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Carbon-13 CIDNP during Photolysis of Di-*tert*-butyl Ketone in Carbon Tetrachloride[1]

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Carbon-13 Fourier transform (FT) NMR was used to observe CIDNP during the photolytic decomposition of di-*tert*-butyl ketone in CCl_4. Recombination of the triplet *tert*-butyl-pivaloyl radical pair (I) was unambiguously established. The polarizations from 2,2-dimethylpropanal (1) and 2,2-dimethylpropanoic acid chloride (3) also result from triplet radical pair I. Other polarized products may come from singlet or triplet radical pair precursors. The observed polarization signs agreed with those predicted for all identified products.

The use of carbon-13 FT NMR to study CIDNP holds great promise as a mechanistic and kinetic tool for the investigation of radical reactions.[2] The major advantages of studying carbon-13 CIDNP are the large chemical shift range and the ability to make all carbons appear as singlets by proton decoupling. In addition, FT NMR techniques enable the entire spectrum to be recorded in a matter of seconds.

As part of our program of defining the pathways of material degradation, we have examined by carbon-13 FT NMR the CIDNP during the photochemical decomposition of di-*tert*-butyl ketone (DTBK) in CCl_4. Analysis of the polarization signs provided insight into the various degradation steps and the multiplicities of radical pair precursors. Proton CIDNP during the photolysis of DTBK has been previously studied using continuous-wave NMR.[3]

Results

Figure 1 shows proton decoupled carbon-13 FT NMR spectra of a 25% DTBK solution in CCl_4 obtained before, during, and after irradiation. The center spectrum, obtained during the first 1000 sec of photolysis, shows emis-

Figure 1. Proton decoupled carbon-13 FT NMR spectra of a 25% DTBK solution in CCl_4 obtained before (top), during (middle), and after (bottom) irradiation. The spectra width is 250 ppm. For each spectrum 100 free induction decays were accumulated at a pulse repetition time of 10 sec.

sion and enhanced absorption signals. These CIDNP signals were assigned to particular carbon atoms by comparing their chemical shifts to those of authentic compounds (Table I). Assignments were aided by observing the carbon–hydrogen splitting patterns in proton coupled spectra. In addition, the proton coupled CIDNP spectra ensured that signals were not being lost in the decoupled spectra due to the exact cancellation of any multiplet effects.

Emission signals occur from C-3 of DTBK, C-1 and C-2 of 2,2-dimethylpropanal (**1**), C-1 of methylpropene (**2**), C-2 of 2-chloro-2-methylpropane (**4**), and $CHCl_3$. The emission signal at 23.9 ppm may be assigned to C-3 of either aldehyde **1** or olefin **2**. Enhanced absorption signals are observed for C-2 of olefin **2**, C-1 of chloride **4**, and all the carbons of 2,2-dimethylpropanoic acid chloride (**3**). Although the signals from C-1 and C-2 of DTBK were affected during photolysis, it was difficult to tell if absorption or emission was occurring because of contributions from unreacted DTBK. Other CIDNP signals of lower intensity were not assignable. The spectrum recorded after photolysis, using the same number of spectral accumulations, contained only signals attributable to C-1 and C-2 of DTBK, C-3 of acid chloride **3**, and C-1 of chloride **4**. Additional signal averaging revealed peaks assigned to $CHCl_3$ and C_2Cl_6.

Table I
Carbon-13 Chemical Shifts of Products Showing CIDNP During the Photolysis of DTBK in CCl_4[a]

Product	Carbon position	Chemical shift, ppm During photolysis[b]	 Authentic product[c]
DTBK	1	28.5[d]	28.5
	2	45.3[d]	45.2
	3	215.2 (E)	215.1
1	1	202.4 (E)	202.2
	2	42.2 (E)	42.5
	3	23.9 (E)[e]	24.0
2	1	110.7 (E)	110.6
	2	140.8 (A)	140.7
	3	23.9 (E)[e]	23.8
3	1	178.6 (A)	178.6
	2	48.9 (A)	49.0
	3	27.1 (A)	27.1
4	1	34.5 (A)	34.5
	2	65.7 (E)	65.6
$CHCl_3$	1	77.2 (E)	77.1

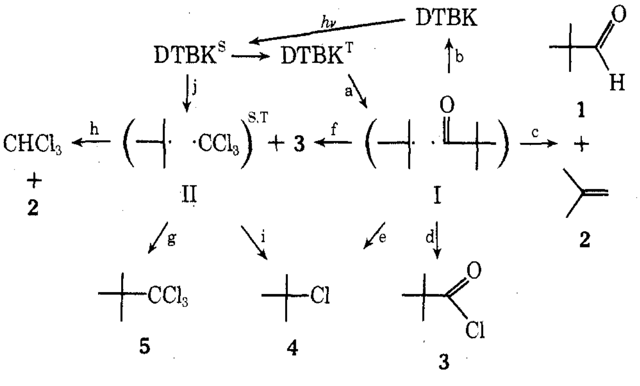
[a] Chemical shifts converted to Me_4Si scale using $\sigma_{Me_4Si} = \delta_{CCl_4} + 96.0$. [b] A = enhanced absorption; E = emission. Unassigned CIDNP signals occurred at 137.8 (E), 111.4 (E), 111.1 (A), 103.4 (E), 98.1 (E), 53.8 (E), 49.7 (A). [c] 25% solutions in CCl_4. [d] Although the intensity of this peak was affected, it was difficult to tell if enhanced absorption or emission was occurring because of signal contribution from unreacted DTBK. [e] This signal may be assigned to C-3 of 1 or 2.

Products **1**, **3**, **4**, $CHCl_3$, C_2Cl_6 as well as 1,1,1-trichloro-2,2-dimethylpropane (**5**), HC_2Cl_5, and C_2Cl_4 were identified by GC–MS analysis.

Discussion

Interpretation of the polarization signs in terms of the CKO theory[4] of CIDNP suggested the mechanistic pathways shown in Scheme I. All the polarization signs may be rationalized by initially invoking the triplet *tert*-butyl–pivaloyl radical pair (I). Some of the polarizations, however, are also consistent with reaction from the singlet *tert*-butyl–trichloromethyl radical pair (II).

Scheme I



The polarizations from DTBK, aldehyde **1**, and acid chloride **3** must result from triplet pair I. Olefin **2** and chloride **4** may come from I, from triplet pair II formed by pair substitution[5] (eq f), or from singlet pair II formed by a singlet exciplex reaction (eq j). In addition, trichloropropane **5** and $CHCl_3$ may result from the singlet or triplet pair II.

Table II
Evaluation of Kaptein's Expression for Products Formed During Photolysis of DTBK in CCl_4[a]

		Radical formation		Product formation				Polarization[b]	
Product	Carbon position	eq[c]	μ	eq[c]	ϵ	Δg[d]	A	Calcd	Exp
DTBK	1	a	+	b	+	+	−	E	*e*
	2	a	+	b	+	+	+	A	*e*
	3	a	+	b	+	−	+	E	E
1	1	a	+	c	+	−	+	E	E
	2	a	+	c	+	−	+	E	E
	3[f]	a	+	c	+	−	+	E	E
2	1	a	+	c	+	+	−	E	E
		f	+	h	+	+	−	E	E
		j	−	h	+	−	−	E	E
	2	a	+	c	+	+	+	A	A
		f	+	h	+	+	+	A	A
		j	−	h	+	−	+	A	A
	3[f]	a	+	c	+	+	−	E	E
		f	+	h	+	+	−	E	E
		j	−	h	+	−	−	E	E
3	1	a	+	d	−	−	+	A	A
	2	a	+	d	−	−	+	A	A
	3	a	+	d	−	−	+	A	A
4	1	a	+	e	−	+	−	A	A
		f	+	i	−	+	−	A	A
		j	−	i	−	−	−	A	A
	2	a	+	e	−	+	+	E	E
		f	+	i	−	+	+	E	E
		j	−	i	−	−	+	E	E
5	1	f	+	g	+	−	+	E	*g*
		j	−	g	+	+	+	E	*g*
	2	f	+	g	+	+	+	A	*g*
		j	−	g	+	−	+	A	*g*
	3	f	+	g	+	+	−	E	*g*
		j	−	g	+	−	−	E	*g*
$CHCl_3$	1	f	+	h	+	−	+	E	E
		j	−	h	+	+	+	E	E

[a] μ is + for triplet pairs and pairs formed from free radical encounters, − for singlet pairs; ϵ is + for cage products, − for escape products; Δg is + for the radical with the larger g factor, − for the radical with the smaller g factor. [b] A = enhanced absorption; E = emission. [c] Equations of Scheme I. [d] g(pivaloyl) = 2.0008;[16] g(*tert*-butyl) = 2.0026;[16] $g(\cdot CCl_3)$ = 2.0091.[17] [e] See Table I, footnote *d*. [f] See Table I, footnote *e*. [g] The chemical shifts of these carbons have not been determined. However, an emission signal was observed in the region where C-1 would be expected to appear (see ref 8).

Table II evaluates Kaptein's expression,[6] $\Gamma = \mu\epsilon\Delta gA$, for the reaction products formed by the indicated pathways. The four terms determine the sense of the polarization. Thus, Γ is positive for enhanced absorption and negative for emission. The multiplicity of the radical pair is given by μ, the type of product-forming reaction is taken into account by the ϵ term, Δg is the sign of the spectroscopic splitting factor difference, and the sign of the electron-nuclear hyperfine interaction constant, A, directly enters the expression.

Triplet Reactions. Spin selection originating in triplet pair I can rationalize the polarization signs for all identified products. Triplet DTBK undergoes α-cleavage (eq a) to form I, which may recombine (eq b), disproportionate (eq c), lead to escape products (eq d, e), or produce triplet pair II by pair substitution[5] (eq f). Pair II may also collapse (eq g), disproportionate (eq h), or lead to escape products (eq i).

Although all the carbons of DTBK are being affected during photolysis, the emission of C-3 is most distinctive. This emission must result from collapse of triplet radical pair I to regenerate starting DTBK (eq b). Carbon-13 CIDNP provides unambiguous evidence that recombination is occurring. This information is difficult to obtain by other photochemical methods. Furthermore, proton CIDNP studies[3] were unable to reveal this reaction, except under stationary nutation conditions.[7]

Table II shows that the polarization from all the carbons of aldehyde **1** can only result from the disproportionation of triplet radical pair I (eq c). Olefin **2** produced in this same process also shows agreement between the experimental and predicted polarization signs. The polarization of all the carbons of chloride **4** and acid chloride **3** are consistent with spin sorting in triplet radical pair I. Escape of the *tert*-butyl and pivaloyl radicals from this cage followed by abstraction of chlorine from solvent would lead to the observed polarizations (eq d, e).

Triplet pair I may undergo pair substitution[5] to give pair II. In this process one of the members of pair I (most probably the more reactive pivaloyl radical) reacts with CCl_4 and is quickly replaced by the trichloromethyl radical. Since spin multiplicity is conserved in this step, new pair II retains triplet character.

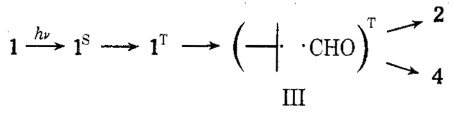
The product from cage collapse of pair II (eq g) is trichloropropane **5**. Although an authentic sample of **5** was not available, there is a weak emission signal in the trichloromethyl carbon region which could be assigned to C-1 of **5**.[8] The production of **5** was confirmed by GC–MS analysis. The emission signal of $CHCl_3$ (eq h) may also be rationalized by this pair substitution mechanism. Unfortunately, the polarization predictions for olefin **2** and chloride **4** are the same for reactions from triplet pair I or triplet pair II, making a definite mechanistic choice impossible.

Singlet Reactions. It has been shown that photoexcitation of *tert*-butyl ketones leads to both singlet and triplet reactive states.[9] More recent evidence points to formation of a singlet exciplex species when the solvent is CCl_4.[3a,10] Scheme I illustrates the decomposition pathways from a singlet DTBK–CCl_4 exciplex.[11] Simultaneous α-cleavage and chlorine abstraction leads selectively to the *tert*-butyl–trichloromethyl radical pair (II), which still retains singlet character (eq j). The acid chloride (**3**) produced in this reaction is not expected to be polarized.[10a] As Table II shows, the polarization signs from products **2**, **4**, **5**, and $CHCl_3$ are predicted to be the same for singlet pair II or a triplet pair II formed by pair substitution and a choice between these two radical pairs cannot be made on the basis of these CIDNP results alone.

Other Reactions. In order to see if secondary photochemical reactions were contributing to the observed polarizations, solutions of compounds **1**, **2**, **3**, and **4** in CCl_4 were photolyzed in the spectrometer.[12]

Aldehyde **1** readily photolyzed and gave rise to major CIDNP signals assigned to C-2 (A) of olefin **2**, C-1 (A) and C-2 (E) of chloride **4**. These polarizations are consistent with reaction from triplet radical pair (III) formed by C–C cleavage (Scheme II). Disproportionation of triplet pair III produces olefin **2** with C-2 in enhanced absorption while escape of *tert*-butyl radicals followed by abstraction gives polarized chloride **4**. The polarization signs are identical with those obtained from the photolysis of DTBK and indicate a

Scheme II



possible complexity in the quantitative analysis of these CIDNP intensities.

Polarizations from the carbons of olefin **2** were not observed during irradiation of **2**. Likewise, CIDNP signals were not detected during the photolysis of acid chloride **3** or chloride **4** under the reaction conditions.

Experimental Section

All chemicals were commercially available and were used without further purification. Solutions were deaerated by a stream of high-purity nitrogen. The products of the photolysis were identified with a Hewlett-Packard Model 5700A/5930A GC–MS system in addition to carbon-13 chemical shifts.

Carbon-13 NMR Measurements. Carbon-13 NMR spectra were obtained at 25.15 MHz on a Varian HA-100 spectrometer modified for pulsed operation and equipped with an external fluorine-19 field-frequency lock.[13] Free induction decays were accumulated and Fourier transformed with a NIC-80 data system. Typically, 100 free induction decays were accumulated using a pulse interval of 10 sec. A 90° pulse took 130 μsec. The probe temperature was 44 ± 2° and 7.5 mm o.d. quartz sample tubes were used. Identical phase corrections were applied to spectra obtained before, during, and after irradiation. Chemical shifts were assigned by comparison with spectra of authentic compounds, which were run as 25% solutions in CCl_4. Chemical shifts were converted to the Me_4Si scale using $\delta_{Me_4Si} = \delta_{CCl_4} + 96.0$.

Photolysis Experiments. Light from a 600-W Hg–Xe arc source was focused through a water filter, Corning filters no. CS-056 and CS-954, and onto the polished end of a quartz rod which terminated 1 mm from the bottom of the sample tube. The combined Corning filters had a measured transmittance of greater than 50% at wavelengths longer than 290 nm and less than 1% at wavelengths shorter than 250 nm. Deaerated 25% solutions of DTBK in CCl_4 were used in the photolysis experiments. For the photolysis of compounds **1**, **2**, **3**, and **4**, 10% solutions were used.

INDO Calculations. The signs of the electron–carbon hyperfine interaction constants for the pivaloyl and *tert*-butyl radicals were obtained using the INDO semiempirical method.[14] Standard geometries were assumed and QCPE program 142 was used for the calculations. All the $A(C^{13})$'s for the pivaloyl radical were calculated to be positive while for the *tert*-butyl radical $A(C^{\alpha})$ is positive and $A(C^{\beta})$ is negative. The $A(C^{13})$ for the trichloromethyl radical is positive.[15]

Registry No.—**1**, 630-19-3; **2**, 115-11-7; **3**, 3282-30-2; **4**, 507-20-0; **5**, 56087-10-6; DTBK, 815-24-7; $CHCl_3$, 67-66-3.

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Secondary Deuterium Isotope Effects and the Conformation of Transition States in the Solvolyses of 3α- and 3β-Cholestanyl Brosylates

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Secondary deuterium isotope effects in ethanolysis of 3β-cholestanyl-*3-d*$_1$ brosylate (**2e**), 3α-cholestanyl-*3-d*$_1$ brosylate (**2a**), 3β-cholestanyl-*2,2,4,4-d*$_4$ brosylate (**3e**), 3α-cholestanyl-*2,2,4,4-d*$_4$ brosylate (**3a**), 3β-cholestanyl-2α-*d*$_1$ brosylate (**4e**), 3α-cholestanyl-2α-*d*$_1$ brosylate (**4a**), and 3α-cholestanyl-2β-*d*$_1$ brosylate (**5a**) were measured. The solvolysis products of unlabeled epimeric brosylates (**1e** and **1a**) were also determined. The deuterium content analyses of olefinic fraction obtained in acetolyses of **3e**, **3a**, **4a**, and **5a** were carried out. The magnitude of the β isotope effects obtained in solvolysis of **3e** ($k_H/k_D = 1.30$), **4e** ($k_H/k_D = 0.95$), and **6e** ($k_H/k_D = 1.18$) leads to the conclusion that the 3β-cholestanyl arensulfonates solvolyze via a chair-like rate-determining transition state. On the other hand, the solvolysis products indicate a half-chair conformation for a product-forming transition state. The isotope effects measured on axial derivatives **3a** ($k_H/k_D = 2.30$), **4a** ($k_H/k_D = 1.13$), and **5a** ($k_H/k_D = 1.60$) discussed together with acetolysis products and the deuterium content of olefins products from **3a**, **4a**, and **5a** suggest a partitioning between k_Δ and k_s processes.

The application of Hammond's postulate[3] to SN1 type reactions implies structural similarities of the cationic intermediate with both ionization and product-forming transition states. One of the best probes of the rate-determining ionization transition state structure are kinetic isotope effects,[4] in particular, owing to their strong conformational dependence, the secondary β-deuterium isotope effects. Product studies, on the other hand, furnish information regarding the structure of the product-forming transition state which, being of lower energy than the rate-determining transition state, resembles the intermediate even more closely.

Recently,[5] we applied both kinetic isotope effects and product analysis in our studies of menthyl tosylate solvoly-