perature for 5 hr, and the reaction was quenched by addition of saturated ammonium chloride solution. The ether layer was washed successively with water and saturated sodium chloride solution, and was then dried and evaporated. The residue was chromatographed on silicic acid–Supercel (250 g). Elution with pentane–ether (4:1) and crystallization from pentane at −70° yielded the tertiary alcohol **23** (115 mg, 55%) as a cream colored solid, which decomposed at 70–80° on attempted melting point determination: homogeneous on tlc; infrared spectrum (CCl_4), bands at 3595 (m) (OH), 2215 (w), 2185 (w) ($RC{\equiv}CR'$), and 1560 cm^{-1} (w) (C=C); electronic spectrum, see Table I and Figure 1; nmr spectrum (CCl_4, see Figure 3), broad singlet at τ 7.85 (hydroxyl) superimposed on multiplet at 7.65–8.00 (allylic methylene) (total 9 H, reduced to 8 H on shaking with D_2O), and singlet at 8.29 (methyl) superimposed on multiplet at 8.20–8.45 (nonallylic methylene) (total 11 H); mass spectrum, molecular ion peak at *m/e* 300.148 (100%) (calcd for ${}^{12}C_{22}{}^{1}H_{20}{}^{16}O$: 300.151), with a fragmentation peak at *m/e* 285 (M − 15, 12.5%). The solid compound was comparatively stable at room temperature; a sample had only slightly decomposed after standing for 1 week in air and light (determined by the electronic spectrum).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.89; H, 6.83.

1-Cyclopentadienylidene-4,5:10,11-bis(tetramethylene)-4,10-cyclotridecadiene-2,6,8,12-tetrayne (33). Freshly distilled cyclopentadiene (0.4 ml) was added to an ice-cooled solution of sodium methoxide [from sodium (50 mg)] in methanol (20 ml) under nitrogen, and the solution was stirred at 0° for 10 min. The ketone **15** (50 mg) in ether (10 ml) was then added, when a deep red-purple color was formed. The reaction was quenched by the addition of water, and the mixture was extracted with ether. The ether layer was washed successively with water and saturated sodium chloride solution. The extract was dried and evaporated under reduced pressure on a rotatory evaporator (bath temperature ~20°), and the deep red solid residue was chromatographed on silicic acid–Supercel (200 g). Elution with pentane–ether (49:1) and crystallization from ether led to the fulvalene **33** (36 mg, 61%) as brick-red needles, which decomposed at 135–140° on attempted melting point determination: homogeneous on tlc; infrared spectrum ($CHCl_3$), see Discussion; (KBr), bands at 2185 (m), 2155 (w) ($RC{\equiv}CR'$), and 1567 cm^{-1} (m) (C=C); electronic spectrum, see Table II and Figure 4; nmr spectrum ($CDCl_3$), see Discussion and Figure 5; mass spectrum, molecular ion peak at *m/e* 332.155 (100%) (calcd for ${}^{12}C_{26}{}^{1}H_{20}$: 332.156), very little fragmentation.

Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.05; H, 6.27.

The fulvalene **33** was moderately soluble in benzene, ether, carbon tetrachloride, or chloroform, and essentially insoluble in pentane or ethanol. The solid gradually decomposed on standing in air and light at room temperature (~50% decomposition after 7 days, determined by the electronic spectrum).

Acknowledgments. G. M. P. is indebted to the Science Research Council for the award of a Research Studentship (1965–1967) and to New Hall, Cambridge, for the award of a Junior Research Fellowship (1967–1968).

The Chemistry of 1,4 Diradicals. I. Intermediates in the Norrish Type II Photocleavage

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Abstract: The photoreactions of methyl *erythro*- and *threo*-3,4-dimethyl-6-ketoheptanoate have been studied. Both *cis*- and *trans*-3-methyl-3-pentenoic acid methyl esters are products of the photocleavage. Reactions of the ketone excited singlet state are shown to be highly stereospecific while those of the triplet component of the reaction show little selectivity.

Difunctional intermediates have been used to rationalize transformations of organic compounds since the earliest studies of reaction mechanisms. 1,4 diradicals have been a commonly invoked member of this class. In recent years, these species and their analogs extended by vinyl conjugation, although never directly observed, have been strongly implicated in the pyrolysis of cyclobutanes[1] and cyclobutanols,[2] the triplet-sensitized cycloaddition reactions of conjugated dienes,[3] and the cycloaddition reactions of highly halogenated olefins,[4] to mention a few.

In a recent elegant contribution, Bartlett and Porter[5] were able to generate these species by decomposition of six-membered ring azo compounds. They found large differences in the stereospecificity of the cyclobutane-forming fraction of this reaction depending on the spin state (singlet or triplet) of the azo precursor to the diradical. This work, coupled with the earlier work of Bartlett,[4] and the more recent work of Turro[6] and Yang[7] leads one to conclude that singlet and triplet states are easily distinguished in the 1,4 diradical system.

The simplicity and convenience of the Norrish type II photocleavage prompted us to explore this reaction as an alternate route to the 1,4 diradical system. In addition, the availability of a range of substrates allows the stereospecificity of the ring closure, cleavage, and internal disproportionation steps to be examined. With these aims in mind we have prepared both *erythro*- and *threo*-3,4-dimethyl-6-ketoheptanoic acid methyl esters and wish to describe the photochemistry of these molecules below.

Synthesis and Results

I (erythro) and II (threo) were prepared from the Diels–Alder adducts between purified maleic anhydride,

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(1) H. R. Berberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 4884 (1961).

(2) E. D. Feit, *Tetrahedron Lett.*, 1475 (1970).

(3) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(4) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

(5) P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

(6) N. J. Turro and P. A. Wriede, *ibid.*, **92**, 321 (1970).

(7) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).

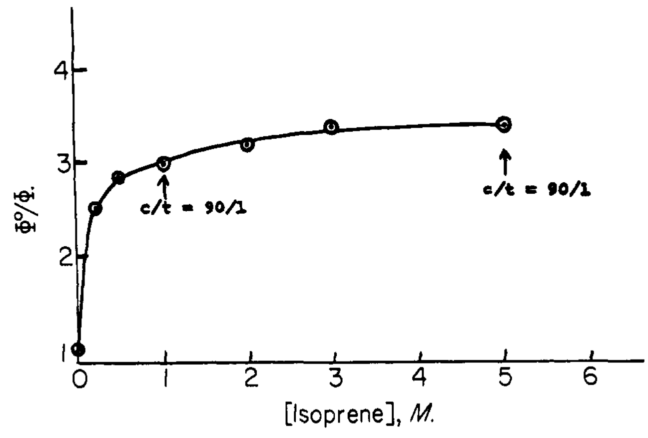


Figure 1. Quenching of photocleavage of I by isoprene.

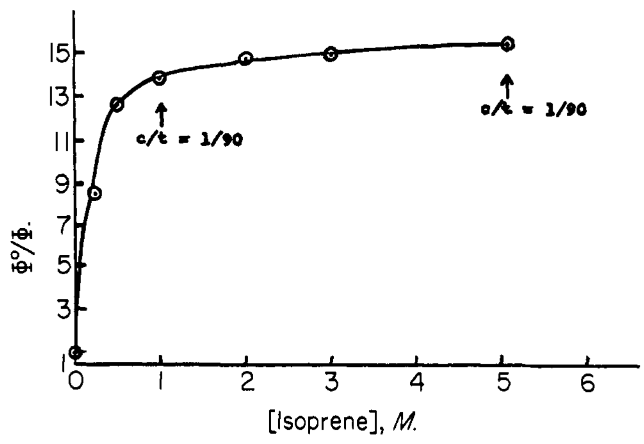
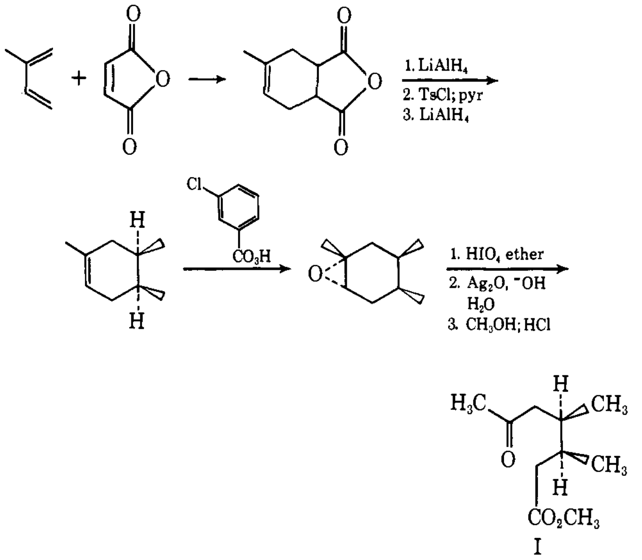


Figure 2. Quenching of photocleavage of II by isoprene.

or dimethyl fumarate, and isoprene. These adducts were each reduced to the trimethylcyclohexenes by treatment with lithium aluminum hydride and conversion of the diols to ditosylates, followed by treatment of the ditosylates with additional lithium aluminum hydride. A keto aldehyde was obtained by epoxidation of the trimethylcyclohexene followed by treatment with periodic acid as described by Ireland.[8] Oxidation to the acid was accomplished with silver oxide. The methyl ester was prepared by Fischer esterification (Chart I).

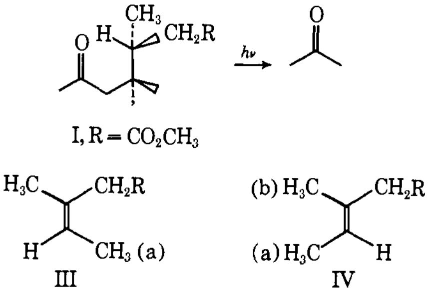
Chart I. Synthesis of I



I

Irradiation of 10% solutions of *erythro*-ketone I in pentane gave acetone and two other products (olefins III and IV) as the only materials of short vapor phase chromatography (vpc) retention time. Smaller amounts of material of longer retention time, presumably cyclobutanols, were also observed, but remain unidentified at this time. The major products were purified by preparative gas chromatography, and the gross structure of the two isolated olefin isomers III and IV was assigned by comparison with material isolated from the dehydration of methyl β-methyl-β-hydroxypentanoate.[9] Samples of the conjugated isomers were also isolated from this dehydration and were available for comparison purposes. The nmr spectra of isomers III and IV allowed the cis–trans relationship to be assigned (see Experimental Section). Thus, for example, in both III and IV the $-CH_3$ (a) (Chart II) appears as a doublet and is easily distinguished from the broad singlet of $-CH_3$ (b); the shielding of $-CH_3$ (b) by $-CH_3$ (a) which is present in IV but not III causes $-CH_3$ (b) in III to resonate at lower field (6.0 Hz) than in IV. This effect has been discussed extensively by Johnson[10a,b] and by Bates,[11] and appears to be widely applicable.

Chart II



When irradiated for shorter periods of time,[12] I (erythro) gave olefins in a ratio of cis:trans = III:IV = 1.9:1. Isomer II (threo) gave olefins in the ratio cis: trans = 1:1.77. In both of the cases the addition of isoprene, a typical ketone triplet quencher, resulted in a diminished yield of olefin and a change in the olefin ratio. This behavior is shown graphically by Figures 1 and 2 with standard Stern–Volmer plots of the data. The ordinate in these figures refers to the ratio of unquenched olefin yields in these experiments.

The details of this behavior will be discussed below. In general terms, however, the unquenchable portion of the photoprocess is attributed to reactions of the singlet excited state of the ketone. The balance, which is quenchable, is due to the ketone excited triplet. These data may be separated into the two states involved, and the ratio of olefins derived from them computed. This is summarized in Table I.

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[8] R. E. Ireland and J. Newhould, *J. Org. Chem.*, **28**, 23 (1963).

[9] G. A. R. Kon and K. S. Nargand, *J. Chem. Soc.*, 2461 (1932).

[10] (a) W. S. Johnson, A. van der Gen, and J. J. Swoboda, *J. Amer. Chem. Soc.*, **89**, 170 (1967); (b) S. F. Brady, M. A. Ilton, and W. S. Johnson, *ibid.*, **90**, 2882 (1968).

[11] R. B. Bates and D. M. Gale, *ibid.*, **89**, 5749 (1967).

[12] In the analytical runs, conversion of ketone to product was generally restricted to <1%. This eliminates complications owing to epimerization of starting material about the δ carbon[7] and sensitized isomerization of the olefin.

Table I. Olefin Ratios from Photolysis Reaction

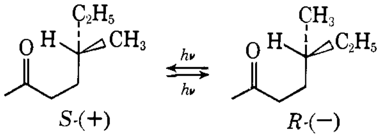
	Singlet, % (c:t)	Triplet, % (c:t)
erythro-I	30 (90:1)	70 (1:1)
threo-II	15 (1:90)	85 (1:1.5)

As is indicated by these figures, the olefin ratio becomes constant at a point shortly after the quenching effect levels off, thus giving added assurance that the triplet component of this reaction is completely quenchable.

Discussion

The Norrish type II processes are surely the most widely studied of all photoreactions and recent studies have served to elucidate many of the fine points of the mechanism.[13] Quenching data similar to that shown in Figures 1 and 2 was first encountered by Wagner and Hammond[13] several years ago. Their explanation, now widely accepted, attributes the quenchable portion of this photolysis to reactions of the lowest ketone triplet state. The balance, which shows only slight or no sensitivity to added quencher, is assigned to reactions of the lowest ketone singlet excited state. There seems to be little doubt that the triplet state reactions proceed through a long-lived intermediate diradical which results from γ hydrogen abstraction by the triplet excited carbonyl. Recent results reported by Yang and Elliott,[7] and shown in Chart III, neatly demonstrate this point of view. These workers found extensive racemization of starting material in the photolysis of (*S*)-(+)-5-methylheptanone, which occurred only from the triplet portion of the reaction. Reversible hydrogen transfer from a long-lived intermediate easily accounts for these data.

Chart III



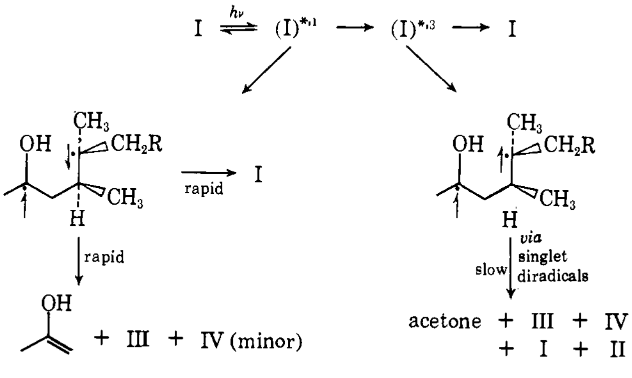
The triplet portion of our photoreaction is also amenable to this interpretation. Abstraction of the γ hydrogen by the triplet excited carbonyl generates a triplet 1,4 diradical species. This intermediate undergoes extensive β–γ bond rotation before decomposing to the olefinic products.

The singlet state reactions have been subject to more controversy; the data of Yang and Elliott,[7] for example, show no detectable racemization of (*S*)-(+)-5-methylheptanone from excited singlet state reactions. However, if the bond-forming reactions of this singlet 1,4 diradical are very rapid relative to bond rotation rates, Yang's data are not inconsistent with a diradical intermediate in the singlet state Norrish reaction. In fact, in an accompanying communication, Yang, Elliott, and Kim[14] argue strongly for such a species on the basis of an extensive study which indicated that the rate of singlet excited state decay to ground state was strongly dependent on the nature of the γ-C–H bond, a result consistent with the reversible formation of a short-lived singlet 1,4 diradical. Other product and rearrangement data from Yang's laboratory also support this point of view.

Alternately, one might choose to view the singlet portion of the Norrish type II process as a formal reversal of the well-known "ene" reaction. Orbital symmetry arguments show that an "ene" reaction follows an allowed course if it proceeds thermally (*i.e.*, in the ground state) in a concerted, "cis–cis" manner. Inspection of models demonstrates that this is the only mode sterically likely, especially for the reverse reaction. The stereochemistry of "ene" reactions has not been nearly so thoroughly studied as the related Diels–Alder reaction; most evidence, however, indicates a stereospecific concerted course.[15] The observed singlet state reactions of ketones could then be attributed to singlet excited state decay to "hot" ground-state species, which undergo a stereospecific reverse "ene" reaction. This mechanism can be ruled out on several levels. (a) Data of Turro and Weiss[16] clearly demonstrate that the abstraction of the γ hydrogen by alkyl ketones is most favorable when the hydrogen is directed toward the half-filled n orbital of the n–π^* excited carbonyl, that is, with the hydrogen lying in the plane of the carbonyl group. However, the optimal geometry for the reverse "ene" reaction requires the hydrogen to be directed toward the π orbitals, either above or below the plane of the carbonyl. Highly stereospecific reactions involving initial interactions between the n orbital and the hydrogen atom in a concerted "hot" ground-state reaction seem somewhat less likely. (b) The high, *but not complete*, stereoselectivity in the formation of the olefin fraction observed in the singlet component of the photolysis of ketones I and II argues strongly for the existence of a short-lived but discrete intermediate.[17] Thus we conclude that while the reactions of this proposed 1,4 diradical singlet are rapid relative to bond rotation, a small amount of leakage to the opposite olefin isomer occurs.

We conclude therefore that the mechanism presented in Chart IV most adequately accounts for the details of the Norrish type II photoreaction. Irradiation of

Chart IV. Photoreactions of Ketone I



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(13) For a recent review and leading references see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, 5, 21 (1968).

(14) N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, 91, 7551 (1969).

(15) The "ene" reaction is reviewed in detail by H. M. R. Hoffman, *Angew. Chem.*, 8, 556 (1969).

(16) N. J. Turro and D. S. Weiss, *J. Amer. Chem. Soc.*, 90, 2185 (1968).

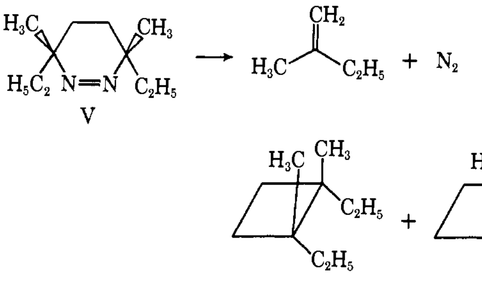
(17) We have been unable to achieve an analytical separation of I from II, and are thus unable to assay either for contamination due to the other isomer. Mixtures of equal parts of I and II are (poorly) resolved by vpc. We are confident, however, that the mode of synthesis, particularly that employed for I, allows the preparation of these compounds in $\gg$99% isomeric purity.

ketone I (for example) leads to the lowest excited singlet state which may decay to the ground state, intersystem cross to the triplet manifold, or produce a *singlet* 1,4 diradical *via* γ hydrogen atom abstraction by the ketone carbonyl. The bond-forming reactions of the species are very rapid relative to β–γ bond rotation and high stereospecificity is maintained in the cleavage step. Yang and coworkers[7,14] have concluded that decay of singlet diradical to ketone ground state (*i.e.*, reverse hydrogen atom transfer) is also a faster process than β–γ bond rotation rates. Our data support this point of view, since the cleavage reaction must be competitive with reverse hydrogen transfer.

Similarly the ketone triplet excited state may decay to ground state or form a *triplet* 1,4 diradical. This species is long lived and extensive loss of configuration due to bond rotation occurs, leading to mixtures of olefins. Reversible hydrogen atom transfer should lead to *loss* of configurational integrity about the γ carbon in this case, an effect noted by Yang[7] but, owing to analytical difficulties, only observed qualitatively in our system.

These results are completely complementary to those reported by Bartlett and Porter[5] for the azo system. For example, decomposition of *meso*-V thermally, or by direct irradiation, led to moderate yields of *meso*-cyclobutane contaminated with only a few per cent more *dl* isomer than was contained in the starting azo compound. Decomposition of the azo compound *via* triplet photosensitization led to mixtures of products (Chart V).

Chart V



Thus, all three major modes of 1,4 diradical decomposition, internal disproportionation, ring closure, and cleavage to olefins, have shown large and similar spin correlation effects despite differences in structure and methods of generation. In the following paper we shall examine the relationship between these species and those derived by other methods and attempt to evaluate the lifetimes of these singlet and triplet species.

Experimental Section

1-Methyl-4,5-*cis*-di(hydroxymethyl)cyclohexene. To a suspension of 30 g (0.79 mol) of lithium aluminum hydride in 800 cm^3 of anhydrous ethyl ether was added portionwise 65 g (0.39 mol) of solid 4-methyl-1,2,3,6-tetrahydrophthalic anhydride,[18] over a period of 1 hr. The base work-up procedure of Amundson and Nelson[19] was followed. The aluminum salts were filtered, extracted three times with ether, and discarded. The solvent was removed, giving 60 g (95%) of a clear viscous liquid which was taken directly to the ditosylate.

Ditosylate of 1-Methyl-4,5-*cis*-di(hydroxymethyl)cyclohexene. The ditosylate was prepared by the addition of 60 g (0.37 mol) of diol in 75 cm^3 of dry pyridine to a stirred, ice–water-cooled mixture of 300 g of *p*-toluenesulfonyl chloride (1.57 mol) in 500 ml of pyridine. After stirring overnight at room temperature, the pink solution containing precipitated pyridine hydrochloride was poured onto 1 l. of ice–water mixture. This mixture was extracted with ether, and the ether layers washed repeatedly to remove excess pyridine. The ether was removed and the solid recrystallized from benzene–hexane to give 130 g (72%) of small white crystals, mp 97.5–99°.

Anal. Calcd for $C_{23}H_{28}O_6S_2$: C, 59.46; H, 6.08; S, 13.80. Found: C, 59.73; H, 6.11; S, 13.60.

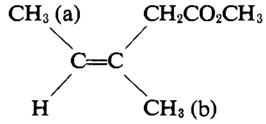
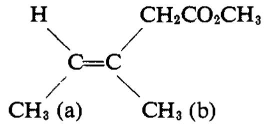
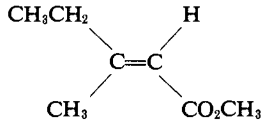
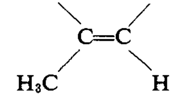
***cis*-1,4,5-Trimethylcyclohexene.** Solid ditosylate, 75 g (0.16 mol) was added to 30 g (0.79 mol) of lithium aluminum hydride in 800 cm^3 of anhydrous ethyl ether over a period of 2 hr. The mixture was allowed to reflux overnight. Base work-up was again employed; after removal of solvent the material was distilled to give 12.6 g (63%) of a clear liquid, bp 149–151° (760 mm).

***trans*-1,4,5-Trimethylcyclohexene.** This was prepared by the procedure of Walborsky and coworkers.[20] The nmr spectra of the cis and trans isomers showed only minor differences.

Methyl *erythro*- or *threo*-3,4-Dimethyl-6-ketoheptanoate. The keto esters were most conveniently prepared by a three-step procedure without isolation of intermediates. Identical procedures were used in both series.

To a stirred solution of 42.7 g of 85% *m*-chloroperbenzoic acid (0.21 mol) in 500 cm^3 of chloroform was added dropwise 26 g (0.21 mol) of trimethylcyclohexene. A slight temperature rise was noted and the mixture was allowed to stir 3 hr at room temperature. The solution was filtered to remove *m*-chlorobenzoic acid, washed with $NaHCO_3$ solution, and dried, and the solvent removed to yield *ca.* 30 g of clear liquid. Distillation, even at reduced pressures, resulted in extensive decomposition and so the undistilled liquid was generally added immediately to a stirred suspension of 48 g of periodic acid (0.21 mol) in 500 cm^3 of ether at room temperature.[8]

Table II. Dehydration Products

(1) 20%					
	CH_3 (a)	CH_3 (b)	CH_2	CO_2CH_3	C=CH
	δ 1.63 ppm d J = 6 Hz	1.75 br s	3.07 s	3.70 s	5.45 q J = 6 Hz
(2) 55%					
	δ 1.61 d J = 6 Hz	1.67 br s	3.00 d (?)	3.68 s	5.40 q J = 6 Hz
(3) 20%					
	CH_3CH_2	CH_3CH_2	CH_3–C=C	CO_2CH_3	C=CH
	δ 1.07 ppm t J = 7 Hz	2.16 q J = 7 Hz	2.15 d J < 1 Hz	3.69 s	5.68 m
(4) 5%					
	δ 1.07 t J = 7 Hz	2.67 q J = 7 Hz	1.90 d J < 1 Hz	3.69 s	5.65 m

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(18) B. Boelselon and A. van der Gract, *Recl. Trav. Chim., Pays-Bas*, **56**, 1203 (1937).

(19) L. H. Amundson and L. S. Nelson, *J. Amer. Chem. Soc.*, **73**, 242 (1951).

(20) H. M. Walborsky, L. Barash, and T. C. Davis, *Tetrahedron*, **19**, 2333 (1963).

Stirring was continued for an additional 3 hr; the mixture was then filtered and the ether washed ($NaHCO_3$), dried, and removed. The crude product showed nmr absorption at δ 2.07 (s, methyl ketone) and 11.3 ppm (t, aldehyde CH). The keto aldehyde was also heat sensitive and was thus carried directly to the keto acid by treatment with silver oxide according to the method of Campaigne and LeSeur.[21] The crude acid (20 g) was treated with 300 cm^3 of methanol with a few drops of added sulfuric acid overnight at room temperature. Methanol was removed and the residue was taken up in ether and washed (H_2O). The ether layer was dried and removed and a slightly yellow liquid was distilled to yield 12 g of clear liquid, bp 65° (15 mm) (31% from trimethylcyclohexene). This keto ester could be conveniently purified by preparative vpc on a 15 ft × $^3/_8$ in. Carbowax column maintained at 190–200°. SE-30 liquid phases were also adequate but less satisfactory. Both isomers showed sharp nmr absorption at δ 2.1 and 3.7 ppm (three protons each) and broad absorption centered around 2.1 and 0.9 ppm. The uv spectra were identical: λ_{max} 280 nm (ϵ 27, pentane).

Anal. Calcd for $C_{10}H_{18}O$: C, 64.49; H, 9.74. Found for *erythro*-IIa: C, 64.38; H, 9.71. Found for *threo*-IIa: C, 64.29; H, 9.79.

Identification of Olefin Isomers. *erythro*-Keto ester (1.3 g) I was irradiated for 5 hr in 20 cm^3 of pentane with a medium-pressure mercury arc using Pyrex filtering. The solvent was then removed and the mixture examined on a 15% SE-30 column, 15 ft × $^3/_8$ in. at 200° revealing starting material (retention time 20 min), two minor products at shorter times (16 and 18 min), and a major product at 6-min retention time. This low molecular weight product was collected from the SE-30 column and further purified on a 20% Carbowax 20M column, 15 ft × $^3/_8$ in., maintained at 110°. Two well-resolved components were observed here and were collected pure. These products were found to be identical with the two major products derived from the dehydration described below; the nmr characteristics of these products are summarized below in Table II.

Alternate Route to Methyl *cis*- and *trans*-2-Methyl-$\Delta^{2,3}$-pentenoate. The preparation and P_2O_5 dehydration of methyl β-methyl-β-hydroxypentanoate have been described by Kon and Nargand[9] and were repeated here with similar findings. Four products were observed on Carbowax 20M at 110° in a ratio of 20:55:20:5 given in order of increasing retention time. Pure samples of the first two are identical with the products derived from the photolysis of the keto ester. The other products appear to be α,β-unsaturated esters. See Table II. This agrees with the findings of the authors above that the β-γ unsaturated isomers represent the bulk of the dehydration mixture.

Quantitative Photolyses. Identical quantities of keto ester and an internal standard (tetradecane) together with varying amounts of isoprene (0–5 *M*) were diluted with pentane so that the ketone concentration was *ca.* 1 *M*. Equal amounts of these solutions were then sealed in 13-mm Pyrex tubes after three freeze–pump–thaw degassing cycles (ultimate pressure *ca.* 10^{-3} mm), and irradiated on a merry-go-round device. A medium-pressure Hg lamp together with Pyrex filtering was employed. Under these conditions the ketone absorbed >95% of the incident light even at the higher diene concentration. These samples were then analyzed in duplicate using matched 15 ft × $^1/_4$ in. 20% Carbowax 20M columns on a Hewlett-Packard F and M Model 5750 gas chromatograph equipped with flame ionization detector, with temperature programming between 110 and 200°.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research through Grant No. 1416-G. The authors wish to thank D. M. Golden, J. I. Brauman, and D. A. Krahulik for helpful conversation.

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(21) N. Rabjohn, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 919.

The Chemistry of 1,4 Diradicals. II. The Interpretation of Spin Correlation Effects

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Abstract: The chemistry of 1,3 and 1,4 diradical species derived from different sources is discussed in terms of their origins and structures. Singlet diradicals produced from azo compounds and Norrish type II photoreactions behave differently from those produced *via* small ring pyrolyses. The properties of these and triplet diradicals are analyzed.

In recent years, many cycloaddition reactions[1] have provided strong evidence for the intermediacy of 1,4 diradicals. Attempts to generate these diradicals by alternate routes have been generally successful, although the species has never been directly observed (Chart I). 1,4 diradicals show three types of reactions in most systems: hydrogen atom transfers (internal disproportionation), ring closure to cyclobutanes, and cleavage to olefins. The stereospecificities of all three reactions have been the subjects of recent study; Bartlett and Porter[2] have studied the decomposition of Ia and Ib to cyclobutanes, Yang and Elliott[3] have studied the photoracemization of II resulting from γ hydrogen atom abstraction by the excited-state carbonyl, and Stephenson, Cavigli, and Parlett[4] have studied the photocleavage of III to *cis*- and *trans*-olefins subsequent to γ hydrogen abstraction. The striking feature of these studies is the large difference in product distribution when singlet or triplet precursors to the diradicals are used. Thus the above examples show high stereospecificity in the reactions which proceed from singlet precursors, and little or no selectivity in the triplet-derived reactions. Since it is reasonably certain that these reactions involve diradical intermediates,[4]

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(1) For example, see: G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964).

(2) P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

(3) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).

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