NOTES *Bull. Chem. Soc. Jpn.*, **55**, *2679—2680 (1982)*

CIDNP Studies of the Oxidation of *N*-(*p*-Tolylsulfonyl)-*N'*-triphenylmethylhydrazine

Masato YOSHIDA,* Akira YANO, and Michio KOBAYASHI

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

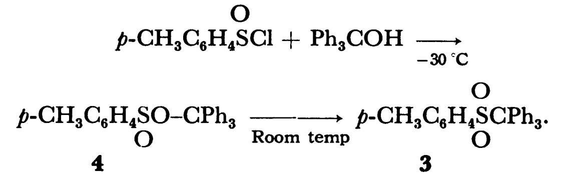
(Received October 8, 1981)

Synopsis. The ^{13}C-CIDNP spectra were observed during the oxidation of *N*-(*p*-tolylsulfonyl)-*N'*-triphenylmethylhydrazine. The formation of sulfone and sulfinic ester as recombination products in a solvent cage was established from the signs of polarization.

In continuing the studies of the decomposition mechanism of the arylazo aryl sulfone,[1] we are interested in the reaction of *p*-tolyl triphenylmethylazo sulfone (**1**). Although *N*-(*p*-tolylsulfonyl)-*N'*-triphenylmethylhydrazine (**2**) is oxidized fairly easily by various oxidizing agents, such as mercury(II) oxide or potassium permanganate, the expected azo sulfone ($Ph_3C{-}N{=}N{-}SO_2{-}Tol\text{-}p$) is too unstable to be isolated as such; it decomposes immediately, with the evolution of nitrogen. The main product is *p*-tolyl triphenylmethyl sulfone (**3**; yield 51.7%), whose formation has been ascribed to the recombination of the *p*-toluenesulfonyl and triphenylmethyl radicals.[2] In order to clarify the details of the decomposition mechanism of *p*-tolyl triphenylmethylazo sulfone, we have studied the ^{13}C-CIDNP spectra observed during the oxidation of *N*-(*p*-tolylsulfonyl)-*N'*-triphenylmethylhydrazine.

Results and Discussion

CIDNP signals appeared when a mixture of *N*-(*p*-tolysulfonyl)-*N'*-triphenylmethylhydrazine (**2**) and yellow mercury(II) oxide in benzene or toluene was inserted into an NMR probe heated to 60—90 °C and the ^{13}C-NMR was measured. One of the spectra thus obtained is shown in Fig. 1. The signals were assigned by comparison with the chemical shifts of the authentic samples. Triphenylmethyl *p*-toluenesulfinate (**4**) was expected to isomerize quickly to the sulfone (**3**) at room temperature, so its chemical shifts were determined as follows: *p*-toluenesulfinyl chloride was added to a solution of triphenylmethanol in carbon tetrachloride in the presence of pyridine in an NMR sample tube at −30 °C, and then its ^{13}C-NMR spectrum was immediately determined at −30 °C. Strong, new ^{13}C-NMR signals assigned to sulfinate (**4**) were observed; when this solution was subsequently warmed to room temperature, though, different signals corresponding to sulfone (**3**) began to appear:



$$p\text{-}CH_3C_6H_4\overset{O}{S}Cl + Ph_3COH \xrightarrow[-30\,^\circ C]{} \underset{\mathbf{4}}{p\text{-}CH_3C_6H_4\underset{O}{S}O\text{-}CPh_3} \xrightarrow[\text{Room temp}]{} \underset{\mathbf{3}}{p\text{-}CH_3C_6H_4\overset{O}{\underset{O}{S}}CPh_3}.$$

The formation of sulfone (**3**) and the sulfinic ester (**4**) as geminate recombination products in a solvent cage is established from the signs of polarization, as is shown in Fig. 1. The generated sulfonyl radical is ambident and acts as either an S- or O-centered radical to give both sulfone and the sulfinic ester, with triphenylmethyl radicals. The azo sulfone (**1**) did not show polarization. This indicates that hydrazine (**2**) is oxidized by mercury(II) oxide to the azo sulfone (**1**), which might decompose to the sulfonyl radical, the triphenylmethyl radical, and nitrogen simultaneously. On the other hand, it has been established that phenylazo *p*-tolyl sulfone (**5**) decomposes to the aryldiazenyl radical and the sulfonyl radical.[1] When a mixture of *N*-phenyl-*N'*-(*p*-tolylsulfonyl)hydrazine (**6**) and yellow mercury(II) oxide in toluene was warmed at 90 °C, the CIDNP signals of not only sulfone and the sulfinic ester, but also of azo sulfone (**5**), were observed. The obtained spectrum was identical with that observed in the thermal decomposition of

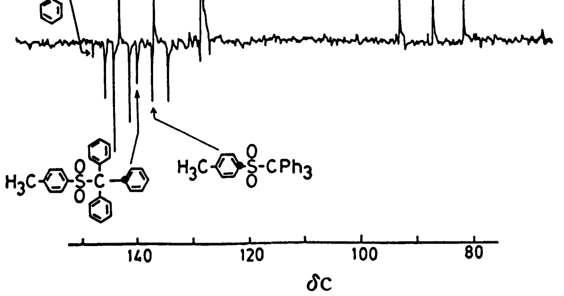
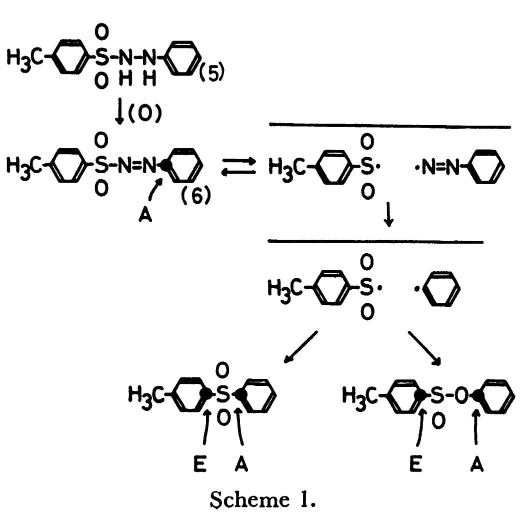


Fig. 1. ^{13}C-CIDNP spectrum in the oxidation of *N*-(*p*-toluenesulfonyl)-*N'*-triphenylmehtylhydrazine in benzene at 60 °C.

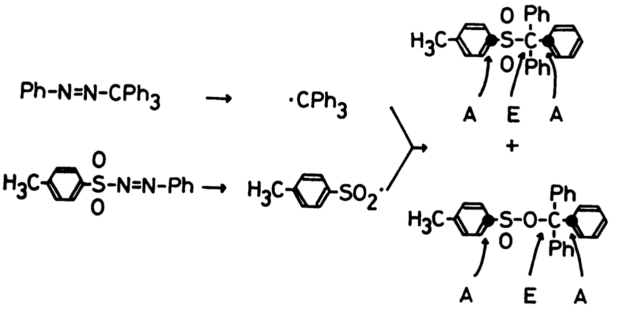


Scheme 1.

phenylazo *p*-tolyl sulfone in toluene.

In order to examine the possibility of the recombination of the sulfonyl radical and the triphenylmethyl radical escaped from the solvent cage, the following two experiments were carried out.

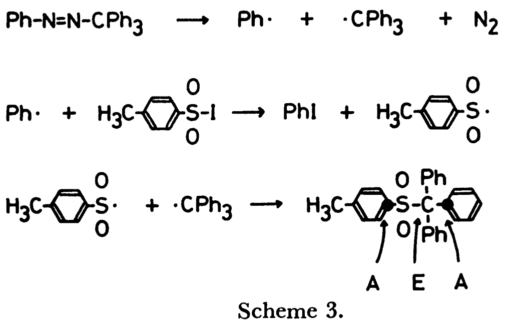
(i) When the ^{13}C-NMR of a mixture of phenylazo *p*-tolyl sulfone and phenylazotriphenylmethane (PAT) in toluene at 90 °C was measured, CIDNP signals assignable to *p*-tolyl triphenylmethyl sulfone (**3**) and triphenylmethyl *p*-toluenesulfinate (**4**) were observed, besides the signals observed in the thermal decomposition of the azosulfone or PAT alone.



Scheme 2.

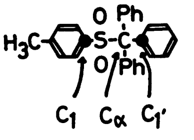
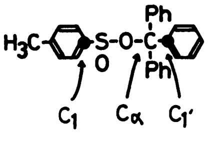
f

(ii) When the ^{13}C-NMR spectrum of a mixture o *p*-toluenesulfonyl iodide and PAT in toluene was measured at 90 °C, the CIDNP signals of *p*-tolyl triphenylmethyl sulfone (**3**) were obtained. The formation of the sulfone can be explained by the following reaction Scheme;



Scheme 3.

The sulfone and the sulfinic ester must be the result o the encounter of free radicals escaped from the original solvent cage, as has been shown before, and the signs of polarization should be the opposite of those obtained in the oxidation of hydrazine (**2**). The predicted signs of the recombination of the encounter of free radical, according to Kaptein's rule[3] are shown below:

		μ	ε	Δg	a	Γ_{ne}
	C_1	+	+	+	(+)[4]	(+)
	C_α	+	+	−	+[5]	−
	$C_{1'}$	+	+	−	−[5]	+
	C_1	+	+	+	(+)[4]	(+)
	C_α	+	+	−	+[5]	−
	$C_{1'}$	+	+	−	−[5]	+

$g = 2\ 0041(\cdot SO_2C_6H_4CH_3\text{-}p)$, $g = 2\ 0026(\cdot CPh_3)$.

Experimental

The ^{13}C-NMR spectra were taken with a JEOL Fx-60 FT-NMR spectrometer. The *N*-(*p*-tolylsulfonyl)-*N'*-triphenylmethylhydrazine was prepared from triphenylmethyl chloride and *p*-tolylsulfonylhydrazine and recrystallized from ethanol. The details have been described in Ref. 1. The *p*-tolyl triphenylmethyl sulfone was obtained from the reaction mixture of *N*-(*p*-tolylsulfonyl)-*N'*-triphenylmethylhydrazin and yellow mercury(II) oxide; it was recrystallized from benzene–ether (mp, 175—178 °C, lit, 171 °C[2]).

References

1) M. Yoshida, N. Furuta, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **54**, 2356 (1981).

2) M. Kojima, N. Kamigata, H. Minato, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **46**, 2501 (1973).

3) R. Kaptein and J. Osterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

4) If one assumes that the hyperifine splitting constant "*a*" of C_1 is positive, the sign in the net polarization, (Γ_{ne}), as calculated according to Kaptein's rule, agrees with the observed mode.

5) M. Karplus and G. K. Frankel, *J. Chem. Phys.*, **35**, 1312 (1961).