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Involvement of Exciplexes in the Photolysis of Aliphatic Ketones in Deuteriochloroform: CIDNP Evidence

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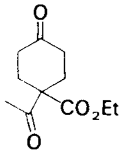
Photolysis of 4-acetyl-4-ethoxyformylcyclohexanone and 4-acetyl-4-phenylcyclohexanone in deuteriochloroform showed an unusual polarization which suggests that a singlet exciplex of the ketone with deuteriochloroform may be involved in the Norrish type I reaction.

KEY WORDS Photolysis Ketones CIDNP Exciplex

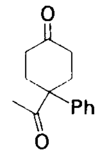
INTRODUCTION

Photolysis of ketones has been extensively studied by chemically induced dynamic nuclear polarization (CIDNP).[1–3] Most of the CIDNP results indicated that the Norrish type I reaction of simple aliphatic ketones produces an acyl–alkyl radical pair which undergoes in-cage recombination and disproportionation reactions and, in addition, out-of-cage hydrogen and/or chlorine abstraction from scavengers or solvents. A triplet multiplicity of the excited state from which the reaction takes place has been proved to be predominant.[4–6] On the other hand, den Hollander *et al.*[7] and Bargon[8] have observed unusual polarizations during the photolysis of α-branched alkanones carried out in the presence of carbon tetrachloride, and have proposed that a singlet exciplex between the ketone and carbon tetrachloride may be involved in the reaction. In other solvents, such as deuteriochloroform, however, no such unusual polarization has been reported.

During the photolysis of 4-acetyl-4-eth oxyformylcyclohexanone (**1**) and 4-acetyl-4-phenylcyclohexanone (**2**) in $CDCl_3$, we observed an unusual polarization which cannot be explained by the general triplet radical pair mechanism. The result, together with the high selectivity of chlorine abstraction from deuteriochloroform as shown by product analysis, suggests that a singlet exciplex between the ketone and deuteriochloroform may be involved in the reaction. This is believed to be the first CIDNP evidence concerning a ketone–deuteriochloroform exciplex as a precursor of the radical pair in the photolysis of ketones. Further, the characteristics of the ketone–$CDCl_3$ exciplex were found to be different from those of the ketone–CCl_4 exciplexes reported previously.[7,8]



R^1COCH_3 (**1**)



R^2COCH_3 (**2**)

EXPERIMENTAL

Compounds **1** and **2** were prepared according to the literature.[9] Sample solutions were deaerated by bubbling argon. The products of the photolysis were identified by gas chromatography–mass spectrometry (GC–MS) with a Hewlett-Packard HP 5988A mass spectrometer and ^1H NMR. NMR measurements were performed at 80.131 MHz on a Bruker AC-80 spectrometer equipped with a photo-CIDNP probe which was maintained at 293 K with a Bruker variable-temperature control unit. The spectrometer was operated in the routine KINETICS mode with a flip angle of 30°. A 0.1 M solution of the sample in $CDCl_3$ was irradiated *in situ* with the full spectrum of a Kratos KPS 255 HR 1000 W xenon lamp.

RESULTS AND DISCUSSION

^1H NMR spectra obtained (a) during and (b) after the irradiation of **1** and **2** in $CDCl_3$ are shown in Figs 1 and 2, respectively. The spectra in Figs 1b and 2b are basically the same as those recorded before the irradiation, indicating that during the short period of irradiation only a very small amount of the sample was photolysed. In order to identify the products, the irradiation was continued for a further 20 min at 293 K, and the products were analysed by GC–MS. This showed a pre-

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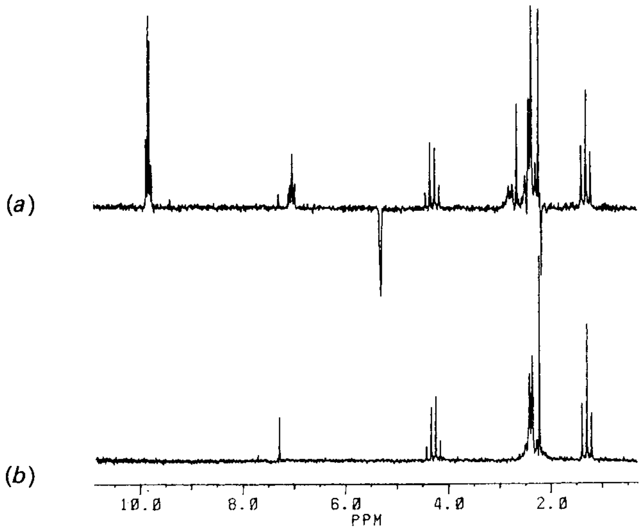


Figure 1. 80 MHz ^1H NMR spectra obtained (a) during and (b) after photolysis of 0.1 M **1** in $CDCl_3$.

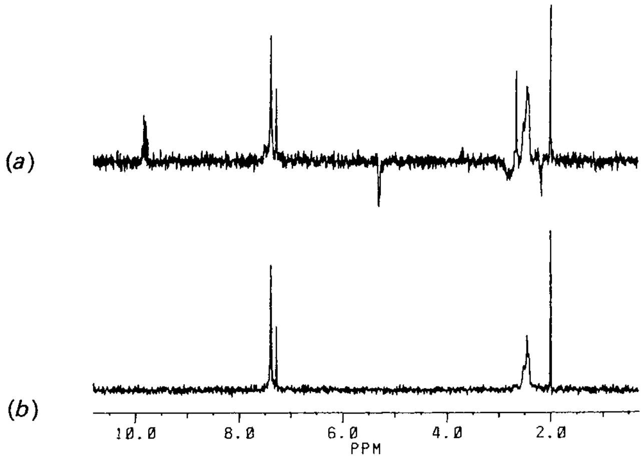


Figure 2. 80 MHz ^1H NMR spectra obtained (a) during and (b) after photolysis of 0.1 M **2** in $CDCl_3$.

Table 1. Assignment and polarization of NMR lines recorded during photolysis of 1 and 2 in $CDCl_3$

Chemical shift (ppm *vs.* TMS) 1	2	Polarization phase 1	2	Compound[a]
2.17	2.17	E	E	CH_3*CHO
9.80	9.80	A	A	CH_3CH*O
5.30	5.30	E	E	CH*DCl_2
2.67	2.67	A	A	CH_3*COCl
7.10		A		$R^1(-H)$[b]
	6.10		A	$R^2(-H)$[b]
2.80		A		$R^1(-H)$[c]
	2.85		E	$R^2(-H)$[c]

[a] Asterisks designate polarized protons.
[b] Olefinic proton.
[c] Allylic proton.

dominant production of CH_3COCl (*m/z* 63, M − CH_3; 43, M − Cl), together with small amounts of CH_3CHO (*m/z*: 44, M; 43, M − H), alkenes [*m/z*: 168, M for $R^1(-H)$ or 172, M for $R^2(-H)$], $CHDCl_2$ (*m/z*: 85, M; 87, M + 2; 89, M + 4), R^1CDCl_2 (*m/z*: 253, M; 169, M − $CDCl_2$) or R^2CDCl_2 (*m/z*: 257, M; 173, M − $CDCl_2$), and a very small amount of $CDCl_2CDCl_2$ (*m/z*: 133, M − Cl; 98, M − 2Cl; 84, $\frac{1}{2}$M). Notably, no CH_3CDO was detected. The assignment of NMR lines based on the chemical shifts and the GC–MS analyses is listed in Table 1. Peaks around 2.4 ppm were superimposed and therefore cannot be assigned unambiguously.

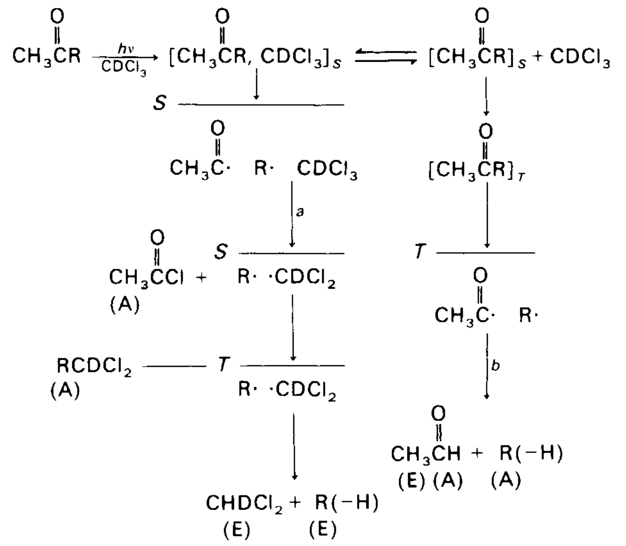
In addition to polarization of acetaldehyde and the alkenes, which must originate from the in-cage disproportionation of the triplet acetyl–alkyl pair, the two spectra revealed some novel features, viz. enhanced absorption for acetyl chloride, emission for $CHDCl_2$, time-dependent polarization for the alkenes and the lack of polarization for $CHCl_3$ and the parent ketones.

In general, photolysis of dialkyl ketones in deuteriochloroform does not produce acyl chloride,[7,9] because the acyl radical decarbonylates rapidly.[10] However, den Hollander *et al.*[7] reported that photolysis of diisopropyl ketone (DIK) in the presence of CCl_4 gave a high yield of isobutyryl chloride which was not polarized. It was proposed that the reaction proceeds via a singlet exciplex between the ketone and CCl_4 as shown in Eqn (1). According to this scheme, polarization for the acyl chloride would not be expected since the α-cleavage of the ketone and the chlorine abstraction take place simultaneously.[11]

$$DIK(S_1) + CCl_4 \rightarrow (DIK,\ CCl_4)_{S_1} \rightarrow RCOCl + {}^{S}\overline{R\cdot\cdot CCl_3} \quad (1)$$

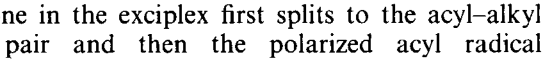
On the other hand, enhanced absorptive acyl chlorides have been observed in the photolysis of di-*tert*-butyl ketone[12] and 2-butanone and 2-pentanone[13] in the presence of CCl_4. The polarization was assumed to arise from chlorine abstraction of the acyl radical, which escaped from the cage, from CCl_4. This assumption, however, has been doubted by Kaptein,[4] since the reaction was found to occur only in CCl_4 and not in several other chlorinated solvents, including $CDCl_3$.[7]

Our new finding was that acetyl chloride was produced in high yield and showed enhanced absorption when the ketones were photolysed in $CDCl_3$. The question is, how does the polarized acetyl chloride arise? CIDNP alone cannot distinguish a singlet in-cage reaction from a triplet out-of-cage reaction, since both give the same phase of polarization.[14] Therefore, one has to search for other evidence. The GC–MS analysis of the products indicated that no CH_3CDO was produced during the reaction, despite the production of a large amount of CH_3COCl and a small amount of CH_3CHO. This means that the acetyl radical did not escape from the cage; had the acetyl radical diffused into the bulk solvent, it would have abstracted deuterium in preference to chlorine[9] from $CDCl_3$ to produce CH_3CDO. Therefore, the mechanism shown in Scheme 1 is suggested for the photolysis of ketones **1** and **2** in $CDCl_3$. This involves a singlet exciplex between the ketone and deuteriochloroform. The cooperation of the singlet exciplex (route *a*) and the triplet acyl–alkyl radical pair (route *b*) can satisfactorily account for all the experimental observations by the Kaptein rule,[14] as shown in Scheme 1.



Scheme 1. Proposed mechanism for the photolysis of **1** and **2** in CDCl$_3$.

The validity of the in-cage chlorine abstraction was further evidenced by the lack of polarization for chloroform in our experiment. Generally, emission for CHCl$_3$ was always observed when photolysis was carried out in deuteriochloroform[7,9] owing to abstraction of deuterium from the solvent and subsequent hydrogen abstraction by ·CCl$_3$ [Eqn (2)]. Since alkyl radicals usually abstract hydrogen or deuterium more readily than chlorine,[9] our observation of exclusive formation of CHDCl$_2$, i.e. high selectivity of chlorine abstraction over deuterium abstraction, implies that the chlorine abstraction did not take place in the bulk solvent. The emissive CHDCl$_2$ may originate from the triplet R·—·CDCl$_2$ pair as shown in Scheme 1.



$$\mathrm{R\cdot + CDCl_3} \begin{cases} \rightarrow \mathrm{RD + \cdot CCl_3} \xrightarrow{\mathrm{R\cdot}} \mathrm{CHCl_3} \\ \rightarrow \mathrm{RCl \bullet \cdot CDCl_2} \xrightarrow{\mathrm{R\cdot}} \mathrm{CHDCl_2} \end{cases} \qquad (2)$$

It should be pointed out that the ketone–CDCl$_3$ exciplex behaves slightly differently from the ketone–CCl$_4$ exciplex reported by den Hollander *et al.*[7] In the ketone–CCl$_4$ exciplex the α-cleavage of the ketone and the chlorine abstraction from CCl$_4$ take place simultaneously in the exciplex, giving the acyl chloride no polarization. In the ketone–CDCl$_3$ exciplex, however, the ketone in the exciplex first splits to the acyl–alkyl radical pair and then the polarized acyl radical abstracts chlorine from the complexed CDCl$_3$, forming the absorptive acyl chloride. The difference may originate from the fact that chlorine abstraction from CDCl$_3$ is slower than that from CCl$_4$.[15] The high selectivity of chlorine abstraction over deuterium abstraction from CDCl$_3$ in the exciplex suggests that a specific configuration of the complex may be required for the reaction.

The coexistence of routes *a* and *b* can also be proved by the fact that the signal intensity of the alkenes is time dependent (Fig. 3). It is seen that although the signal intensities of acetaldehyde (9.80 and 2.17 ppm) were almost unchanged during the photolysis, the signal intensities of the alkene changed considerably with time.

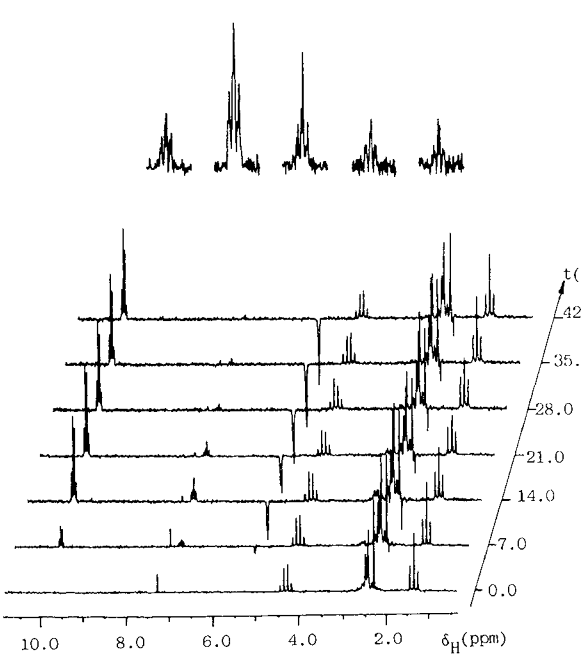


Figure 3. Time dependence of the ^{1}H NMR signal during the photolysis of **1** in CDCl$_3$. The inset illustrates the expansion of the peak at 7.10 ppm.

For **1**, the enhanced absorptions at 7.10 and 2.80 ppm reached their maxima around 14 s after turning on the light, and then the intensity decreased rapidly. With **2**, a weak enhanced absorption appeared at the beginning of the irradiation and disappeared quickly, while an emission at 2.85 ppm appeared and increased gradually in intensity. The results can be explained by the competition between routes *a* and *b* (Scheme 1). Both pathways would produce the same alkene. However, since the *g* value of the alkyl radical (2.0025) is greater than that of the acetyl radical (2.0007), but smaller than that of ·CDCl$_2$ (2.0080),[4] the alkene derived from routes *a* and *b* should give an opposite polarization. The different behaviour of **1** and **2** is a reflection of the different ease of formation of the exciplex for the two compounds. The influence of the structure of ketones on the stability of exciplexes has been discussed by Bargon.[8] The absence of polarization for the parent ketones and the high yield of acetyl chloride demonstrate that route *a* must be the main pathway in our reactions.

It was noted that the structure of the ketones can influence the mechanism of photolysis appreciably. For instance, photolysis of dibenzyl ketone in CDCl$_3$ did not give any product derived from the solvent.[16] Photolysis of diisopropyl ketone in CDCl$_3$ gave emissive CHCl$_3$ but no indication of the formation of any exciplex.[7] In the present case the specific structures of **1** and **2** may play a role in the formation of the exciplex. Further investigations of the structural dependence of the formation of the exciplex are in progress.

Acknowledgements

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REFERENCES

1. H. Fischer, *Pure Appl. Chem.* **41**, 475 (1975).
2. G. L. Closs, R. J. Miller and O. D. Redwine, *Acc. Chem. Res.* **18**, 196 (1985).
3. I. R. Gould, B. H. Baretz and N. J. Turro, *J. Phys. Chem.* **91**, 925 (1987).
4. R. Kaptein, in *Advances in Free Radical Chemistry*, edited by G. H. Williams, Vol. 5, p. 319. Elek Science, London, 1975.
5. J. K. Vollenweider, H. Fischer, J. Hennig and R. Leuschner, *Chem. Phys.* **97**, 217 (1985).
6. N. J. Turro, *Modern Molecular Photochemistry*, p. 528. Benjamin Cummings, Menlo Park (1978).
7. J. A. den Hollander, R. Kaptein and P. A. T. M. Brand, *Chem. Phys. Lett.*, **10**, 430 (1971).
8. J. Bargon, in *Proceedings of 28th IUPAC Macromolecular Symposium*, p. 297, IUPAC, Oxford, (1982).
9. P. G. Frith and K. A. McLauchlan, *J. Chem. Soc., Faraday Trans. 2* **72**, 87 (1976).
10. N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro and J. C. Dalton, *J. Am. Chem. Soc.* **92**, 6874 (1970).
11. N. A. Porter and P. M. Iloff, Jr., *J. Am. Chem. Soc.* **96**, 6200 (1974).
12. W. B. Moniz, C. F. Poranski, Jr, and S. A. Sojka, *J. Org. Chem.* **40**, 2947 (1975).
13. S. P. Vaish, R. D. McAlpine and M. Cocivera, *Can. J. Chem.* **52**, 2978 (1974).
14. R. Kaptein, *J. Chem. Soc., Chem. Commun.* 732 (1971).
15. J. S. Keute, D. R. Anderson and T. H. Koch, *J. Am. Chem. Soc.* **103**, 5434 (1981).
16. L. J. Johnston, P. D. Mayo and S. K. Wong, *J. Am. Chem. Soc.* **104**, 307 (1982).