# Photo-CIDNP Studies of 2-Butanone and 3-Pentanone in Solution

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The results of photolysis of 2-butanone and 3-pentanone as studied by chemically induced dynamic nuclear polarization (CIDNP) and electron spin resonance spectroscopy (e.s.r.) are reported. In aqueous solutions and *t*-butanol only the ethyl radical is detected by means of e.s.r., indicating  $\alpha$  cleavage to be a major path involving excited states. This observation is further supported by the n.m.r. spectra which are obtained during irradiation of these ketones in D<sub>2</sub>O and a mixture of CD<sub>3</sub>CN-D<sub>2</sub>O (1:1 by volume) containing carbon tetrachloride. Several compounds are detected with their protons spin polarized. A mechanism involving radical reactions is proposed which is consistent with the experimental results.

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On rapporte les résultats de la photolyse de la butanone-2 et de la pentanone-3 tels qu'étudiés par polarisation nucléaire dynamique induite chimiquement (CIDNP) et par spectroscopie de résonance paramagnétique électronique (r.p.e.). En solution aqueuse et dans le *tert*-butanol on ne détecte par r.p.e. que des radicaux éthyles indiquant que le clivage  $\alpha$  est une route importante pour les états excités. Cette observation est corroborée par des données de r.m.n. obtenues durant l'irradiation de ces cétones dans D<sub>2</sub>O et dans un mélange de CD<sub>3</sub>CN-D<sub>2</sub>O (1:1 par volume) contenant du tétrachlorure de carbone. On détecte plusieurs composés ayant des protons avec des spins polarisés. On propose un mécanisme impliquant des réactions radicalaires; ce mécanisme est en accord avec les données expérimentales.

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### Introduction

In our earlier paper (1) we reported the results of photolysis of acetone as studied by chemically induced dynamic nuclear polarization (CIDNP). In this case,  $\alpha$  cleavage and intermolecular hydrogen abstraction involving the triplet state of acetone were the main photochemical reactions responsible for the CIDNP effects. The present study is an extension of our earlier work to other ketones, namely 2-butanone and 3-pentanone, to ascertain if  $\alpha$  cleavage and hydrogen abstraction steps occur for these systems also. In this paper, we report CIDNP evidence which supports the occurrence of the  $\alpha$ -cleavage step. We obtained no evidence in support of hydrogen-abstraction step.

#### Experimental

#### Nuclear Magnetic Resonance

The proton n.m.r. spectra at 100 MHz were obtained at 15 °C using a Varian HA-100-15 spectrometer, which was modified to operate on a time-sharing mode. This enabled us to use a quartz probe built in our laboratory (2) and take the n.m.r. spectrum while the sample was being irradiated. The radiation source was a 1000 W Hanovia mercury-xenon arc lamp. Filtering the light to transmit

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radiation having wavelengths greater than 310 nm reduced the intensity of polarization without altering any details.

#### Electron Spin Resonance

The e.s.r. spectra were obtained at 9.6 GHz (X band) using Varian  $\dot{E}$ -12 and Bruker BE-414 spectrometers. These spectra were obtained during irradiation with the full spectrum of a 1000 W mercury-xenon lamp at room temperature. The solutions were flowed at a rate of about 1 ml per s.

#### Chemicals

2-Butanone (Aldrich) and 3-pentanone (Aldrich) were fractionally distilled and the purity was checked using g.l.c. and n.m.r. Deuterioacetonitrile and  $D_2O$  were obtained from Stohler Isotope Chemicals, and carbon tetrachloride (spectroquality) from Matheson, Coleman and Bell. These solvents were used as received. Other solvents used were also reagent grade.

#### Results

### Electron Spin Resonance

The e.s.r. spectrum obtained during irradiation of 8% 2-butanone in water is given in Fig. 1. The spectrum is assigned to the ethyl radical on the basis that the hyperfine splittings 27.0 G for CH<sub>3</sub> and 22.1 G for CH<sub>2</sub> protons are similar to those reported in the literature ( $A_{\beta} = 26.9$  G and  $A_{\alpha} = 22.4$  G) at -180 °C (3).

When *t*-butanol was used as a solvent, no new



FIG. 1. Electron spin resonance of 8% 2-butanone in water at room temperature obtained during irradiation with the full spectrum of a mercury-xenon lamp. The large line in the center is a cell signal. The theoretical reconstruction is given below the experimental spectrum as a stick figure.

lines were observed, however the intensity of ethyl radical spectrum was improved. When 3pentanone was photolyzed in the cavity of the e.s.r. spectrometer in *t*-butanol, only the spectrum of ethyl radical was again observed although the intensity of the spectrum was stronger than when 2-butanone was used. Ethyl radicals can be generated by the following reactions:

$$C_{2}H_{5}COCH_{3} \xrightarrow{h\nu} C_{2}H_{5} + \cdot COCH_{3}$$

$$C_{2}H_{5}COC_{2}H_{5} \xrightarrow{h\nu} C_{2}H_{5} + \cdot COC_{2}H_{5}$$

Since we were not able to observe any signal corresponding to  $CH_3CO$  or  $C_2H_5CO$  radicals, these radicals are probably too short lived to be detected under our experimental conditions. Furthermore, the observation of only the ethyl radical (resulting from  $\alpha$  cleavage) suggests that the hydrogen abstraction involving excited triplet or singlet states may be less important for these ketones. The n.m.r. results are consistent with this observation.

## Nuclear Magnetic Resonance

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The n.m.r. spectra obtained during irradiation of an air-saturated solution of 0.11 M 2-butanone and 0.10 M 3-pentanone in D<sub>2</sub>O are shown in Fig. 2. These spectra were obtained using the full spectrum of a 1000 W mercury-xenon arc lamp. When irradiation is stopped after exposing the samples for a few minutes, the spectrum of each ketone is observed without enhancement and all other signals disappear. The temperature in the n.m.r. probe was maintained at 15 °C although the irradiated portion of sample was hotter.

As is evident in these spectra, a number of compounds are formed during irradiation. The



FIG. 2. Proton nuclear magnetic resonance spectra obtained at 100 MHz for an air-saturated solution during irradiation of: (A) 0.10 M 3-pentanone in  $D_2O$  at 1000 Hz sweep-width. Spectrum a at increased sensitivity and at 1000 Hz sweep-width: spectrum b at 500 Hz sweepwidth and at different higher gains. (B) 0.11 M 2-butanone in  $D_2O$  at 1000 Hz sweep-width. Spectrum c at increased sensitivity and at 1000 Hz sweep-width; spectrum d at 500 Hz sweep-width and at different higher gains. Dashed lines indicate the intensity of larger signal of the multiplet after irradiation. The stick diagram refers to calculated relative intensities on the basis of radical pair [CH<sub>3</sub>CH<sub>2</sub>·  $\cdot$ COCH<sub>3</sub>]<sup>T,F</sup> where *i* denotes recombination and *ii* denotes disproportionation. Numbers on the top of the signals refer to assignments given in Table 1.

spectrum 2A was obtained for 3-pentanone and the spectrum 2B for 2-butanone. As is clear from the figure, both compounds show very similar spectra and exhibit either enhanced absorption or emission indicating non-Boltzmann nuclear spin polarization. Assignment of these lines is given in Table 1. Compounds were identified either by adding them to the solution or by their literature chemical shifts. The lines at 1.25 and at 4.00 p.p.m. in Fig. 2 were not identified. The calculated spectra based on the theory given elsewhere (4) are also shown as stick diagrams for 2-butanone in Fig. 2.

In the presence of nitric oxide no polarizations were observed. The rates for triplet quenching of ketones by nitric oxide in the gas phase are estimated to be diffusion controlled (5). Additional

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	Position <sup>a</sup>		CIDNP <sup>b</sup>		
Resonance	2-Butanone	3-Pentanone		CCl <sub>4</sub> <sup>c</sup>	Compound <sup>d</sup>
1	0.86	0.86	Е		CH <sub>3</sub> CH <sub>3</sub>
2	1.02		A(A/E)	A(A/E)	$CH_3CH_2COCH_3$
3		1.02	A(A/E)	A(A/E)	$CH_{3}CH_{2}COCH_{2}CH_{3}$
4	2.23		E	E	CH <sub>3</sub> CH <sub>2</sub> CO <i>CH</i> <sub>3</sub>
5	2.28		Е		<i>CH</i> <sub>3</sub> CHO
6		2.52	E(A/E)	E(A/E)	$CH_{3}CH_{2}COCH_{2}CH_{3}$
7	2.56		E(A/E)	E(A/E)	CH <sub>3</sub> CO <i>CH</i> <sub>2</sub> CH <sub>3</sub>
8	5.10		Α		$CH_3CH(OH)_2(hydrate)$
9		4.96	Α		$CH_{3}CH_{2}CH(OH)_{2}(hvdrate)$
10	5.30	5.36	Α	Е	CH <sub>2</sub> CH <sub>2</sub>
11		9.57	А	A <sup>e</sup>	CH <sub>3</sub> CH <sub>2</sub> CHO
12	9.74		А	A <sup>e</sup>	CH <sub>3</sub> CHO
13	1.30	1.31		Е	$CH_{3}CH_{2}CCl_{3}$
14	1.50	1.50		E(E/A)	$CH_{3}CH_{2}CI$
15	2.06			A	<i>CH</i> <sub>3</sub> COOH
16	2.80	2.82		А	$CH_3CH_2CCI_3$
17	3.72	3.66		E(E/A)	$CH_3CH_2Cl$
18	7.64	7.67		E -	CHCl <sub>3</sub>

TABLE 1.	Assignment of n.m.r.	lines observed during	; irradiation	of 2-butanone	and 3-pentanone	in D <sub>2</sub> O				
or $CD_3CN-D_2O(1:1 \text{ by volume})$										

In p.p.m. relative to TMS as external standard. Absorption A, emission E, and multiplet A/E and E/A with A and E, respectively, at lower field. In CD<sub>3</sub>CN-D<sub>2</sub>O mixture.

Position refers to italicized groups. eVery weak

information about the photoreactions of these ketones was obtained by trapping experiments using carbon tetrachloride which acts as a freeradical scavenger. Since carbon tetrachloride does not dissolve appreciably in  $D_2O$ , a mixture of equal volumes of deuterioacetonitrile and  $D_2O$  was used as a solvent. The spectra in this solvent, in the presence of 0.07 M carbon tetrachloride, are given in Fig. 3. The spectrum without CCl<sub>4</sub> differs only slightly from that obtained in pure  $D_2O$ . The difference is that the hydrates of the corresponding aldehydes were not observed in the mixed solvent, probably due to lower intensities. Also some more lines appeared at 0.9 and 1.3 p.p.m. which are presently not conclusively identified although their chemical shifts fall in the same region as those for butane. As is evident from Fig. 3, new polarized products are observed. Both 2-butanone and 3-pentanone again show very similar spectra. When irradiation is stopped after exposing the samples for a few minutes, the spectrum of each ketone is observed without enhancement, and all other signals disappear. The assignments of the resonances are listed in Table 1. Except for 1,1,1-trichloropropane, all assignments were confirmed by adding the compound to the solution.

As indicated in Table 1, acetic acid is formed

when  $CCl_4$  is present. We suggest that it results from the hydrolysis of acetyl chloride which is a radical trapping product during photolysis of 2-butanone. One would expect to observe propionic acid in the same way from the hydrolysis of  $C_2H_5COCl$  formed by the trapping of propionyl radical generated during photolysis of 3pentanone in presence of CCl<sub>4</sub>. However we were not able to observe any lines due to the acid or the acid chloride. 1,1,1-Trichloropropane  $(CH_3CH_2CCl_3)$  (triplet at 1.3 p.p.m. and quartet at 2.8 p.p.m.) could not be obtained commercially and we were not able to obtain literature values of the chemical shifts for this compound. However, we report its presence on the grounds discussed later. The signals (absorption) at 3.97 p.p.m. and the singlet (emission) at 6.6 p.p.m. could not be identified. The calculated spectra are given as stick diagrams in the case of the 2-butanone system but not for the 3-pentanone system because the results are very similar for both cases.

### Discussion

The spectra obtained in Fig. 2 can be explained according to following scheme in terms of reactions involving radical-pairs. The photoreactions in the case of 3-pentanone could be explained in



FIG. 3. Proton nuclear magnetic resonance spectra obtained at 100 MHz for an air-saturated solution during irradiation of: (A) 0.1 M 3-pentanone in CD<sub>3</sub>CN-D<sub>2</sub>O (1:1 by volume) solutions in presence of 0.07 M CCl<sub>4</sub>. Spectrum a was taken at higher gain. Sweep-width 1000 Hz. (B) 0.11 M 2-butanone in  $CD_3CN-D_2O$  (1:1 by volume) solutions in the presence of 0.07 M CCl<sub>4</sub>. Spectrum b was taken at higher gain. Dashed lines indicate the larger signal of the multiplet after the irradiation is stopped. Stick diagrams refer to calculated relative intensities on the basis of radical pairs i to vi, where i denotes [CH<sub>3</sub>CO· CH<sub>2</sub>CH<sub>3</sub>]<sup>T</sup>, recombination; iii [CH<sub>3</sub>CO·  $(CH_2CH_3]^T$ , trapped; iv  $[CH_3CH_2 \cdot CCl_3]^F$ , trapped; v [CH<sub>3</sub>CH<sub>2</sub>··CCl<sub>3</sub>]<sup>F</sup>, recombination; vi [CH<sub>3</sub>CH<sub>2</sub>··CCl<sub>3</sub>]<sup>F</sup> disproportionation. Figures 3A and 3B were recorded at about twice the gain used for Figs. 2A and 2B.

a similar fashion. In this scheme, the brackets indicate a radical pair and the superscripts indicate that the radical pair has a triplet T and/or free-radical F, precursor. The signs beneath the products indicate the calculated signs for the n.m.r. signals for the proton, (+) for enhanced adsorption, and (-) for emission.

According to Scheme 1, a molecule of 2-butanone is excited into a singlet state, which goes to a triplet state via intersystem crossing. The radical pair formed in eq. 2 via the triplet state of the ketone could have three pathways. It could recombine to give the parent molecule in the ground state (eq. 3) or it could disproportionate to give acetaldehyde and ethylene (eq. 4). For the third path, the radical pair could dissociate and the free radicals could undergo other reactions such as eq. 6 (discussed below) or reassociate. Comparison of the observed signs in Table 1 with the calculated signs for the products indicates that this scheme is consistent with our experimental results. The calculations were based on a model in which non-Boltzmann nuclear spin polarization occurs as a result of reaction via a radical pair (6). Details of the theory given in earlier publications (4), will not be repeated here.

For calculations, literature values for the isotropic g factors and electron-nuclear hyperfine coupling constants were used (3), and positive values were used for the indirect nulcear-nuclear coupling constants for vicinal protons of the products. Since some of the parameters used in the calculation are somewhat arbitrary, only the relative values of intensities are meaningful. Consequently for a compound exhibiting only one n.m.r. line, the calculated relative intensities have not been illustrated, unless a comparison with another line is possible. As a result in Fig. 2, the calculated relative intensities are illustrated only for acetaldehyde, ethylene, and 2-butanone. When comparing the calculated and experimental spectra for 2-butanone, one must take into account the fact that the experimental spectrum is a superposition of spectra due to some molecules having Boltzmann polarization and others having non-Boltzmann polarization. The intensity due to Boltzmann polarization during irradiation could be approximated as equal to the intensity of the spectrum after irradiation (indicated by dashed lines in Fig. 2). When this intensity is subtracted from the spectrum obtained during irradiation, agreement between calculated and experimental intensities is obtained for the 2-butanone molecule.

According to eq. 4, acetaldehyde and ethylene are formed via a disproportionation step involving  $[CH_3CO \cdot CH_2CH_3]^{T,F}$ . While the calculation based on this radical pair gives the proper signs for the polarization of acetaldehyde carbonyl hydrogen vs. the ethylene hydrogen, the relative intensities do not agree as well as might be expected. That is, relative to the acetaldehyde carbonyl hydrogen, the experimental value for ethylene appears smaller than the calculated value. This lower than expected value for the ethylene intensity might be explained by the fact CAN. J. CHEM. VOL. 52, 1974

 $CH_3COCH_2CH_3 \xrightarrow{h\nu} CH_3COCH_2CH_3^S \longrightarrow CH_3COCH_2CH_3^T$ 

 $CH_3COCH_2CH_3^T \longrightarrow [CH_3CO \cdot \cdot CH_2CH_3]^T$ 

 $[CH_{3}CO\cdot \cdot CH_{2}CH_{3}]^{T,F} \xrightarrow{CH_{3}COCH_{2}CH_{3}} (-) (-) (+) \xrightarrow{H_{2}O} CH_{3}CH(OH)_{2} (+) (-) (+) (-) (+) (-) (+) \xrightarrow{(-)} (+) (-) (+)$ 

 $\begin{array}{c} \cdot \operatorname{CH}_2\operatorname{CH}_3 + \operatorname{CH}_3\operatorname{COCH}_2\operatorname{CH}_3 & \longrightarrow & \operatorname{CH}_3\operatorname{CH}_3 + \operatorname{CH}_3\operatorname{COCHCH}_3 \\ (+) & (-) & (-) \end{array}$ 

#### SCHEME 1

that we observed the evolution of gas from the n.m.r. sample during irradiation. On the other hand, we cannot rule out the possibility that the difference between calculated and observed relative intensity may be due in part to different relaxation times and/or some additional contribution to the polarization from other steps. The possibility of an additional step also is suggested by radical trapping experiments discussed below.

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[1]

[2]

[3]

[4]

[5]

[6]

The polarization observed for ethane may be accounted for by eqs. 5 and 6. According to this mechanism, dissociation of [CH<sub>3</sub>CO··CH<sub>2</sub> CH<sub>3</sub>]<sup>T,F</sup> results in free radicals whose nuclei are initially polarized. If these radicals react to form diamagnetic products at rates which are competitive with nuclear spin – lattice relaxation rates, the polarization is carried over into the products. Thus, we suggest that the rate for eq. 6 is competitive with relaxation rates. Other steps are possible but either do not account for the polarization or are not consistent with other facts. For example, disproportionation in [CH<sub>3</sub>CO··CH<sub>2</sub>  $CH_3$ <sup>T,F</sup> results in positive rather than negative polarization for ethane and would require the formation of ketone (or acetic acid, its hydrolysis product) which is not observed. Disproportionation in  $[CH_3CO \cdot CH_2CH_3]^{s}$  gives the correct sign for ethane polarization but is not consistent with the CCl<sub>4</sub> trapping results discussed below. Thus we conclude that eqs. 5 and 6 provide the main contribution to the ethane polarization.

*n*-Butane formed by a coupling reaction via  $[C_2H_5, C_2H_5]^F$  will have net zero polarization but would exhibit a multiplet effect. In CD<sub>3</sub>CN-D<sub>2</sub>O there are some lines where butane spectrum is expected; however its presence is not conclusively proved.

In the case of 2-butanone in  $D_2O$ , spin-polarized acetaldehyde hydrate (methine proton quartet at 5.1 p.p.m.) is observed and similarly for 3-pentanone in  $D_2O$ , spin-polarized propionaldehyde hydrate (methine proton, triplet at 4.96 p.p.m.) is observed. Since the rates of hydration of these aldehydes are known to be competitive (7, 8) with the spin-lattice relaxation rates, the polarization for the methine hydrogen of each hydrate may be explained by a process in which the polarization of the carbonyl hydrogen in the aldehyde (eq. 4) is carried into the hydrate as a result of the hydration process.

In the presence of carbon tetrachloride, the following scheme is suggested when 2-butanone is photolyzed in  $CD_3CN-D_2O$  solutions. A similar mechanism should hold for 3-pentanone. According to this scheme in eq. 2, 2-butanone forms a radical pair via its excited triplet state. The radical pair could either combine as in eq. 3 or could dissociate (eq. 5). After dissociation, acetyl and ethyl radicals cannot recombine be-



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give products: acetyl chloride (eq. 8), ethyl chloride (eq. 7), and CCl<sub>3</sub> radical. The acetyl chloride signal is not observed because it is rapidly hydrolyzed in aqueous solution to spinpolarized acetic acid whose enhanced absorption signal is observed. For 3-pentanone, neither spin-polarized propionyl chloride nor propionic acid is observed, indicating either that nuclear spin-polarized propionyl radical is not trapped by 0.07 M CCl<sub>4</sub> or that the polarization is weak because the hyperfine coupling constant for the CH<sub>2</sub> proton of this radical is small (9). According to eqs. 9, 10, and 11, [CH<sub>3</sub>ĊH<sub>2</sub> ĊCl<sub>3</sub>]<sup>F</sup> can combine to form CH<sub>3</sub>CH<sub>2</sub>CCl<sub>3</sub>, disproportionate to form ethylene and CHCl<sub>3</sub>, and dissociate with the subsequent formation of ethyl chloride by a trapping step with  $CCl_4$ . Except for ethyl chloride, the agreement between calculated and

observed signs of polarization can be seen by comparing Table 1 with the signs given in Scheme 2. In addition, this scheme is consistent with the fact that the signal due to ethane is not observed when  $CCl_4$  is present (Fig. 3). When carbon tetrachloride is added for radical trapping experiments, the polarization in the parent compound is reduced. The reduction is evident by comparing Fig. 2 with Fig. 3 which was obtained at twice the gain used in Fig. 2. This reduction cannot be considered to be conclusive evidence for polarization due to [CH<sub>3</sub>CO CH<sub>2</sub>- $CH_3$ <sup>1<sup>t</sup></sup> since  $CCl_4$  might also be acting as a triplet quencher. For the aldehydes, the polarization for the carbonyl hydrogen is reduced much more than that for the parent ketone. Although this reduction indicates that the aldehyde polarization results from F as well as T pairs, it seems unlikely that the F type polarization comes

 $CCl_4$ 

(+) (-)

CH<sub>3</sub>CH<sub>2</sub>Cl (+) (-)

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solely from  $[CH_3\dot{C}O\dot{C}H_2CH_3]^F$  since the reduction is not the same for both the aldehyde and the ketone. Consequently an additional free radical reaction is probably responsible for at least part of the polarization observed for the aldehydes in the absence of carbon tetrachloride. This additional path may also be indicated by the discrepancy between calculated and observed polarizations for acetaldehyde and ethylene discussed above. The nature of this path is not obvious to us. It is difficult to use this evidence as an indication of a hydrogen abstraction mechanism as observed for acetone (1) because additional products would be expected and we have not detected them. If this process occurs, it does not appear to make a major contribution to the observed polarization.

For comparison, the calculated relative intensities are shown in Fig. 3 to illustrate the agreement between calculated and observed values. The only exception is ethyl chloride whose observed relative intensities do not conform to the calculated values based on either eq. 7 or eq. 11 (indicated in Fig. 3 as *iii* and *iv*, respectively). However, good agreement is obtained for both the CH<sub>3</sub> and CH<sub>2</sub> resonances if the calculated values based on eq. 7 are added to those based on eq. 11. For this reason we suggest that eqs. 7 and 11 make comparable contributions to the polarization observed for ethyl chloride. Alternative mechanisms such as contributions from singlet and triplet pairs do not give the proper relative intensities.

The assignment of the quartet at 2.80 p.p.m. and the triplet at 1.3 p.p.m. to 1,1,1-trichloropropane cannot be considered conclusive since we have not added the compound to the solution and have been unable to find a report of its spectrum. We base this assignment on indirect evidence. For example, compounds such as ethyl chloride, propionyl chloride, and propionic acid have been ruled out because their chemical shifts differ substantially from 2.80 and 1.3 p.p.m. Other compounds have been ruled out on the basis of multiplicity in addition to chemical shift. Second, the chemical shifts for the protons of trichloroisobutane are CH<sub>3</sub>, 1.30 p.p.m. and CH, 2.73 p.p.m. (10). and the chemical shift for 1,1,1-trichloroethane is 2.80 p.p.m. (1). Finally, as can be seen in Table 1 and in Fig. 3, the identical spectrum (including relative intensities) is

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observed when 3-pentanone replaces 2-butanone. Since  $\alpha$  cleavage of both compounds can provide ethyl radicals, 1,1,1-trichloropropane would be expected in both cases. The calculated relative intensities based on  $[CH_3CH_2 \cdot CCl_3]^F$  are given in Fig. 3 (denoted v) to illustrate the agreement with observed values.

At CCl<sub>4</sub> concentrations which are substantially higher than 0.07 M, CIDNP evidence has been obtained (10, 11) for the reaction of excited singlet state ketones with CCl<sub>4</sub>. Furthermore, for more highly branched di-t-butyl ketone, quenching data indicate reaction occurs via excited singlet and triplet states (12). In the case of 2butanone and 3-pentanone, the maximum concentration attainable for CCl<sub>4</sub> in the mixed solvent is not large enough to provide the opportunity to detect the singlet mechanism. At any rate, our results do not preclude the possibility that both the singlet and triplet mechanism occur. Our results indicate only that Schemes 1 and 2 provide the main contribution to the CIDNP effects observed for 2-butanone and 3-pentanone in D<sub>2</sub>O and D<sub>2</sub>O-CD<sub>3</sub>CN.

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