly to either olefins or cyclobutanes and largely avoids deactivation to a thermally equilibrated 1,4 diradical.



Stephenson and Brauman's analysis unfortunately rests on a comparison between the loss of stereochemistry due to rotation about a tertiary radical center in the photochemically generated singlet 1,4 diradical and the loss of stereochemistry due to rotation about a secondary radical center in the thermally generated singlet 1,4 diradical. The rate of rotation about a secondary radical has been estimated to be an order of magnitude greater than the rate of rotation about a tertiary radical center.[21] The fact that a secondary diradical is more prone to rotation than a tertiary one is consistent with the negative entropy of activation associated with more ponderous rotors.[22]

The only valid comparison between thermally and photochemically generated singlet 1,4 diradicals must involve radicals of similar structure. It can be seen from Table V that cleavage of 1,4 diradicals to olefins proceeds with greater than 95% retention of stereochemistry when isomeric products arise from rotation about a carbon–carbon bond of a tertiary radical. This is true for both the photochemical and the thermal generation of singlet 1,4 diradicals. The 98.9% stereospecificity observed by Stephenson[5] in the singlet photolysis of **7** and **8** and the 95–97% stereospecificity observed by Bartlett[17] in the singlet photolysis of the cyclic azo compounds **9** are in good agreement with the 98% stereospecificity observed by Bartlett[16] in the thermolysis of **9**. The lack of photoracemization of (*S*)-(+)-5-methyl-2-heptanone from the singlet state seen by Yang[3] and the lack of interconversion of *cis-* and *trans*-1,1,2,2-tetramethylcyclobutane-$d_6$ during thermolysis[22] are also consistent with the rate of cleavage of singlet 1,4 diradicals being much faster than rotation about a tertiary radical center.

In contrast, lower stereospecificities have been observed in cases where isomeric products result from rotation about a carbon–carbon bond of a secondary radical. The 95% stereospecificity observed by us in the formation of olefins from the trans conformation **6** of the 1,4 diradical formed in the singlet photolysis of **1** and **2** is in good agreement with the 90% retention of stereochemistry observed by Walters in the formation of 2-butenes from the thermolysis of *trans*-1,2-dimethylcyclobutane. Similarly, the 90% stereospecificity of olefin formation from the cis conformation **5** of the 1,4 diradical formed in the singlet photolysis of **1** and **2** is roughly paralleled by the 64% retention of stereo-

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[17] P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

[18] N. J. Turro and P. J. Wriede, *ibid.*, **92**, 320 (1970).

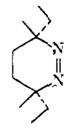
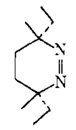
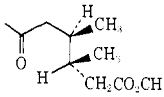
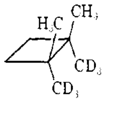
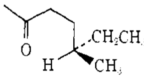
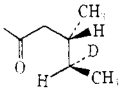
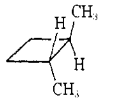
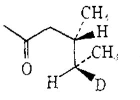
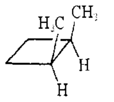
[19] L. M. Stephenson and J. I. Brauman, *ibid.*, **93**, 1988 (1971).

[20] H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 4884 (1961).

[21] R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969), and references therein.

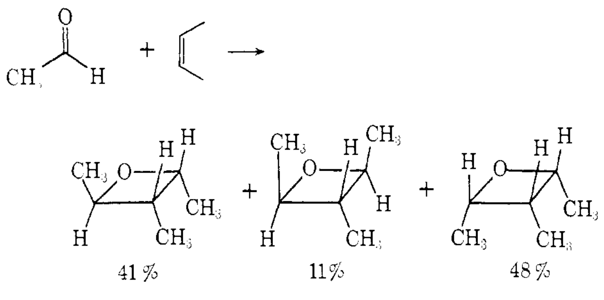
[22] J. A. Berson, D. C. Tompkins, and G. Jones II, *ibid.*, **92**, 5799 (1970), and references therein.

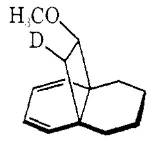
**Table V.** Stereochemistry of Cleavage of Singlet 1,4 Diradicals

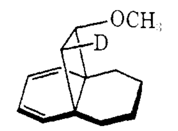
| Photochemical reactions | | | Thermal reactions | | |
|---|---|---|---|---|---|
| Radical precursor | Retention of stereochemistry in cleavage, % | Ref | Radical precursor | Retention of stereochemistry in cleavage, % | Ref |
| Tertiary radicals | | | | | |
|  | 95–97 | 17 |  | >98 | 17 |
|  | 98.9 | 5 |  | Starting material does not isomerize | 22 |
|  | Starting material does not isomerize | 3 | | | |
| Secondary radicals | | | | | |
|  → 6d | 95 | -- |  | 90 | 20 |
|  → 5d | 90 | -- |  | 64 | 20 |

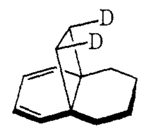
chemistry observed in the formation of 2-butenes in the thermolysis of *cis*-1,2-dimethylcyclobutane.[20]

In other studies of secondary 1,4 diradicals, Yang and Eisenhardt have examined the stereochemistry of the photocycloaddition of acetaldehyde to *cis*- and *trans*-2-butene, which they have suggested proceeds *via* the $^1$n–$\pi^*$ state.[23] A mechanism involving singlet 1,4 biradicals was suggested to explain the >4% loss of stereochemistry in the addition to *trans*-2-butene and the >11% loss of stereochemistry in the addition to *cis*-2-butene. Paquette and Thompson have recently reported the stereochemistry of several cyclobutane pyrolyses which proceed through semistabilized 1,4 diradicals.[24] The pyrolysis of the 4,4,2-propella-2,4-dienes **10** and **11** gave methyl 2-deuteriovinyl ether with respectively 97 and 77% retention of stereochemistry. Paquette and Thompson found only 66% retention of stereochemistry in the pyrolysis of **12**, which proceeds *via* a primary diradical intermediate.




10


11


12

The above analysis indicates that there are no major differences in the behavior of photochemically and thermally generated singlet 1,4 diradicals. All differences in the stereospecificity of reactions proceeding *via* singlet 1,4 diradicals were adequately explained by the greater ease of rotation about secondary radicals compared with tertiary radicals. If "hot" diradicals are involved in the singlet photochemical reactions, then the "hot" diradicals and thermally equilibrated diradicals must have very similar relative rates of internal bond rotation and bond scission. Consequently, while Stephenson and Brauman's[19] postulate of photochemically generated "hot" singlet 1,4 diradicals cannot be eliminated, there are no experimental data which require such an explanation.

Bartlett's less complex explanation of spin correlation effects, however, is in good agreement with our results and accounts not only for the higher stereospecificity of the singlet reactions compared with the triplet reactions but also for the greater stereospecificity observed in the singlet reactions of tertiary 1,4 diradicals than in those of secondary diradicals which have lower rotational barriers and a greater tendency to give isomeric products. The greater stereospecificity seen in the cleavage of the trans conformation **6** of the secondary 1,4 diradical than in the cis conformation **5** is also

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[23] N. C. Yang and W. Eisenhardt, *J. Amer. Soc., Chem.* **93**, 1277 (1971).

[24] L. A. Paquette and G. L. Thompson, *ibid.*, **93**, 4920 (1971).

**Table VI.** Sample Calculation of Stereospecificity

| | *trans*-2-Butene | | *cis*-2-Butene | |
|---|---|---|---|---|
| | $d_0$ | $d_1$ | $d_0$ | $d_1$ |
| *threo*-**2** | 48.38 ± 0.29 | 5.32 ± 0.11 | 3.43 ± 0.07 | 26.07 ± 0.27 |
| 3.5 ± 1.0% *erythro*-**1** | 0.18 ± 0.02 | 2.32 ± 0.66 | 0.36 ± 0.10 | 0.15 ± 0.04 |
| 2.9 ± 0.2% $d_0$ ketone | 2.08 ± 0.14 | | 0.55 ± 0.04 | |
| Pure threo ketone | 46.12 ± 0.32 | 3.00 ± 0.67 | 2.52 ± 0.13 | 25.92 ± 0.27 |

$$\text{Stereospecificity for transfer of H} = \frac{cis\text{-}d_1}{cis\text{-}d_1 + trans\text{-}d_1} = \frac{25.92 \pm 0.27}{(25.92 \pm 0.27) + (3.00 \pm 0.67)} = 89.6 \pm 2.4$$

$$\text{Stereospecificity for transfer of D} = \frac{trans\text{-}d_0}{trans\text{-}d_0 + cis\text{-}d_0} = \frac{46.12 \pm 0.32}{(46.12 \pm 0.32) + (2.52 \pm 0.13)} = 94.8 \pm 0.9$$

in agreement with the expectation that **5** will undergo rotation more rapidly than **6** to relieve the interaction of the cis methyl groups.

## Experimental Section

**Deuterium Bromide.** Freshly distilled phosphorus tribromide (42.5 g, 0.15 mol) was added dropwise to $D_2O$ (11 g, 0.55 mol) at 0°. The reaction mixture was then stirred at room temperature overnight. Deuterium bromide was directly condensed into a −78° trap on a vacuum line as it was formed. Vacuum distillation into a graduated tube gave 12.5 ml of DBr (34.6 g, 0.42 mol, 95% yield).

***erythro*-2-Bromobutane-*3-d₁* (3).** The procedure of Skell and Allen[8] was modified to reduce the risk of an uncontrolled exothermic reaction. *trans*-2-Butene (32.0 ml, 0.36 mol) and freshly prepared DBr (12.0 ml, 0.41 mol) were condensed in a flask on a vacuum line at liquid nitrogen temperature. The flask was warmed to −78° (Dry Ice–isopropyl alcohol) in a Pyrex dewar and opened to the vacuum line which contained a safety manometer. The stirred solution was irradiated with a 275-W Westinghouse sun lamp for approximately 30-sec intervals or until the pressure in the system reached about 200 mm due to a temperature rise in the reaction mixture.[25] The material was cooled to −78° before irradiation was again initiated. After about 10 min total irradiation time it was no longer necessary to interrupt the irradiation. The mixture was then irradiated for an additional 2 hr at −70° to insure complete reaction. Excess DBr and 2-butene were distilled under high vacuum from the reaction flask at −78° into a trap at −198°. The reaction flask was then removed from the line, and the contents were immediately washed with 75 ml of saturated sodium bicarbonate and dried ($MgSO_4$) to give **3** (41.4 g, 83.6% yield). The ir spectrum of **3** was identical with that reported by Skell.[8]

***threo*-2-Bromobutane-*3-d₁* (4).** Reaction of *cis*-2-butene with DBr as above gave a 95% yield of **4**, whose ir spectrum was identical with that reported by Skell.[8]

**Dehydrobromination of 3 and 4.** Following the procedure of Skell, Allen, and Helmkamp,[9] a mixture of 0.25 g of the bromide and 10 ml of freshly prepared 1.0 *M* potassium ethoxide was sealed in a 15-mm Pyrex tube under vacuum and heated to 70 ± 2° for 2 hr. The relative per cent yields of the butenes (determined by gas chromatography) and the deuterium content of the butenes (determined by mass spectral analysis) are listed in Table I. From these data, it is calculated that the erythro bromide is 95.0% pure, containing 2.9% $d_0$ material and 2.1% threo bromide.[26] The threo bromide is calculated to be 92.6% pure, with 4.2% erythro bromide and 3.2% $d_0$ bromide present.

***erythro*-4-Methyl-2-hexanone-*5-d₁* (1).** Reaction of *threo*-2-bromobutane-*3-d₁* (**4**) (90.0 g, 0.65 mol) with the potassium salt of ethyl acetoacetate anion (0.67 mol) in 450 ml of dry *tert*-amyl alcohol[27] at 100° for 30 hr, followed by saponification and decarboxylation,[28] yielded the *erythro*-ketone **1** (19.7 g, 27% yield), which was further purified by preparative vpc at 125° using a 20 ft × 3/8 in. 30% FFAP column: uv max (95% EtOH) 279 mμ (ε 19); ir (neat) 2137 (C–D) and 1709 cm⁻¹ (C=O); nmr ($CCl_4$) δ 2.23 (2 H m, $CH_2CO$), 2.03 (3 H, s, $CH_3CO$), 1.87 (1 H, m), 1.2 (1 H, m, CHD), 0.85 (6 H, br d, $J$ = 6.5 Hz, $CH_3$); mass spectral analysis at 14 eV gave 96.8 ± 0.2% $d_1$ and 3.2 ± 0.2% $d_0$.

***threo*-4-Methyl-2-hexanone-*5-d₁* (2).** Reaction of *erythro*-2-bromobutane-*3-d₁* (10.0 g, 0.073 mol) with the potassuim salt of ethyl acetoacetate anion (0.074 mol) in 125 ml of dry *tert*-amyl alcohol at 100° for 30 hr, followed by saponification and decarboxylation, gave *threo*-ketone **2** (2.1 g, 25%). The ketone was further purified by preparative vpc at 125° using a 20 ft × 3/8 in. 30% FFAP column. Uv, ir, and nmr of **2** were indistinguishable from those of **1**. Mass spectral analysis at 14 eV gave 94.1% $d_1$ and 2.9 ± 0.2% $d_0$.

**Photolysis of Ketones.** Photolyses were carried out in sealed degassed 15-mm Pyrex tubes strapped to a quartz immersion well. A Hanovia high-pressure quartz mercury vapor lamp, inserted into a Pyrex filter sleeve, was used as the light source. Each ketone was uv and vpc pure. Solutions were prepared with olefin-free heptane and were 1.0 *M* in ketone and 1–2 *M* in nonane, an internal vpc standard. Distilled piperylene was used for quenching studies. The per cent conversion was monitored by vpc.

**Separation and Gas Chromatographic Analysis of Butenes.** The butenes produced in a given reaction were taken onto a vacuum line, distilled through a −78° trap, and collected at −198°. The butene isomers were separated on a 15 ft × 1/4 in. 20% UCON-HB-280X-P column at −15°. Relative per cent yields were determined from peak areas on a Hewlett-Packard Model 5750 flame ionization gas chromatograph. The data in Tables I and III are each the average of at least three determinations (probable error ±0.3%). Retention times were: 1-butene, 28 min; *trans*-2-butene, 38 min; and *cis*-2-butene, 45 min.

**Mass Spectral Analyses.** Deuterium analysis was carried out on an AEI-MS-903 instrument at 11.6 eV. Blank samples of each butene isomer (Matheson) were run under identical conditions, and it was demonstrated that there was no $M - 1$ peak. The deuteruim content of each sample in Tables I and III is the average or a minimum of six scans (probable error ±0.2%). It was found that reproducible results were best obtained by operating at slow scanning rates.

**Calculation of Stereospecificity.** Table VI presents a sample calculation of the stereospecificities given in Table IV. The following procedure was used to calculate the stereospecificity of olefin formation in the singlet photolysis of **2**. The gas chromatographic and mass spectral data in Table III were used to calculate the percentages of *trans*-2-butene-$d_0$ and -$d_1$ and of *cis*-2-butene-$d_0$ and -$d_1$ formed in the photolysis of **1**, **2**, and undeuterated ketone in the presence of 3.0 *M* piperylene. Next the distribution of products expected from the undeuterated and diastereomeric ketones present in the sample was calculated and subtracted from the products obtained from photolysis of **2** to obtain the unnormalized product distribution expected from the photolysis of pure threo ketone. The stereospecificities given in Table IV were then calculated from these product distributions.

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(25) When continuous irradiation was used on this scale, the exothermic reaction caused a rapid increase in pressure in the system and the reaction mixture blew out of the flask.

(26) M. Svoboda, J. Zavada, and J. Sicher, *Collect. Czech. Chem. Commun.*, 32, 2104 (1967).

(27) W. B. Renfrow, Jr., *J. Amer. Chem. Soc.*, 66, 144 (1944).

(28) J. R. Johnson and F. D. Hager, "Organic Syntheses," Collect. Vol. I, H. Gilman, Ed., Wiley, New York, N. Y., 1964, p 351.