

# Photochemistry of 2,2,12-trimethylcyclododecanone and 2,2,12,12-tetramethylcyclododecanone: product distribution, photo-CIDNP and magnetic isotope effect<sup>†</sup>

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## Abstract

The primary photochemical process of 2,2,12-trimethylcyclododecanone (**1a**) and 2,2,12,12-tetramethylcyclododecanone (**1b**) is exclusively C<sub>1</sub>–C<sub>2</sub>  $\alpha$  cleavage to form biradicals **2a** and **2b** which then disproportionate to form enals. This contrasts with the strong preference for  $\gamma$ -hydrogen abstraction for the parent cyclododecanone. The preference of  $\alpha$  cleavage over  $\gamma$ -hydrogen abstraction for the methyl-substituted large ring cycloalkanones is explained by the faster rate of  $\alpha$  cleavage due to stabilization of the intermediate biradical by methyl substitution. No nuclear polarization can be observed in the photochemically induced dynamic nuclear polarization (photo-CIDNP) of **1a** in the absence of radical scavengers. Measurement of the <sup>13</sup>C isotopic content of the photoproducts shows that the major enal product is slightly enriched in <sup>13</sup>C in the absence of radical scavengers through isotopomer separation via the magnetic isotope effect. However, the recovered **1a** is not enriched in <sup>13</sup>C. The addition of radical scavengers, such as molecular oxygen, CBrCl<sub>3</sub> or CCl<sub>4</sub>, causes dramatic nuclear polarization and an increase in the <sup>13</sup>C enrichment of the enal product. The presence of radical scavengers opens up a competitive pathway which serves as the spin (or isotopomer) sorting process required for both the generation of T<sub>0</sub>-S biradical CIDNP and isotope enrichment. In the absence of radical scavengers, the observation of the slight <sup>13</sup>C enrichment in the enal product and the absence of nuclear polarization result from the slow decarbonylation process which is fast enough to serve as an isotopomer sorting process, but not fast enough to serve as a spin sorting process.

## 1. Introduction

The photolysis of five- and six-membered cycloalkanones has been extensively studied [1–5]. The dominant primary process in the photolysis of these medium ring ketones is  $\alpha$  cleavage (type I reaction) rather than  $\gamma$ -hydrogen abstraction (type II reaction). In contrast, for cyclododecanone and other unsubstituted large ring cycloalkanones, the major products of photolysis are cyclobutanol derivatives resulting from  $\gamma$ -hydrogen abstraction [6–9]. 2-Methylcyclododecanone undergoes both  $\alpha$  cleavage and  $\gamma$ -hydrogen abstraction, since the methyl group can stabilize the biradical produced by  $\alpha$  cleavage and thereby accelerate the rate of  $\alpha$  cleavage [10, 11]. The photolysis of large ring 2-phenylcycloalkanones and 2,*n*-diphenylcycloalkanones (*n* = 9, 10, 11, 12,

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15) produces exclusive  $\alpha$  cleavage [12] since the phenyl group can stabilize the biradical resulting from  $\alpha$  cleavage. In chemically induced dynamic electron polarization (CIDEP) studies of the biradicals produced from the photolysis of 2,2,12-trimethylcyclododecanone (**1a**) and 2,2,12,12-tetramethylcyclododecanone (**1b**), Closs and Forbes [13] observed intense electron spin polarization due to strong electron–nuclear hyperfine coupling (HFC) within the biradical. Tarasov *et al.* [14] reported the first investigation of the magnetic isotope effect on the photolysis of **1a**. They observed very low  $^{13}\text{C}$  enrichment in the recovered **1a**, which seems inconsistent with the CIDEP results. In principle CIDEP, the magnetic isotope effect and chemically induced dynamic nuclear polarization (CIDNP) (for reviews, see ref. 15) all have the same origin, *i.e.* the electron–nuclear hyperfine interaction in the biradical.

In this report, we investigate the role of the HFC interaction in the biradical chemistry of the title compounds. To elucidate the reaction mechanism, the product distribution (as a function of the temperature and solvent polarity), magnetic isotope effect and photo-CIDNP were investigated. It was observed that the enal isomer, a product that has not been reported previously [14], was slightly enriched in  $^{13}\text{C}$ . The addition of radical scavengers, such as molecular oxygen,  $\text{CBrCl}_3$  or  $\text{CCl}_4$ , increased the  $^{13}\text{C}$  content of the enal product, but not the recovered **1a** (the  $^{12}\text{C}$  is sorted from the  $^{13}\text{C}$  through the scavenging reactions, *i.e.* the scavenged products are enriched in  $^{12}\text{C}$  relative to natural abundance). In the absence of radical scavengers, no photo-CIDNP effect was observed. The presence of radical scavengers caused dramatic nuclear polarization in the starting ketone, the enal isomer and the corresponding scavenged product(s). The effect of radical scavengers [16–19] can be rationalized by the creation of a competing pathway to serve as a spin (or isotopomer) sorting process.

## 2. Experimental details

### 2.1. Synthesis of **1a** and **1b** [20]

KH (Aldrich, 30 ml, 262 mmol), washed twice with 50 ml of pentane, was added to a flask which contained 220 ml of distilled tetrahydrofuran (THF). Cyclododecanone (Aldrich, 9.0 g, 49.4 mmol) was transferred into the flask over a period of 10 min. Methyl iodide (Aldrich, 13.5 ml, 217 mmol) was added to the flask over a period of 30 min. The reaction mixture was stirred for an additional 30 min. During work-up, 30 ml of water was added. After the separation the aqueous layer was extracted with several 15 ml portions of ethanol. The organic extracts were dried with anhydrous  $\text{K}_2\text{CO}_3$  and combined. Distillation of the organic layer gave 9.5 g (98%) of **1a** (pentane, 99.6% pure by gas chromatography (GC)) which was purified by recrystallization. In the synthesis of **1b** from **1a**, a mixture of **1a** (12.5 mmol), KH (7.56 ml, 66.0 mmol) and 57 ml of distilled THF was refluxed at 70 °C for 22 h. Methyl iodide (8.54 ml, 137 mmol) was then added to the reaction mixture over a period of 30 min. The reaction mixture was stirred for another 30 min, and then quenched by the addition of 19 ml of water. After work-up, **1b** was purified by preparative vapor phase chromatography (VPC) (column, 2 m; carbowax). Both **1a** and **1b** were characterized by their spectral properties: mass spectrometry (MS) (Hewlett Packard GC/MS, model 5988A),  $^1\text{H}$  300 MHz nuclear magnetic resonance (NMR) (VXR 300, ppm,  $\text{CDCl}_3$ , tetramethylsilane (TMS)), Fourier transform IR (FTIR) (Perkin–Elmer, FT 1600) and UV (Perkin–Elmer 559A). Compound **1a**: MS, 224 ( $\text{M}^+$ );  $^1\text{H}$  NMR, 3.18 ppm (M, 1H), 1.98 (M, 2H), 1.05–1.6 (M, 16H), 1.05 (d, 3H), 1.05 (s, 6H); FTIR, 1699.3  $\text{cm}^{-1}$  (carbonyl); UV, 294 nm ( $\epsilon=23$ ). Compound **1b**: MS, 238 ( $\text{M}^+$ );  $^1\text{H}$  NMR, 1.55 ppm (t, 4H), 1.1–1.4 (M, 14H), 1.2 (s, 12H); UV, 295 nm ( $\epsilon=24$ ).

## 2.2. Photolysis of **1a** and **1b**

A solution of **1a** or **1b** (2–5 mmol) was placed in an NMR tube and bubbled with argon for 10 min. The sample was irradiated using a medium pressure mercury lamp (450 W) fitted with an aqueous potassium chromate filter solution. The conversion was maintained below 30%. For the low temperature photolysis, the NMR tube containing the solution of **1a** or **1b** was immersed in a Dewar flask constructed so that one side was transparent to UV and visible light. The product distributions were determined by gas chromatography using a 25 m capillary column (Hp-1, cross-linked methyl silicone gum).

## 2.3. Spectral data for the photolysis products of **1a** and **1b**

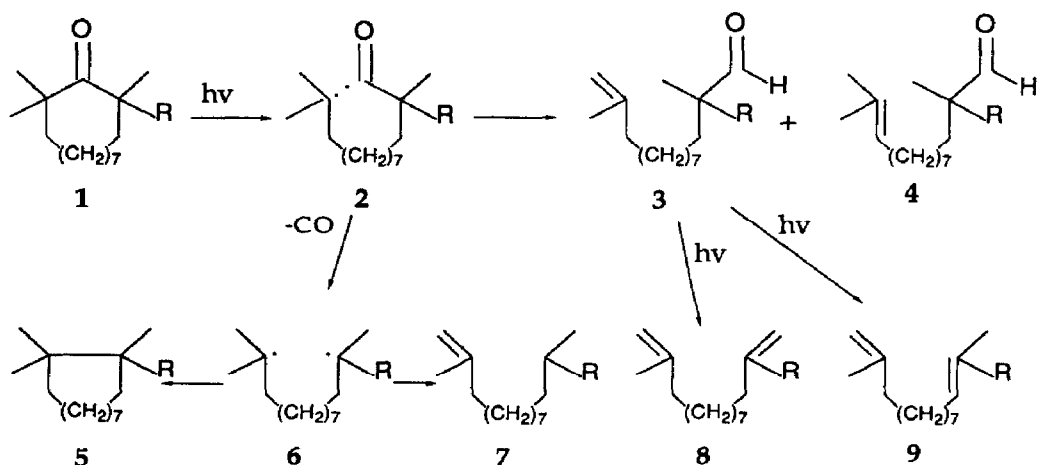
The photolysis products were separated by preparative VPC (2 m, carbowax), and characterized by GC/MS and 300 MHz  $^1\text{H}$  NMR (ppm,  $\text{CDCl}_3$ , TMS). **3a**: GC/MS, 224 ( $\text{M}^+$ );  $^1\text{H}$  NMR, a mixture with **4a** (**3a**:**4a**=41:6), 9.64 (d, 1H), 4.7 (m, 2H), 2.0 (t, 2H), 1.7 (s, 3H), 1.2–1.6 (m, 17H), 1.1 (d, 3H). **4a**: GC/MS, 224 ( $\text{M}^+$ );  $^1\text{H}$  NMR, 9.64 (d, 1H), 5.14 (t, 1H), 2.0 (m, 2H), 1.6 (s, 6H), 1.2–1.6 (m, 17H), 1.1 (d, 3H). Mixture of **5a**, **7a** and **8a** (ratio, 26:100:9): **5a**: GC/MS, 196 ( $\text{M}^+$ ); **7a**: GC/MS, 196 ( $\text{M}^+$ );  $^1\text{H}$  NMR, 4.70 (d, 2H), 2.0 (t, 2H), 1.72 (s, 3H); **8a**: GC/MS, 194 ( $\text{M}^+$ );  $^1\text{H}$  NMR 5.80 (m, 1H), 4.95 (m, 2H), 4.70 (d, 2H). **9a**: GC/MS, 194 ( $\text{M}^+$ );  $^1\text{H}$  NMR of mixture of **9a** with **7a** and **8a** shows internal olefinic hydrogen at 5.14 (m). **3b**: GC/MS, 238 ( $\text{M}^+$ );  $^1\text{H}$  NMR, 9.48 (s, 1H), 4.68 (m, 2H), 2.0 (t, 2H), 1.72 (s, 3H), 1.2–1.5 (m, 14H), 1.08 (s, 6H). **4b**: GC/MS, 238 ( $\text{M}^+$ );  $^1\text{H}$  NMR, 9.48 (s, 1H), 5.14 (t, 1H), 2.0 (m, 2H), 1.62 (s, 6H), 1.2–1.5 (m, 14H), 1.08 (s, 6H). **5b**: GC/MS, 210 ( $\text{M}^+$ ). **7b**: GC/MS, 210 ( $\text{M}^+$ ). **8b**: GC/MS, 208 ( $\text{M}^+$ ). **9b**: GC/MS, 208 ( $\text{M}^+$ ). Mixture of **5b**, **7b**, **8b** and **9b** (ratio, 11:100:49:23):  $^1\text{H}$  NMR of the mixture shows both terminal and middle olefinic hydrogens, 4.68 (s), 5.12 (t); ratio of integrals of 4.68 ppm to 5.12 ppm is about 14.

## 2.4. Photo-CIDNP and magnetic isotope effect experiments

The CIDNP experiments were performed using a Bruker-IBM 250 MHz FTNMR spectrometer. The NMR probe was modified with a quartz light pipet equipped with two mirrors at both ends to allow the passage of collimated light into the NMR chamber. A 1000 W high pressure mercury lamp (Oriol) fitted with a  $\text{CoSO}_4$  aqueous filter solution was used as the light source. All solutions were purged by argon gas for 5 min before the experiments, except for the experiments with molecular oxygen as scavenger, when the solutions were purged with pure oxygen for 5 min before the measurements. In the magnetic isotope effect experiments, a solution of the photo-products was injected into a Hewlett Packard GC/MS (model 5988A), and the  $^{13}\text{C}$  content of the products was analyzed in the chemical ionization (CI) mode and the isotopic composition was computed as described previously [16].

## 3. Results and discussion

Scheme 1 shows the reaction mechanism of the photolysis of **1a** and **1b**. Regiospecific  $\alpha$  cleavage of the  $\text{C}_1\text{--C}_2$  (most substituted) bond generates triplet biradical **2**, which undergoes intersystem crossing, followed by either intramolecular disproportionation to generate isomers **3** and **4** or recombination to regenerate the starting ketone. The biradical **2** also undergoes a minor degree of decarbonylation, as shown by the product analysis, to generate biradical **6**, which is stabilized by cyclization and disproportionation



a: R = H; b: R = CH<sub>3</sub>

Scheme 1. Photochemistry of 2,2,12-trimethylcyclo-dodecanone and 2,2,12,12-tetramethylcyclo-dodecanone.

TABLE 1

Product distribution of the photolysis of 1a

Solvent	<i>T</i>	Conversion (%)	Yield (%)				
			3+4	3/4	5+7+8	9	Unknown
Hexane	RT	25	91	11	2.3	2.3	1.0
	-78 °C	19	94	16	2.4	1.0	1.0
Benzene	RT	21	95	13	1.4	0.8	1.0
	MeCH	RT	23	91	11	3.0	3.2
DMF	-78 °C	22	92	15	0.5	3.3	-
	RT	25	80	14	3.0	2.0	-
	-78 °C	27	72	19	0.4	5.5	-

MeCH, methylcyclohexane; DMF, *N,N*-dimethylformamide; RT, room temperature. Estimated error limits are no more than  $\pm 10\%$  of the reported values.

to products 5 and 7 respectively. The formation of biradical 6 is confirmed by time-resolved electron spin resonance (TRESR) studies on 1a and 1b [13]. The ESR spectrum of acyl alkyl biradical 2 is observed after a short time delay (0.25  $\mu\text{s}$ ) following the photolysis of 1. The spectrum corresponding to biradical 6 increases after a delay of about 1  $\mu\text{s}$ . For 2-methylcyclohexanone, a lower limit of a 50-fold preference for the cleavage of the C<sub>1</sub>-C<sub>2</sub> bond over the C<sub>1</sub>-C<sub>6</sub> bond has been established [2], while no C<sub>1</sub>-C<sub>12</sub> cleavage is observed for 1a.

Tables 1 and 2 show the product distributions of the photolysis of 1a and 1b in several solvents at two temperatures. At low conversion (less than 30%), the decarbonylation products 5, 7, 8 and 9 are produced in relatively small amounts compared

TABLE 2

Product distribution of the photolysis of **1b**

Solvent	<i>T</i>	Conversion (%)	Yield (%)				
			3+4	3/4	5+7+8	9	Unknown
Hexane	RT	24	68	14	3.0	0.7	5.8
	-78 °C	23	76	24	2.3	0.2	-
Benzene	RT	25	84	15	6.6	0.6	1.2
MeCH	RT	22	76	18	3.1	0.4	-
	-78 °C	21	86	24	6.0	-	-
DMF	RT	22	80	23	-	-	-
	-78 °C	27	83	31	2.9	1.0	-

MeCH, methylcyclohexane; DMF, *N,N*-dimethylformamide; RT, room temperature. Estimated error limits are no more than  $\pm 10\%$  of the reported values.

with the enal products. The highly efficient intramolecular disproportionation of biradical **2** leads to the formation of the major product enals **3** and **4**. From  $^{13}\text{C}$  isotope enrichment in the photolysis of **1b**, Tarasov *et al.* [14] found that the efficiency of separation of the isotopes was very low, and concluded that this was due to the low reversibility of acyl alkyl biradical **2b**. The photolysis of **1a** and **1b** in methanol does not produce new products, which excludes the formation of ketene by intramolecular disproportionation of biradical **2**. More importantly, for the photolysis of **1a** and **1b**, no  $\gamma$ -hydrogen abstraction products are detected, although cyclobutanol derivatives account for 17% of the products in the photolysis of 2-methylcyclododecanone [10]. This result is expected since biradical **2** is more stable, and is therefore formed faster than the radical formed by the  $\alpha$  cleavage of 2-methylcyclododecanone. The product distributions, as listed in Tables 1 and 2, show that the photolysis of **1b** results in a slightly larger amount of decarbonylated products than the photolysis of **1a**, whereas **1a** gives slightly more enal products than **1b**. This result suggests that the decarbonylation process of the primary biradical is more efficient due to the enhanced stabilization of the secondary biradical by substituents at the  $\alpha$  positions. Previous studies [12] have shown that photolysis of 2,12-diphenylcyclododecanone results in more than 90% decarbonylation products and photolysis of 2-phenylcyclododecanone gives more than 90% isomerization products; these results are consistent with the above suggestion.

The "external" enals **3a** and **3b** are formed preferentially to the "internal" enals **4a** and **4b** in the disproportionation process, which is consistent with Weiss's reported photolysis of 2-methylcyclododecanone in which an enal analogous to **3** is the major product [10, 11]. In contrast, substituted cyclohexanone photolysis gives primarily enals analogous to **4** [12]. The **3** to **4** ratio for **2a** and **2b** is higher than ten. It is also higher than that for 2-methylcyclododecanone (**3** to **4** ratio of about eight [11]). This result is probably obtained because the radicals from **1a** and **1b** have twice as many methyl hydrogens as the biradical from the photolysis of 2-methylcyclododecanone. The **3** to **4** ratio increases with increasing polarity of the solvent. This ratio is also much higher at  $-78\text{ }^\circ\text{C}$  than at room temperature. The dependence of the product ratio on the solvent polarity implies that the transition state for the formation of terminal enal **3** is probably more polar than that for enal **4**. The formation of **3** is more favored in a polar solvent. The temperature effect on the ratio of **3** to **4** suggests

that the formation of the terminal alkene is kinetically controlled, and is favored by lowering the temperature of the reaction. Furthermore, the non-bonding interactions and the strain energy for the formation of **4** are larger than for the formation of **3** [11]. Consequently, higher temperatures will favor the formation of the enal **4**. A similar temperature effect on the product distribution was also observed by Coyle [21] in a study of the photolysis of 2-*t*-butyl-cyclohexanone.

The photo-CIDNP effect of **1a** was studied in a magnetic field of 58.3 kG (corresponding to a 250 MHz  $^1\text{H}$  FTNMR or 68.9 MHz  $^{13}\text{C}$  FTNMR spectrometer). The  $^{13}\text{C}$  and  $^1\text{H}$  photo-CIDNP spectra are shown in Figs. 1 and 2 respectively. In the absence of radical scavengers, no nuclear polarization is observed (see Fig. 1(b)). However, dramatic nuclear polarization in **1a**, **3a** and the corresponding scavenged products is observed when radical scavengers, such as molecular oxygen,  $\text{CBrCl}_3$  or  $\text{CCl}_4$  (see Figs. 1(a), 1(c) and 1(d) respectively), are introduced into the reaction mixture. Because of their instability, the products resulting from oxygen scavenging were not isolated, so that the polarization bands are assigned, as listed in Table 3, by comparison with the authentic products. In the presence of molecular oxygen, it is proposed that the triplet intermediate biradical **2a** reacts to form the biradical **10a**, which undergoes recombination or disproportionation to form **11a** or **12a** respectively. The two enhanced absorption peaks at 176.7 and 173.8 ppm (Fig. 1(a)) exhibit an

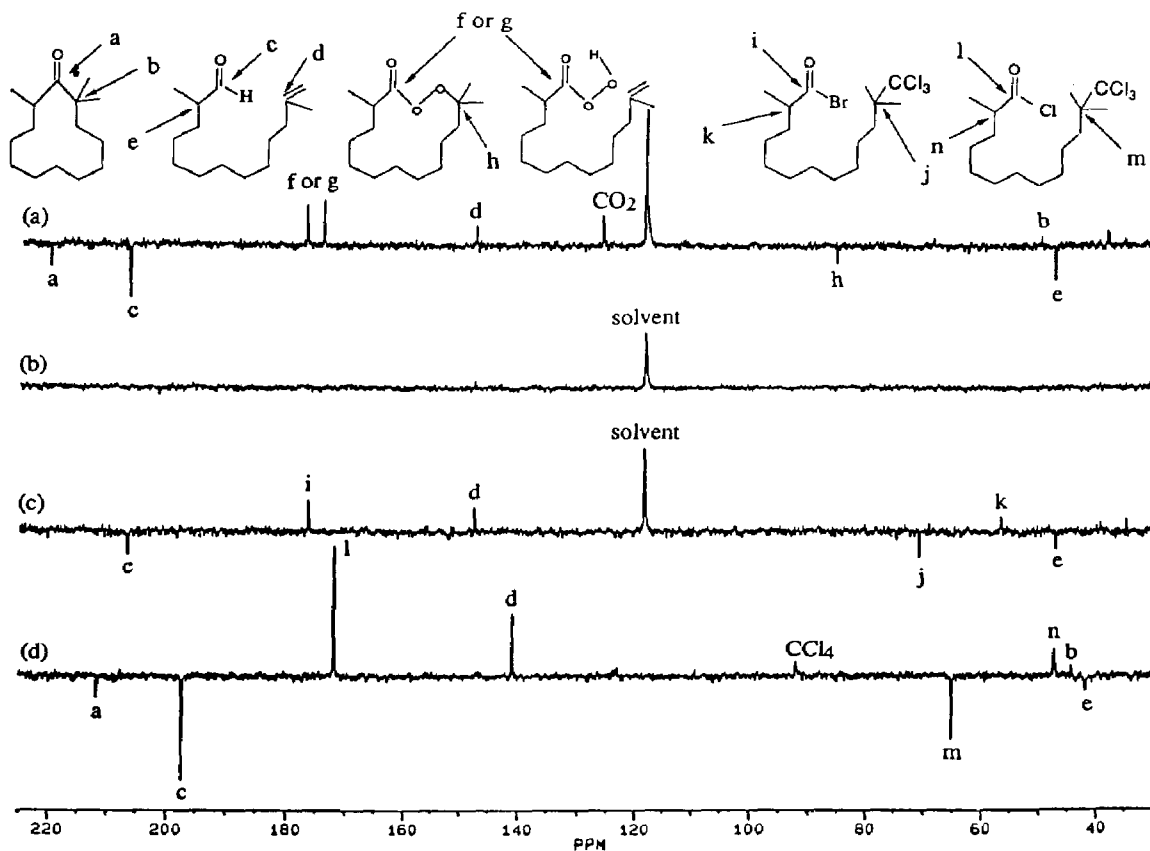


Fig. 1.  $^{13}\text{C}$  CIDNP of a 30 mM solution of **1a** in  $\text{CD}_3\text{CN}$  in the presence of molecular oxygen (a), in the absence of molecular oxygen (b), in the absence of molecular oxygen but with the addition of 20 mM  $\text{CBrCl}_3$  (c) and in neat  $\text{CCl}_4$  solvent (d).

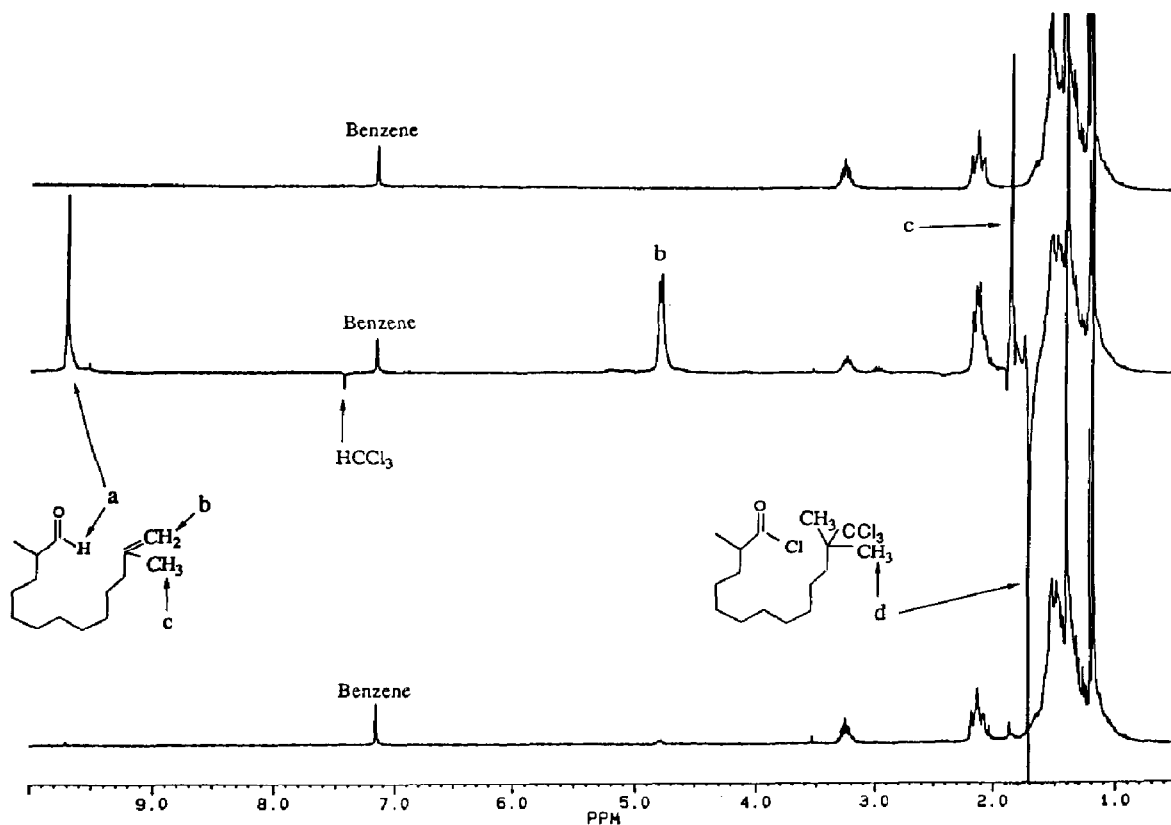
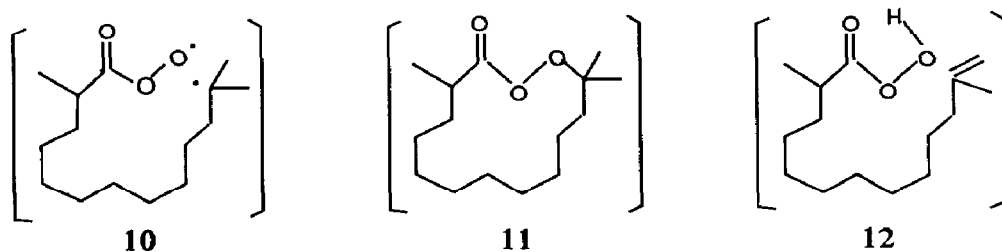


Fig. 2.  $^1\text{H}$  CIDNP of a 30 mM solution of **1a** in neat  $\text{CCl}_4$  solution (250 MHz): before (top), during (middle) and after (bottom) irradiation. A capillary tube containing benzene- $d_6$  solvent was inserted into the sample tube to lock the NMR frequency.

opposite polarization phase from the recombination products (220 ppm of **1a** and 206.3 ppm of **3a**), and are therefore assigned to the carbonyls of **11** and **12**. The emissive polarization peak at 85 ppm, corresponding to C–O-type carbons, is therefore assigned to the  $\text{C}_2$  of **11**. The intermediate biradical **10** undergoes decarbonylation to generate  $\text{CO}_2$ , as shown by the enhanced absorption of  $\text{CO}_2$  at 125.7 ppm.

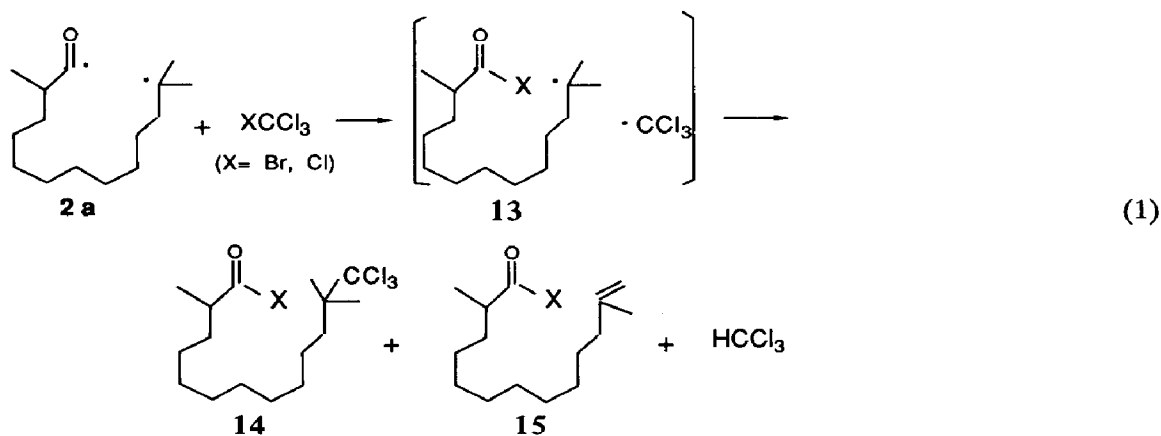


In the presence of  $\text{CBrCl}_3$  or  $\text{CCl}_4$ , the acyl radical center abstracts a halogen atom to form the intermediate radical pair **13**, followed by radical pair recombination or disproportionation to give products **14**, **15** and  $\text{HCCl}_3$  (see eqn. (1)).

TABLE 3

$^{13}\text{C}$  and  $^1\text{H}$  chemical shifts and CIDNP polarization phases of carbons and protons of various products (E, emission, A, absorption)

Compound	Nucleus	Chemical shift
1a	C=O	220 ppm ( $\text{CD}_3\text{CN}$ , E), 216.3 ppm ( $\text{CCl}_4$ , E)
	2-C	49.2 ppm ( $\text{CD}_3\text{CN}$ or $\text{CCl}_4$ , A)
3a	C=O	206.3 ppm ( $\text{CD}_3\text{CN}$ , E), 201.9 ppm ( $\text{CCl}_4$ , E)
	2-C	46.8 ppm ( $\text{CD}_3\text{CN}$ , E), 46.4 ppm ( $\text{CCl}_4$ , E)
	12-C	147.2 ppm ( $\text{CD}_3\text{CN}$ , A), 145.5 ppm ( $\text{CCl}_4$ , A)
	C(=O)H	9.7 ppm ( $\text{CCl}_4$ , d, A)
	=CH <sub>2</sub>	4.78 ppm ( $\text{CCl}_4$ , d/d, A)
	13-CH <sub>3</sub>	1.85 ppm ( $\text{CCl}_4$ , A)
14 <sub>Br</sub>	C=O	176 ppm ( $\text{CD}_3\text{CN}$ , A)
	2-C	70.6 ppm ( $\text{CD}_3\text{CN}$ , E)
	12-C	56.6 ppm ( $\text{CD}_3\text{CN}$ , A)
14 <sub>Cl</sub>	C=O	176.3 ppm ( $\text{CCl}_4$ , A)
	2-C	51.8 ppm ( $\text{CCl}_4$ , A)
	12-C	69.8 ppm ( $\text{CCl}_4$ , E)
	13-CH <sub>3</sub>	1.7 ppm ( $\text{CCl}_4$ , E)
CO <sub>2</sub>	C	125.7 ppm ( $\text{CD}_3\text{CN}$ , A)
HCCl <sub>3</sub>	H	7.4 ppm ( $\text{CCl}_4$ , E)



Previous studies [16–18] demonstrate that the reactivity of acyl radicals towards perhalomethane is at least three orders of magnitude higher than that of alkyl radicals. Therefore the halogen abstraction by the acyl radical center is most probably the first step in the quenching of biradical **2a** by perhalomethane [16, 17].

The disproportionation process of the intermediate radical pair **13** is shown by the formation of HCCl<sub>3</sub>, which exhibits emissive polarization at 7.4 ppm (Fig. 2(b)). The proton of HCCl<sub>3</sub> comes from one of the gem-dimethyl protons of **13**. Therefore, the polarization phase of HCCl<sub>3</sub> is the same as the dimethyl protons of product **14**, which shows emissive polarization at 1.72 ppm (Fig. 2(b)). After normalization for the number of protons, the polarization intensity of HCCl<sub>3</sub> is much smaller than that



of the dimethyl protons of **14**, which implies that the recombination pathway is the major annihilation process of radical pair **13**. The electron  $g$  factor is approximately 2.0007 for the acyl radical center [22] and 2.0025 for the alkyl radical center [23]. The HFC constants of the carbons and protons of biradical **2a** are as follows:  $a_{C=O} = 114$  G,  $a_{2-C} = 47$  G [22],  $a_{12-C} = 25$  G and  $a_{H,13-CH_3} = 22$  G [23]. The polarization phases of carbons and protons follow Kaptein's net rule [24]. For example, for the carbonyl carbon of **3a**, an emission is predicted from Kaptein's rules:  $(\mu)(\epsilon)(\sigma)(\Delta g) = (+)(+)(-)= -, E$ .

The polarization phases of the scavenged products are opposite to the corresponding carbon (or proton) of the recombination products (Figs. 1 and 2). The observation that the overall polarization is a mixture of enhanced absorption and emission is a signature of  $T_0$ -S CIDNP. The  $T_0$ -S CIDNP mechanism requires competing pathways such as cage reactions and cage escape to serve as spin sorting processes for the generation of nuclear polarization. In radical pair systems, a common competing radical escape is irreversible diffusional separation of the radical pair, which is not available for biradicals due to the connection of the two radical centers by a molecular chain. In the present system, the decarbonylation process, a chemical process, is not fast enough to compete with the cage reactions of biradicals **1a** and **2a**. Therefore the  $T_0$ -S CIDNP mechanism is not observed. (Another type of polarization mechanism,  $T_{\pm}$ -S, usually occurs in short biradicals ( $n \leq 3$ ,  $n$  is the number of carbons between the two radical centers) at high fields, or in medium biradicals ( $4 \leq n \leq 7$ ) at low fields). For long chain biradicals, such as **2a**, a large external magnetic field will split the  $T_{\pm}$  triplet sublevels away from the S singlet state, which results in the "quenching" of the  $T_{\pm}$ -S CIDNP mechanism [25].) The lack of an effective spin sorting process seems to be a very common cause for the failure of observation of CIDNP of many long chain biradicals [16-19]. The introduction of radical scavengers, such as molecular oxygen,  $CBrCl_3$  or  $CCl_4$ , opens up a competing pathway to serve as the spin sorting process for the generation of  $T_0$ -S CIDNP for both biradicals and results in dramatic nuclear polarization, which offers valuable information concerning the reaction mechanism. Different scavengers have characteristic quenching rates for various types of radicals. Our previous study indicates that intense nuclear polarization occurs only when the radical scavenging rate is comparable with the radical cage recombination [16, 17]. A much slower or faster scavenging rate will cause a reduction in the CIDNP intensities to below the level of observation.

The generation of nuclear polarization is due to effective electron-nuclear hyperfine-induced intersystem crossing (ISC) which dominates in the ISC process of "open chain" biradical conformers (*i.e.* biradical conformations with 6-10 Å end-to-end separation). Another ISC mechanism, spin-orbit coupling (SOC), dominates in triplet biradicals with closed chain conformations. The SOC-induced ISC is available for both magnetic and non-magnetic nuclei, while the HFC-induced ISC is a unique characteristic property of magnetic nuclei. The observation that the polarization of **3a** is much higher than that of **1a** (see Figs. 1 and 2) implies that most of the "open chain" biradical conformers follow the disproportionation pathway to give product **3a**, *i.e.* recombination is a minor pathway as suggested by Tarasov *et al.* [5]. Since the factors leading to both CIDNP and the magnetic isotope effect are essentially the same, and are due to the electron-nuclear hyperfine interaction involved in the ISC process, we examined the  $^{13}C$  content of both **3a** and recovered **1a** (see Table 4). In the absence of radical scavengers, the product **3a** is only slightly enriched in  $^{13}C$  [5]. The addition of radical scavengers (5 mM  $CBrCl_3$  or in neat  $CCl_4$ ) increases the  $^{13}C$  enrichment of **3a**. However, the recovered **1a** is not enriched in  $^{13}C$ , which is consistent with the results reported

TABLE 4

$^{13}\text{C}$  enrichment of the photoproducts of **1a** in  $\text{CH}_3\text{CN}$  (with or without the presence of  $\text{CBrCl}_3$ ) and neat  $\text{CCl}_4$

Condition	<b>1a</b>		<b>3a</b>	
	Conversion	$\beta^a$ (%)	Absolute yield <sup>b</sup>	$\beta$ (%)
In $\text{CH}_3\text{CN}$ (no scavenger)	32	0	68	31
	49	0	59	34
In $\text{CH}_3\text{CN}$ (5 mM $\text{CBrCl}_3$ )	55	6	33	50
	58	6	38	56
In $\text{CCl}_4$	45	0	34	40
	74	0	29	64

<sup>a</sup> $\beta$  is defined as follows: (observed  $^{13}\text{C}$  (%) of the product minus  $^{13}\text{C}$  (%) of the unphotolyzed starting ketone)/1.108%, where 1.108% is the natural abundance of  $^{13}\text{C}$ . The error limit of  $\beta$  is estimated to be  $\pm 30\%$ , mainly the result of instrumental errors in the analysis.

<sup>b</sup>Absolute yield is obtained from the observed yield divided by the conversion.

by Tarasov *et al.* [5] in the absence of radical scavengers. As in  $T_0$ -S CIDNP, isotope separation through the magnetic isotope effect also requires a competing pathway to serve as the isotopomer sorting process which allows the escape of those biradicals associated with  $^{12}\text{C}$  (which have a slower ISC rate than those associated with  $^{13}\text{C}$ ). In the absence of a competing pathway, all biradicals containing either  $^{13}\text{C}$  or  $^{12}\text{C}$  will sooner or later undergo the same cage process to couple into the same product(s). In this situation, no net isotope separation results. The addition of radical scavengers opens up a new exit channel to remove those biradicals with  $^{12}\text{C}$ , and results in an increase in the  $^{13}\text{C}$  content of the recombination products. Since the isotope separation is due to the HFC-induced ISC process, and not to the SOC-induced ISC process, the slightly  $^{13}\text{C}$ -enriched **3a** should mainly come from the open chain biradical conformers, and the recovered **1a** from the closed chain biradical conformers. The observation that the addition of radical scavengers increases the  $^{13}\text{C}$  content of product **3a** implies that some of the open chain biradical conformers are scavenged during their lifetime. In the absence of radical scavengers, the observation that the slow decarbonylation process of biradical **2a** may serve as a competing process for isotope separation, but not for CIDNP, indicates that the effective range of the isotopomer sorting process of this particular system is probably wider than that of the spin sorting process.

A final issue of interest is whether the absolute rate of decarbonylation from the biradical is significantly different from the rate for an analogous monoradical. Since decarbonylation of the primary biradical is competitive with ISC and halogen abstraction, a rough estimation of these rates can be made by comparison of the rates of free radical models, or by setting one known rate as the "clock" for the estimation of the other rates. In TRESR measurements [13], the primary biradical **2b** was detected at 0.25  $\mu\text{s}$  after laser excitation, and the secondary biradical at 1  $\mu\text{s}$  after laser excitation. These results show the rate of decarbonylation of **2b** to be of the order of approximately  $10^6 \text{ s}^{-1}$ . In comparison, the monoradical analog of **2b**, the *t*-butyl acyl radical  $[(\text{CH}_3)_3\text{CO}]$ , is reported [26] to possess a decarbonylation rate of approximately  $7 \times 10^5 \text{ s}^{-1}$ , *i.e.* a rate of the same order as that deduced for the biradical.

## 4. Conclusions

Stabilization by the methyl substituents causes the primary photochemical process of **1a** and **1b** to be exclusively  $\alpha$  cleavage, in contrast with the exclusive  $\gamma$ -hydrogen abstraction typical of unsubstituted large ring cycloalkanones. The preferential formation of the enal product **3** is the result of the slow decarbonylation rate and the effective disproportionation of the intermediate biradical **2**. Photo-CIDNP and magnetic isotope effect studies show that most of the open chain biradical conformers undergo efficient intramolecular disproportionation rather than recombination. The addition of radical scavengers, such as molecular oxygen,  $\text{CBrCl}_3$  or  $\text{CCl}_4$ , results in dramatic nuclear polarization and increases the  $^{13}\text{C}$  enrichment of the enal product **3a** (and presumed, but not measured,  $^{12}\text{C}$  enrichment of the scavenged products), but not the recovered starting ketone **1a**. The effect of the scavengers can be rationalized in terms of the introduction of a competing process, which serves as the required spin (or isotopomer) sorting process.

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