buffer, 600 volt, 60 min: 0.59×Lys]: $[\alpha]_D^{25}$ −75° (c=0.3, 5% aqueous AcOH); amino acid analysis (acid hydrolysis)[7,11]: Arg 1.98, Lys 5.20, Asp 4.11, Thr 4.00, Ser 3.16, Glu 8.16, Pro 2.02, Gly 1.00, Ala 3.04, Val 6.00, Leu 8.06, Tyr 1.36, Phe 1.08 (recovery, 76%).

The synthetic peptide was active in the induction of thymocyte differentiation from prothymocyte *in vitro*[10] (Table I) and the potency of the synthetic hormone was more than 10 times the potency of the synthetic tridecapeptide corresponding to the sequence 29—41 of the hormone.[12] Since it has been fully confirmed by Schlesinger, *et al.*[3] that the fragment 29—41 exhibited approximately 10% activity by weight when compared with natural Tp, the activity of our synthetic hormone would consequently be comparable to that of natural Tp. Further biological characterization of this synthetic hormone is now in progress in these laboratories.[13]

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11) After enzymatic hydrolysis by chymotrypsin and aminopeptidase-M, the amino acid composition of the product was also good agreement with the theory.
12) The tridecapeptide (29—41) was prepared by the conventional stepwise elongation method: $[\alpha]_D^{26}$ −34.0° (c=0.1 in 50% AcOH); Rf^7 (cellulose) 0.54.
13) The detailed biological studies will be reported elsewhere by Drs. Kawaji, Takaoki and Sugino.

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Oxidation of 4'-Substituted Benzenesulfenanilides with Lead Dioxide. Electron Spin Resonance Studies of Benzenesulfenanilidyl Radicals

Benzenesulfenanilidyl radicals (3) were generated by the oxidation of benzenesulfenanilides (4'-OMe (**1a**), 4'-Me (**1b**), 4'-Cl (**1c**), 4'-H (**1d**)) with lead dioxide, and their electron spin resonance (ESR) and visible spectra were investigated. The radicals generated from **1a** and **1b** in benzene were fairly stable and gave well-resolved ESR spectra, whereas those from **1c** and **1d** were less stable and gave poorly resolved ESR spectra. The oxidations of **1a** and **1b** gave the corresponding phenazines as the final products, whereas those of **1c** and **1d** did not.

Keywords——benzenesulfenanilides; oxidation of sulfenanilides; oxidation with lead dioxide; electron spin resonance; benzenesulfenamidyl radicals; nitrene; imido intermediate; synthesis of phenazines

In the previous paper[1] we reported the results on the controlled potential electrolyses of benzenesulfenanilides (4'-OMe (**1a**), 4'-Me (**1b**), 4'-Cl (**1c**), 4'-H (**1d**)) and 2-nitrobenzenesulfenanilides (4'-OMe (**2a**), 4'-Me (**2b**), 4'-Cl (**2c**), 4'-H (**2d**)) in acetonitrile. Electrolyses of **1a**, **1b**, **2a**, **2b**, and **2c** gave the corresponding 2,7-disubstituted phenazines, whereas those of **1c**,

1) H. Sayo, K. Mori, and A. Ueda, *Chem. Pharm. Bull.* (Tokyo), **25**, 525 (1977).

1d, and **2d** did not. Lecher, *et al.*[2] found that the oxidation of *p*-toluenesulfenanilide with lead dioxide in benzene gives a red solution, which was ascribed to the formation of a new class of nitrogen-centered radicals. Miura, *et al.*[3] have recently found that stable dibenzenesulfenamidyl radicals are formed on the oxidation of dibenzenesulfenamides with lead dioxide in benzene, and reported Electron Spin Resonance (ESR) and visible spectra of the radicals.

In order to elucidate the mechanism of the formation of the phenazines, we have now studied the oxidation of benzenesulfenanilides with lead dioxide both in benzene and in acetonitrile, and found that fairly stable benzenesulfenanilidyl radicals (**3**) are formed in these system.

A benzene solution of **1a** (1 mM, 10 ml) was deoxygenated by passage of nitrogen through the solution, and then treated with PbO_2 (25 mg), and the resulting solution was filtered immediately. At first a visible spectrum of the filtrate showed a λ_{max} at 593 nm, which is responsible for the blue color. The absorbance at 593 nm decreased gradually with time with a half-life ($t_1/_2$) of *ca.* 90 min, while new λ_{max}'s appeared at 405 and 427 nm and their absorbances increased with time. The oxidations of **1b** and **1c** also gave blue solutions, λ_{max} 594 ($t_1/_2$=*ca.* 30 min) and 606 nm ($t_1/_2$=*ca.* 2 min), respectively. On the other hand, a green color observed on the oxidation of **1d** was so transient that the λ_{max} could not be determined.

Table I. ESR Spectral Data of Benzenesulfenanilidyl Radicals (3) in Benzene

Radical	4′-X	Coupling constant (G)							*g*-Value
		A_N	$A_{2\text{-H}}$	$A_{3\text{-H}}$	$A_{4\text{-H}}$	$A_{2'\text{-H}}$	$A_{3'\text{-H}}$	$A_{4'\text{-X}}$	
3a	OCH_3	9.50	0.60	0.20	0.625	3.85	1.10	0.65	2.0055
3b	CH_3	9.50	0.725	0.225	0.75	3.75	1.20	4.70	2.0059
3c	Cl	9.40	0.325	0.75	0.325	3.65	1.275	—	2.0062
3d	H	8.60	0.775	0.275	0.80	3.70	1.25	4.20	2.0061

As for ESR experiments, the oxidation was carried out in degassed benzene in order to get well-resolved ESR spectra. The radicals **3a** and **3b** showed well-resolved ESR spectra and had life-times of a day in degassed benzene. On the other hand, **3c** and **3d** showed poorly resolved spectra and decomposed thoroughly in an hour. The coupling constants are sum-

Table II. Results of Oxidation of 4′-Substituted Benzenesulfenanilides with Lead Dioxide

Compd. No.	Concn. (mg/ml)	Solvent	PbO_2 (g)	Reaction		Products identified	Yield (mg)
				Temp. (°C)	Time (hr)		
1a	116/50	C_6H_6	0.53	30	2	2,7-dimethoxyphenazine	33.1
						diphenyldisulfide	36.9
1b	160/74	C_6H_6	1.28	35	22	2,7-dimethylphenazine	26.7
						diphenyldisulfide	46.4
1c	25/10	C_6H_6	0.05	40	4	*a*)	
1d	20/10	C_6H_6	0.05	40	4	*a*)	
1a+**1b**	187+172/160	CH_3CN	1.0	40	15	2,7-dimethoxyphenazine	19.7
						2,7-dimethylphenazine	6.4
						2-methoxy-7-methylphenazine	15.3

a) Products were not identified.

2) H. Lecher, K. Koberle, and P. Stocklin, *Chem. Ber.*, **58**, 423 (1925).
3) Y. Miura, N. Makita, and M. Kinoshita, *Tetrahedron Lett.*, **1975**, 127; *idem*, *Bull. Chem. Soc. Japan*, **50**, 482 (1977).

marized in Table I, together with g-values. The nitrogen coupling constants and g-values of **3** are smaller than those of dibenzenesulfenamidyl radicals.[3] On the other hand, the values of A_H in the aniline part are larger than those in the phenylthinyl part. The unpaired electron is, therefore, distributed mainly on the aniline part.

The results of a large scale oxidation of **1** are summarized in Table II. Although the oxidations of **1a** and **1b** gave the corresponding phenazines as the final products, those of **1c** and **1d** did not. The rate of formation of 2,7-dimethylphenazine was much slower than that of 2,7-dimethoxyphenazine at the same temperature. The following schemes are suggested for the oxidations of **1a** and **1b**.

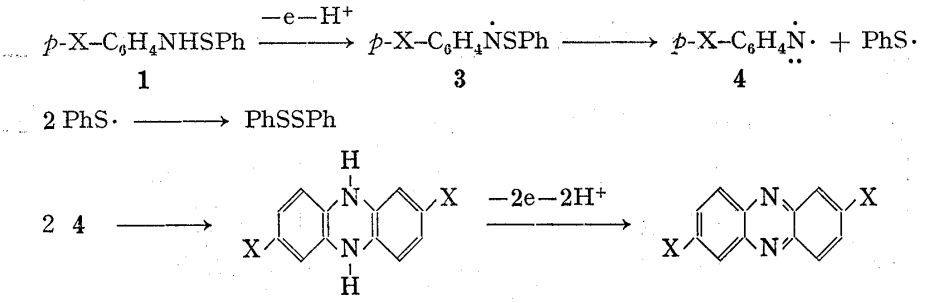

Chart 1

The oxidation of an equimolar mixture of **1a** and **1b** was carried out in acetonitrile, because the rate of formation of 2,7-dimethylphenazine was faster in acetonitrile than in benzene. A crossover product, 2-methoxy-7-methylphenazine, was obtained besides the 2,7-disubstituted phenazines. The isolation of the crossover product favors the nitrene pathway.[4] Detailed studies are now in progress.

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