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Phenylazo *p*-Tolyl Sulfone as a Source of Phenyl Radical[1]

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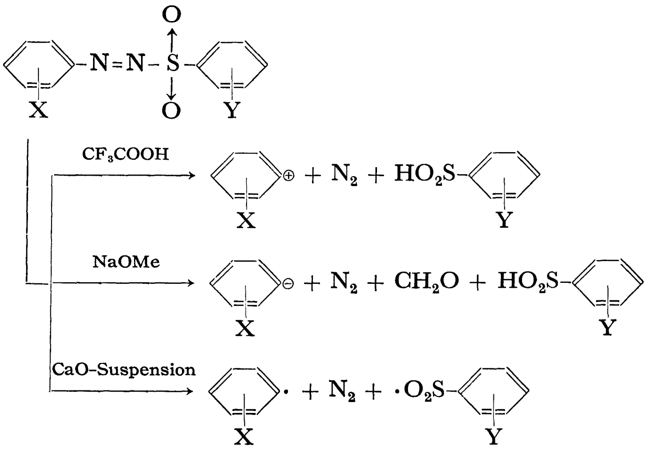
Mechanism of the decomposition of phenylazo *p*-tolyl sulfone(I) was investigated. Orientations and partial rate factors of substituted biphenyls produced by the decomposition of I in benzene-substituted benzene mixtures were used as the criteria for judging the nature of the decomposition. When CaO- or MgO-suspension was present, autocatalytic heterolysis of I was suppressed to some extent, but for complete suppression 20—40 w/v % CaO or MgO was necessary. Pyridine and quinoline were found to be effective for suppression of the autocatalysis. When sufficient amount of pyridine, quinoline, MgO or CaO were present, orientations and partial rate factors for phenylation of substituted benzene were similar to those obtained by phenyl radical produced by benzoyl peroxide on *N*-nitrosoacetanilide. The rate of decomposition of I was determined in PhC_2H_5, $PhOCH_3$, PhCl, $PhNO_2$, pyridine and DMF in the presence of pyridine. An isokinetic relationship was found to hold for activation parameters for the decomposition in these solvents, and the isokinetic temperature was 88.6°C. Values of activation enthalpy and entropy were rather large; $\Delta H^{\neq}=39.6$ kcal/mol and $\Delta S^{\neq}=34.4$ e.u./mol in DMF.

When trifluoroacetic acid is present in the medium, phenylazo *p*-tolyl sulfone decomposed heterolytically, yielding phenyl cation, nitrogen and *p*-toluenesulfinic acid.[2] Bunnett and Happer reported that when sodium methoxide is present *o*-halophenylazo phenyl sulfone yielded *o*-halophenyl anion, nitrogen, formaldehyde and benzenesulfinic acid.[3] Rosenthal and Overberger reported that in the presence of suspended calcium oxide phenylazo phenyl sulfone decomposed homolytically, yielding phenyl and benzenesulfonyl radicals.[4] Kice and Gabrielsen reported that phenylazo methyl sulfone also decomposed homolytically when suspended calcium oxide was present.[5]



Azosulfones are interesting compounds as the source for aryl radicals and arenesulfonyl radicals, but it seems that the conditions which guarantee completely homolytic decomposition of azosulfones have not been established yet. It is not certain that to what extent the

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[1] Organic Sulfur Compounds, Part XXV.

[2] M. Kobayashi, H. Minato, and N. Kobori, This Bulletin, **43**, 219 (1970).

[3] J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **32**, 2701 (1967).

[4] C. G. Overberger and A. J. Rosenthal, *J. Amer. Chem Soc.*, **82**, 108, 117 (1960).

[5] J. L. Kice and R. S. Gabrielsen, *J. Org. Chem.*, **35**, 1004 (1970).

heterolytic decomposition of azosulfones is suppressed when suspended calcium oxide is present. Further detailed investigation of the mechanism of decomposition of azosulfones seemed desirable. Such investigation was carried out in our laboratories, and the effectiveness of added bases such as calcium oxide, magnesium oxide, pyridine, and quinoline was determined. In order to determine whether or not phenyl cation is being produced, orientations and partial rate factors for phenylation in aromatic solvents were measured. These results will be described in this paper.

Experimental

Materials. Aromatic solvents were purified according to conventional methods.[2]

Phenylazo *p*-tolyl sulfone was synthesized by the reaction between benzenediazonium chloride and sodium *p*-toluenesulfinate, and recrystallized from methanol; mp 90—91°C (decomp.).

Pyridine and quinoline were refluxed over potassium hydroxide and then distilled; pyridine, 114—115°C/760 mmHg, quinoline, 137°C/45 mmHg.

Calcium oxide was ground to fine powder and then used. Magnesium oxide which is available as fine powder was used as received.

Kinetic Measurements. A flask containing a mixture of 60 m*l* of a solvent and 8—13 mmol of pyridine was placed in a constant temperature bath. After the temperature of the mixture reached that of the bath, 3 mmol of I was dissolved (the concentration is about 0.05 mol/*l*). Amounts of nitrogen gas generated were measured by a gas buret.

Analysis of Phenylated Products. Three mmol of I was dissolved in aromatic solvents (a mixture of 0.12 mol of benzene and 0.12 mol of a substituted benzene) containing 3—20 mmol of pyridine or quinoline, and a flask containing the solution was placed in a constant temperature bath.

Since azobenzene is one of the products and it interferes the gas-chromatographic determination of biphenyls, it had to be removed by reduction. To the reaction mixtures containing anisole, chlorobenzene or ethylbenzene, zinc powder and methanolic hydrochloric acid were added and azobenzene was reduced; then the mixture was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The reaction mixtures containing benzonitrile or nitrobenzene were washed with a 5% sodium carbonate solution and water, dried over anhydrous magnesium sulfate, and then concentrated.

When calcium oxide or magnesium oxide was used in place of pyridine or quinoline, the reaction mixtures were filtered and then treated in a similar manner.

Biphenyls in the concentrated mixtures were determined by a Hitachi K-53 Gas Chromatograph.

Results and Discussion

Rosenthal and Overberger reported that when 0.13—0.33 w/v% calcium oxide was present the autocatalysis by acidic products (arenesulfinic acids and arenesulfonic acids) were prevented and the decomposition followed a first-order rate law.[4] We determined the orientations and partial rate factors for the phenylation of substituted benzenes (0.12 mol benzene +0.12 mol a substituted benzene) with I in the absence of CaO and in the presence of 0.5 g CaO (0.5 g CaO corresponds to 2.19 w/v% in the case of benzene-chlorobenzene). The results are shown in Table 1.

Partial rate factors in the presence of 0.5 g CaO are quite different from those in the absence of CaO, but they are still different from the partial rate factors for phenylation with phenyl radical produced from benzoyl peroxide[6] or *N*-nitrosoacetanilide.[7] This finding indicates that the autocatalytic heterolysis is not completely suppressed. Therefore, the amounts of calcium oxide suspension were increased. Since magnesium oxide is commercially available as powder much finer than calcium oxide, some experiments were carried out in the presence of magnesium oxide. The results of experiments with benzene-chlorobenzene are shown in Table 2.

When 5.0 g of MgO was present (21.9 w/v%), the orientations and partial rate factors are similar to those by phenyl radical, and no further change was observed when amounts of magnesium oxide were increased. Therefore, the orientations and partial rate factors for

Table 1. Orientations and partial rate factors for the phenylation of PhX with *p*-TsN_2Ph (a) in the absence of CaO and (b) in the presence of 0.5 g CaO[a]

X in PhX		Orientations(%)			Partial rate factors			Yield of total biphenyls (%)
		o-	*m*-	*p*-	k_o/k	k_m/k	k_p/k	
OCH_3	a)	57.8	14.8	27.4	2.37	0.61	2.26	
	b)	68.8	16.4	14.8	3.99	0.95	1.73	
C_2H_5	a)	49.5	24.5	26.0	1.41	0.70	1.48	14.0
	b)	51.3	30.2	18.5	2.08	1.23	1.49	13.0
Cl	a)	53.0	20.3	26.7	1.13	0.43	1.14	21.9
	b)	57.3	22.7	20.0	2.89	1.15	2.01	32.6
CN	a)	43.1	36.9	20.0	0.89	0.71	0.77	
	b)	51.8	22.0	26.2	2.68	1.16	2.75	
NO_2	a)	38.0	62.0	0	0.60	0.98	0	12.8
	b)	47.5	23.7	28.8	2.45	1.23	2.98	18.0

[a] Each experiment was carried out with a mixture of 0.12 mol of benzene and 0.12 mol of a substituted benzene. Reaction temperature; 60.0°C

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6) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon press, Oxford (1960), pp. 68, 73,

7) R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

TABLE 2. ORIENTATIONS AND PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhCl WITH *p*-TsN_2Ph IN THE PRESENCE OF VARIED AMOUNTS OF CaO OR MgO[a)]

Additive	Weight (g)	Orientations(%)			Partial rate factors		
		o-	*m*-	*p*-	k_o/k	k_m/k	k_p/k
CaO	0.5	57.3	22.7	20.0	2.89	1.15	2.01
	10.0	59.6	22.7	17.7	3.77	1.47	2.30
	20.0	60.0	22.1	17.9	3.91	1.44	2.34
MgO	1.0	60.0	22.0	19.0	2.73	0.96	1.73
	5.0	60.2	21.4	18.4	4.67	1.66	2.59
	10.0	61.5	22.0	16.4	4.37	1.57	2.35

a) Reaction temperature: 60.0°C

TABLE 3. ORIENTATIONS AND PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhX WITH *p*-TsN_2Ph IN THE PRESENCE OF 5.0 g MgO[a)]

X in PhX	Orientations (%)			Partial rate factors			Yield of total biphenyls (%)
	o-	*m*-	*p*-	k_o/k	k_m/k	k_p/k	
OCH_3	68.6	19.9	11.5	5.79	1.67	1.94	
C_2H_5	53.5	30.5	16.0	2.20	1.26	1.36	8.4
Cl	60.9	21.7	17.4	4.52	1.67	2.60	32.6
CN	57.4	14.3	28.3	6.15	1.53	6.06	
NO_2	64.6	8.6	27.1	13.33	1.81	11.25	39.0

a) Reaction temperature: 60.0°C

the phenylation of various substituted benzenes were determined in the presence of 5.0 g magnesium oxide. The results are shown in Table 3. These values are comparable to those reported for phenylation with phenyl radical.[6,7)]

Since the systems containing calcium oxide and magnesium oxide are heterogeneous, variation of the size of particles and the rate of stirring influence on the results of experiments. Some organic compounds usable in place of calcium oxide are desirable for reproducibility and convenience in the experiments generating phenyl radicals from azosulfones. Experiments were carried out with pyridine and quinoline as organic weak bases, and the results are shown in Tables 4 and 5. Both orientations and partial rate factors are similar to those obtained with 5.0 g magnesium oxide, and these data show that both pyridine and quinoline are effective in preventing autocatalytic heterolysis of I.

Abramovitch and Saha[8)] reported that in the presence of pyridine benzenediazonium salts decompose homolytically according to a scheme shown below.

TABLE 4. ORIENTATIONS AND PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhX WITH *p*-TsN_2Ph IN THE PRESENCE OF PYRIDINE[a)]

X in PhX	Orientations (%)			Partial rate factors			Yield of total biphenyls (%)
	o-	*m*-	*p*-	k_o/k	k_m/k	k_p/k	
OCH_3	65.0	22.5	12.5	4.91	1.69	1.89	
C_2H_5	49.1	32.6	18.3	2.00	1.33	1.49	12.6
Cl	58.3	23.0	18.8	3.32	1.31	2.16	48.7
NO_2	64.5	7.7	27.8	10.36	1.26	8.70	54.4

a) [pyridine]/[*p*-TsN_2Ph]=2—8 (mol ratio) Reaction temperature: 60.0°C

TABLE 5. ORIENTATIONS AND PARTIAL RATE FACTORS FOR THE PHENYLATION OF PhX WITH *p*-TsN_2Ph IN THE PRESENCE OF QUINOLINE[a)]

X in PhX	Orientations (%)			Partial rate factors			Yield of total biphenyls (%)
	o-	*m*-	*p*-	k_o/k	k_m/k	k_p/k	
OCH_3	65.8	21.4	12.8	4.79	1.56	1.89	
C_2H_5	53.5	30.1	16.4	2.02	1.14	1.24	13.2
Cl	60.6	22.8	16.6	3.63	1.36	1.99	46.7
CN	49.4	15.6	35.0	5.20	1.66	7.38	
NO_2	65.7	8.3	26.0	11.07	1.42	8.78	47.8

a) [quinoline]/[*p*-TsN_2Ph]=1.6—10.0 (mol ratio) Reaction temperature: 60.0°C

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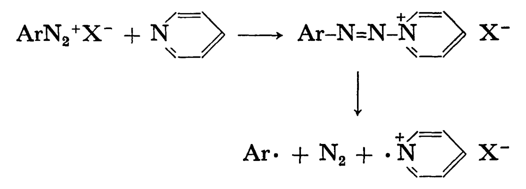
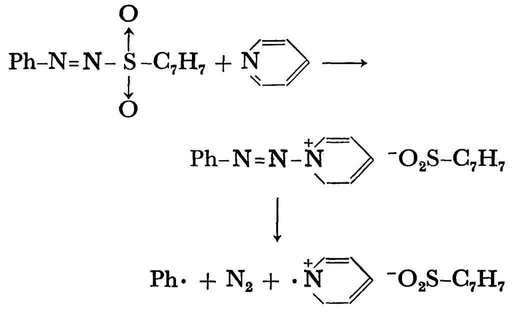
8) R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **21**, 3297 (1965).



In the presence of pyridine, I could undergo a similar reaction.



However, such possibility can be rejected on the basis of the following considerations; a) magnesium oxide and calcium oxide can be used in place of pyridine and similar results are obtained, b) the infrared spectrum of I in pyridine showed no absorptions at 2260—2280 cm^{-1} ascribable to a diazonium salt, c) rates of decomposition of I in the presence of pyridine are quite different from those of diazonium salts in the presence of pyridine, and d) orientations and partial rate factors obtained with I in the presence of pyridine are considerably different from those obtained with diazonium salts in the presence of pyridine.

Figure 1 shows the Hammett plots of *para* partial rate factors against Hammett σ values. The ρ values obtained from the right half line was 1.21 (at 60°C), which is comparable to the ρ value for phenylation with *N*-nitrosoacetanilide (1.27, at 20°C) or that with benzoyl peroxide (1.14, at 80°C), but somewhat different from that with phenylazotriphenylmethane (0.93, at 60°C).[9] These data show that the phenylation with phenyl radical is very little dependent on the temperature but considerable dependent on the source of phenyl radical.

The effect of temperature on the phenylation with phenyl radical has not been investigated in detail. Therefore it has not been established whether or not it is meaningful to compare the orientations and partial rate factors obtained at different temperatures with different phenyl radical sources. In order to clarify this question, orientations of phenylation with I at various temperatures were measured, and the results are shown in Table 6. When the temperature was raised, phenylation at *ortho* position gradually decreased and phenylation at *meta* or *para* position gradually increased. Such tendency was greatest for the phenylation of chlorobenzene. However, the changes are not so significant even in the case of chlorobenzene. These findings indicate that activation energies for phenylation at *ortho*, *meta*, and *para* positions do not differ greatly. This finding supports the commonly accepted interpretation that the similarity in the data on the phenylations with benzoyl peroxide or *N*-nitrosoacetanilide at different temperatures must arise from the same intermediate, phenyl radical.

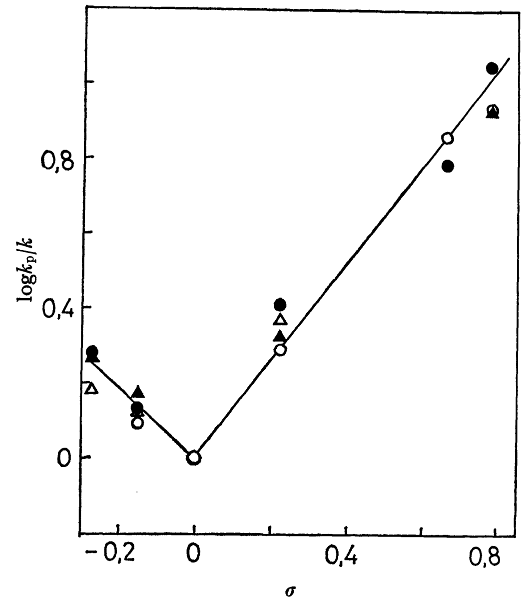


Fig. 1. Hammett plot for phenylation with p-TsN$_2$Ph in the presence of pyridine, quinoline, MgO, and CaO.
ρ=1.21 (at 60°C)
▲ Pyridine ● MgO
○ Quinoline △ CaO

The rates of decomposition of I in various solvents were determined by measuring the nitrogen gas evolved. As shown in Fig. 2, autocatalysis is observed in the absence of calcium oxide or pyridine (curve b) where-

TABLE 6. ORIENTATIONS FOR THE PHENYLATION OF PhX WITH p-TsN$_2$Ph IN THE PRESENCE OF PYRIDINE AT VARIOUS TEMPERATURES[a)]

Reaction Temp. (°C)	PhOCH$_3$			PhC$_2$H$_5$			PhCl			PhNO$_2$		
	o-	*m*-	*p*-	*o*-	*m*-	*p*-	*o*-	*m*-	*p*-	*o*-	*m*-	*p*-
60.0	65.0	22.5	12.5	49.1	32.6	18.3	58.3	23.0	18.8	64.5	7.7	27.8
80.0				50.2	32.7	17.1	51.5	28.7	19.8	60.6	11.2	28.2
85.4	63.7	20.8	15.5	48.2	34.8	17.0	50.2	29.1	20.7	59.9	12.3	27.8
90.6	64.3	20.8	14.9	45.8	36.0	18.2	52.2	28.5	19.3	60.8	12.0	27.2
93.1				48.0	33.7	18.3						
95.6							51.8	28.8	19.4	60.5	11.6	27.9
99.1	61.9	22.1	16.0									

a) [pyridine]/[p-TsN$_2$Ph]=2—4 (mol ratio)

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[9] M. Kobayashi, H. Minato, N. Watanabe, and N. Kobori, This Bulletin, **43** 258 (1970).

Table 7. First-order rate constants for the decomposition of p-TsN$_2$Ph in the presence of pyridine[a]

Reaction Temp. (°C)	Solvent ε	PhC$_2$H$_5$ 2.41	PhOCH$_3$ 4.30	PhCl 5.61	Pyridine 12.3	PhNO$_2$ 34.6	DMF 36.7
				$k\times10^4$ (sec^{-1})			
80.0		1.32		0.494	0.489	0.671	0.591
85.4		1.97	0.793	1.08	1.04	1.16	1.11
90.6		5.06	1.51	2.52	1.79	2.24	3.78
93.1		5.92					
95.6			2.94	5.38	3.42	5.15	5.33
99.1			4.82				

a) [p-TsN$_2$Ph]$_0$=0.05 mol/l, [pyridine]$_0$/[p-TsN$_2$Ph]$_0$=2—4 (mol ratio), except the decomposition in pyridine as the solvent.

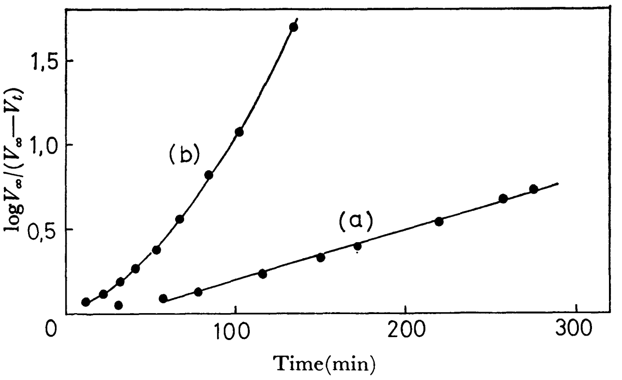

Fig. 2. Rate of decomposition of p-TsN$_2$Ph in PhCl at 85.4°C. V: volume of nitrogen evolved, [p-TsN$_2$Ph]$_0$=0.05 mol/l a) [pyridine]=0.135 mol/l b) [pyridine]=0

as the rates of decomposition followed a first-order rate equation when pyridine is present (line a). The molar ratio, [pyridine]/[I], was kept in the range of 2—4, and the rate constants, k, were not influenced by the concentration of pyridine. First-order rate constants for the decomposition of I in solvents of various dielectric constants were determined in the presence of pyridine, and the results are shown in Table 7.

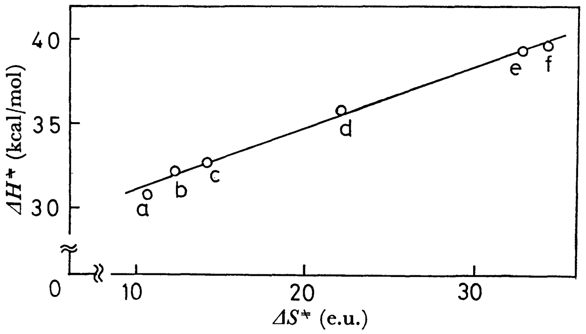

Fig. 3. Isokinetic relationship for the decomposition of p-TsN$_2$Ph in the presence of pyridine in various solvents. β=88.6°C; a, PhC$_2$H$_5$ b, C$_5$H$_5$N c, PhNO$_2$ d, PhOCH$_3$ e, PhCl f, DMF

Table 8. Activation parameters for the decomposition of p-TsN$_2$Ph in the presence of pyridine

Solvent	$\Delta H^{\ddagger}$(kcal/mol)	$\Delta S^{\ddagger}$(e.u.)
PhC$_2$H$_5$	30.8	10.7
pyridine	32.2	12.3
PhNO$_2$	32.6	14.1
PhOCH$_3$	35.9	22.2
PhCl	39.4	32.8
DMF	39.6	34.4

Rate constants in Table 7 are not dependent on the dielectric constants of media, and this fact also supports the homolytic nature of the decomposition of I in the presence of pyridine. Activation parameters for the decompositions in these solvents were obtained, and shown in Table 8. An isokinetic relationship holds for these activation parameters, as shown in Fig. 3, and the isokinetic temperature, β, was 88.6°C.

Variation in activation parameters in these solvents is fairly large, but cannot be rationalized easily. However, it is of interest to note that activation entropies for decomposition of this azosulfone are rather large compared with those of common radical initiators with similar activation enthalpies; this azosulfone, in chlorobenzene, $\Delta H^{\ddagger}$=39.4 kcal/mol, $\Delta S^{\ddagger}$=32.8 e.u., t-butyl peracetate,[10] in chlorobenzene, $\Delta H^{\ddagger}$=38 kcal/mol, $\Delta S^{\ddagger}$=17 e.u., di-t-butyl peroxide,[11] in t-butylbenzene, $\Delta H^{\ddagger}$=37.8 kcal/mol, $\Delta S^{\ddagger}$=13.8 e.u. Because of these rather large activation entropies, this azosulfone decomposes at temperatures lower than those used for di-t-butyl peroxide or t-butyl peracetate. Compounds decomposing with activation entropies comparable to those of this azosulfone are phenylazo phenyl sulfides; van Zwet and Kooyman reported that E_a and $\Delta S^{\ddagger}$ for the decomposition of p-tolylazo p-t-butylphenyl sulfide in benzene were 36 kcal/mol and 33 e.u., respectively.[12]

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[10] P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

[11] J. H. Raley, F. F. Rust, and W. E. Vaughan, *ibid.*, **70**, 1337 (1948).

[12] H. van Zwet and E. C. Kooyman, *Rec. Trav. Chim., Pays-Bas*, **86**, 1143 (1967).