Tetrahedron Vol. 37, pp 569 to 573
Pergamon Press Ltd., 1981 Printed in Great Britain

0040-4020/81/0201-0569/$02.00/0

THERMOCHROMISM AND PHOTOCHROMISM OF ARYL SUBSTITUTED ACYCLIC AZINES[1]

UNCATALISED AND ACID-CATALISED THERMAL ISOMERISATION

K. APPENROTH, M. REICHENBÄCHER, R. PAETZOLD*
Sektion Chemie der Friedrich-Schiller-Universität Jena, DDR

(*Received in Germany* 1 *April* 1980)

Abstract –The photochemical *E–Z* isomerisation of the benzophenone-9-anthraldehyde azine (**1**), benzophenone-9-acridine-aldehyde azine (**2**) and 9-anthraldehyde azine (**3**) is thermally reversible. The thermal reaction gives the same isomers as the photochemical reaction. We have studied the mechanism of the thermal isomerisation of these azines. Our results are in accordance with an inversion of the N atom which is connected with a rotation movement about the N–N single or the C=N double bond.

In the investigation of variously substituted 2,3-diazabutadienes (azines) of the general formula (Fig. 1), we have shown that photochromism based on an *E–Z* isomerisation about the C=N bond is a general property of this class of compounds[2,3] and have studied the mechanism of both the unsensitised and the sensitised photochemical *E–Z* and *Z–E* isomerisation of the azines.[4]

All observed photochemical reactions of the azines are also accompanied by thermal reactions. The mechanism of the thermal isomerisation about the C=N bond has been investigated in detail particularly in aniles and hydrazones.[9] Although many analytical investigations (especially by NMR spectroscopic methods) of thermally produced mixtures of isomers of both alkyl substituted[5-8] and aryl substituted azines[5,6,8] have been carried out, no results have hitherto been reported on the kinetics and mechanism of the thermal isomerization of these compounds.

Besides an *E–Z* isomerisation about the C=N double bond of the 2,3-diazabutadienes, the possibility of conformer formation about the N–N single bond should be considered. Such conformer mixtures consisting of the thermodynamically stable s-*trans* and a *gauch*-form could be detected only with alkyl substituted azines.[5,6,8]

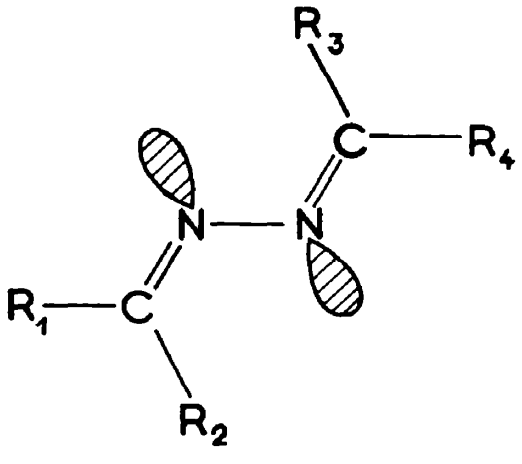

Fig. 1. 2,3-Diazabutadiene (azine).

To investigate the mechanism of the thermal isomerisation of the azines we selected representatives of both photochemical $A \rightleftharpoons B$ and $A \rightleftharpoons B \rightleftharpoons C$ systems[3] and studied the solvent and substituent effects on the kinetics of the thermal reactions, the results of which are reported in this communication.

RESULTS

Thermal isomerisation

Benzophenone-9-anthraldehyde azine, **1**, (*E* form: $R_1 = R_2$ = phenyl; $R_3 = H$; R_4 = 9-anthranyl) and benzophenone-9-acridinealdehyde azine, **2**, (*E* form: $R_1 = R_2$ = phenyl; $R_3 = H$; R_4 = 9-acridinyl) belong to the class of azines forming a reversible $E \overset{h\nu}{\underset{h\nu}{\rightleftharpoons}} Z$ system in solution.[3] This light-induced *E–Z* isomerisation is also thermally reversible. The thermal *Z–E* isomerisation runs through the same isosbestic points as does the photoisomerisation and the ED diagrams[10] are strictly linear, as expected. The reaction obeys a first order rate law. The free enthalpy of activation and the activation entropy are solvent-dependent (Table 1).

9-Anthraldehyde azine, **3**, (*EE* form: $R_1 = R_4$ = 9-anthranyl; $R_2 = R_3 = H$) shows the reversible consecutive photoreaction $EE \rightleftharpoons EZ \rightleftharpoons ZZ$.[3] Upon irradiation with light of different wave length, photostationary states may be obtained enabling a separate investigation of the dark reactions. The composition of the isomers obtained by irradiation of a solution of **3** (λ_{exc} = 436 nm) amounts to 56% *ZZ*, 38% *EZ* and 6% *EE* forms. The spectral changes of the following dark reactions yield a straight line in the *E* diagram which is parallel to the line *ZZ–EZ* in Fig. 2. Consequently, only the $ZZ \rightarrow EZ$ reaction is pursued. Deviations from the linearity appear only at temperatures above 50° or after longer duration, as under these conditions the $EZ \rightarrow EE$ isomerisation is already in considerable evidence.

Upon irradiation with λ_{exc} = 480 nm the $EE \rightarrow EZ$ reaction is selectively induced. The *E* diagram of the following thermal reaction is identical with the

Table 1. Solvent dependence of the free enthalpy of activation, the activation enthalpy as well as the activation entropy of the thermal *Z–E* isomerization of **1** and **2**

Solvent	**1** (T = 298 K)			**2** (T = 304 K)		
	ΔG^* kJ/mol	ΔH^* kJ/mol	ΔS^* J/mol·K	ΔG^* kJ/mol	ΔH^* kJ/mol	ΔS^* J/mol·K
Paraffin	99,5					
n-Decane	99,9					
Cyclohexane	100,5	103,8	10,0	97,1	88,8	-27,2
n-Hexane	100,5					
Ether	101,1					
THF	100,4	103,8	11,5	100,8	86,3	-47,7
Toluene	100,4	104,3	13,4	100,0	86,3	-45,2
Dioxane	100,5			101,9		
Acetone	101,6			102,1	86,7	-50,6
DMFA	101,0			102,2		
Acetonitril	103,0	103,4	1,4	102,8		
DMSO	101,2			102,3		
Methylenchloride	102,3					
i-Propanol	103,0	100,9	-7,2			
Ethanol	103,6	100,9	-8,8	103,4	85,0	-60,3
Methanol	103,8	100,1	-12,6			

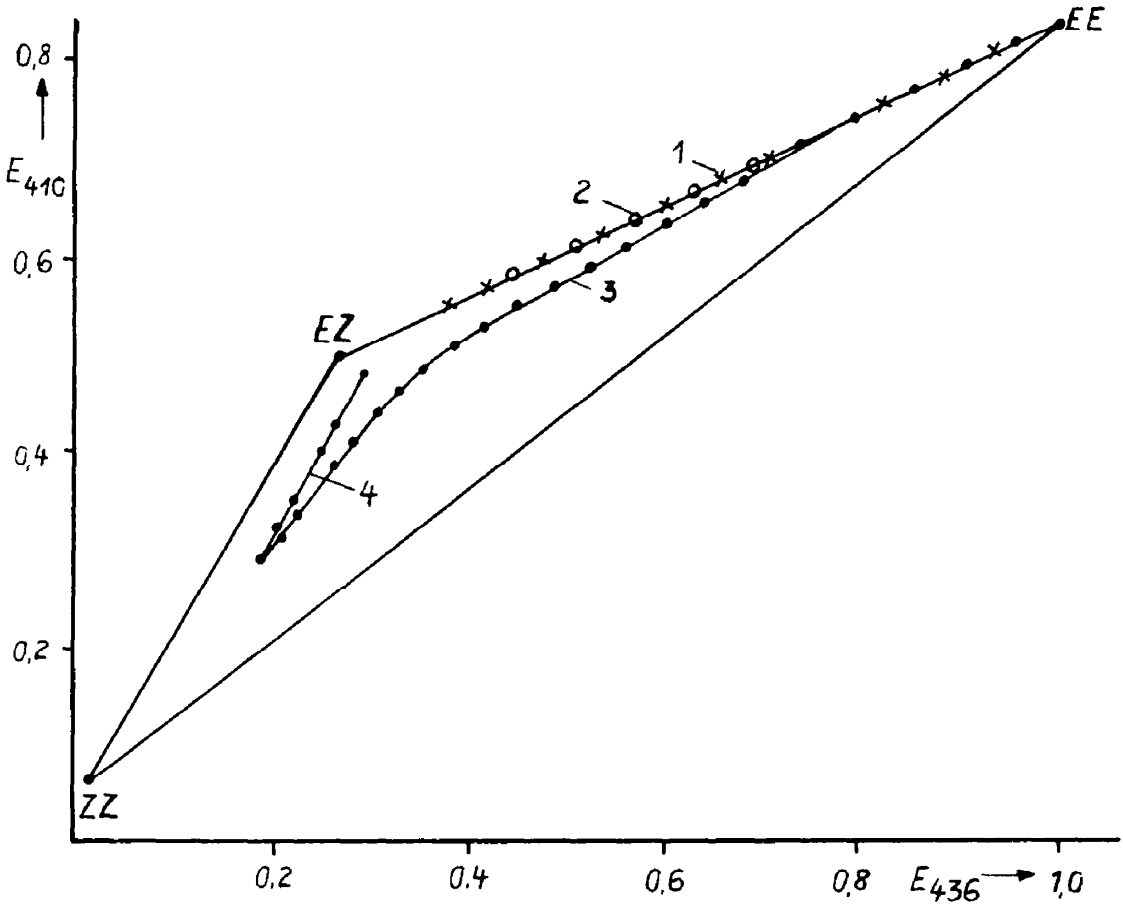

Fig. 2 E diagram of both the photochemical and the dark reactions of **3** in toluene. λ_{exc} = 480 nm (1(×)) and the following dark reaction (2(○)); λ_{exc} = 436 nm (3) and the following dark reaction (4).

photochemical isomerisation $EE \rightarrow EZ$ (Fig. 2). Consequently, under these conditions only the $EZ \rightarrow EE$ isomerisation obeying first order kinetics takes place. The activation parameters for both dark reactions are listed in Table 2.

Thermal E–Z isomerisation (thermodynamic equilibrium)

Some aryl substituted azines are thermochromic; in solution and in a molten state a thermal equilibrium exists between different isomers. Thus, the spectral changes of the dark reaction started with the photostationary state do not completely revert to the initial spectrum of the *E* isomer. The end state depends on the temperature and is obtained in like manner starting with the pure *E* form.[2,3] The thermodynamic data are given in Table 3. Because of the very small spectral changes the experimental determination of the kinetic parameters of the thermal *E–Z* isomerisation is not possible.

Catalysed thermal Z–E isomerisation

We have investigated the influence of both acids and bases on the thermal *Z E* isomerisation. The acids suitable for the investigation of the catalysed thermal reaction are extremely restricted because with most (mainly strong) acids a positive acichromic effect is obtained whereby the photochromic properties of the azines are lost.[11] We have found that benzoic acid in ethanol is a proper system for the investigation of the acid-catalysed thermal *Z–E* isomerisation.

Table 2. Activation parameters of the thermal isomerisation of **3** in toluene (T = 293 K)

Parameter	ZZ ⟶ EZ	EZ ⟶ EE
$\Delta G^{\neq}$ / kJ·mol^{-1}	97,6	110,7
$\Delta H^{\neq}$ / kJ·mol^{-1}	97,5	113,5
$\Delta S^{\neq}$ / J·mol^{-1}·K^{-1}	- 0,4	9,6

The graph of the experimentally determined rate constants of thermal *Z–E* isomerisation vs concentration of the benzoic acid is linear. The activation parameters obtained from the temperature dependence of the slope of the rate constant are given in Table 4. The existence of a pure acid catalysed *Z–E* isomerisation is confirmed by the linear ED diagram.

Bases do not have any catalytic influence on the thermal reaction $Z \rightarrow E$. To investigate this effect we employed molar concentrations of dimethyl-, diethyl- and triethylamine in ethanol as well as potassium hydroxide in an ethanol/water solution.

DISCUSSION

Thermal Z E isomerisation

Considering only the geometric motion of ligands during a thermal isomerisation about the C=N double bond the following mainly mechanistic pathways can be distinguished:[9] inversion of the imine N atom causing the ligand to move in the plane of the double bond and involving a linear transition state or rotation about the C=N double bond with the loss of π-bond energy while the molecule is in the transition state. Rotation about the C=N double bond should have a barrier comparable to or even higher than that of rotation about the corresponding C=C double bond, and the experimental values are generally higher than 160 kJ.mol^{-1}.[12] Even in compounds with a much smaller C=N bond order by conjugation effects, rotation barriers are higher than 130 kJ.mol^{-1}.[9,12,15] Considering that an essential weakening of the C=N bond by conjugation does not take place in the azines (the C=N stretching wavenumbers of the azines are obtained in the region of about 1600 cm^{-1}, expected for the C=N double bond), the experimentally determined activation barriers smaller than 100 kJ.mol^{-1} rule out a pure rotation mechanism for the *Z–E* isomerisation.

To estimate the required free enthalpies of activation for a pure inversion of the C=N isomerisation, we have made use of the corresponding hydrazones comparable with the azines.[16,17] Using the empirical procedure of Kessler[17] we calculated the

Table 3. Thermodynamic data of the *E Z* isomers of **1** and **2** in toluene

Parameter	1 (T = 293 K)	2 (T = 304 K)
ΔG / kJ·mol^{-1}	8,75	9,93
ΔH / kJ·mol^{-1}	16,8	19,3
ΔS / J·mol^{-1}·K^{-1}	29,3	29,3

Table 4. Activation parameters of the benzoic acid-catalized thermal *Z E* isomerization of **1** and **2** in ethanol

Parameter	1 (T = 298 K)	2 (T = 304 K)
$\Delta G^{\neq}$ / kJ·mol^{-1}	86,9	82,3
$\Delta H^{\neq}$ / kJ·mol^{-1}	53,2	36,4
$\Delta S^{\neq}$ / kJ·mol^{-1}	-113,5	-150,7

free enthalpies of activation of inversion of hydrazones Ph–N=CH–R (R = 2-naphthyl, 1-naphthyl, 9-anthranyl) and CH_3–N=CHR (R = 1-naphthyl, pentamethylphenyl) from the experimentally determined inversion barriers of related N-phenylimines[18] and N-methylimines.[13,19] The values of the calculated inversion barriers lie between 160 and 180 kJ.mol^{-1}. Therefore, energetic reasons make a pure inversion mechanism improbable for the *Z*–*E* isomerisation.

The free enthalpies of activation of some naphthaldehyde phenylhydrazones reported by Condorelli *et al.*[20,21] are about 106 kJ.mol^{-1}. A such drastic lowering of activation barriers is not understandable even considering a steric hindrance in the *Z* isomer.[21] In order to support our calculated inversion barriers, we tried to determine using the Kessler method[9] the free enthalpies of activation of 9-anthraldehyde diphenylhydrazone not investigated by Condorelli but related to the azines considered in this work. After careful elimination of acid traces the photochemically produced *Z* isomer does not show any indication of thermal *Z*–*E* isomerisation at 60 even after several hours. Therefore, the free enthalpy of activation at 60 has to be greater than 120 kJ.mol^{-1}, as expected.

Moreover, the analysis of the isomer composition is in contradiction to an inversion of the thermal isomerisation of the *Z* form. Thus, the unambiguously proved *Z* → *E* reaction of **1** and **2** is only possible by a double inversion of the N atoms. But the activation barrier required for this process is still higher than that needed for a single inversion.[22] The conditions in **3** show this with even greater clarity. Thus, the *ZZ* form might directly isomerise to the *EE* form by double inversion. But a direct *ZZ* → *EE* reaction does not take place as proved by *E* diagram (Fig 2). Moreover, the *ZZ* → *EZ* isomerisation is not at all possible by an inversion mechanism but is unequivocally observed in experiments.

For this reason, the experimental results of isomerisation of the azines can be interpreted neither by a pure inversion mechanism nor by a pure rotation. The question arises what kind of isomerisation mechanism provides the low activation barriers. It is known for the imines that the inversion barriers are considerably lowered if the inverted lone electron pair takes part in conjugation with a π-electron system.[23] Azines can affect this inversional-like mechanism in two ways:

(1) Inversion is connected with rotation about the N–N single bond with a smaller activation energy. Thus, the lone electron pair can take part in the π-electron system of the second azomethine moiety (inversion-NN-rotation mechanism).

(2) Inversion is coupled with rotation about the C=N bond. During this intermediate mechanism,[24] the p orbital of the N atom forming the CN–π-bond becomes a lone electron pair in the rotation transition state favourable to participation in the conjugation with the π-system (inversion-CN-rotation mechanism).

The experimental results with azines are in accordance with both mechanisms. An experimental distinction between these isomerisation mechanisms—for instance with the aid of solvent effects—may be difficult to realise because the solvent effects can become incalculable if besides the inverting N atom there are several heteroatoms present in the molecule,[26] this is true of the azines.

The experimentally ascertained solvent dependence of the rate constants of thermal *ZE* isomerisation is mainly caused by the solvent influence on the free enthalpy of activation (Table 1). In polar, especially protic solvents, the activation entropy is negative. The stronger solvent interaction in the transition state causing negative activation entropy may be explained only by an enhanced basicity of the N atom in that state. Single and multiple regression analyses with the acceptor and donor number[27] as well as the viscosity of the solvents revealed that only the acceptor number provides a significant contribution. The dependence of the activation parameters of **1** on the acceptor number (AN) of solvents obeys the following equations:

$$\Delta G^*/\text{kJ·mol}^{-1} = 100{,}18 + 0{,}0873\,(\text{AN})$$

$$\Delta H^*/\text{kJ·mol}^{-1} = 102{,}5 - 0{,}1005\,(\text{AN})$$

$$\Delta S^*/\text{J·mol}^{-1}\text{K}^{-1} = 12{,}23 - 0{,}557\,(\text{AN}).$$

The fact that only the acceptor ability but not the donor strength of solvents exerts an influence on the isomerisation barrier does not provide evidence for a rotation mechanism with an electrophile and nucleophile centre in the transition state but does not allow us to decide between an inversion-NN-rotation and an inversion-CN-rotation mechanism.

E–Z *Isomerisation (thermodynamic equilibrium)*

We have found that aryl substituted azines with substituents of sterically various kinds form a thermodynamic equilibrium in solution. As the small spectral changes do not permit experimental determination of the activation parameters, no distinction between conformers (perhaps by rotation about the N–N or C–C(aryl) bond) or *E*–*Z* isomers in the thermodynamic equilibrium is possible. However, the following experimental data of **1** and **2** prove the existence of *E Z* isomers in the thermodynamic equilibrium. The tlc separated thermoproduct possesses the same R_f value and the same photochemical behaviour as the electronic spectra of both forms are identical and the spectral changes of the corrected absorption spectra agree with those of the photochemical *E*–*Z* isomerisation.

The experimentally determined *Z* rate of about 3% in the thermodynamic equilibrium is in contrast with the hitherto existing known results of aryl substituted azines according to which it was only possible to detect isomers in the thermal equilibrium if all substituents were sterically equal or similar.[5,6] This condition is not fulfilled by **1**, **2** and **3**. However, similar sterically inhibited imines and nitrones likewise exhibit a considerable *Z* rate in the thermal equilibrium.[28]

Obviously, the thermodynamically stable *E* isomer is more destabilized by torsion about the C–C(aryl) bond with the anthranyl and acridinyl substituted azines than the *Z* form which anyhow already strongly twisted whereby the enthalpy difference between both isomers is lowered and the rate of the less stable *Z* isomer increases. It is therefore understandable why the thermodynamically stable *E* isomer of benzaldehyde azine ($R_1 = R_4$ = phenyl, $R_2 = R_3 = H$) is the only isomer which could be detected[5] and, as we have

found, the electron absorption spectra of benzophenone *p*-nitrobenzaldehyde azine ($R_1 = R_4$ = phenyl, R_2 = *p*-nitrophenyl, R_3 = H) does not provide any indication of the existence of a thermal equilibrium, not even at 60 . By contrast with **1**, **2** and **3**, sterically strongly effective substituents are absent in these two compounds.

Acid-catalysed Z E isomerisation

The presence of acids considerably lowered the free enthalpy of activation of the thermal *Z–E* isomerisation (Table 4); the strong negative activation entropy is in accordance with a bimolecular reaction.

The presence of acids does not affect the absorption spectra. Neither does it supply the fluorescence typical of protonated azines.[29] There is therefore no detectable rate of the azine in the protonated form, even at molar concentrations of benzoic acid. However, it is known that in consequence of the high exchange rate even catalytic amounts of effective protons are sufficient to lower the activation barriers dramatically[30] therefore, the catalytic effect of the benzoic acid may quite well be based on the interaction of the azine N atom with the proton. However, the protonation of the N atom prevents an inversion of the acid-catalysed C=N isomerisation. But the experimentally ascertained activation barriers are decidedly too low for a rotation. By Jennings conception[12] a reversible nucleophile addition (possible by the benzoate anion or traces of water) is simultaneously effected on the C=N bond polarized by protonation. This temporarily takes on single bond character and the low activation enthalpies are understandable as rotation barriers about a single bond.

EXPERIMENTAL

Materials. The azines were prepared under exclusion of actinic light according to known procedures,[31] or analogously if synthesized for the first time. We will report elsewhere on the synthesis and the spectroscopic properties of these compounds.[32] The solvents used were purified by the usual methods.[33]

Kinetic parameters. The uncatalysed thermal *Z–E* isomerisation was analyzed directly from the measured absorbance by known methods for the determination of rate constants.[14] The activation parameters are calculated by the temp dependence of the rate constants according to the Arrhenius and the Eyring equations. The rate constant of the *ZZ EE* isomerisation of **3** was calculated according to the method of Mauser.[10]

The rate constant of an acid-catalysed thermal reaction is determined by the equation:[34]

$$k = k_0 + k_s\,[\text{acid}]$$

k–total rate constant

k_0 uncatalised rate constant

k_s catalized rate constant

k_s was calculated by the slope of the k rs concentration of benzoic acid plot and according to the Eyring equation, the activation parameters were calculated from the temp dependence of this slope. The dissociation of the acid and its temp dependence is not considered, as usual.[12]

Spectra were recorded with a spectrometer CARY model 17 (Varian) or Specord UV/VIS (VEB Carl Zeiss Jena).

REFERENCES

[1]4 Communication, 3. Communication, see Ref. 4.
[2]R Paetzold, K. Appenroth and M. Reichenbächer, *Z. Chem.* **16**, 446 (1974).
[3]K. Appenroth, M. Reichenbächer and R. Paetzold, *J. Photochem.* **14**, 39 (1980).
[4]K. Appenroth, M. Reichenbächer and R. Paetzold, *J. Photochem* **14**, 51 (1980).
[5]J. Elguero, R. Jacquier and C. Marzin, *Bull. Soc. Chim. Fr.* 1374 (1969).
[6]D. S Malament and J. M. McBride, *J. Am. Chem. Soc.* **92**, 4586 (1970).
[7]J. F. Ogilvie and K. C. Cole, *Spectrochim. Acta* **A27**, 877 (1971).
[8]J. Elguero, R Jacquier and C. Marzin, *Bull. Soc. Chim. Fr.* 713 (1968).
[9]H. Kessler, *Angew. Chem.* **82**, 237 (1970); *Tetrahedron* **30**, 1861 (1974).
[10]H Mauser, *Formale Kinetik*. Berthelsmann-Universitätsverlag, Düsseldorf (1974).
[11]K Appenroth, M. Reichenbacher and R. Paetzold, in preparation; see also K. Gustav and S. Vettermann, *Wiss. Z. FSU Jena* in print
[12]W. B. Jennings, S. Al-Showiman, M S. Tolley and D. R. Boyd, *J. Chem. Soc.* Perkin 2, 1535 (1975).
[13]W. B. Jennings and D. R. Boyd, *J. Am. Chem. Soc.* **94**, 7187 (1972).
[14]W. B. Jennings, D. R. Boyd and L. C Waring, *J. Chem. Soc.* Perkin 2, 610 (1976).
[15]W. B. Jennings and S. D. Worley, *Tetrahedron Letters* 1435 (1977).
[16]D. Wurmb-Gerlich, F Vögtle, A Mannschreck and H. A. Staab, *Liebigs Ann.* **708**, 36 (1967).
[17]H.-O Kalinowski, H. Kessler, D. Leibfritz and A. Pfeffer, *Chem. Ber.* **106**, 1023 (1973).
[18]G. Wettermark and E. Wallström, *Acta Chem. Scand.* **22**, 675 (1968).
[19]W. B. Jennings, S. Al-Showiman, D. R. Boyd and R. M. Campbell, *J. Chem. Soc.* Perkin 2, 1501 (1976).
[20]G. Condorelli, L. L. Costanzo and S. Piastarà, *Ann. Chim.* **61**, 383 (1971).
[21]G. Condorelli, L. L. Costanzo, S. Pistarà and S. Giuffrida, *Z. Phys. Chem.* (Frankfurt am Main) N. F **90**, 58 (1974).
[22]J. E. Anderson, *J. Am. Chem. Soc.* **91**, 6374 (1969).
[23]E. Haselbach and E. Heilbronner, *Helv. Chim. Acta* **51**, 16 (1968).
[24]H. Kessler and D. Leibfritz, *Chem. Ber* **104**, 2143 (1971).
[25]H.-O. Kalinowski, H. Kessler and A. Walter, *Tetrahedron* **30**, 1137 (1974)
[26]J. M. Lehn, *Fortschr. chem. Forschg.* **15**, 311 (1970).
[27]V. Gutmann, *Electrochim. Acta* **21**, 661 (1976).
[28]J. Bjorgo, D. R. Boyd, D. C. Neil and W B. Jennings, *J. Chem. Soc.* Perkin 1, 254 (1977).
[29]A. Weller and H. Wolf, *Liebigs Ann.* **657**, 64 (1962).
[30]A. Lidén and J. Sandström, *Tetrahedron* **27**, 2893 (1971).
[31]D. Kolbah and D. Koruncev, *Methoden der organischen Cheme* (4th Edited by Houben-Weyl), Vol. X/2. G. Thieme Verlag Stuttgart (1967).
[32]M. Reichenbächer, K. Appenroth and R. Paetzold, *J. prakt. Chem.* in preparation.
[33]A. Weissberger and E. S. Proskauer, *Techniques of Organic Chemistry: Organic Solvents*, Vol. II. Interscience, New York (1935).
[34]G Wettermark, M. E. Langmuir and D. G. Anderson, *J. Am. Chem. Soc.* **87**, 476 (1965).