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PHENYLAZOTRIORGANOSILANES AS SILYLATED PHENYLDIAZENES; A CONVENIENT PRECURSOR FOR PHENYLDIAZENE

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Summary

Phenylazotriphenyl- (Ia) and phenylazotrimethyl-silane (Ib) react with alcohols to give the corresponding alkoxytriorganosilane and benzene as the major products. Spectroscopic investigations (UV) suggested that phenyldiazene was formed as an intermediate which afforded the final reaction products. Chemical evidence for the formation of phenyldiazene was obtained by the reaction of Ia with methanol-*d* in nonane. Phenylazotriorganosilanes are convenient precursors for phenyldiazene.

Introduction

Kosower and coworkers have previously described generation of phenyldiazene from the precursors such as $\text{PhN}=\text{NCO}_2\text{Me}$ and $\text{PhN}=\text{NCO}_2\text{K}$ [1–4]. We now report that phenylazotriphenylsilane (Ia) [5] and phenylazotrimethylsilane (Ib) * react readily with alcohols such as methanol and ethanol to form phenyldiazene, such silylated azo compounds serve as new and more convenient precursors for the diazene, since they can be easily obtained in large amounts [5–7] and are soluble in common organic solvents; also the reaction system for the generation of the diazene is simple.

Results and discussion

In a degassed sealed tube, Ia reacted with ethanol at room temperature to give benzene and ethoxytriphenylsilane, together with small amounts of azobenzene, biphenyl and hydrazobenzene. Evolution of nitrogen also was ob-

* This compound (b.p. 100–103°C/18 mmHg) can be prepared by the methods described in refs. 5, 6 and 7.

TABLE 1

REACTIONS OF PHENYLAZOTRIORGANOSILANES (I) WITH ALCOHOLS ^a

Run	Reactants	mmol	Reaction time (h)	Products (mmol) (%) ^b
1	Ia	0.26	16	Ph ₃ SiOEt (0.23) (88), PhH (0.17) (65), PhN=NPh (0.01), Ph-Ph (0.01), PhNHNHPh (trace)
	EtOH	6.29		
2	Ia	0.40	10	Ph ₃ SiOMe (0.27) (68), PhH (0.24) (60), PhN=NPh (0.01), Ph-Ph (0.01)
	MeOH	8.11		
3	Ib	0.92	0.5	Me ₃ SiOEt (0.85) (92), PhH (0.61) (66), PhN=NPh (0.01), Ph-Ph (trace)
	EtOH	14.3		
4	Ib	0.88	0.5	Me ₃ SiOMe (0.66) (75), PhH (0.46) (52), PhN=NPh (0.05), Ph-Ph (0.01).
	MeOH	14.0		

^a All the reactions were carried out at room temperature in evacuated sealed tubes. ^b GLC yields based on the azosilane used (an external standard was used).

served. The reaction of Ib gave results analogous to Ia (Table 1).

Spectroscopic investigations (UV) showed that an air-sensitive product was formed in the reaction. Thus, an UV spectrum of a fresh reaction mixture obtained from Ia in ethanol showed an absorption maximum at 263 nm (ethanol) and this peak remained substantially unchanged under nitrogen or in vacuo, but on contact with air, its intensity diminished rapidly. In a control experiment, phenyldiazene * generated from PhN=NCO₂K/Et₃N · HCl reaction in ethanol showed similar spectroscopic behavior. Neither Ia (in acetonitrile) ** nor hydrazobenzene (in ethanol) † exhibited an absorption maximum in this region. Thus, the air-sensitive compound is suggested to be phenyldiazene and, except for the alkoxy silane, the final stable products could have been derived from the diazene.

In order to obtain more detailed understanding of the reaction, treatment of Ia with methanol in an inert solvent was studied and afforded similar results to those of the reactions without solvent (Table 2). When Ia was treated with methanol-*d* in a ten-fold excess of *n*-nonane, there was 37% incorporation of deuterium in the benzene formed (Run 4). Although the value of the incorporation is not so large, this finding indicates that benzene-*d*₁ was formed in a solvent cage via phenyldiazene-1-*d* derived from the reaction of Ia with methanol-*d*. In this connection, Huang and Kosower have reported that phenyldiazene decomposes bimolecularly yielding benzene and nitrogen, and also proposed, from the result of 73% incorporation of deuterium in the reaction of PhN=NCO₂⁻ K⁺ with Et₃ND⁺ Cl⁻ in acetonitrile, a mechanism involving the formation of radical reaction partners within a solvent cage [3]. Interestingly, Simamura and coworkers have investigated the reduction of benzenediazonium tetrafluoroborate to benzene with trialkyltin and silicon deuteride in solvents such as THF and acetonitrile. They found that the reaction gave a 40% incorpo-

* Phenyldiazene has been shown to have an absorption maximum at 260 and 270 nm in acetonitrile and phosphate buffer solution, respectively (see refs. 2 and 3).

** λ_{max} 294 nm.

† λ_{max} 247 nm (245–250 mμ; see ref. 8).

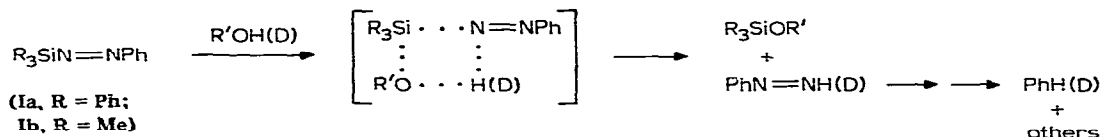
TABLE 2

REACTIONS OF PHENYLAZOTRIPHENYLSILANE (Ia) WITH METHANOL AT ROOM TEMPERATURE ^a

Run	Reactants, mmol	Solvent, ml	Time (h)	Products, mmol (%) ^b	Ratio PhD/PhH ^d			
1	Ia MeOH	1.13 8.01	n-Heptane	3	2	Ph ₃ SiOMe	0.90(80) ^c	
						Benzene	0.84(74)	
	Ph-Ph	0.04(18)						
	PhN=NPh	0.02(4)						
	Ph ₃ SiOMe	0.92(85) ^c						
2	Ia MeOD	1.08 6.96	n-Heptane	3	2	Benzene	0.81(75)	
						Ph-Ph	0.05 (10)	
	PhN=NPh	0.01(3)						
	Ph ₃ SiOMe	0.72(73) ^c						
	Benzene	0.63(64)						
3	Ia MeOD	0.98 20.95			0.5	Ph-Ph	0.02(4)	61/39
						PhN=NPh	0.01(3)	
	Ph ₃ SiOMe	0.72(73) ^c						
	Benzene	0.63(64)						
	Ph-Ph	0.02(4)						
4	Ia MeOD	12.43 47.61	n-Nonane	25	2	PhN=NPh	0.02(4)	
						Ph ₃ SiOMe	10.68(86) ^c	
	Benzene	9.32(75)						
	Ph-Ph	0.37(6)						
	PhN=NPh	0.13(2)						

^a The reaction was carried out in an open system under nitrogen. ^b GLC yield based on the amount of Ia, starting material (an external standard was used). ^c Isolated yield. ^d Measured by mass spectrometry with an ionization potential of 10 eV.

ration of deuterium into benzene, and proposed the formation of phenyldiazene-1-*d* as the intermediate [9]. From these observations of the previous workers together with ours, it is likely that the present reaction proceeds as follows:



It should be noted that the organosilyl azo compounds can be regarded as *N*-silylated phenyldiazenes and that the silyl groups could be easily replaced by a hydrogen of the protic compounds (alcohols), as evidenced by the present reactions.

Experimental

IR spectra were recorded as neat liquid or KBr pellets with a Hitachi EPI-G3 spectrometer, and NMR spectra were measured in CCl₄ solution using a Varian A-60D spectrometer. GLC analyses were conducted using Ohkura Model 802 and 1700 gas chromatographs. Mass spectral analyses were conducted using a JEOL Model JMS-07 spectrometer.

UV spectroscopic measurements

The spectroscopic measurements were carried out in a specially devised glass

apparatus using samples from which oxygen had been removed by degassing through at least three freeze-thaw cycles on a vacuum line.

Phenylazotriphenylsilane (Ia) was mixed with ethanol by breaking a thin glass diaphragm and the resulting solution was introduced into a quartz UV cell in the system. The solution exhibited an absorption maximum at 263 nm and this peak remained substantially unchanged, but by the introduction of air into the system its intensity diminished rapidly. This spectroscopic behavior was the same as that observed with phenyldiazene prepared from potassium phenyldiazene carboxylate and triethylamine hydrochloride in acetonitriles as described by Huang and Kosower [3]. The final spectrum of the sample showed that of ethoxytriphenylsilane (λ_{\max} 263 nm in the fine structure of four peaks at 248, 259, 264 and 270 nm).

Similarly, potassium phenyldiazene carboxylate [2,3] was mixed with an ethanol solution containing triethylamine hydrochloride. The spectrum (λ_{\max} 263 nm) of the resulting solution was identical with that of phenyldiazene as described in the literature [3]. Upon contact with air, the intensity of the spectrum diminished and the shape of the final spectrum was the same as that described in the literature.

Product studies

A. Reactions of Ia and Ib with alcohols (ethanol and methanol). In a typical example, phenylazotriphenylsilane (Ia, 0.26 mmol) was mixed with ethanol in an evacuated sealed glass tube and allowed to react at room temperature for 16 h, during which time solid Ia dissolved and the blue color of the mixture changed to light orange. GLC analysis of the resulting mixture showed that ethoxytriphenylsilane (0.23 mmol; 88%) and benzene (0.17 mmol; 65%) were formed. In addition, azobenzene, biphenyl and hydrazobenzene were detected (Table 1). Ethoxytriphenylsilane was isolated and identified by comparison of its NMR and IR spectra with those of an authentic sample.

B. Reaction of Ia with methanol in n-heptane. Phenylazotriphenylsilane (Ia, 1.13 mmol) was added to methanol (8.01 mmol) in n-heptane (3 ml) under nitrogen. The clear solution was stirred at room temperature for 2 h and, at this stage, the blue color of the solution disappeared. GLC analysis of the reaction mixture indicated that the reaction gave methoxytriphenylsilane, benzene, biphenyl and azobenzene in yields of 80, 74, 18 and 4%, respectively (Table 2, Run 1).

C. Reactions of Ia with methanol-d in n-nonane. The reaction was carried out in a similar manner to that described above (B), except for the use of MeOD in place of MeOH. The products thus formed were shown to be methoxytriphenylsilane, benzene, biphenyl and azobenzene (Run 4 in Table 2). The mass spectrum of the benzene fraction isolated by GLC showed that it consisted of a mixture containing 37% benzene-d₁ (PhD) and 63% ordinary benzene (PhH).

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