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Michael Reaction. IV.[1] $NaNH_2$ Catalyzed One Stage Reaction Between Phenylacetic Acid Dialkylamides and Cinnamic Acid Methyl Ester or Dialkylamides. Influence of Reaction Conditions on the Stereochemistry

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The $NaNH_2$ catalyzed one stage reaction between phenylacetic acid dialkylamides and cinnamic acid methyl ester or dialkylamides was studied under various conditions. Conditions were found for easy preparation of each of the both possible diastereomeric derivatives of 2,3-diphenylglutaric acid. It was proved that catalytic amounts of $NaNH_2$ take part in the reaction. It is assumed that the observed *erythro/threo* equilibrium ratios are determined by an isomerization via two different carbanions (at C_2 and C_4) of the reaction products.

(Keywords: 2,3-Diphenylglutaric acid derivatives; Second order asymmetric transformation; Sodium amide catalyzed; Stereochemistry)

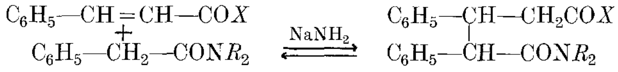
Michael Reaktion. IV. $NaNH_2$*-katalysierte Eintopfreaktion von Dialkylamiden der Phenylessigsäure mit Methylestern oder Dialkylamiden der Zimtsäure. Einfluß der Reaktionsbedingungen auf die Stereochemie der Reaktion*

Die $NaNH_2$-katalysierte Eintopfreaktion von Dialkylamiden der Phenylessigsäure und Methylestern oder Dialkylamiden der Zimtsäure wurde unter verschiedenen Reaktionsbedingungen untersucht. Es wurden die optimalen Bedingungen zur Darstellung jedes der beiden möglichen diastereomeren Derivaten der 2,3-Diphenylglutarsäure ermittelt. Die Teilnahme katalytischer Mengen von $NaNH_2$ wurde bewiesen. Es wird angenommen, daß das beobachtete *erythro/threo*-Gleichgewichtsverhältnis von der Isomerisierung über zwei verschiedene Carbanionen (C_2 und C_4) bestimmt wird.

Introduction

The preparative potentialities of the alcoxide catalyzed *Michael* reaction leading to compounds with two vicinal chiral centers have been extensively studied[2]. Only in a few cases both diastereomers have been isolated[3–11] and even in fewer ones their configuration have been established[4, 11]. Attempts for directing the stereochemistry of the reaction have not been reported, although the influence of the reaction conditions has been demonstrated[11a]. The observed stereochemical results have received scant attention[11]. Solid $NaNH_2$ has been used in a few cases, while the stereochemistry in its presence has been examined only by *Hauser*[12]. In earlier investigations we showed that the reaction between phenylacetic and cinnamic acid esters and dialkylamides in the presence of $NaNH_2$ in ether under conditions of free evaporation of the solvent caused by exothermicity leads to a mixture of diastereomeric 2,3-diphenylglutaric acid esteramides[13], amidesters[14] or diamides[15] in which the *erythro/threo* ratio depends on the reacting compounds. Unfortunately, we were not able to interpret the observed stereochemical results because of the quite undefined reaction conditions i.e. reaction in the melt, possibility of second order asymmetric transformation etc.

In the present work an attempt will be made to elucidate the influence of the conditions of the reaction (solvent, reaction time, temperature and concentration) on the stereochemical course of the interaction between phenylacetic acid dialkylamides and methyl cinnamate or cinnamic acid dialkylamides in order to find conditions for its direction.



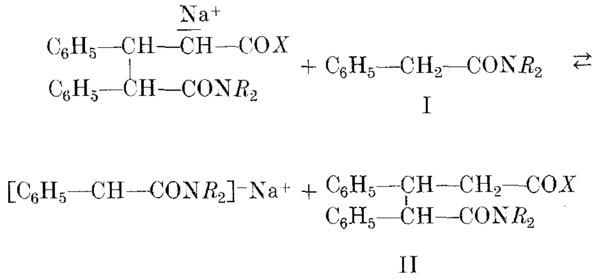
$$\begin{array}{c} C_6H_5\text{—}CH{=}CH\text{—}COX \\ + \\ C_6H_5\text{—}CH_2\text{—}CONR_2 \end{array} \xrightleftharpoons{NaNH_2} \begin{array}{l} C_6H_5\text{—}CH\text{—}CH_2COX \\ \qquad\;\; | \\ C_6H_5\text{—}CH\text{—}CONR_2 \end{array}$$

No.	X	NR_2	No.	X	NR_2
9	OCH_3	$N(CH_3)_2$	**13**	$N(CH_3)_2$	$N(C_6H_{11})_2$
10	OCH_3	$N(i\text{-}C_3H_7)_2$	**14**	$N(CH_2CH_2)_2O$	$N(CH_2CH_2)_2O$
11	OCH_3	$N(C_6H_{11})_2$	**15**	$N(C_2H_5)_2$	$N(CH_2CH_2)_2O$
12	OCH_3	$N(CH_2CH_2)_2O$			

Results

The following CH-acids and acceptors were used: dimethylamide (**1**), diisopropylamide (**2**), dicyclohexylamide (**3**) and morpholide (**4**) of phenylacetic acid and methyl cinnamate (**5**), dimethylamide (**6**), diethylamide (**7**) and morpholide (**8**) of cinnamic acid in the "classical" one stage (one flask) variation of the *Michael* reaction in ether, tetrahydrofurane, hexamethylphosphoramide, dimethylsulphoxide or benzene.

In some of the examined cases it was found that the reaction proceeds in high yields even in the presence of catalytic amounts of $NaNH_2$ (see Tables). The following reaction of metal exchange between the reaction product and the initial dialkylamide is of great importance for the course of the reaction in these cases:



$$\begin{array}{l} \overset{Na^+}{\overline{}} \\ C_6H_5-CH-CH-COX \\ C_6H_5-\overset{|}{C}H-CONR_2 \end{array} + \underset{\text{I}}{C_6H_5-CH_2-CONR_2} \rightleftarrows$$

$$[C_6H_5-CH-CONR_2]^-Na^+ + \underset{\text{II}}{\begin{array}{l} C_6H_5-CH-CH_2-COX \\ C_6H_5-\overset{|}{C}H-CONR_2 \end{array}}$$

Such an exchange should take place even when an equimolar amount of $NaNH_2$ is used, because of its restricted solubility. The metallation of I by the sodium derivative of II in homogeneous medium should be favoured. An evidence for that is the strong evolution of ammonia during the hydrolysis of the reaction mixture. The degree of conversion to products of the *Michael* reaction when catalytic amount of metal is used depends, according to *Ingold*[16] mainly on the equilibrium between the neutral forms of the reactant and the adduct.

Most of the reaction products discussed in the present haper were described in Ref.[14, 15]. Data on the products of the reaction of **2** with **5** i.e. **10**, **3** with **5**-**11** and **3** with **6**-**13** are given in the experimental part. The configurational assignment of these products as well as the analysis of the diastereomeric mixtures is based on the differences in the location of the signals of the C_6H_5, $COOCH_3$ and $CON(CH_3)_2$ protons in the NMR spectra of the isomers[14, 15, 17]. The following results were obtained in the various solvents employed:

A. *Ether* (Table 1)

The rate of the reaction in this solvent is relatively low and the possibility of temperature variations rather limited. It is because of this probably that the reaction between **2** and **3** with **5** does not proceed, irrespective of the reduced CH-acidity of these compounds (compare with the reaction in *THF*). The stereochemistry does not depend on the temperature, concentration and structure of the reactants.

The reversibility of the reaction was studied on pure diastereomers. Under the reaction conditions *threo*-**9** dissociates insignificantly (3%) in 6 hours. Traces of the *erythro*-isomer were detected by *TLC*. Under the same conditions *erythro*-**9** remains unchanged. The concentration and the amount of the catalyst do not influence the results. The reaction appears to be practically irreversible or the reproduction of the reaction conditions, because of the restricted solubility of the products and of the metallation agent, is strongly inhibited.

Table 1. *Formation of* **9, 10, 11** *and* **14** *in ether*

X	NR_2		Conc. (mol/l)	Temp. (°C)	React. time (min)	Yields (%)	*E/T*
OCH_3	$N(CH_3)_2$	**9**	1.0[a]	34	5	47	58/42
					60	90	56/44
				22	60	34	58/42
			0.1	22	30	20	58/42
					360	32	56/44
OCH_3	$N(i\text{-}C_3H_7)_2$	**10**	1.0	34	120	0	—
OCH_3	$N(C_6H_{11})_2$	**11**	1.0	34	120	0	—
$N(CH_2CH_2)_2O$	$N(CH_2CH_2)_2O$	**14**	1.0[a]	34	20	76	52/48
			0.1	22	30	25	50/50

[a] Heterogeneous medium.

B. *Tetrahydrofuran* (*THF*) (Table 2)

The reaction rates in this solvent (compare the yields for short reaction times) decrease in the following orders: **12** ≈ **9** > **10** ≈ **11** and **13** > **11**. The first of them (the same acceptor) corresponds to the CH-acidity of the donors. The second one (the same donor) does not correspond to the electrophilicity of the acceptors. The observed ratio **13** > **11** is probably determined by the metal exchange rate, which should be higher when $X = N(CH_3)_2$ because of the larger difference between the acidities of I and II than when $X = OCH_3$. The conversion in the case of **11** for longer reaction intervals is higher than that of **13** similary to all cases when methyl cinnamate takes part. The decrease in the yield of **9** is due to the side reactions (21% by-products were isolated by TCL).

The stereoselectivity of the reaction is low. The ratio of $E/T = 60/40$ seems to be preferred one, although some deviation can be observed at short reaction intervals in the cases of **10, 11** and **13**. The *E/T* ratios in these cases are probably due to "mixed control" over the stereochemistry at the beginning of the reaction. The stereochemistry of the reaction remains unaffected by the heterogeneity of the mixture (see Table 2) or reduced amounts of $NaNH_2$.

The isomerization and dissociation data of the pure diastereomers are shown in Table 3. The reaction is reversible at 64° in all examined cases. Compounds **9** and **14** undergo fastest isomerization accompanied by considerable dissociation. This is an evidence for the reversibility of the "aldol" stage of the reaction. Isomerization leads to the same E/T ratio as in the case of synthesis. Longer reaction intervals are connected with an increase of by-products. Because of the existence of a second CH-acid center at C_2 we cannot exclude the possibility of its isomerization by epimerization. The reaction is practically irreversible at 22° probably for the same reasons already mentioned in the discussed of the results obtained in ether; it is most unlikely that the kinetic controled ratio at 22° is the same as the equilibrium one at 64°.

Table 2. *Formation of* **9**-**15** *in THF*

X	NR_2	Conc. (mol/l)	Temp. (°C)	React. time (min)	Yields (%)	E/T
OCH_3	$N(CH_3)_2$	**9** 0.312	64	15	82	54/46
				60	55	54/46
		0.312[a]	64	15	55	58/42
				60	87	60/40
		2.0[b]	64	3-4	92	57/43
		0.5	22	30	14	59/41
				120	23	55/45
OCH_3	$N(i\text{-}C_3H_7)_2$	**10** 0.312	64	15	15	70/30
				60	49	68/32
				120	81	60/40
OCH_3	$N(C_6H_{11})_2$	**11** 0.312	64	15	12	67/33
				60	55	62/38
				120	82	58/42
OCH_3	$N(CH_2CH_2)_2O$	**12** 0.312	64	15	83	58/42
				60	70	57/43
$N(CH_3)_2$	$N(C_6H_{11})_2$	**13** 0.312	64	15	58	30/70
				60	50	60/40
				120	44	56/44
$N(CH_2CH_2)_2O$	$N(CH_2CH_2)_2O$	**14** 0.312	64	15	88	50/50
				60	85	50/50
$N(C_2H_5)_2$	$N(CH_2CH_2)_2O$	**15** 0.312	64	15	84	58/42
				60	85	53/47

[a] 0.2 mol $NaNH_2$. [b] Heterogeneous medium.

C. *Hexamethylphosphoramide* (*HMPA*) (Table 4)

In this medium the reaction is reversible in all examined conditions (see Table 4). The diastereomers **9** exhibited the highest degree of

Table 3. *Isomerization in THF*

X	NR_2	Configu-ration	Conc. (mol/l)	Temp. (°C)	React. time (min)	Yields (%)	Degradation products[a] (%)	*E*/*T*
OCH_3	$N(CH_3)_2$	*threo*-**9**	0.312	64	15	79	18/—	59/41
					60	50	19/15	59/41
			0.5	22	120	98	—	0/100
		erythro-**9**	0.312	64	15	82	15/—	59/41
					60	52	20/18	60/40
			0.5	22	120	97	—	100/0
OCH_3	$N(i\text{-}C_3H_7)_2$	*threo*-**10**	0.312	64	15	92	—	0/100
					120	63	13/—	61/39
		erythro-**10**			15	96	—	100/0
					120	72	18/—	60/40
OCH_3	$N(C_6H_{11})_2$	*threo*-**11**	0.312	64	15	79	13/—	29/71
					60	58	16/8	58/42
		erythro-**11**			15	82	15/—	90/10
					60	52	18/7	62/38
$N(CH_2CH_2)_2O$	$N(CH_2CH_2)_2O$	*threo*-**14**	0.312	64	15	71	23/3	47/53
					60	67	28/4	57/43
		erythro-**14**			15	73	24/3	52/48
					60	62	26/8	56/44

[a] Initial compounds vs. by-products.

Table 4. *Formation of* **9**, **10**, **11** *and* **13** *in HMPA*

X	NR_2		Conc. (mol/l)	Temp. (°C)	React. time (min)	Yields (%)	*E*/*T*
OCH_3	$N(CH_3)_2$	**9**	0.416	22	5	73	38/62
					10	69	67/33
					30	65	71/29
				0	10	75	13/87
					60	90	30/70
			2.5	22	2–3[c]	82	20/80
					120	75	90/10
OCH_3	$N(i\text{-}C_3H_7)_2$	**10**	0.416	22	10	62	8/92
					30	94	24/76
					30	94	24/76
					60	90	65/35
					120	81	70/30
			0.625	60	5	78	71/29
OCH_3	$N(C_6H_{11})_2$	**11**	0.416	22	10	72	12/88
					30	90	28/72
					60	88	66/34
					120	81	70/30
			0.625	60	5	90	70/30
			2.5	22	20[b]	86	21/79
					60[c]	89	31/69
			2.5[a]	22	20[b]	25	19/81
					60[c]	90	7/93
$N(CH_3)_2$	$N(C_6H_{11})_2$	**13**	0.416	22	10	78	26/74
					120	54	48/52
			0.625	60	5	69	70/30

[a] 0.2 mol $NaNH_2$. [b] Homogeneous medium. [c] Heterogeneous medium.

Table 5. *Isomerization in HMPA at 22° and concentration 0.416 mol/l*

X	NR_2	Configuration	React. time (min)	Yields[a] (%)	*E*/*T*
OCH_3	$N(CH_3)_2$	*threo*-**9**	15	47	40/60
			30	40	57/43
			60	29	60/40
		erythro-**9**	15	62	77/23
			30	55	72/28
OCH_3	$N(i\text{-}C_3H_7)_2$	*threo*-**10**	60	57	78/22
		erythro-**10**	15	92	93/7
			60	68	75/25
OCH_3	$N(C_6H_{11})_2$	*threo*-**11**	15	90	30/70
			60	60	75/25
		erythro-**11**	15	90	95/5
			60	71	87/13

[a] The rest is a mixture of degradation and by-products in which the latter predominates.

dissociation. The rate of regeneration of the diastereomeric mixtures is low. The difference consists of starting compounds and by-products with a predomination of the latter. Compounds **10** and **11** show a lower amount of by-products. The isomerization rates in both diastereomeric series change in the order **9** > **11** ≈ **10** as observed during the synthesis. The stereochemical results correspond satisfactorily to the E/T ratios obtained during synthesis ($E/T = 70/30$).

Table 6. *Formation of* **9, 10, 11** *and* **13** *in DMSO*

X	NR_2		Conc. (mol/l)	Temp. (°C)	React. time (min)	Yields (%)	E/T
OCH_3	$N(CH_3)_2$	**9**	0.5	22	10	35	60/40
					60	43	60/40
					120	37	69/31
			1.25	22	2-3[a]	63	57/43
					15	60	90/10
					60	48	95/5
OCH_3	$N(i\text{-}C_3H_7)_2$	**10**	1.25	22	5[a]	78	22/78
					60	68	0/100
OCH_3	$N(C_6H_{11})_2$	**11**	1.25	22	5[a]	49	20/80
					60	51	6/94
$N(CH_3)_2$	$N(C_6H_{11})_2$	**13**	1.25	22	5[a]	48	57/43
					60	52	30/70

[a] Heterogeneous medium.

The reaction in this solvent is very fast and the yields are over 80% (Table 5). A perceptible decrease in yields occurs at longer reaction times because of the consumption of methyl cinnamate and reaction products. This consumption rises with the increase of temperature. The *threo*-isomers are favoured at the beginning of the reaction (**10, 11, 12**) or at low temperatures (**9**) and probably are products of "mixed control". Further isomerization leads to the predomination of the corresponding *erythro*-isomers. The concentration of 2.5 mol/l leads to a second order asymmetric transformation and isolation of the practically pure less soluble isomer. In the case of **9** this is the *erythro*-isomer. *threo*-**11** is less soluble, but isomerization via the solution leads to an increased amount of the *erythro*-isomer in the reaction mixture. Pure *threo*-isomer in this case can be obtained by reducing the amount of the catalyst as isomerization agent.

D. *Dimethylsulphoxide* (*DMSO*) (Table 6)

The reaction in this solvent is also reversible and proceeds with considerable complications because of side reactions including also reaction with the solvent (sulphur-containing by-products were isolatet in some cases). The stereoselectivity of the reaction is the same as in *HMPA*. The heterogeneous reaction conditions are great significance for obtaining practically pure less soluble isomers (*erythro*-**9**, *threo*-**10** and *threo*-**11**).

E. *Benzene*

The only studied case in this solvent was the synthesis of **9** at 80° and concentration of 0.312 mol/l. The yields after 15 and 60 min are 47% and 68%, respectively. The *E*/*T* ratio is 58/42, as in ether and *THF*. The reaction is reversible at this temperature.

Discussion

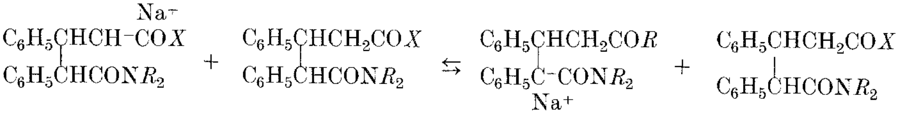
The reaction in *HMPA* and *DMSO* are of significant importance from the point of view of synthetic organic chemistry. *threo*-Isomers can be prepared easily in *HMPA* at room temperature and short reaction times. Longer reaction times or increased temperatures favour the formation of the *erythro*-isomers. Second order asymmetric transformation in *HMPA* or *DMSO* afforded the practically pure less soluble isomers.

The reaction is reversible over a wide range of experimental conditions. The question of the reversibility at low temperatures in ether and *THF* is left open.

The predominating of one of the diastereomers at the beginning of the reaction in *THF* and *HMPA* is due probably to the "mixed control" over the configuration. Some differences between **10, 11** and **13** in *THF* are unclear.

The *E*/*T* equilibrium ratio does not depend on the reaction conditions and reactants. It is approximately 60/40 in aprotic nonpolar media (benzene, ether and *THF*) and about 70/30 in polar ones. The isomerization leads to the same ratios.

Taking into consideration that under conditions of a one stage reaction neutral molecules are formed, we assume that the following reaction of metal exchange can also take place:



$$\begin{array}{l} \qquad\qquad Na^{+} \\ C_6H_5CHCH{-}COX \\ C_6H_5CHCONR_2 \end{array} + \begin{array}{l} C_6H_5CHCH_2COX \\ C_6H_5CHCONR_2 \end{array} \leftrightarrows \begin{array}{l} C_6H_5CHCH_2COR \\ C_6H_5C{-}CONR_2 \\ \qquad Na^{+} \end{array} + \begin{array}{l} C_6H_5CHCH_2COX \\ C_6H_5CHCONR_2 \end{array}$$

A **B**

The conversion of **A** into **B** has been postulated in some earlier works on the *Michael* reaction[18] catalyzed by alkoxides but its mechanism has been not discussed.

The formation of the carbanion **B** leads to isomerization by epimerization at C_2 either via metal exchange with other CH-acids present in the reaction mixture or during the hydrolysis at the end of the reaction. As already mentioned **B** could be formed also during the isomerization of the pure diastereomers either via metal exchange or by direct metallation at C_2. It is most likely, that the observed *E/T* equilibrium ratios are determined by both reversible formation of **A** and epimerization of **B**.

In our next work on the two stage *Michael* reaction between the same compounds we intend to present the stereochemical results under kinetic and thermodynamic conditions.

Experimental

All data listed in the tables are the result of at least 2-3 experiments.

Synthesis of pure diastereomers **10, 11** *and* **13**

The *threo* compounds were isolated by recrystallizing the diastereomeric mixtures obtained after 10 min in *HMPA* at 22°. The mixtures obtained in the same solvent after 5 min at 60° afforted the corresponding *erythro*-isomers. The results of the synthesis and new diastereomeric compounds are described below:

Compound and configuration	Yield %	M. p. °C	Solvent	Analysis %N calc.	Analysis %N found	C_6H_5 (ppm) interval
erythro-**10**	48	108-110	Benzene/Hexane	3.67	3.76	7.30-7.90
threo-**10**	51	154-156	Ethanol	3.67	3.84	7.00-7.30
erythro-**11**	42	137-139	Heptane	3.03	3.21	7.25-7.65
threo-**11**	55	170-172	Ethanol	3.03	3.41	7.05-7.25
erythro-**13**	32	133-135	Benzene/Hexane	5.90	6.16	7.20-7.70
threo-**13**	47	169-171	Benzene/Hexane	5.90	6.13	7.05-7.20

Syntheses in different solvents

Equimolar amounts of freshly ground $NaNH_2$ were added in a single portion to the solution of the starting compounds (the concentration is given in the Tables). The reaction mixture was stirred under dry nitrogen at the corresponding temperature for the listed time intervals. A few milliliters of water were added at the end of the reaction. Further treatment depended on the solvent.

1. *Ether and benzene*

a. Heterogeneous reaction mixture. In the case of **9** the solid product was washed with water after filtration to remove the starting dialkylamide, dried in the air and stirred in heptane to remove the unreacted methyl cinnamate (TLC showed absence of reaction products in the washings). Compound **14** was treated as in 1-b.

b. Homogeneous reaction mixture. Evaporation of the ether, dissolution of the residue in chloroform, drying the chloroform extracts and evaporation of the solvent led to a viscous oil. The pure diastereomeric mixture was isolated by preparative TLC (silica gel G, type 60) using ether as eluant and chloroform for extracting the products. The loss of material during separation did not exceed 6%.

2. *Tetrahydrofuran*

The reaction mixture under homogeneous conditions was worked up as described in 1-b [in the case of **10** and **11** the elution system was ether/heptane (3:2)]. The heterogeneous reaction mixtures was worked up as in 1-a.

3. *Hexamethylphosphoramide*

A ten-fold excess of water was added at the end of the reaction and the solution was saturated with sodium chloride, filtered and washed with water. TLC showed that the solid residue was a pure mixture of diastereomers. No diastereomers were observed in the filtrate (TLC of chloroform extract).

4. *Dimethylsulphoxide*

The products were isolated as in 3. Small amounts of a mixture of diastereomers was found in the *DMSO* filtrate (TLC).

Isomerization of the pure diastereomers

The isomerization was conducted under homogeneous conditions at the same concentration as used in the synthesis. Equimolar amounts of $NaNH_2$ were added to the solution of the diastereomer. The products were isolated as described earlier. Preparative TLC was employed in some cases to evaluate the distribution of reactants and products.

References

[1] Part III: *J. Stefanovsky* and *L. Viteva*, Comun. Dept. Chem. Bulg. Acad. Sci. **4**, 159 (1971).

[2] *E. D. Bergmann*, *D. Ginsburg*, and *R. Pappo*, Organic Reactions, Vol. 10, p. 179. New York: Wiley. 1959.

[3] *W. Borsche*, Ber. dtsch. chem. Ges. **42**, 4496 (1909).

[4] *S. Avery*, J. Amer. Chem. Soc. **50**, 2512 (1928); *S. Avery* and *M. W. Maclay*, J. Amer. Chem. Soc. **51**, 2833 (1929).

[5] *G. M. Badger*, *J. E. Campbell*, and *J. W. Cook*, J. Chem. Soc. **1949**, 1084.

[6] *C. F. Koelsch*, J. Amer. Chem. Soc. **65**, 437, 2459 (1943).

[7] *R. Connor*, *C. L. Fleming*, and *T. Clayton*, J. Amer. Chem. Soc. **58**, 1386 (1936).

[8] *H. Rupe* and *L. Stern*, Helv. Chim. Acta **10**, 859 (1927).

[9] *E. P. Kohler*, J. Amer. Chem. Soc. **38**, 889 (1916); *E. P. Kohler* and *C. F. H. Allen*, J. Amer. Chem. Soc. **46**, 1522 (1924).

[10] *R. W. Helmkamp, L. J. Tanghe*, and *J. T. Plati*, J. Amer. Chem. Soc. **62**, 3215 (1940).

[11] a. *A. M. Baradel, J. Dreux, R. Longeray, P. Lazio*, and *H. Riviere*, Bull. Soc. Chim. Fr. **1966**, 3545; b. *A. M. Baradel, J. Dreux*, and *R. Longeray*, Bull. Soc. Chim. Fr. **1970**, 253, 255 and 258.

[12] *R. B. Meyer* and *C. R. Hauser*, J. Org. Chem. **26**, 3183, 3187 (1961).

[13] *J. Stefanovsky* and *A. Bozilova*, Mh. Chem. **99**, 798 (1968).

[14] *J. Stefanovsky* and *L. Viteva*, Comun. Dept. Chem. Bulg. Acad. Sci. **4**, 99 (1971); C. A. **75**, 88 270 v (1971).

[15] *J. Stefanovsky* and *L. Viteva*, Comun. Dept. Chem. Bulg. Acad. Sci. **4**, 159 (1971); C. A. **76**, 24 872 f (1972).

[16] *K. Ingold*, Structure and Mechanism in Organic Chemistry, p. 692. New York: Cornell University Press. 1953.

[17] *S. L. Spassov*, Tetrahedron (London) **25**, 3631 (1969).

[18] *C. K. Ingold* and *W. J. Powell*, J. Chem. Soc. **119**, 1976 (1921).