THE RITTER REACTION OF THE ACRYLONITRILE OLIGOMER

Václav JANOUT and Pavel ČEFELÍN
Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

Received December 10th, 1979

The Ritter reaction of oligomeric models of poly(acrylonitrile) with tert-butyl alcohol in tetramethylene sulphone leads to the respective N-tert-butylamides and proceeds *via* the second-order kinetics. The rate constants increase only little on passing from the monomeric to the trimeric model. The decrease in the activation enthalpy ΔH^* is almost compensated for by the decrease in the activation entropy parameter. No effect of the neighbouring functional group on the reaction kinetics could be observed. A new conformational equilibrium is established during the reaction.

The preparation of model compounds of poly(acrylonitrile) of the $CH_3CH(CN)\,[CH_2CH(CN)]_nCH_3$ type has been investigated by several authors[1-3]; further attention has been mainly concentrated on the study of the spectral properties of such compounds in order to explain the configurational and conformational structure of poly(acrylonitrile)[4-13]. The relationship between the reactivity of these model compounds and the reactivity of poly(acrylonitrile) has been investigated only sporadically, namely, for acid catalyzed hydrolysis[14], thioamidation[15] and thermal transformations[16], with the aim of obtaining information on the structure of products of similar reactions on poly(acrylonitrile). The alkylation of the nitrile group to yield the alkylamide group was recorded in 1930 by Weiland and Dorrer[18], but the reaction of nitriles with alkenes and alcohols in sulphuric acid, giving rise to N-substituted amides, was first described by Ritter[17]. Very good yields can be obtained by using suitable sources of carbenium ions[19]. The reaction mechanism was suggested already by Ritter in the introductory paper, but it could be confirmed only in kinetic studies of a later date[20-22]:

$$\mathrm{R{-}C\bar{N}} + \overset{+}{\mathrm{C}}\!\leqq \;\rightleftharpoons\; \mathrm{R{-}C{\equiv}\overset{+}{N}{-}C}\!\leqq \;\leftrightarrow\; \mathrm{R{-}\overset{+}{C}{=}\bar{N}{-}C}\!\leqq \;\xrightarrow{\mathrm{H_2O},\,-\mathrm{H}^+}$$

$$\longrightarrow \mathrm{R{-}C(OH){=}\bar{N}{-}C}\!\leqq \;\rightleftharpoons\; \mathrm{R{-}CONH{-}C}\!\leqq \qquad (A)$$

For the transient state of formation of the alkylnitrilium grouping in the presence of sulphuric acid, the nitrile is assumed to interact with the carbenium ion, which forms the ion pair with the sulphate anion[22]. In the nitrile series the reaction has no limitation; the effect of structure on reactivity has not been investigated systematically. In the various sources of carbenium ions the reaction is restricted to such systems which are able to form carbenium ions with a reasonable degree of stability[19]. Reactions of dinitriles of propanedioic, butanedioic and pentanedioic acid showed some different features compared with the unequivocal reaction of mononitriles. Yields obtained under conditions resembling those in which the mononitriles react completely decrease for dinitriles below 50%. The reaction of butanedioic acid dinitrile with 2-methylpropene does not give rise to N,N'-ditert-butyldiamide of butanedioic acid; instead, a monotopically substituted diamide was isolated as the only product. Formation of an intermediate cyclic imide structure[23] is assumed in the reaction.

This paper reports an investigation of the course and kinetics of the Ritter reaction of oligomeric models of poly(acrylonitrile) with the general formula *I* (Scheme *A*) with tert-butyl alcohol in tetramethylene sulphone. Their choice was motivated by the intention to offer a description of the effect of structure on the course and kinetics of the Ritter reaction on poly(acrylonitrile). Isobutyronitrile (*Ia*) was chosen as a model of the isolated nitrile group having surroundings similar in the first approximation to those of the CN group in the poly(acrylonitrile) chain. The study of the reactivity of diastereoisomers of 2,4-pentanedicarbonitrile (*Ib,c*) and 2,4,6-heptanetricarbonitrile (*Id*) includes an investigation of the effect of the adjacent functional group and the effect of its configuration on the chain.

$$CH_3CH(CN)[CH_2CH(CN)]_nCH_3$$

I

Ia: $n = 0$, isobutyronitrile
Ib: $n = 1$, D,L-2,4-pentanedicarbonitrile (*R*, *R*)
Ic: $n = 1$, *meso*-2,4-pentanedicarbonitrile (*R*, *S*)
Id: $n = 2$, 2,4,6-heptanetricarbonitrile (mixture of stereoisomers)

$$CH_3CH(CONHC(CH_3)_3)\,[CH_2CH(CONHC(CH_3)_3]_nCH_3$$

II

IIa: $n = 0$, N-tert-butylisobutyramide
IIb: $n = 1$, N,N'-ditert-butyl-2,4-pentanedicarboxamide
IIc: $n = 1$, *meso*-N,N'-ditert-butyl-2,4-pentanedicarboxamide
IId: $n = 2$, N,N',N''-tritert-butyl-2,4,6-heptanetricarboxamide

Scheme *A*

N-tert-Butylamides *II* (Scheme *A*) as products of the Ritter reaction between tert-butyl alcohol and model compounds *I* were prepared under conditions identical with those used in the kinetic measurements. In all the cases the reaction is unambiguous and the respective products can be isolated in satisfactory yields (Table I). In the presence of an equivalent amount of catalyzing sulphuric acid and of a strongly polar solvent, tetramethylene sulphone, no side reactions observed by Ritter occur[23] if sulphuric acid is the catalyzing agent and solvent at the same time, and is thus present in a considerable excess with respect to the concentration of nitrile groups.

Characteristics of the infrared spectra of amides *II* are given in Table II. The infrared spectra of solutions of diastereoisomers of N,N'-ditert-butyl-2,4-pentanedicarboxamide show that in both cases the stablest conformation is that stabilized by the intramolecular hydrogen bond. After an analysis of geometrical aspects of the possibilities of its formation in the case of the individual diastereoisomers it may be said that:

In the case of D,L-diastereoisomer *IIb* the stablest conformation is TG. For the initial D,L-rac. diastereoisomer of 2,4-pentanedicarbonitrile the stablest reported conformations are TT and GG (refs[4,5,8,24]).

In the case of *meso*-diastereoisomeric ditert-butylamide *IIc* the conformer stabilized with the intramolecular hydrogen bond is of the TT and GG type. The initial dinitrile *Ic* has the stablest conformation TG (refs[5,8,24]). For conformation TT, no local

TABLE I

Characteristics of Products of the Ritter Reaction between Tert-Butyl Alcohol and Oligomeric Models of Poly(acrylonitrile) *Ia*–*d* in Tetramethylene Sulphone

Compounds were recrystallized from hexane. NMR spectra were recorded in $CDCl_3$, UV spectra were recorded in ethanol.

Amide II (mol.mass)	Yield, % m.p., °C	Calculated/Found % C	% H	% N	^{1}H-NMR τ, ppm	UV nm
IIa	86·5	67·13	11·89	9·79	4·65 s, 1 H, NH	198·6
(143·1)	119	67·22	12·00	9·65	7·90 m, 1 H, CH	
					8·65 s, 9 H, $C(CH_3)_3$	
					8·90 d, 6 H, CH_3	
IIb	80	66·66	11·11	10·37	4·10 s, 2 H, NH	198
(270·2)	169	66·50	11·20	10·33	7·80 m, 2 H, CH	
					8·45 m, 2 H, CH_3	
					8·70 s, 18 H, $C(CH_3)_3$	
					8·95 d, 6 H, CH_3	
IIc	85	66·66	11·11	10·37	4·25 s, 2 H, NH	198
(270·2)	159	66·20	11·27	10·22	7·95 m, 2 H, CH	
					8·15 m, 2 H, CH_2	
					8·70 s, 18 H, $C(CH_3)_3$	
					8·95 d, 6 H, CH_3	
IId	80	66·49	10·83	10·58	4·30 s, 3 H, NH	198
(397·3)	232	66·52	11·00	10·48	7·50 m, 3 H, CH	
					8·30 m, 4 H, CH_2	
					8·70 s, 27 H, $C(CH_3)_3$	
					8·95 d, 6 H, CH_3	

minimum was found by a semiempirical calculation of the stability of possible conformers[24].

Hence, in the course of the Ritter reaction of tert-butyl alcohol with dimeric models of poly(acrylonitrile) *Ib,c* a new conformational equilibrium is established, different from that of the initial diastereoisomeric dinitriles *Ib,c*. The different absorption values of product *IIb,c* in the infrared and ^{1}H-NMR spectra also indicate that no configurational changes take place within the detectable range.

The course of the Ritter reaction between nitriles *I* and tert-butyl alcohol in tetramethylene sulphone in the presence of sulphuric acid of the constant concentration 0·5M was examined by gas chromatography, by measurements of the concentrations of tert-butyl alcohol and nitrile, and in the case of nitrile *Ia* also by the determination

TABLE II
IR Spectra of N-Tert-Butylamides *II*
Concentrations given in mol/l.

Amide	Solution	Absorption, cm^{-1}
IIa	KBr	3 310, 3 200, 3 078, 2 970, 2 935, 2 875, 2 770, 1 645, 1 545, 1 480, 1 445, 1 390, 1 360, 1 310, 1 260, 1 220, 1 095, 955, 930, 915, 862, 765, 675
IIb	KBr	3 300, 3 200, 3 065, 2 975, 2 940, 2 880, 2 770, 1 645, 1 540, 1 480, 1 450, 1 385, 1 370, 1 360, 1 330, 1 285, 1 260, 1 245, 1 225, 1 150, 1 110, 1 050, 1 035, 1 015, 955, 930, 910, 895, 860, 765, 735, 680
	CCl_4 ($c = 0{\cdot}02$)	3 430, 3 310, 2 960, 2 920, 2 870, 2 840, 1 675, 1 650, 1 495, 1 475, 1 450, 1 445, 1 385, 1 360, 1 305, 1 285, 1 265, 1 250, 1 220, 1 175, 1 140, 1 075, 960, 920, 900
	CCl_4 ($c = 0{\cdot}001$)	3 460, 3 324, 2 969, 2 930, 2 872, 2 844
IIc	KBr	3 400, 3 270, 3 200, 3 080, 2 990, 2 970, 2 930, 2 870, 2 770, 1 745, 1 530, 1 475, 1 450, 1 430, 1 390, 1 375, 1 360, 1 355, 1 335, 1 320, 1 283, 1 275, 1 250, 1 220, 1 145, 1 100, 1 075, 1 045, 1 035, 1 000, 960, 940, 925, 910, 890, 880, 845, 785, 770
	CCl_4 ($c = 0{\cdot}02$)	3 430, 3 330, 2 960, 2 920, 2 860, 1 675, 1 650, 1 496, 1 475, 1 450, 1 445, 1 385, 1 370, 1 360, 1 260, 1 235, 1 210, 1 190, 1 140, 950, 580
	CCl_4 ($c = 0{\cdot}001$)	3 450, 3 342, 2 965, 2 930, 2 870, 2 844
IId	KBr	3 305, 3 200, 3 080, 2 975, 2 935, 2 875, 2 770, 1 645, 1 545, 1 480, 1 453, 1 418, 1 392, 1 362, 1 315, 1 300, 1 260, 1 230, 1 200, 1 150, 1 110, 1 085, 1 035, 950, 930, 910, 885, 850, 740, 675

of the increasing concentration of the product, N-tert-butylisobutyramide. No stable intermediate arises in the given experimental arrangement, and the reaction follows the second-order kinetics. The overall reaction order determined by the method of half-times of fractional times is 1·9, the reaction order with respect to nitrile is unity (refs[20,22]); hence, the reaction is described by the kinetic equation

$$v = k\,.\,[\mathrm{RCN}]\,.\,[\text{t-BuOH}]\,. \qquad (1)$$

The effect of concentration of the catalyzing sulphuric acid on the kinetics of the reaction between nitrile *Ia* and tert-butyl alcohol was investigated in the concentration range (c_a) 0·5 – 1·5M-H_2SO_4 at 25°C (tetramethylene sulphone, concentration of reaction components 1M):

c_a, mol l^{-1}:	0·5	0·75	1·0	1·5
k, 10^{-5} l mol^{-1} s^{-1}:	8·3	14·3	27·5	82·5
H_0:	−4·05	−4·5	−4·9	−5·55

The logarithm of the rate constant is linearly dependent on the Hammet acidity function[25], in accordance with observations of Glikmans and coworkers[22] concerning the reaction between acrylonitrile and 2-methyl-2-propene. The slope of our linear dependence is −1·48. Thus, with respect to the theory of the kinetics of acid catalyzed reactions, it may be written that

$$k = k'\,.\,h^{1.48} \qquad (2)$$

and the kinetic equation of the reaction between isobutyronitrile and tert-butyl alcohol in tetramethylene sulphone at 25°C has the form

$$v = k'\,.\,h^{1.48}\,.\,[\text{isobutyronitrile}]\,.\,[\text{t-BuOH}]\,, \qquad (3)$$

where h is the acidity function, for which $H_0 = -\log h$. At a single concentration of sulphuric acid, 0·5M, the rate constants (k) of reactions of all the model compounds *I* with tert-butyl alcohol (equimolar ratio of reaction groups, [t-BuOH] = 1M) were determined at 25, 35 and 40°C. Under the given conditions they are independent of the extent of reaction within the range under investigation (Fig. 1). The activation parameters of all reactions were calculated using the Eyring–Polonyi equation and assuming that the acidity function is temperature-independent; this assumption seems to be plausible, as indicated by the data published so far[26] (Table III).

The reaction sequence *A* is preceded by the equilibrium of the reaction between tert-butyl alcohol and sulphuric acid. The formation of its product, namely, of the carbenium ion or of its ion pair with the sulphate anion, is regarded by some authors as the slowest step of the whole reaction sequence of the Ritter reaction[27]. Using experimental data found by Dostrovski and Klein in the investigation of the kinetics of the reaction between tert-butyl alcohol and sulphuric acid[28], it may be calculated that the activation energy of this preceding reaction is much lower than the activation enthalpy values of the Ritter reaction reported in this paper. Consequently, the rate constants given in Table III describe the slowest process, obviously consisting in the formation of the alkylnitrilium grouping. Compared with the reaction of isobutyronitrile, only a slight rise in the rate constants can be seen for the two dimeric models and for the trimeric model, due to the decrease in the activation enthalpy values. The decrease in the values of the entropic activation parameter acts against the direction of this shifts. Contributions of the individual stereoelectronic factors and solvation phenomena, both of which affect the reactivity of the nitrile group in the propagating chain of molecules of the model compounds, act against each other and almost compensate one another. The reactivity of model compounds satisfies isokinetic relations, as can be seen in the relation $\Delta H^* - \Delta S^*$ (Fig. 2). The difference between the reactivities of diastereoisomers *Ib,c* is insignificant. Although it followed from the calculation[24] and from results of the investigation of the equilibrium between the two diastereoisomers in an alkaline medium[29], where the labile α-hydrogen atom is exchanged, that the D,L-diastereoisomer *Ib* is the stabler structure, the difference between the energies of the basic state was not reflected in the values of the measured activation parameters. The difference in the activation enthalpy of reactions of both diastereoisomers is compenasted for by the entropic factor, obviously in relation with the different solvation effects which may be expected for different diastereoisomers.

The independence of the rate constant of the extent of reaction (Fig. 1) of dinitrile *Ib,c* and of the trimeric model *Id* allows us to conclude that the presence of a newly

TABLE III

Rate Constants and Activation Parameters of the Ritter Reaction between Oligomeric Models *I* and Tert-Butyl Alcohol in Tetramethylene Sulphone (0·5M-H_2SO_4)

Oligomer	$k \cdot 10^5$, l mol^{-1} s^{-1} 298 K	308 K	313 K	ΔH^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}
Ia	8·3	30	53	91·5	109·1
Ib	10·2	38	55	81·7	67·3
Ic	10·4	36	56	84·4	74·4
Id	12·4	40	66	78·6	60·2

formed functional group in the propagating chain of model compounds does not affect the reactivity of the adjacent unreacted nitrile group.

EXPERIMENTAL

The melting points were determined with a Boetius melting point microapparatus and were not corrected. The IR spectra were recorded with a Perkin–Elmer 621 spectrometer. The NMR spectra were measured with a PS 100 JEOL apparatus, the UV spectra were recorded with a Perkin–Elmer Hitachi 340 spectrometer. Gas chromatographic measurements were performed with a Perkin–Elmer F 30, FID, apparatus, with nitrogen as the carrier gas.

Chemicals

The solvents used were repurified and dried by standard procedures.

Isobutyronitrile (Ia) was prepared by a procedure described in the literature[30]. A redistilled product, b.p. 102°C, was employed in the kinetic measurements.

2,4-*Pentanedicarbonitrile* (Ib,c) was prepared by the decarboxylation of 2,4-dicyano-2-pentanecarboxylic acid in a 78% yield by the method used by Clark[2]. Rectification on a Vigreux column yielded both diastereoisomers with purity higher than 96%.

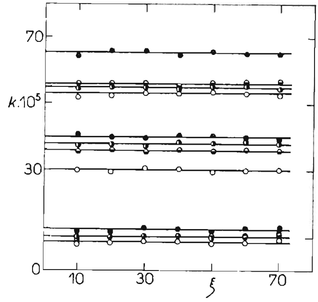

FIG. 1

Rate Constants (l mol^{-1} s^{-1}) of Reactions of Model Compounds *I* with Tert-Butyl Alcohol in Tetramethylene Sulphone (0·5M-H_2SO_4) to the Extent of Reaction (ξ) 70%

Compounds: ○ *Ia*, ◒ *Ib*, ◑ *Ic*, ● *Id*.

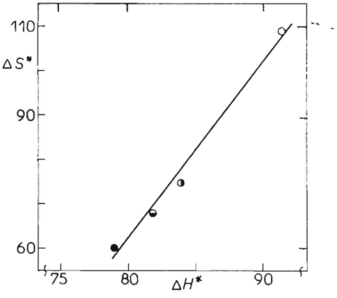

FIG. 2

Correlation of the Activation Enthalpy (kJ mol^{-1}) and Activation Entropy (J . K^{-1} mol^{-1}) of Reactions of Model Compounds *I* with Tert-Butyl Alcohol in Tetramethylene Sulphone (0·5M-H_2SO_4)

Compounds: ○ *Ia*, ◒ *Ib*, ◑ *Ic*, ● *Id*.

2,4,6-*Heptanetricarbonitrile* (Id) was prepared by the decarboxylation of 2,4,6-tricyano-4-heptanecarboxylic acid according to the literature[1]. An attempt to separate the individual diastereoisomers using a reported procedure[10] was unsuccessful, similarly to other authors[3]. A product recrystallized from methanol, m.p. 70—72°C, was used in the measurements. IR spectrum (KBr pellet, cm^{-1}): 2995, 2950, 2920, 2890, 2245, 1460, 1388, 1355, 1345, 1305, 1283, 1260, 1220, 1150, 1125, 1095, 1065, 950, 780, 630, 550. ^{1}H-NMR spectrum (DMSO-d_6, τ) 6·95 (m, 2 H, —CH(CN)—), 8·00 (m, 4 H, —CH_2—), 8·60 (d, 6 H, —CH_3). For $C_{10}H_{13}N_3$ (175·1) calculated: 68·57% C, 7·42% H, 24·00% N; found: 68·45% C, 7·51% H, 23·87% N.

2,4-*Dicyano-2-pentanecarboxylic and* 2,4,6-*tricyano-4-heptanecarboxylic acid* were prepared by the hydrolysis of the respective esters. Ethyl ester of 2,4-dicyano-2-pentanecarboxylic acid was prepared according to Clark[2] by Michael's addition of ethyl cyanoacetate on methacrylonitrile, followed by methylation of the adducts with methyl iodide. It was found that the content of the mono- and bis-adduct greatly varied in Michael's addition depending on the temperature and concentration of the catalyzing sodium ethoxide. At a lower concentration of C_2H_5ONa the formation of bis-adduct is preferred, while in the presence of an equimolar amount the mono-adduct is mainly formed. The overall extent of addition increases with increasing temperature. The bis-adduct was obtained after the usual treatment of the reaction mixture[1,2] and after removal by distillation of the unreacted ethyl cyanoacetate and of the mono-adduct of 2,4-dicyano-valerate by crystallization of the distillation residue from a saturated ethanolic solution. This procedure is a better method for the preparation of a precursor of the trimetric model of poly(acrylonitrile) compared with the procedure used earlier[1]. Ethyl-2,4,6-tricyano-4-heptanecarboxylate thus obtained has the m.p. 55—7°C. IR spectrum (KBr pellet, cm^{-1}): 3000, 2950, 2920, 2890, 2245, 1745, 1455, 1445, 1390, 1375, 1340, 1300, 1285, 1270, 1240, 1160, 1135, 1120, 1105, 1065, 1045, 1035, 1020, 1000, 955, 920, 885, 865, 810, 760, 640, 620, 590, 550, 510, 440. For $C_{13}H_{17}N_3O_2$ (274·2) calculated: 63·16% C, 6·89% H, 17·00% N; found: 63·07H C, 6·97% H, 17·06H N.

The Ritter Reaction

To an equivalent amount of nitrile dissolved in 2 ml of tetramethylene sulphone, a mixture of 0·296 g (4 mmol) tert-butyl alcohol, 1·5 ml tetramethylene sulphone and 0·2 g conc. H_2SO_4 was added. The temperature of the reaction mixture was maintained at 35°C for 8 hours. After that, the mixture was added to 4 ml of a 1M aqueous NaOH solution. The crystalline product precipitated from the solution was separated, washed with water and recrystallized from hexane.

The reactions for kinetic measurements were carried out in tetramethylene sulphone solutions of tert-butyl alcohol and of the respective nitrile and of H_2SO_4 with an equivalent amount of the reaction components at 25, 35, 40°C. The concentration of tert-butyl alcohol was 1M, that of H_2SO_4 was 0·5M (the concentrations used in measuring the dependence of the rate constant on the acidity function were also 0·75M, 1M and 1·5M). The samples were taken in regular intervals, and the reaction was stopped by adding the samples to the same volume of a 1M aqueous NaOH solution. The resulting mixture was then analyzed by gas chromatography.

REFERENCES

1. Takata T., Taniyama M.: Chem. High Polym. *16*, 693 (1959).
2. Clark H. G.: Makromol. Chem. *63*, 69 (1963).
3. Balard H., Meybeck J.: Eur. Polym. J. *13*, 16 (1977).
4. McMahon P. E., Tincher W. C.: J. Mol. Spectrosc. *15*, 180 (1965).

5. Alexander L. E., Engman R., Clark H. G.: J. Phys. Chem. *70*, 252 (1966).
6. Matsuzaki K., Uryu T., Okada M.: J. Polym. Sci. B*4*, 487 (1966).
7. Murano M., Yamadera R.: Chem. High Polym. *23*, 497 (1966).
8. Murano M., Yamadera R.: J. Polym. Sci. *A1—5*, 1855 (1967).
9. Kirby J. R., Brandrup J., Peebler L. H.: Makromol. *1*, 64 (1968).
10. Murano M., Yamadera R.: J. Polym. Sci. *A1—6*, 843 (1968).
11. Matsuzaki K., Uryu T., Okada M., Shiroki H.: J. Polym. Sci. *A1—6*, 1475 (1968).
12. Murano M.: Rev. Phys. Chem. Jap. *39*, 93 (1969).
13. Balard H., Fritz H., Meybeck J.: Makromol. Chem. *178*, 2393 (1977).
14. Valk G., Peters M., Husung L.: Forschungsb. Landes Nordheim-Westfalen *1971*, 2212.
15. Levites L. M., Gabrielan G. A., Schtschabligin M., Kudryavcev G. I., Rogovin T. A.: Vysokomol. Soedin. *16B*, 268 (1974).
16. Takata T., Taniyama M.: J. Polym. Sci. 2*A*, 1567 (1964).
17. Ritter J. J., Minieri P. P.: J. Amer. Chem. Soc. *70*, 4045 (1948).
18. Wieland H., Dorrer E.: Chem. Ber. *63*, 404 (1930).
19. Krimen K. I., Cota D. J.: Org. Reactions *17*, 213 (1969).
20. Deno N. C., Edwards T., Perizzolo C.: J. Amer. Chem. Soc. *79*, 2108 (1958).
21. Weil I., Goebel G., Tulp E. R., Cahn A.: Amer. Chem. Soc., Div. Petrol. Chem., Prepr. *8*, 95 (1963).
22. Glikmans G., Tors B., Hellin M., Coussemant F.: Bull. Soc. Chim. Fr. *1966*, 1376.
23. Benson F. R., Ritter J. J.: J. Amer. Chem. Soc. *73*, 4128 (1969).
24. Sýkora J.: This Journal *33*, 3514 (1968).
25. Arnett E. M., Douty C. F.: J. Amer. Chem. Soc. *86*, 409 (1964).
26. Gelbstein A. I., Schtscheglova G. G., Temkin M. I.: Zh. Neorg. Khim. *61*, 506 (1956).
27. Meyers A. I., Sircar J. C.: *Chemistry of Cyano Group,* p. 70. Interscience, London 1970.
28. Dostrovski I., Klein F. S.: J. Chem. Soc. *1955*, 791.
29. Clark H. G.: J. Polym. Sci. *A16*, 3455 (1968).
30. Bachman W. E.: Org. Synthesis *25*, 61 (1954).

Translated by L. Kopecká.