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Preliminary communication

HOMOLYTIC DECOMPOSITION OF PHENYLAZOTRIPHENYLSILANE IN CARBON TETRACHLORIDE

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Summary

Phenylazotriphenylsilane was thermally and photochemically decomposed in carbon tetrachloride. From product analyses and ESR studies of the reactions, it is concluded that the decomposition presumably involves homolytic fission of Si—N and N—C bonds of the compound.

We have prepared arylazotriphenylsilanes in high purity [1] and this makes it possible to investigate this type of compound in some detail. While phenylazotrialkylsilanes have been reported to be ineffective as vinylic polymerization initiators [2], there still remains the possibility for azosilanes to be thermal or photochemical sources of silyl radicals by analogy to phenylazotriphenylmethane (PAT) [3—7]. We now present evidence for the homolytic fission of Si—N and N—C bonds of phenylazotriphenylsilane (I) in carbon tetrachloride.

Compound I in carbon tetrachloride decomposed at 110°C to give triphenylchlorosilane, chlorobenzene, azobenzene, chloroform, biphenyl and chlorobiphenyl. In addition to these products, tetraphenylsilane and hexachloroethane, and three or four unidentified compounds were detected. In the photochemical reaction of I the products formed were virtually the same as those of the thermal reaction. The results are summarized in Table 1.

For the elucidation of the mode of decomposition, ESR techniques seemed appropriate. Thus, a carbon tetrachloride solution of I changed from blue to dark green in color when it was heated; at this stage the reaction was incomplete (see Table 1, note *a*). The solution, the dark green color of which remained unchanged for a long time in the absence of air at room temperature, was quickly transferred to an ESR tube, sealed in vacuo, and examined by ESR spectroscopy. Separately, an identical solution of I was irradiated to afford a similar reaction mixture, the color of which was also dark green. The resulting solution was also studied by ESR. At room

TABLE 1

DECOMPOSITION OF PHENYLAZOTRIPHENYLSILANE IN CARBON TETRACHLORIDE [a]

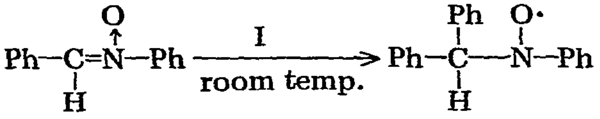
Reactants (mmol)	Products (mmol)	Thermal reaction (110°C, 44 h)	Photochemical reaction (22°C, 18h) [b]
$Ph_3SiN{=}NPh$		1.00	1.00
CCl_4		14.20	13.70
	Ph_3SiCl	0.92	0.98
	PhCl	0.23	0.20
	PhH	0.06	0.02
	Ph—Ph	0.02	0.01
	$Ph{-}C_6H_4Cl$	0.06	0.01
	PhN=NPh	0.13	0.07
	$CHCl_3$	0.08	0.02
	C_2Cl_6	+	+
	Ph_4Si	+	+
	Others [c]	+	+

[a] Each run was carried out in a Pyrex sealed tube and reaction was complete when the blue color of the solution changed to the orange-red via the dark green. The products, isolated by preparative GLC, were characterized by means of NMR, IR and mass spectroscopy. [b] Reactant solution was externally illuminated with light of wavelength longer than 3300 Å through a filter (0.1 *M* naphthalene solution in cyclohexane; 10 mm thick) using a 400-W high-pressure mercury lamp. [c] Three or four unidentified compounds were detected by GLC at high temperature.

temperature, samples from the two reactions gave strong broad complex signals, indicating the production of stable radicals. This fact, together with the occurrence of the products listed in Table 1, strongly suggests that the reactions proceed through homolytic processes (eqn. 1).

$$\underset{\text{(I)}}{Ph_3SiN{=}NPh} \rightarrow [Ph_3Si\text{- - -}N_2\text{- - -}Ph] \rightarrow Ph_3Si\cdot + N_2 + \cdot Ph \qquad (1)$$

In order to obtain further confirmation of such homolytic processes, ESR spin trapping for short-lived radicals [8] using α,*N*-diphenylnitrone (II) in benzene was tested and the hyperfine structure of the phenyl radical adduct (III) derived from I was observed at room temperature (eqn.2). The



$$\underset{\text{(II)}}{Ph{-}\underset{\mid}{\overset{}{C}}{=}\overset{O}{\overset{\uparrow}{N}}{-}Ph}\atop{\;\;H} \xrightarrow[\text{room temp.}]{\text{I}} \underset{\text{(III)}}{Ph{-}\overset{Ph}{\underset{H}{C}}{-}\overset{O\cdot}{N}{-}Ph} \qquad (2)$$

(II) (III)

coupling constants thus obtained were almost identical to those of the literature [9] [III: *a*(N) 10.3, *a*(H) 2.7, *a*(N—Ph(*o*-H))2.6, *a*(N—Ph(*m*-H)) 0.8, *a*(N—Ph(*p*-H)) 3.5 gauss]. In control experiments under similar conditions, the same spectrum was obtained by mixing PAT with the nitrone, but PAT and compound I in the absence of the nitrone exhibited no signals. On the other hand, attempts to detect the triphenylsilyl radical under the various ESR conditions failed. Other efforts to verify this radical, in contrast with trialkylsilyl radicals [10,11], also have been reported to be unsuccessful [12].

Further investigations of the decomposition and its mechanism are now underway.

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