

CIDNP Investigation of Aminyl Radicals Formed by Thermolysis of Triazenes¹⁾

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Thermolysis of asymmetric triazenes Ar-N=N-NH-R **1** produces anilines Ar-NH_2 **2**, hydrocarbons R-H **3**, and *N*-alkylated anilines Ar-NH-R **4** as the main reaction products. ¹H- and ¹³C-CIDNP experiments show polarization of nuclei in Ar-NH_2 , Ar-NH-R , R-H and some additional products (especially ring alkylated anilines). These observations are in agreement with the formation of an intermediate radical pair $[\text{Ar-NH}\cdot\cdot\text{R}]$ which must have been formed *via* homolysis of the tautomeric form ArNH-N=N-R **1'**. Temperature-dependent ¹³C-NMR spectra show a rapid equilibrium between **1** and **1'** at room temperature and above, the tautomeric form **1** being predominant. From the CIDNP spectra the signs of the ¹H and ¹³C hyperfine couplings of aminyl radicals $\text{Ar-NH}\cdot$ and alkyl radicals $\text{R}\cdot$ have been determined.

Recently an important role of free radicals in the reactions of onium compounds with nucleophiles was pointed out.^{1,2)} Electron transfer from nucleophiles to onium ions should initially lead to the primary radical pair I, Scheme 1, from which cage and escape products and/or secondary cages II might be formed. Alternatively, a direct ionic recombination of both components could occur to form a homopolar bond which consecutively would homolyse into the same radical pairs.

As a mechanistic model of one of these reactions, namely, the reaction of aryldiazonium salts with strongly nucleophilic amines or amide anions,³⁾ we have examined the thermolysis of 1-aryl-3-alkyltriazenes **1** in various

solvents at 125–135 °C.

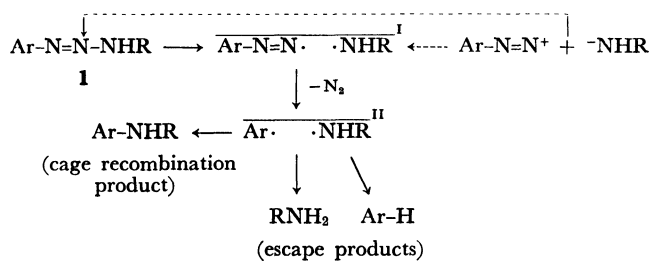
Contrary to the expectation (derived from the structure of triazenes **1**) that arenes ArH and amines R-NH_2 as escape products and *N*-alkylaniline derivatives as the cage recombination products would be formed predominantly in hydrogen-donating solvents as shown in Scheme 1, anilines Ar-NH_2 **2** have been found as the main products indicating the preferential formation of arylaminyl (anilino) radicals in these reactions. Therefore we wish to propose Scheme 2 as revealed by the ¹H- and ¹³C-CIDNP investigations and by the product analysis of the thermal decomposition of the triazenes.

Experimental

The triazenes **1** were synthesized in analogy with the preparation of 1-phenyl-3-methyltriazene⁴⁾ or purchased from Willow Brook Labs. Inc., Waukesha, Wisc., USA. The samples were crystallized from petroleum ether before use. The authentic samples for the reaction products are commercially available except *N*-methyl-*p*-toluidine **4a**, *N*-benzyl-*p*-toluidine **4b** and 2-benzyl-4-methylaniline **5b**. These were prepared according to the literature.^{5,6)}

The ¹H-NMR spectra were obtained on a Hitachi R-20 B (60 MHz) spectrometer and a Bruker HFX-90 (90 MHz) spectrometer (δ ppm from TMS). In typical CIDNP experiments, solutions of 38 mg of triazene in 0.4 ml of solvent (Hitachi) or 70 mg in 1 ml of solvent (Bruker) were heated in the spectrometer probe. CIDNP spectra were registered at 130 °C by a continuous wave scan of 600 Hz/200 s on both instruments. For the Bruker instrument an internal deuterium lock made of DMSO-*d*₆ was sealed in a 2 mm capillary and placed concentrically in a sample tube of 5 mm o.d., using a perforated vortex plug to allow for gas escape.

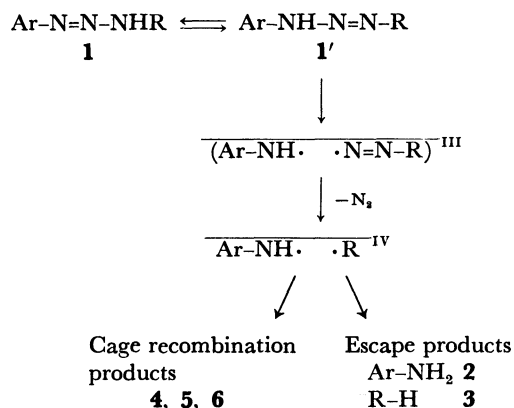
The ¹³C-NMR spectra were obtained at 25.15 MHz on a JEOL PS 100 PFT spectrometer and at 22.628 MHz on the Bruker HFX-90 instrument. The internal deuterium lock described above was used with both instruments. The diameter of the capillary was raised to 4 mm and to 5 mm as a consequence of the 8 mm o.d. (JEOL) and 10 mm o.d. (Bruker) sample tubes. Further conditions for the JEOL instrument: a radiofrequency 45° pulse of 11 μ s was applied with a repetition time of 1.0 s over the spectrum width of 6.25 KHz. Accumulation of the FID signals was started at 30 s after insertion of a sample solution (185 mg of **1b** in 1 ml of a solvent, for



1a: Ar = *p*-tolyl, R = CH₃

1b: Ar = *p*-tolyl, R = CH₂-C₆H₅

Scheme 1.



Scheme 2.

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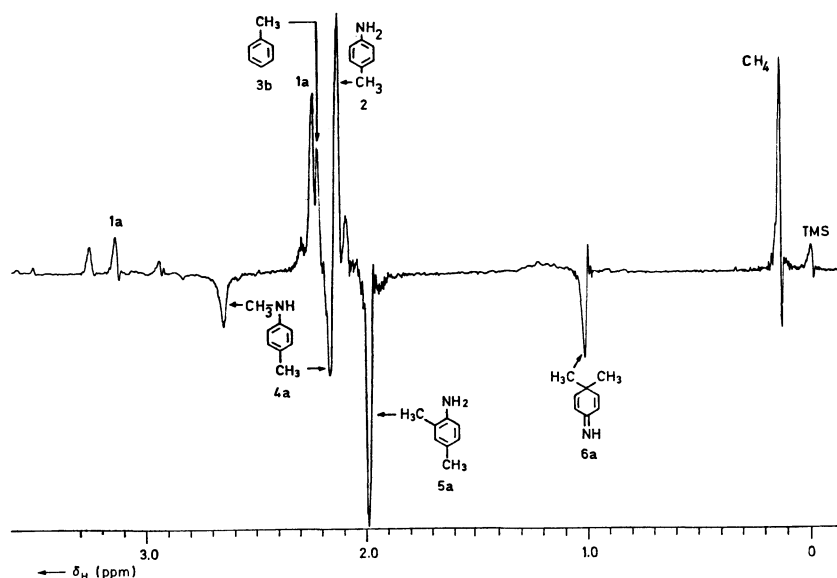


Fig. 1. ^1H -CIDNP spectrum (90 MHz) obtained on a solution of 3-methyl-1-*p*-tolyltriazene **1a** in *o*-dichlorobenzene decomposing at 130 °C.

TABLE 1. ^1H -CIDNP (δ ppm FROM INTERNAL TMS) IN THE THERMOLYSIS OF **1a** IN 1,1,2,2-TETRACHLOROETHANE (TCE), *trans*-DECALIN (DC), AND 1,2-DICHLORO BENZENE (DCB)

TCE ^{a)}	DC	DCB	Assignment	No. of compound	CIDNP
0.20	0.18	0.13	CH_4	3a	strong A
1.18	—	1.01	$\text{NH}-\text{C}_6\text{H}_4-\text{CH}_3$	6a	E
2.12	2.04	1.98	$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{CH}_3$	5a	strong E
2.22	2.16	2.13	$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_3$	2	weak A
2.38	—	2.15	$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{CH}_3$	5a	weak E ^{b)}
2.38	—	2.15	$\text{H}_3\text{C}-\text{NH}-\text{C}_6\text{H}_4-\text{CH}_3$	4a	weak E ^{b)}
2.79	2.76	2.64	$\text{H}_3\text{C}-\text{NH}-\text{C}_6\text{H}_4-\text{CH}_3$	4a	E
2.98	—	—	CH_3Cl	7	short-lived E
6.41	6.28 ^{c)}	—	$\text{H}_3\text{C}-\text{NH}-\text{C}_6\text{H}_3(\text{H})-\text{CH}_3$	4a	A ^{b,d)}
6.54	6.42 ^{c)}	—			A ^{b,d)}
6.41	6.28 ^{c)}	—	$\text{H}_2\text{N}-\text{C}_6\text{H}_3(\text{H})-\text{CH}_3$	5a	A ^{b,d)}
6.54	6.42 ^{c)}	—			A ^{b,d)}
6.47	6.32	—	$\text{H}_2\text{N}-\text{C}_6\text{H}_3(\text{H})-\text{CH}_3$	2	E
6.59	6.46	—			E
6.86	6.75	—	$\text{H}_2\text{N}-\text{C}_6\text{H}_3(\text{H})-\text{CH}_3$	2	A
6.99	6.88	—			A
2.30	2.27	2.24	$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{NH}-\text{CH}_3$	1a	no
3.21	3.19	3.14			no

a) No additional weak emission signals at δ 0.88 and 1.00 in TCE can be assigned. b) Due to the overlap of shift values of **4a** and **5a**, discrimination is not possible. c) Shifts of authentic sample taken at 37 °C with Varian A 60: 6.24, 6.38 ppm. d) No CIDNP observed in TCE. e) Shifts of authentic sample taken at 37 °C with Varian A 60: 6.23, 6.37 ppm.

example) into the preheated NMR probe and was continued until the sum of 300 was obtained. Further condition for the Bruker instrument: *ca.* 300 mg of triazene **1a** in 2 ml of solvent was decomposed. The probe was preheated at 80 °C and accumulation started 40 s after the temperature had reached 130 °C. A 10 μ s pulse was applied 1024 times with a repetition time of 0.4 s over the spectrum width of 5.0 KHz. In each case the sample temperature was controlled as usual by preheated nitrogen flow and thermostatted by a heat-sensor in an effluent gas stream.

Unless otherwise stated, the assignment of both the ^1H - and ^{13}C -CIDNP signals was made by careful comparison of chemical shifts with those of the authentic samples under the same experimental conditions. This was effectively done by adding

small amounts of the authentic sample to the reaction mixture right before and after recording the CIDNP spectra and observing the corresponding increase in absorption intensity of the signals in question. Product analyses were performed by vapor phase chromatography on Shimadzu GC-4A and on Perkin Elmer F-7 instruments in the usual manner using authentic samples for comparison. The amount of nitrogen-plus methane evolved was determined volumetrically by means of a thermostatted azotometer.

Results and Discussion

a) ^1H -CIDNP Results. All the results are summarized in Tables 1 and 2. The aliphatic region

TABLE 2. ^1H -CIDNP (δ ppm FROM INTERNAL TMS) IN THE THERMOLYSIS OF **1b** IN 1,1,2,2-TETRACHLOROETHANE (TCE), *trans*-DECALIN (DC) AND 1,2-DICHLOROBENZENE (DCB)

TCE	DC	DCB	Assignment	No. of compound	CIDNP
1.21		1.09		6b	weak E
2.20	2.16	2.12		2	strong A
2.18		2.19		4b	weak E ^{b)}
2.21		2.19		5b	weak E ^{b)}
2.28		2.22		3b	A
2.77	2.69	2.65		6b	E
2.94	2.88	2.87		8	A
3.84	3.80	3.78		5b	strong E
4.25	4.16	4.20		4b	weak broad E
4.55				9	very weak E
6.46	6.32	}		2	E
6.59	6.46			2	E
6.85	6.74	}		2	A
7.00	6.88			2	A
	6.35	}		4b	A ^{b)}
	6.48			4b	A ^{b)}
6.47	6.34	}		5b	b)
6.60	6.47			5b	b)
	6.79	}		4b	b)
	6.95			4b	b)
7.18	7.12			3b	later E
7.21				5b	E
7.23				8	A
7.34	7.21			4b	E
2.39	2.25	2.34		1b	no
4.89	4.67	4.82		1b	no
7.36				1b	no

a) Assignment tentative. b) Due to overlap, assignment of the anilino part CIDNP signals to **4b** or **5b** is impossible.

of a typical ^1H -CIDNP spectrum of the thermolysis of **1a** in *o*-dichlorobenzene at 130 °C is reproduced in Fig. 1. At this temperature the intensity of the *N*-methyl and aromatic methyl singlets at δ 3.14 and 2.24, respectively, due to **1a** decreases with a half-life of 2–3 min. A strongly polarized absorption due to methane is noted at δ 0.13 throughout a 10–12 min period of the reaction. There are several emission singlets in the methyl region of the spectrum. The one at δ 1.01 is tentatively assigned to the methyl protons of 4,4-dimethyl-cyclohexa-2,5-dien-1-imine **6a**.^{7,8)} The strongest emission at δ 1.98 corresponds to the *ortho*-methyl group of 2,4-dimethylaniline **5a**. Both the aromatic methyl and *N*-methyl protons of *N*-methyl-*p*-toluidine **4a** cause weak emission signals at δ 2.15 and 2.64, respectively. The signal of the aromatic *p*-methyl protons of **5a**, also for which emission is predicted, coincides with that of **4a**. At δ 2.13 the methyl signal of *p*-toluidine **2** itself is observed in weakly enhanced absorption. Some toluene has also been formed as can be seen from the signal at δ 2.22.

The thermal decomposition of the triazene **1a** in 1,1,2,2-tetrachloroethane and in *trans*-decalin supplements the above CIDNP experiments. In 1,1,2,2-tetrachloroethane a short-lived emission at δ 2.98 is considered to be due to methyl chloride **7** formed in 12% yield (vapor phase chromatography) specifically in this solvent. In the aromatic region, the high-field part of the AA'BB' pattern is emissive while the low-field half is slightly enhanced during the first 5 min period of the reaction. Although the AA'BB' multiplet due to the aromatic ring protons of *p*-toluidine and its *N*-methyl derivative **4a** is quite similar under these conditions and also the doublet of H-6 of 2,4-dimethylaniline **5a** is found at the same shift values as H-2,6 of **4a**, we might conclude that the CIDNP effect is derived from the main reaction product *p*-toluidine. At a later stage of the reaction (8–15 min) we note a new emission singlet at the chemical shift corresponding to the aromatic protons of toluene. At the end of the reaction (30 min

after the start) in 1,1,2,2-tetrachloroethane, the signals at δ 1.18, 2.12, and 7.18 are barely detected as absorptions, suggesting the formation of only a small amount of imine **6a**, aniline **5a**, and toluene, respectively (*vide infra*).

In *trans*-decalin the high-field half of the AA'BB' pattern shows emission for *p*-toluidine and enhanced absorption for **4a/5a**. The latter two, of course, cannot be distinguished.

The ^1H -CIDNP experiments with 1-*p*-tolyl-3-benzyl-triazene **1b** (Ar = *p*-CH₃C₆H₄, R = CH₂Ph; Table 2) in principle support our results obtained from thermolysis of **1a**. Therefore, they are not discussed in detail. It should be mentioned, however, that toluene **3b** is formed mainly *via* the benzyl radical and that bibenzyl **8** also shows CIDNP.

b) ^{13}C -CIDNP Results. A nearly full interpretation of the polarized signals during thermolysis of **1a** has been successfully achieved and is given in Table 3. As shown in Fig. 2 (decalin solution), the aliphatic region is not very informative since most of the aromatic *C*-methyl signals coincide and are compensated due to alternating polarizations. Thus it depends on small changes of the reaction conditions, whether the signal at δ 20.6–20.7 ppm is in weak absorption or emission.

The CIDNP pattern of the aliphatic region of **1a** in *o*-dichlorobenzene is shown in Fig. 3 with a clear-cut emission mode of the 20.6 ppm line. The low CIDNP intensity of the aromatic *C*-methyl signals might be due to short spin-lattice relaxation times of these carbon atoms as a result of spin rotation mechanisms available for the methyl groups. On the other hand, those methyl groups originating from the methyl radical of the radical pair III (Scheme 2) show reasonable enhancement factors. This is true for the *N*-methyl carbon of **4a** and for the 2-methyl group of **5a**, which are clearly detected as being in enhanced absorption in or close to the region of the solvent signals. Consequently, lower ^{13}C -hyperfine coupling constants a_1 of the aromatic methyl carbon atoms in arylaminyl radicals with

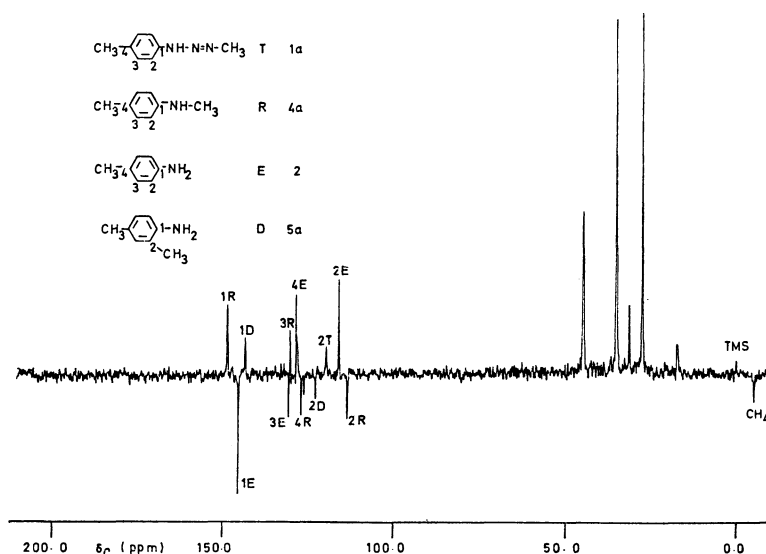


Fig. 2. ^{13}C -CIDNP spectrum (22.628 MHz, PFT) obtained on a solution of **1a** in *trans*-decalin.

TABLE 3. ^{13}C -CIDNP^{a)} IN THERMOLYSIS OF **1a** AT 135 °C

TCE		DC		DCB		Assignment	CIDNP
A ^{b)}	B ^{b)}	A ^{b)}	B ^{b)}	A ^{b)}	B ^{b)}		
-4.0	-4.9	-4.6	-5.1	-3.5	-4.9	CH ₄ (3a)	E
17.7	16.9	16.9	16.9	17.2	16.9	2-CH ₃ (5a)	A
20.4	20.7	20.7	20.6	20.4	20.7	4-CH ₃ (4a)	vwA ^{c)}
20.6	20.7	20.7	20.6	20.6	20.7	4-CH ₃ (2)	vwE ^{c)}
21.8		21.4		21.4		CH ₃ (3b)	
28.7	27.9	—	—	—	—	CH ₃ Cl (7)	wA
31.0	31.0	31.1	31.1	30.0	30.9	N-CH ₃ (4a)	A
39.5	36.8	—	—	—	—		wE
112.5	113.0	113.0	113.2	111.7	113.0	C-2 (4a)	E
116.0	115.6	115.8	115.7	115.3	115.6	C-2 (2)	sA
	119.2		119.3		119.5	C-2 (1a)	
123.2	122.5	122.4	122.4	122.6	122.4	C-2 (5a)	E
125.6	125.4	125.8	125.6	125.5	—	C-4 (3b)	wE
126.2	126.5	126.2	126.5	125.0	126.2	C-4 (4a)	E
128.2	127.5	127.6	127.5	127.9	127.4	C-4 (2)	A
128.7	128.5	128.4		129.1		C-3 (3b)	
129.2		—	—	—	—		A
129.6	129.5	128.6		129.3		C-2 (3b)	
129.7	129.5	130.0	129.6	129.0	129.5	C-3 (4a) (1a)	wA
130.5	130.0	130.4	129.9		130.0	C-3 (2)	wE
	134.7				134.7	C-4 (1a)	
138.2		137.7		137.6		C-1 (3b)	
140.7	139.9	—	—	—	—		A
142.8	142.1	142.5	142.5	142.6	142.4	C-1 (5a)	A
144.7	144.0	144.8	144.6	144.7	144.5	C-1 (2)	sE
					146.7	C-1 (1a)	
147.1	147.3	147.9	147.8	146.7	147.6	C-1 (4a)	A

a) Shifts are given in δ ppm from internal TMS; TCE=1,1,2,2-tetrachloroethane, DC=*trans*-decalin, DCB=1,2-dichlorobenzene; w=weak, vw=very weak, s=strong. b) A: 25.15 MHz spectra; B: 22.628 MHz spectra. c) The signal at 20.6–20.7 ppm is due to the overlap of the 4-methyl signals of **2** and **4a**. Thus it depends on small variations of the reaction conditions (solvent, temperature, concentration) whether it appears in weak emission or weak enhanced absorption.

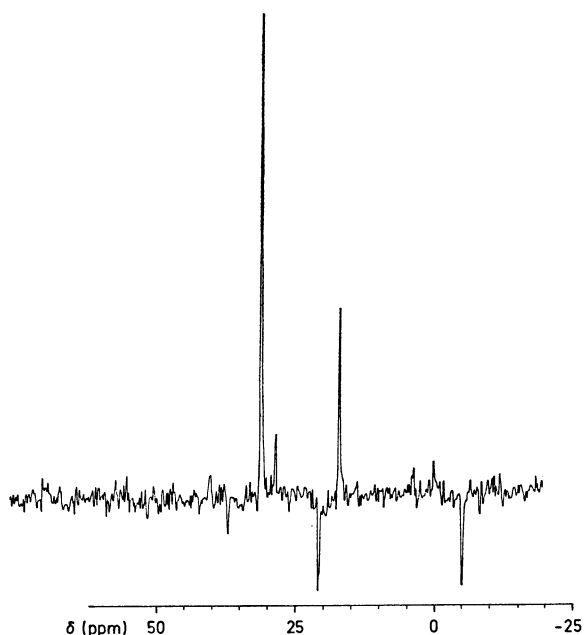


Fig. 3. The ^{13}C PFT CIDNP pattern of the aliphatic region of a reacting solution of **1a** in *o*-dichlorobenzene.

respect to a_{CH_3} seem to be mostly responsible for the low intensity.

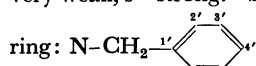
The methane resonance at $\delta=5$ is found in emission. In the case of ^1H - ^{13}C coupled spectra the methane signal appears as a quintet ($J_{\text{H-C}}=125$ Hz) showing a relatively large Δg effect (superimposed multiplet and net effect) which seems to be reasonable (*vide infra*).

In the aromatic region the spectrum is more complicated. All the observed resonances can, however, be assigned to compounds **2**, **4a**, and **5a**, already determined by ^1H -CIDNP as recombination and escape products. The signs of polarization at C-1, C-2, C-3, and C-4 for *p*-toluidine **2** are E, A, E, and A, respectively. The positionally alternating signs are inverted in *N*-methyl-*p*-toluidine **4a**. In striking contrast to the methyl carbons, we note that, while the aromatic C-1 and C-4 are the weakest in the thermally equilibrated spectra because of the lack of the nuclear Overhauser effect under wide-band proton decoupling, these carbons show strongest polarization (see Table 3). The greater T_1 values for these quaternary carbons are considered mainly to be responsible for the apparent increase in enhancement. The enhancement factors of the ^{13}C -signals of toluene **3b** are small; the effect cannot always be reproduced. ^{13}C -signals of **6a** could not be

TABLE 4. ^{13}C -CIDNP^{a)} IN THE THERMOLYSIS OF **1b**

TCE	DC	Assignment	CIDNP
20.4	20.7	CH_3 (2 , 4b , 5b)	vwA
21.4	21.4	CH_3 (3b)	vwE
25.3	—		wE
37.2	37.8	CH_2 (5b)	A
49.8	49.8	N-CH_2 (4b)	A
113.7	114.0	C-2 (4b)	E
116.0	115.9	C-2 (2)	sA
117.2	—		A
121.7	119.5	C-2 (1b)	
126.0	125.8	C-4 (3b)	E
127.0	127.3	C-5 and C-4' (5b)	wA
127.6	127.1	C-4 (4b) and (5b)	E
128.0	127.6	C-4' (4b) ^{b)} and C-4 (2)	A
128.4	127.9	C-4 (2)	sA
129.0	128.7	C-2' or C-3 (3b)	A
129.4	128.9	C-3 (3b)	A
129.8	129.5	C-2 (3b)	E
130.5	130.1	C-3 (2)	E
131.0		C-3 or C-2' (4b) ^{b)}	A
137.6	137.7		E
	137.9	C-1 (3b)	A
140.8	140.9	C-1' (4b) ^{b)}	sE
—	142.2		A
142.7	143.1	C-1 (5b)	A
144.7	144.8	C-1 (2)	sE
147.0	147.0	C-1 (4b)	sA
155.3	—		E

a) Shifts are given in δ_{ppm} from internal TMS; resonance frequency 25.15 MHz; TCE=1,1,2,2-tetrachloroethane, DC=*trans*-decalin; w=weak, vw=very weak, s=strong. b) Numbering of the *N*-benzyl



detected, which is not unreasonable due to the small amount of **6a** present and to the unknown line positions.

The ^{13}C -CIDNP results obtained on **1b** (Table 4, Fig. 4) support our findings with **1a**, although the

spectrum is more complicated, since R in Scheme 2 is now $\text{CH}_2\text{C}_6\text{H}_5$. The signals of **6b** could not be assigned so far.

c) *Product Analyses.* A typical thermolysis of a 0.33–0.39 M solution of **1a** in decalin at 130 °C gives the following products as revealed by VPC analyses: *p*-toluidine (**2**), 38%; *N*-methyl-*p*-toluidine (**4a**), 11%; toluene (**3b**), 4%; 2,4-dimethylaniline (**5a**), 5%. The intensities of further peaks in VPC are not greater than 0.9%. Therefore, the cyclohexadienimine **6a** is formed in yields <1%. An experiment performed in 1,2-dichlorobenzene as solvent (0.33 M) showed the following product analysis: **2**, 40%; **4a**, 13%; **3b**, 2%; **5a**, 7%. Ditolylamine and bitolyl derivatives were difficult to determine by VPC; bibenzyl was not detected.

p-Azotoluene could be isolated by preparative thin-layer chromatography in 3–4% yield (thermolysis in 1,2-dichlorobenzene). Methane was determined volumetrically together with nitrogen evolved. Provided that 96–97% of the theoretical amount^{9a)} of nitrogen is formed, the yield of methane can be calculated to be about 44–45% (in decalin) and 11–12% (in 1,2-dichlorobenzene).

d) *Mechanistic Implications.* *Chemical Aspects:* While the thermal decomposition of 1,3-diaryltriazenes has been thoroughly reported,¹⁰⁾ little is known on the mechanism of similar reactions of 3-alkyl-1-aryltriazenes,¹¹⁾ aside from kinetic measurements and a study of gaseous products.^{9b)} All the results of our present work appear to be well interpreted in terms of Scheme 2; the tautomeric form **1'** decomposes to give *p*-tolylaminyl-methyldiazenyl radical pair. Elimination of nitrogen molecule from the latter component of the pair should be very facile ($\geq 10^7$ – 10^9 s⁻¹) and leads to *p*-tolylaminyl-alkyl radical pair IV $\text{p-CH}_3\text{-C}_6\text{H}_4\text{-NH}\cdot\text{R}\cdot$. There are three positions available for the *p*-tolylaminyl radical to cage-recombine with the alkyl radical as shown in Scheme 3 by the canonical structure of the former. The first one should lead direct to *N*-alkyl-*p*-toluidine **4**. The other two are expected to

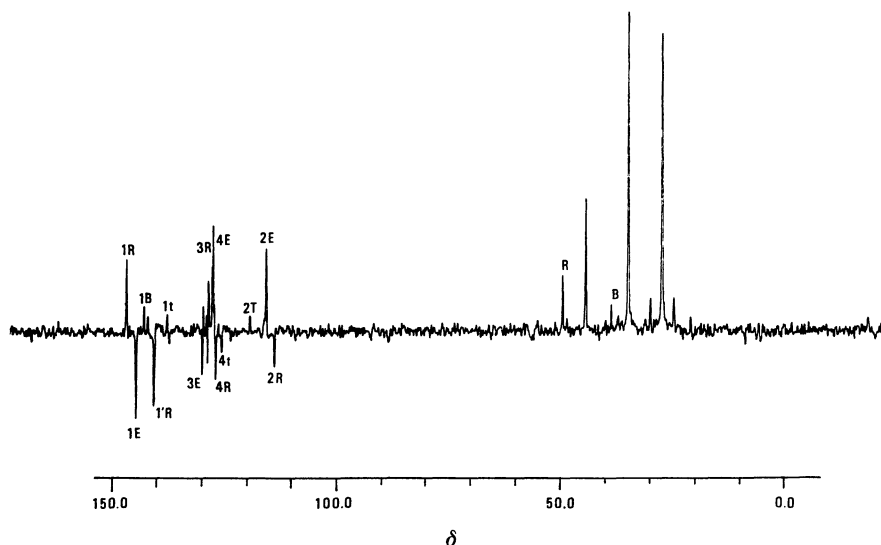
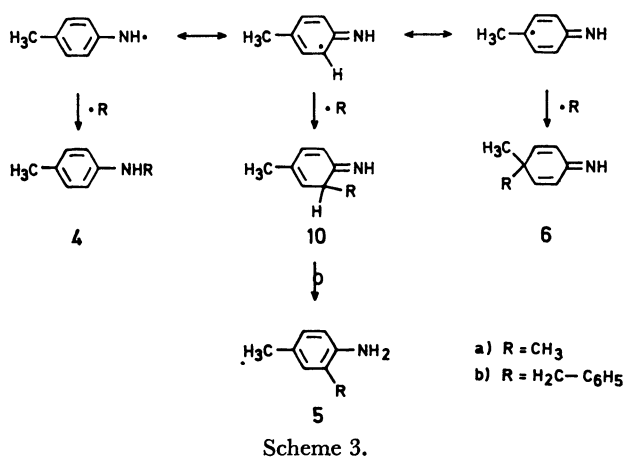


Fig. 4. ^{13}C -CIDNP spectrum (25.15 MHz PFT) of a decomposing solution of 3-benzyl-1-*p*-tolyltriazene **1b** in decalin at 125 °C.

give the corresponding cyclohexadienimines **6** and **10**. The 2-alkyl-4-methyl derivative out of these two appears to be susceptible to 1,3-prototropy under the experimental conditions to form 2-alkyl-4-methylaniline **5** as the final product. This 1,3-prototropy must be much faster than the relaxation time (spin-lattice) of the protons.¹²⁾ Thus the memory of polarization in pair IV is transferred to the rearranged **5**, while the steady-state concentration of **10** is considered too low to be detected by NMR even if intensities of their signals might be enhanced by CIDNP.

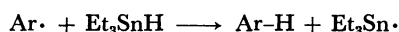
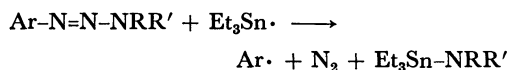
p-Tolyl-alkylaminyl radical pair II $\overline{p\text{-CH}_3\text{-C}_6\text{H}_4\cdot\text{NHR}}$ in Scheme 1 cannot explain the formation of



these two recombination products (**5** and **10**). The predominant formation of *p*-toluidine **2** instead of toluene in thermolysis of **1a** as one of the escape products is also consistent with Scheme 2. Our mechanistic interpreta-

tion that **1** decomposes *via* its tautomeric 1-alkyl-3-aryltriazene form **1'** is further supported by the thermal stability of 1-*p*-tolyl-3,3-dimethyltriazene which decomposes only at 245–250 °C³⁾ in contrast to 120–130 °C of **1**. The formation of a more stable arylaminyl radical as compared to methylaminyl radical is considered to be a driving force of the reaction going by way of **1'**. The thermochemically calculated N–H bond dissociation energies of aniline and methylamine are 92.3 and 97.8 (105.0 observed) kcal/mol,¹³⁾ respectively, supporting the above explanation.

The formation of toluene in 2–5% yield (as compared to 36–38% of *p*-toluidine **2** in thermolysis of **1a**) might indicate the small contribution of Scheme 1 to these reactions; toluene could then be formed by escape of *p*-tolyl radicals from the cage II $p\text{-CH}_3\text{-C}_6\text{H}_4\cdot\text{NHCH}_3$ followed by abstraction of the hydrogen atom from solvents. On the other hand, we have precedents for the formation of arenes either by the following induced decomposition reaction of triazenes^{14a)}



or by the thermolysis¹⁴⁾ of a pentaza-1,4-diene [Ar–N=N(CH₃)–N=N–Ar] which could be formed under the reaction conditions.

Discussion on CIDNP: According to the theory of S-T₀ transitions in the radical pair models of CIDNP,¹⁵⁾ the sign of polarization is given by $\mu \cdot a_i \cdot \Delta g \cdot \varepsilon$, where Δg is the difference in the *g* factors in the radical pair, *a_i* is the hyperfine coupling constant of ¹H and ¹³C of interest, μ is minus for singlet precursors and plus for triplet and random phase reactions, and ε is taken as

TABLE 5. ISOTROPIC HYPERFINE COUPLING CONSTANTS; SIGNS AS DETERMINED BY CIDNP

Radical	Nucleus	<i>a</i> -Values [G]		Signs determined by CIDNP
		Experimental	Calculated	
$\text{CH}_3\cdot$	H	23.0 ¹⁷⁾	(–) 23.0 ^{a)}	–
	C	38.3 ¹⁸⁾	(+) 38.5 ^{a)}	+
	H-2	5.13 ²¹⁾	– 6.31 ²²⁾	} – ^{b)}
	H-3	1.77 ²¹⁾	+ 3.55 ²²⁾	
	H-4	6.17 ²¹⁾	– 5.54 ²²⁾	
	H-5	16.34 ²¹⁾	– 16.72 ²²⁾	–
	C-1	14.45 ²³⁾	– 12.33 ²²⁾	–
	C-2		+ 11.64 ²²⁾	+ ^{c)}
	C-3		– 8.52 ²²⁾	–
	C-4		+ 10.42 ²²⁾	+
	C-5	24.45 ²³⁾	+ 32.30 ²²⁾	+
	H-2	6.0 ^{d)}	– 5.43 ^{d)}	–
	H-3	2.1 ^{d)}	+ 3.09 ^{d)}	+
	H-5	14.0 ^{d)}	– 20.46 ^{d)}	–
	H-6		+ 5.2 ^{e)}	+
	C-1			–
	C-2			+
	C-3			–
	C-4			+
	C-6			+

a) Calculated values taken from Ref. 18, signs taken from Ref. 15. b) Average of H-2, H-3, H-4, the signals of which coincide. c) CIDNP signals coincide with those of other C-atoms. d) The values of the unsubstituted phenylaminyl radical taken from Ref. 17. e) Estimated from $\rho^{\pi}_{\text{C-4}} = 0.179$ in Ref. 17.

plus for cage recombination and minus for escape products. In $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}\cdot\text{R}$ the arylaminyl radical has a larger g value (*ca.* 2.0030^{16,17}) than the alkyl counterpart $\text{R}\cdot$ ($g_{\text{CH}_3}=2.0026$,¹⁸ $g_{\text{CH}_2-\text{H}_5\text{C}_6}=2.0025$ ¹⁷). The pertaining hyperfine coupling constants available from literature ESR data and/or estimated from calculations are summarized in Table 5.

The sings for $\cdot\text{CH}_3$, and $\text{H}_3\text{CC}_6\text{H}_4\text{NH}\cdot$ (thermolysis of **1a**) derived from CIDNP correspond nicely to the calculated ones (Table 5), thus providing an experimental proof for the sign of hfs which can otherwise be difficult to determine experimentally.¹⁹ To the best of our knowledge, the sings and values of a_i for p -tolylaminyl itself do not appear to have been determined by other methods.²⁰

The observed proton enhanced absorption and carbon emission for *methane* are due to opposite a_i sign (negative for hydrogen and positive for carbon) in the methyl radical. When CIDNP signal is emission in p -toluidine **2**, the corresponding nucleus in N -methyl- p -toluidine **4a** shows a signal of enhanced absorption. The contrasting sign inversion of polarization is interpreted in terms of recombination *vs.* escape products: different sign in ϵ . The positional sign alternation clearly demonstrated in C-1 through C-4 of **2** and **4a** corresponds to sign alternation in the hyperfine coupling as shown in Table 5.

While N -methyl- p -toluidine **4a**, 2,4-dimethylaniline **5a** and 4,4-dimethylcyclohexa-2,5-dien-1-imine **6a** which are considered to be derived from the same cage are formed in a ratio of about 1:0.5:0.08, the observed relative intensities of their proton emission signals due to the entering methyl group are 1:9.3:2.6. This means that the enhancement factor for the N -methyl

group of N -methyl- p -toluidine should be unduly small. The trend may be ascribed to smaller T_1 value of these protons due to quadrupole relaxation by the nitrogen atom.

The toluene formed from **1a** shows clear-cut CIDNP (emission) only of C-4. This would be compatible with Scheme 1, since only C-1 (this position is C-4 in toluene) of p -tolyl has a large (positive) a_i value.²⁴ A weak enhanced absorption, sometimes observed for the methyl protons, may be also explained by a p -tolyl σ -radical ($a_{\text{CH}_3}=2.4\text{ G}$ ²⁵). The *delayed emission* for the aromatic protons of toluene in 1,1,2,2-tetrachloroethane (TCE) may be considered as being derived from a secondary decomposition reaction of the intermediately formed azo compounds, *e.g.* $p\text{-CH}_3\text{C}_6\text{H}_4\text{-N=N-X}$ in which X will be a fragment or some combination of TCE employed as a solvent. The polarized methyl chloride observed in TCE must also emanate from a secondary pair, since simple chlorine abstraction by polarized methyl radicals escaped from pair IV should result in the opposite CIDNP sign.

The hyperfine signs derived from the CIDNP observed in the thermolysis of **1b** again support Scheme 2 with respect to p -tolylaminyl and benzyl radicals (Table 5). Only an effective sign of averaged hyperfine coupling can be obtained on the ring protons of the benzyl radical since these protons show singlets in the products, **4b**, **5b**, and **8**. There is a deviation, however, for the aromatic protons of the later-appearing toluene. Applying the Kaptein rules, one would expect from the observed emission an average plus sign for the a_i values of H-2, H-3, H-4 of benzyl. However, according to the MO calculations (Table 5) and the observations on **4b**, **5b**, and **8**, the overall sign should be negative. A

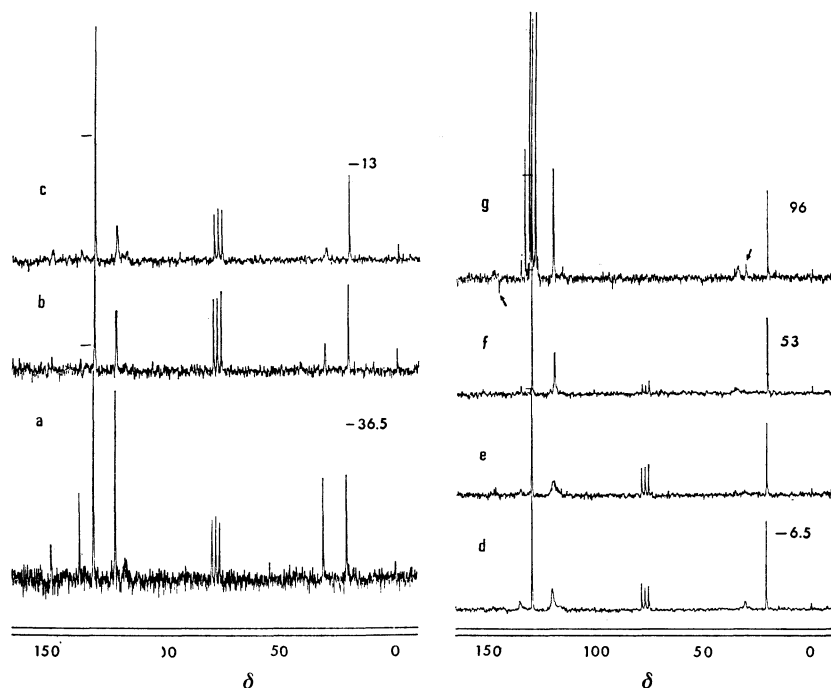


Fig. 5. ^{13}C -NMR spectra (20.1 MHz) of 3-methyl-1- p -tolyltriazene **1a** in CDCl_3 at various temperatures: (a)–(f) in CDCl_3 and (g) in *o*-dichlorobenzene.

The arrows in (g) show CIDNP signals already coming out.

reasonable explanation stems from the fact that the above mentioned effect can be observed only in TCE. Obviously in this solvent some of the reaction products (e.g. **3b**) can be formed *via* different pathways (see also discussion of methyl chloride formation in thermolysis of **1a** in TCE). In the reaction path *via* pair IV ($R = CH_2Ph$) especially the nuclei in the recombination products **4b** and **5b** and in bibenzyl **8** are polarized, whereas in some other reaction (not involving the benzyl radical) the ring protons of the later-formed toluene are polarized preferentially. One candidate for a radical component in such a pair would be the *p*-tolyl radical (ring proton hfs signs expected to be >0 ; ring carbon hfs signs the same as in the benzyl radical).²⁴⁾

e) *Tautomerism in 1a* The occurrence of tautomerism in **1a** assumed to account for the chemical product formation and CIDNP in the thermolysis of this compound has been independently confirmed by IR-²⁶⁾ and ¹H-NMR²⁷⁾ spectroscopy. An additional support has been obtained in this work by the temperature dependent ¹³C-NMR spectra. As shown in Fig. 5, all the ¹³C signals (due to **1a**) are sharp at $-36.5^\circ C$ in $CDCl_3$ and consistent with structure **1a**, namely, 1-*p*-tolyl-3-methyltriazene. The singlets due to *N*-CH₃, C-1, C-2, and C-4 start to broaden at about $-25^\circ C$. This broadening is so effective that *N*-methyl and C-1 carbons cannot be seen at $2-53^\circ C$. Only the singlet at δ 129.4 due to C-3 remains constant in its peak height. The *N*-methyl signal becomes again observable at temperatures only higher than $60^\circ C$. The position is, however, shifted to the lower field by 3.9 ppm, indicating the enhanced rate of prototropy and increase in the population of tautomeric 1-methyl-3-*p*-tolyltriazene structure **1a'** at higher temperatures. Closer inspection of the spectrum at -36.5° (Fig. 5) reveals that there is an additional weak singlet at δ 54.0 which could be due to *N*-methyl carbon of **1a'**. In the case of the signal of C-2 (120.0 ppm) we note at $-36.5^\circ C$ a "satellite" of very low intensity on the highfield side (115.6 ppm) which might be attributed to C-2 of **1a'**. At about $2^\circ C$ the two signals coalesce and at $53^\circ C$ we observe the fast exchange singlet at 119.1 ppm.

f) *CIDNP, its Advantages and Limitation in Mechanistic Studies.* ¹H- and ¹³C-CIDNP investigations have shown that triazenes **1** may thermolyse *via* the tautomeric form **1'** and that radical pairs like IV can be intermediates, thus qualitatively proving the conclusions drawn from chemical product analysis. It is even possible to give the hfs signs of carbon and hydrogen atoms of *p*-tolyl-aminyl unambiguously, although no ESR spectrum of this radical has been measured.

New reaction paths, hitherto not taken into account,⁹⁾ e.g. formation of **5** and **6**, were discovered. One of these compounds, **6**, still resists chemical isolation and separate preparation until the present day. On the other hand, the CIDNP technique of a level employed in this study does not necessarily give quantitative account of the decomposition of all the triazene molecules. The chemical product analyses of the thermolysis of **1a** show a large excess of "escape" products, **2** and **3a**, over the "recombination" products **4a**, **5a**, **6a**. The formation of methane **3a** (0.33 M

solution of **1a**) depends a great deal on the solvent used: 46% (in decalin) and 12% (in tetrachloroethane). This effect has also been found for other 3-alkyl-1-aryl-triazenes in solvents of the corresponding hydrogen donating ability.^{9b)} The amount of *p*-toluidine **2** does not differ much in decalin and tetrachloroethane. This indicates that a part of the reaction might proceed *via* ionic pathways induced by traces of water or acid present in the system.^{27,28)}

We would like to add that, whereas it is difficult to interpret our CIDNP data in terms of pair III only, we were not able to disclose the positive role of the methyl-diazenyl radical in Scheme 2. If there is an internal return to **1'** by recombination, it is usually the case in which CIDNP is detected in the starting material as exemplified by the photolysis of phenylazocumene.²⁹⁾ Our failure to detect CIDNP in the starting material may be due to a shorter life-time of the methyl-diazenyl as opposed to the phenyldiazenyl radicals. Either prototropic tautomerism in the starting materials (*vide supra*) or quadrupole relaxation due to the nitrogen atoms could also be responsible for making the possible CIDNP effect in **1** obscure.³⁰⁾

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