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Studies of Poly-2-vinylpyridine. VI. Thermodynamic Data on Solutions of Poly-2-vinylpyridine in Various Solvents

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The viscosities of dilute solutions of several fractions of poly-2-vinylpyridine have been measured in methanol, isopropanol, chloroform, benzene, dioxane, and methyl ethyl ketone at different temperatures, ranging from 15 to 65°C. The osmotic pressures of dilute solutions of fractions of the polymer have been measured in dioxane at 10, 25, 40, and 65°C. The data have then been analysed using the theories of Flory and Fox and of Kurata and Stockmayer. The results obtained are as follows: (1) the entropy parameters, ψ_1, for the solutions of poly-2-vinylpyridine in methanol and isopropanol are negative, while the critical miscibility temperatures, θ, are positive and extraordinary high; (2) ψ_1 is positive and θ is negative in chloroform; (3) These parameters behave regularly in benzene and dioxane. Qualitatively the same results have also been obtained with the poly-4-vinylpyridine fraction in several solvents, including methanol and chloroform. These results show that in alcohols and chloroform the temperature coefficient of the solubility of polyvinylpyridines is negative, and indicate the presence of strong interaction between segments and solvents, probably due to hydrogen-bond formation.

In the preceding paper[1] some properties of poly-2-vinylpyridine solution in ethanol have been described: the entropy parameter, ψ_1, from the viscosity data is negative; the critical consolute temperature, θ, from the same data is extraordinary high, and both the heat and the entropy of dilution obtained from the data of osmotic pressure are negative. It has been concluded that these peculiarities may be the result of the strong interaction between the segment and solvent itself, probably because of the hydrogen-bond formation between the nitrogen atom in the pyridine ring and the hydroxyl group in the solvent molecule.

The same results have been reported for the poly-4-vinylpyridine-*t*-butanol-benzene system[2] and the polyacrylic acid - dioxane system.[3] The negative value of ψ_1 has also been reported for the polymethacrylonitril - methyl ethyl ketone system.[4] However, the reports on such peculiar properties are very limited, and it is considered to be important to confirm the conclusions of the preceding paper by performing similar experiments in other acidic solvents which are capable of hydrogen-bond formation, and also in neutral or basic solvents which are not. In this report, thermodynamic data on poly-2-vinylpyridine solutions in methanol, isopropanol, and chloroform, and on such solutions in benzene, dioxane and methyl ethyl ketone as slovents of the latter category are presented. The results of complementary experiments on poly-4-vinylpyridine in several solvents will also be described.

Experimental

The fractions of poly-2-vinylpyridine, E-2, K-2, and C-1, were the same as those used in a previous study.[5] The unfractionated poly-2-vinylpyridine, 2U$_0$ was obtained by block polymerization in a sealed tube at 60°C, and was purified by repeated precipitations in methyl ethyl ketone by addition of ligroin.

Poly-4-vinylpyridine was prepared by the suspension method.[6] Thirty-five grams of the polymer were fractionated into 8 fractions by the column-elusion method. The fourth fraction, 4F-4, was used in this study.

The intrinsic viscosity and osmotic pressure were measured by the methods described in a previous paper.[1] The solvents were dried and fractionally distilled according to usual methods.[7]

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1) S. Arichi, This Bulletin, **41**, 548 (1968).

2) A. G. Boyes and U. P. Strauss, *J. Polymer Sci.*, **22**, 463 (1956).

3) S. Newman, W. R. Krigbaum, C. Laugier and P. J. Flory, *ibid.*, **14**, 451 (1954).

4) H. Morawetz, "Macromolecules in Solution," Interscience Publishers, Inc., New York (1965).

5) S. Arichi, This Bulletin, **39**, 439 (1966).

6) J. B. Berkowitz, M. Yamin and R. M. Fuoss, *J. Polymer Sci.*, **28**, 69 (1958).

7) A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," Interscience Publishers, Inc., New York (1955).

Results

Temperature Variation of the Intrinsic Viscosity. The intrinsic viscosities of the solutions of the poly-2-vinylpyridine fraction, E-2, in methanol, isopropanol, and chloroform; those of the K-2 fraction in benzene, dioxane, and methyl ethyl ketone, and those of $2U_0$ in methanol at various temperatures are shown in Table 1. The experimental results for the poly-4-vinylpyridine fraction, 4F-4, in methanol, isopropanol, chloroform, and pyridine are summarized in Table 2.

The relations between the intrinsic viscosities and the temperature for poly-2-vinylpyridine fractions in various solvents are shown in Fig. 1, and those for the poly-4-vinylpyridine fractions, in Fig. 2.

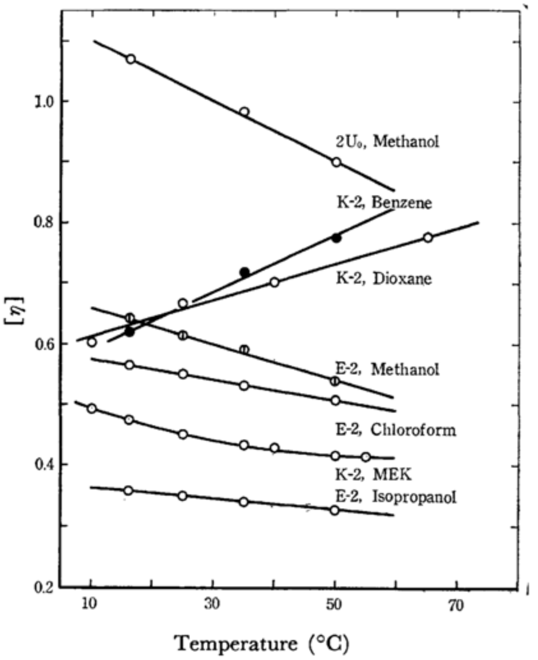

Fig. 1. Plots of the intrinsic viscosities of poly-2-vinylpyridine fractions in various solvents *vs.* temperature.

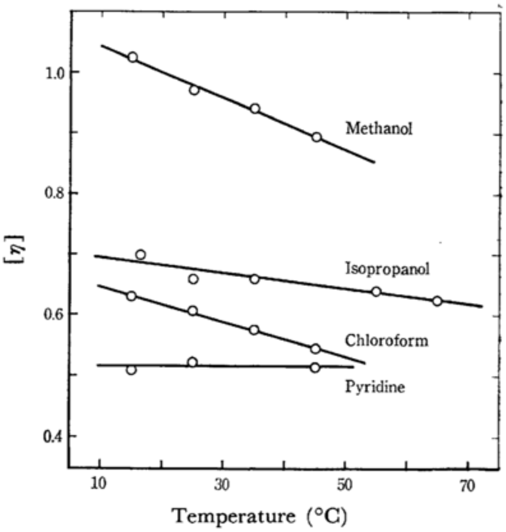

Fig. 2. Plots of the intrinsic viscosities of poly-4-vinylpyridine fractions *vs.* temperature.

TABLE 1. THE INTRINSIC VISCOSITIES OF POLY-2-VINYLPYRIDINE FRACTIONS IN VARIOUS SOLVENTS AT DIFFERENT TEMPERATURES

Fraction	Solvent	[η] Temperature (°C)						
		10	16.2	25	35	40	50	65
E-2	Methanol		0.640	0.614	0.583		0.540	
$2U_0$	Methanol		1.068		0.982		0.901	
E-2	Chloroform		0.566	0.549	0.531		0.510	
E-2	Isopropanol		0.358	0.349	0.344		0.328	
K-2	Benzene		0.620		0.719		0.775	
K-2	Dioxane	0.601		0.668		0.701		0.701
K-2	MEK	0.495	0.479	0.452	0.434	0.430	0.415	

TABLE 2. THE INTRINSIC VISCOSITIES OF POLY-4-VINYLPYRIDINE FRACTIONS IN VARIOUS SOLVENTS AT DIFFERENT TEMPERATURES

Fraction	Solvent	[η] Temperature (°C)						
		15	16.5	25	35	45	50	65
4F-4	Methanol	1.025		0.970	0.942	0.895		
4F-4	Chloroform	0.630		0.606	0.575	0.545		
4F-4	Isopropanol		0.700	0.660	0.660		0.640	0.625
4F-4	Pyridine	0.510		0.522		0.515		

As may be seen in these figures, the temperature coefficients of the intrinsic viscosities of both poly-2-vinylpyridine and poly-4-vinylpyridine fractions in methanol, isopropanol and chloroform are negative, as are those of poly-2-vinylpyridine1) and poly-4-vinylpyridine6) in ethanol. On the contrary, the coefficients are positive or almost zero in the case of neutral or basic solvents, such as benzene and pyridine, as is usual in a nonpolar polymer - nonpolar solvent system. Methyl ethyl ketone is a typical basic solvent,8) but the temperature coefficient for the system of poly-2-vinylpyridine-methyl ethyl ketone is rather negative.

Although the results shown in Figs. 1 and 2 seem to support our previous conclusion1,8) that, for polyvinylpyridine, acidic solvents are good solvents and neutral or basic solvents, poor solvents, further examinations were made by analysing the data using the Flory-Fox9) and Kurata-Stockmayer10) theories.

As is well known, the thermodynamic interactions between polymer segments and solvent molecules are represented by the following equations, (1) and (2), given by Flory and Fox9) and by Kurata and Stockmayer10) respectively:

$$(K_T/K_0)(\alpha_\eta{}^5-\alpha_\eta{}^3)/M^{1/2} = 2C_{\mathrm{M}}\psi_1(1-\theta/T) \tag{1}$$

$$(K_T/K_0)(1-\alpha_\eta{}^{-2})(\alpha_\eta{}^2+1/3)^{3/2}/M^{1/2} = (3^5/2^3)1.10C_{\mathrm{M}}\psi_1(1-\theta/T) \tag{2}$$

where the symbols are the same as those used in the previous paper.1)

It has been reported1) that the value of the Flory constant, K, for poly-2-vinylpyridine, as estimated from the intrinsic viscosity data in ethanol, is considerably larger than those in the neutral or basic solvents. Now, let us suppose that the values of the Flory constant, K_i, for the samples of poly-2-vinylpyridine with a homogeneous molecular weight in methanol and chloroform are the same as those in ethanol at a certain temperature,1) and that those in neutral or basic solvents are all equal to the value11) of 8.2×10^{-4}, regardless of the temperature and the kind of solvent. As for isopropanol, it has already been pointed out that, because of the steric hindrance, the interaction between this solvent and the nitrogen atom in the pyridine ring of poly-2-vinylpyridine is relatively small compared with that in other primary alcohols.8) In fact, the values of the intrinsic viscosity in isopropanol in this study are very small. Consequently, it was supposed that the value of K_i for this solvent is nearly equal to that of the neutral solvent: 8.2×10^{-4}.

Using the following equations,10) the values of K_w were calculated, assuming that the molecular-weight distribution for each polymer fraction is represented by the exponential-type molecular-weight distribution function:12)

$$K_w = K_i q_w \tag{3}$$

$$q_w = \Gamma(h+1.5)/(h+1)^{1/2}\Gamma(h+1) \tag{4}$$

where h is the parameter of the molecular-weight inhomogeneity and is defined by the following equation:

$$M_w/M_n = (h+1)/h \tag{5}$$

The values of K_w thus calculated are shown in Table 3.

TABLE 3. THE VALUES OF K USED FOR CALCULATION OF EQS. (1) AND (2)

Fraction	$M_w\times10^{-4}$	$M_n\times10^{-4}$	M_w/M_n	q_w
E-2	12.01	7.42	1.62	0.955
K-2	52.06	18.07	2.88	0.924

For methanol and chloroform solutions

Temp. (°C)	$K_i\times10^4$ a)	$K_w\times10^4$ E-2	$K_w\times10^4$ K-2
10	13.7	13.1	12.7
25	13.0	12.4	12.0
40	12.2	11.7	11.3
65	11.5	11.0	10.6

For benzene, dioxane, methyl ethyl ketone and isopropanol solutions

Temp. (°C)	$K_i\times10^4$ b)	$K_w\times10^4$ E-2	$K_w\times10^4$ K-2
10—65	8.20	7.83	7.58

a) The values from Ref. 1.
b) The value from Ref. 2.

The values of α_η were calculated by inserting the values of $[\eta]$, K_w, and M_w into the following equation:9)

$$\alpha_\eta{}^3 = [\eta]/K_w M_w{}^{1/2} \tag{6}$$

Plots of the left-hand side of Eq. (1) for data of the intrinsic viscosity of poly-2-vinylpyridine in various solvents against the reciprocal temperature, $1/T$, are shown in Fig. 3, and those for Eq. (2) are shown in Fig. 4. These figures show the relation to be linear for all the solvents used. The slopes of the lines for benzene and dioxane are normal, while those for the other solvents are negative, in contrast to the case with ordinary polymer-solvent systems.

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8) S. Arichi, H. Matsuura, Y. Tanimoto and H. Murata, This Bulletin, **39**, 434 (1966).

9) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).

10) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolymer. Forsch.*, **3**, 196 (1963).

11) S. Arichi, *J. Sci. Hiroshima Univ., Ser.* **A-II**, **29**, 97 (1965).

12) S. Arichi, S. Mitsuta, N. Sakamoto and H. Murata, This Bulletin, **39**, 428 (1966).

TABLE 4. THERMODYNAMIC DATA, ψ_1 AND θ, ESTIMATED FROM THE DATA OF TEMPERATURE VARIATION OF THE INTRINSIC VISCOSITY AND THE OSMOTIC SECOND VIRIAL COEFFICIENT, A_2

Solvent	θ (°K)			ψ_1		
	From A_2	From $[\eta]$		From A_2	From $[\eta]$	
		Eq. (1)	Eq. (2)		Eq. (1)	Eq. (2)
Methanol		482.8	450.0		−0.03	−0.02
Chloroform		−297.4	−173.9		0.01	0.01
Isopropanol		443.2	412.6		−0.03	−0.02
Benzene		275.4	278.8		0.07	0.04
Dioxane	268.9	267.6	272.5	0.28	0.05	0.03
MEK		258.9	249.3		−0.04	−0.01

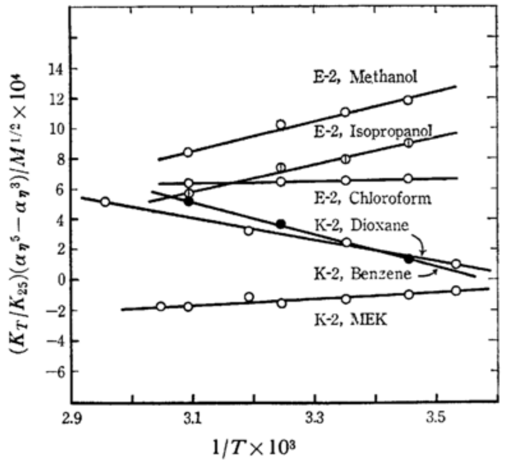

Fig. 3. Plots of the left hand side of Flory-Fox equation, Eq. (1), *vs.* the reciprocal temperature.

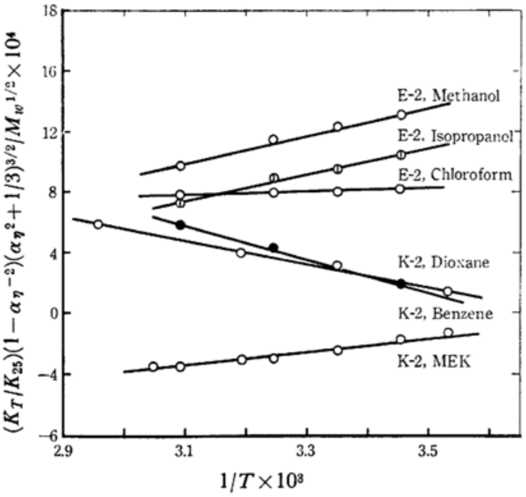

Fig. 4. Plots of the left hand side of Kurata-Stockmayer equation, Eq. (2), *vs.* the reciprocal temperature.

The equations of the linear lines in Figs. 3 and 4 were obtained by the least-square method; the values of the thermodynamic parameters, ψ_1 and θ, were calculated to be as shown in Table 4.

Thermodynamic Interaction Parameters Obtained from the Temperature Dependence of the Osmotic Pressure. The thermodynamic interaction parameters were estimated from the measurement of the temperature variation of the osmotic second virial coefficient, A_2. According to the Flory theory,[13] the relation between A_2 and T is shown by the following equation:

$$A_2=(\bar{v}^2/V_1)\psi_1(1-\theta/T)F(X) \tag{7}$$

where $\bar{v}$ is the specific volume of the polymer, and V_1, the molar volume of the solvent; $F(X)$ depends mainly on the thermodynamic interaction parameters but also partly on the molecular weight of the polymer and on the temperature, but at the temperature of θ, $F(X)$ takes a definite value of 1.

In order to compare the data on the intrinsic viscosity with those on osmotic pressure, measurements were carried out for solutions of the C-1 fraction in methanol, chloroform, and dioxane and for a solution of the F-2-3 fraction in methyl ethyl ketone. Unfortunately, the experiments succeeded only in the dioxane solution. In the other solutions the temperature variations of the second virial coefficient were very small, and, in addition, the leak of solute molecules from the membrane at relatively high temperatures could not be avoided. Thus, experimental accuracy was not good enough for the data to serve as the basis of further discussion.

Plots of the reduced osmotic pressure, π/c, against the concentration, c, at each temperature are shown in Fig. 5 for the solution of the poly-2-vinylpyridine fraction, C-1, in dioxane. As may be seen in this figure, the points lie on linear lines, so the osmotic third virial coefficient was neglected. In Fig. 6 the values of A_2 obtained by the least-square method are plotted against T. These plots are also represented by a linear line, whose equation was calculated by the least-square method; the value of θ was determined to be 268.9°K. This value of θ was then inserted into Eq. (7). Plots of $\psi_1F(X)$ against T are shown in Fig. 7,

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[13] P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

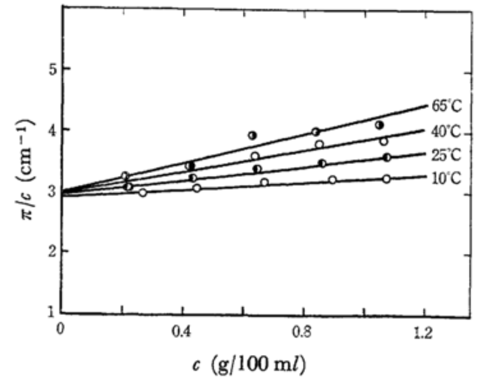

Fig. 5. Plots of the reduced osmotic pressure *vs.* the concentration of poly-2-vinylpyridine fraction, C-1, in dioxane at various temperatures.

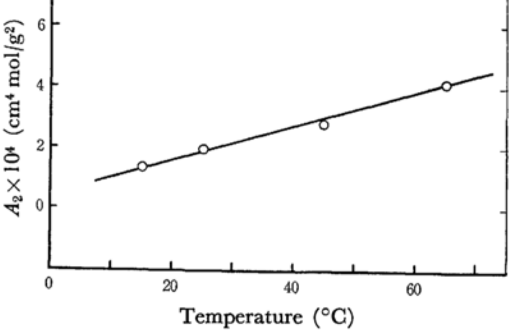

Fig. 6. Plots of the second virial coefficient *vs.* temperatures for the solution of poly-2-vinylpyridine fraction, C-1, in dioxane.

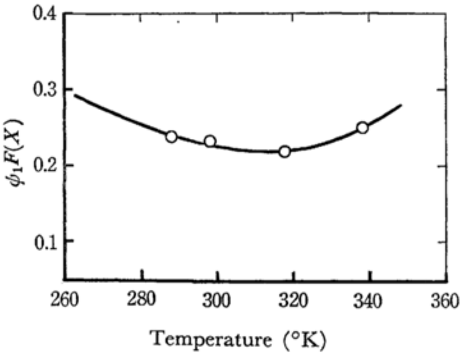

Fig. 7. Plots of $\psi_1F(X)$ *vs.* temperature for the solution of poly-2-vinylpyridine fraction, C-1, in dioxane.

from which the value of ψ_1 is obtained as 0.28 for the system of poly-2-vinylpyridine - dioxane.

Discussion

As may be seen in Table 4, the estimated values of θ for benzene, dioxane, and methyl ethyl ketone are somewhat lower than room temperature and seem probable. The value of θ for chloroform is negative, while those for methanol and isopropanol are positive and extraordinary high. On the other hand, the value of ψ_1 for chloroform is positive, while those for methanol and isopropanol are negative. The heat of dilution for chloroform is, therefore, negative, indicating that chloroform is a very good solvent for this polymer. For the solutions of methanol and iospropanol, both the heat and the entropy of dilution are negative, as in the results for the poly-2-vinylpyridine - ethanol system.[1)]

The hydrogen-bond formation, as described in a previous paper,[1)] is considered to be the main reason for the peculiar findings on the thermodynamic interaction parameters in poly-2-vinylpyridine solutions in alcohols and chloroform. Nevertheless, it seemed useful to confirm that the peculiarity is not due to the presence of some impurities in the polymer. With this object, measurements of the temperature variation of the intrinsic viscosity in methanol with the 2U$_0$ polymer and those of several solvents for poly-4-vinylpyridine were carried out; the results are shown in Table 1 and Fig. 1 for the former, and in Table 2 and Fig. 2 for the latter. respectively. In order to avoid any possibility of contamination, the poly-2-vinylpyridine sample, 2U$_0$, was thermally polymerized in a sealed tube without any initiator or solvent, and was carefully purified by reprecipitation. As may be seen in Fig. 1, the behavior of the intrinsic viscosity of 2U$_0$ in methanol is just the same as that of K-2 in the same solvent. The behavior of the intrinsic viscosity of poly-4-vinylpyridine, fraction 4F-4, in pyridine is not so peculiar, while those in alcohols and chloroform are just the same as those of poly-2-vinylpyridine in the same solvents. From these results, it may be concluded that the peculiar behavior of the intrinsic viscosity is not due merely to the presence of some impurities in the samples.

The value of θ for the solution of poly-2-vinylpyridine in a neutral solvent, benzene, as estimated from the data on the intrinsic viscosity, seems appropriate, though the value is rather lower than the value obtained from the dependence of the consolute temperature on the polymer-chain length.[5)]

The value of θ for the solution of poly-2-vinylpyridine in dioxane agrees well with that obtained from the osmotic second virial coefficient. It is noteworthy that the value of ψ_1 obtained from the osmotic pressure data is larger than that obtained from the intrinsic viscosity data.

As for the solution of poly-2-vinylpyridine in methyl ethyl ketone, various parameters which indicate that the θ temperatures lie near room temperature were described in a previous paper.[11)] For example, at 25°C the long-range interaction parameter, B, obtained from Fixman's plots is negative; the osmotic second virial coefficient, A_2, is negative, and the exponent, ν, in the Mark-Houwink-Sakurada equation is smaller than 0.5, which is theoretically the smallest value.[10]

The values of α_η obtained from the viscosity data in methyl ethyl ketone in this study are again smaller than 1 in the temperature range of 10—45°C. The osmotic second virial coefficients, A_2, were almost zero throughout the 10—40°C temperature range measured in steps of 5°C. The application of the viscoisity data to Eq. (2) gives 249.3°K and -0.01 for θ and ψ_1 respectively. In fact, the phaseseparation experiments showed that the critical temperature for the poly-2-vinylpyridine fraction, H-3 ($M_w=14.9\times10^4$), is about 247°K.

These results show that the dilution of the solution is exothermic and that methyl ethyl ketone brings poly-2-vinylpyridine to the suspected θ state over a very wide range of temperature. Similar results have been reported by Fujita and others[14] for the polychloroprene - methyl ethyl ketone system. It is not yet clear what kind of chemical interaction is the source of the solution properties in the poly-2-vinylpyridine - methyl ethyl ketone system, but it is possible that the alcoholic –OH group produced by keto-enol tautomerism in methyl ethyl ketone[15] plays some role.

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[14] K. Hanafusa, A. Teramoto and H. Fujita, *J. Phys. Chem.*, **70**, 4004 (1966).

[15] A. Gero, *J. Org. Chem.*, **19**, 1960 (1954); **26**, 3156 (1961).