THERMODYNAMICS OF VINYL ETHERS-XI†

THE EFFECT OF THE ALKOXY GROUP ON THE RELATIVE STABILITIES OF 2-ALKOXY-3-METHYL-1-BUTENES AND CORRESPONDING 2-BUTENES

E. TASKINEN

Department of Chemistry, University of Turku, 20500 Turku 50, Finland

(Received in the UK 18 October 1973; Accepted for publication 26 August 1974)

Abstract—The effect of the alkoxy group (RO-; R=Me, Et, MeOCH₂CH₂, ClCH₂CH₂, *i*-Pr, *s*-Bu, (Et)₂CH, C₆H₃) on the relative stabilities of 2-alkoxy-3-methyl-1-butenes and corresponding 2-butenes has been studied by chemical equilibration in cyclohexane solution at various temperatures. The relative stability of the latter isomer is favored by (a) increasing size, (b) increasing electron-attracting character, and (c) increasing conjugative power of the R group. The last-mentioned point is especially important; in the case R = phenyl, the value of Δ H° (g, 298·15 K) of the isomerization of the former to the latter is 12–13 kJ mol⁻¹ more negative than in cases where conjugation between the ether oxygen and the R group is not possible.

In a previous part of this series,¹ thermodynamics of the isomerization of 2-methoxy-3-methyl-1-butene [1a, R=Me in equation (1)] to 2-methoxy-3-methyl-2-butene 1b were



studied. The values of the standard enthalpy and entropy of isomerization were found to be considerably more positive than those of the reaction between the corresponding hydrocarbons, viz. 3 - methyl - 1 - butene $\rightleftharpoons 2$ methyl - 2 butene. This was assumed to be due mainly to the rotation of the methoxy group from the planar s-cis configuration in 1a to a nonplanar configuration in 1b.^{1.2} In the present work the effect of the R group on the thermodynamics of reaction (1) was studied.

RESULTS

The values of the mean equilibrium constant K and its standard error at various temperatures are shown in Table 2. From the values of K, standard Gibbs free energies of isomerization were calculated and these were then plotted as a function of T. If the free energy of isomerization was found to be a linear function of T (showing $\Delta C_p^o = 0$), the values of ΔH^o and ΔS^o of isomerization at 298.15 K were obtained by a least-squares treatment of ΔG^o vs T ($\Delta G^o = \Delta H^o - T\Delta S^o$).¹ In many cases, however, ΔG^o proved to be a nonlinear function of temperature. In those cases the values of K were fitted to the following equation:³

$$\ln K = A + B/T + C \ln T$$
 (2)

[†]Part X: E. Taskinen and P. Ylivainio, Acta Chem. Scand. B 29, 000 (1975).

The use of this equation requires that ΔH° is a linear function of temperature ($\Delta C_{p}^{\circ} = constant$). This condition was satisfactorily (within experimental error) fulfilled. The fitting was performed on an IBM 1130 computer. The values of ΔG° , ΔH° , ΔS° and ΔC_{p}° for the isomerization $a \rightarrow b$ in the liquid phase at 298.15 K are shown in Table 3. The values of the standard enthalpy and standard entropy of vaporization at 298.15 K were calculated from the normal boiling points (see Experimental) using the equations derived in.⁴ After this, the values of ΔH° and ΔS° of isomerization in the ideal gas state at 298.15 K could be evaluated. The results are collected in Table 4.

DISCUSSION

A convenient basis for comparison of the results of the present work with the thermodynamics of the reaction between the corresponding olefins is provided by

$$i - Pr - CH = CH_2 \equiv Me - CH = CMe_2$$
(3)

for which $\Delta H^{\circ} = -13.6 \text{ kJ mol}^{-1}$, $\Delta S^{\circ} = 5.1 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta C_{p}^{\circ} = -13.6 \text{ J K}^{-1} \text{ mol}^{-1}$ in the gas phase at 298.15 K.⁵ Table 4 shows that as the size of the R group increases, the values of $\Delta H^{\circ}(g)$ and $\Delta S^{\circ}(g)$ of reaction (1) approach those of reaction (3) without, however, reaching them completely. Similarly, in many cases the values of $\Delta C_{p}^{\circ}(1)$ of reaction (1) (Table 3) are practically equal to the value of $\Delta C_{p}^{\circ}(g)$ of reaction (3), provided that the R group is sufficiently bulky [of course, $\Delta C_{p}^{\circ}(1)$ and $\Delta C_{p}^{\circ}(g)$ are not strictly comparable, but apparently this approximation does not render the comparison invalid]. Seemingly, most of these results can be explained by considering the effect of the size of the alkoxy group on the configurational equilibria in the **a** and **b** isomers.

In principle, the rotation of the alkoxy group around the O-Cvinyl bond leads to three possible rotamers, viz. s-cis,

Table 1. NMR data for some 2-alkoxy-3-methyl-1-butenes **a** and 2-alkoxy-3-methyl-2-butenes **b**. The spectra were recorded in CCL at 60 MHz with TMS as internal standard. The chemical shifts are shown in τ values (ppm) and the coupling constants in Hz

(1) (2) (CH ₃) ₂ CH	(3) H	(1) CH ₃	(2) .CH,
C=	=C(H	R C=	⊧с́ Сн,
Ŕ	(4)		(3)
8		b	

R	Structure	1	2	3	4	5	6	7	8	\mathbf{J}_{12}	J ₃₄	J 56
CH ₃ CH ₂	8	8.96	7.71	6.33	6.24	8.71	~ 6.3			7.1	2.1	7.1
(5) (6)	Ь	8 ∙26	8-41	8.41		~ 8.7	~6.3					
CH ₁ OCH ₂ CH ₂	8	8.96	7.75	6.40	6.21	6.67	6-2 -	- 6.4		6.9	1.8	
(5) (6) (7)	Ь	8 ·27	8.41	8.41		6.67	6.2 -	- 6.6				
CICH ₂ CH ₂	1	8.94	7.69	6.1	- 6.4	6-1	- 6.4			6.9		
(5) (6)	b	8.27	8.40	8.40		6-1	- 6.4					
(CH ₃) ₂ CH		8·98	7.77	6.34	6.18	8.79	5.78			6.8	1.9	6.5
(5) (6)	ь	8·29	8 ∙41	8.41		8.88	6·11					
CH ₃ CH ₂ (CH ₃)CH	2	8.94	7.76	6.35	6.20	~ 9.0	~ 8.7	~ 8.8	6.10	6.0	1.8	
(5) (6) (7) (8)	Ь	8·29	8.41	8.41		~ 9.0	~8.7	~ 8.8	~ 6.1			
(CH ₁ CH ₂) ₂ CH	8	8.96	7.73	6-37	6.23	9.10	8∙54	~6.2			1.7	
(5) (6) (7)	b	8.30	8.42	8.42		9.10	8∙54	6.33				
C ₆ H ₅ (5)	b	8∙26	8·39	8∙26		2.€	5-3-3					

Table 2. Values of the mean equilibrium constant K and its standard error for the iodine-catalyzed reaction 2-alkoxy-3-methyl-1-butene **a** = 2-alkoxy-3-methyl-2-butene **b** in cyclohexane solution at various temperatures. n denotes the number of independent determinations

R	T/K	Catalyst conc. mol dm ⁻³	Substr. conc. mol dm ⁻³	Start from	n	K(a≓b)
Et	293.2	0.006	0.9	8	4	0.593 ± 0.013
	303-2				6	0.639 ± 0.010
	313-2				4	0.690 ± 0.012
	323-2				4	0.728 ± 0.004
	333-2				4	0·769 ± 0·008
	333-2				4	0·778 ± 0·008
	343-2				2	0.796 ± 0.016
	343-2				3	0.797 ± 0.002
	353-2				4	0.815 ± 0.009
	355-2				3	0.888 ± 0.006
	362.7				3	0.922 ± 0.006
	366-2				3	0.943 ± 0.009
	375-2				2	0.955 ± 0.015
	389.2				3	1.089 ± 0.016
MeOCH ₂ CH ₂	298.2	0.004	0.6	Ь	2	0.838 ± 0.012
	325-2			-	1	0.947
	346-2				3	1.078 ± 0.007
	356-2				3	1.110 ± 0.019
	360.2				3	1.108 ± 0.015
	363-2				3	1.147 ± 0.013
	363-2				3	1.174 ± 0.011
	368-2				3	1.150 ± 0.009
	373-2				3	1.233 ± 0.014
	393-2				3	1.287 ± 0.008
	399-2				2	1.348 ± 0.013
	418·2				2	1.414 ± 0.001

		Catalyst conc.	Substr. conc.	Start		
R	T/K	mol dm ⁻³	mol dm ⁻³	from	n	K(a≓b)
CICH ₂ CH ₂	279·0	0.003	1.0		2	1·163 ± 0·010
	279-0			b	2	1·195 ± 0·011
	293·2	0.006		8	2	1.272 ± 0.008
	298·2	0.003		8	2	1·257 ± 0·007
	298-2			ь	2	1·276 ± 0·007
	305-2			1	3	1.310 ± 0.008
	305-2			Ь	3	1·330 ± 0·010
	313-2				3	1·367 ± 0·006
	313-2			b	3	1.372 ± 0.008
	323-2	0.006		8	3	1.366 ± 0.012
	333·2			8	4	1.436 ± 0.021
	343-2			8	2	1-478 ± 0-015
	380-2			2	4	1.650 ± 0.025
	396 -2			2	3	1.810 ± 0.005
i–Pr	284.7	0.002	0.4	b	2	1.438 ± 0.003
	313-2				2	1.597 ± 0.002
	323-2			8	3	1.685 ± 0.005
	333-2			b	2	1.639 ± 0.005
	343-2				2	1.703 ± 0.004
	381-2			2	2	1.768 ± 0.010
	385-2				2	1.770 ± 0.015
	379-2			b	2	1.796 ± 0.007
s-Bu	293-2	0.002	0.7	b	6	1.586 ± 0.006
	303-2			2	2	1.404 ± 0.002
	313-2			D	3	1.433 ± 0.024
	323.2			D	4	1.440 ± 0.004
	342.7			D 6	ć	1.476 ± 0.005
	343.2				2	1.470 ± 0.003
	361.2			0 1	1	1.527 + 0.005
	371.7			b b	2	1.527 ± 0.005 1.551 ± 0.005
	390.7			Б	1	1.529 ± 0.012
	399.7				, ,	1.554 ± 0.009
	401.2			h	8	1.541 ± 0.007
(Et)-CH	283.2	0.004	0.6	ĥ	1	1.066
(20)2011	303.2	• •••	•••		2	1.131 ± 0.012
	323.2			2	4	1.206 ± 0.011
	343-2				3	1.232 ± 0.018
	359-2				3	1.277 ± 0.011
	373-2			2	2	1.283 ± 0.008
	402.2			2	3	1.313 ± 0.013
	422·2			b	3	1.327 ± 0.005
C°H3	293·2	0.008	0-3	b	2	139·0 ± 1·8
	313-2				3	109·7 ± 2·3
	333-2				2	87·4±1·4
	343-2				3	83·7 ± 0·7
	356-2				2	72·9 ± 1·3
	360-2				3	66·4 ± 1·0
	374-2				2	56.9 ± 0.1
	401·2				2	51.8 ± 0.5

Table 2.—Continued

s-trans and gauche rotamers the first two of which have planar structures; in the latter rotamer, however, the R

s-cis (planar)

s-trans (planar)

gauche (nonplanar)

group lies either below or above the plane formed by the group C=C-O (see refs 1 and 2, and the references cited therein). It seems likely² that in compounds like isomers b of this study, the gauche rotamer is predominant (irrespective of the size of the R group) because of steric interactions between the R group and the alkyl groups attached to the double bond in the two possible planar

Table 3. Thermodynamic data for the isomerization of 2-alkoxy-3-methyl-1-butene to 2alkoxy-3-methyl-2-butene in cyclohexane at 298.15 K. The errors are twice the standard errors

	AC9/1-1	A 179/1/11-1	A 5%/I W-1 mol-1	AC%/I V-1 mol-1
ĸ			45/JK IIIOI	
Me ⁴	2.270 ± 0.035	6.48 ± 0.26	14.1 ± 0.8	
Et	1.241 ± 0.086	5·71 ± 0·58	15.0 ± 1.7	-
MeOCH ₂ CH ₂	0.486 ± 0.074	4.69 ± 0.38	14.1 ± 1.0	-
CICH ₂ CH ₂	-0.603 ± 0.034	$3 \cdot 17 \pm 0 \cdot 28$	12.6 ± 0.9	-
CICH ₂ CH ₂ *	-0.603 ± 0.026	2.67 ± 0.50	11.0 ± 1.6	14 ± 14
i–Pr	-1.043 ± 0.049	2.7 ± 0.8	12.4 ± 2.4	-24 ± 17
s-Bu	-0.821 ± 0.028	1.56 ± 0.46	8.0 ± 1.5	-11 ± 10
(Et) _b CH	-0.281 ± 0.020	2.25 ± 0.26	8.5 ± 0.8	-15 ± 5
C ₆ H ₅	-12.08 ± 0.16	-9.3 ± 1.0	9.3 ± 2.8	

"From ref. 1.

^bCalculated from equation (2).

Table 4. Thermodynamic data for the isomerization of 2-alkoxy-3methyl-1-butene to 2-alkoxy-3-methyl-2-butene in the gas phase at 298-15 K

R	$\Delta H^{\circ}/kJ \text{ mol}^{-1}$	$\Delta S^{\circ}/J K^{-1} mol^{-1}$
Me°	9·46±0·33	17·9 ± 1·0
Et	8.82 ± 0.61	18.8 ± 1.8
MeOCH ₂ CH ₂	7.43 ± 0.43	17.0 ± 1.1
CICH,CH,*	6.08 ± 0.41	15.6 ± 1.0
i–Pr	5.5 ±0.9	15.7 ± 2.5
s-Bu	4.91 ± 0.50	11.7 ± 1.6
(Et) ₂ CH	5.42 ± 0.33	12.5 ± 1.0
C ₆ H ₅	-7.4 ± 1.1	11.0 ± 2.9

^a From ref 1, with values of the standard enthalpy and standard enthalpy of vaporization revised according to relevant equations given in ref 4.

^b The values of Δ H° and Δ S° in the liquid phase were derived from a linear least-squares treatment of Δ G° against T.

configurations. On the other hand, the s-cis configuration is possible for isomers a if the R group is not too bulky. Energetically, the s-cis configuration (in a) is favourable for small R groups but the entropy apparently favors the nonplanar rotamer owing to a more restricted rotation of the R group in the planar rotamer.² Moreover, it is likely that the gauche rotamer has a higher heat capacity than any of the planar rotamers because of the more unhindered rotation of the R group in the nonplanar configuration. Hence, as the size of the R group increases, the relative concentration of the gauche rotamer in the a isomer raises while the b isomer always exists mainly in the gauche configuration, irrespective of the size of the R group. Thus the enthalpy, entropy and heat capacity of isomer a, relative to those of the b isomer increase with the size of R, and correspondingly, the values of ΔH° , ΔS° and ΔC_p° of isomerization decrease in the same sequence.

In addition to the steric effect, the value of ΔH° of isomerization is also dependent on the polar character of the R group. The higher the electron-withdrawing character of the group, the weaker is the conjugation between the lone-pair electrons of the oxygen atom and



the π electrons of the ethylenic linkage of the vinyl group. A weak conjugation strenghtens the double bond character of the ethylenic linkage thereby increasing the stabilizing effect of the alkyl groups on the double bond.⁶ As there are more alkyl groups attached to the double bond in the **b** isomer, electron-withdrawing R groups favour the stability of the **b** isomer. However, separation of the contributions of the steric and polar factors on the value of ΔH° is hardly possible.

The reaction 8a=8b (R = phenyl) deserves special attention for in this case the value of ΔH° of isomerization is exceptionally negative. Evidently, the value of ΔH° of this reaction cannot be satisfactorily explained solely by means of the steric and polar effects discussed above. No doubt the electron-withdrawing power of the phenyl group is stronger than that of any of the other R groups used in this study (σ^* -values⁷ 0.600 for phenyl, 0.385 for ClCH₂CH₂, the most electronegative of the other R groups) but, in addition, the phenyl group also competes with the vinyl group for the lone-pair electrons of oxygen by means of its resonance effect;⁸ the carbon-carbon double bond stretching frequency of the vinyl group of phenyl vinyl ether^{9,10} is abnormally high for a vinyl ether showing that conjugation of the π electrons of the vinyl group with the lone-pair electrons of the oxygen atom has essentially decreased. This effect also strengthens the double bond character of the vinyl group leading to an increased stability of the b isomer.

EXPERIMENTAL

The NMR spectra were recorded in CCL at 60 MHz with TMS as internal reference. The chemical shifts are shown in τ value (ppm). Because of the very low concentration of 8a in the synthetic product, its NMR spectrum could not be recorded. The spectra are shown in Table 1.

2-Ethoxy-3-methyl-1-butene and isomer (2a and 2b). The diethyl acetal of methyl isopropyl ketone was prepared from methyl isopropyl ketone, triethyl orthoformate and ethanol using the procedure described by House and Kramar.¹⁷ The product (b.p. 425·2-426·0 K at 103·5 kPa) was obtained in 69% yield. It was distilled from a small amount of toluene-p-sulfonic acid to give a mixture of ethanol and the desired vinyl ethers, which was collected at 350-389 K/103·5 kPa. The ethanol was removed from the mixture by extraction with water, the organic layer was dried (K_2CO_3) and redistilled to give an 81% yield of an approximately equimolar mixture of 2a and 2b, boiling temperature 374-388 K/103·0 kPa.

2-(2-Methoxyethoxy)-3-methyl-1-butene and isomer (3a and 3b). A small amount of toluene-p-sulfonic acid was added into an equimolar mixture of the dimethyl acetal of methyl isopropyl ketone' and 2-methoxyethanol, and the mixture was fractionated at atmospheric pressure to remove the most volatile reaction product, methanol, after which fractionation was continued at 337-341 K/2.7 kPa. The yield was 40%.

2-(2-Chloroethoxy)-3-methyl-1-butene and isomer (4a and 4b). 2-Chloroethanol was slowly added to an equimolar amount of 2a and the mixture was subjected to fractional distillation to remove ethanol as the product of the alcohol exchange reaction. An 85% yield of a mixture of 4a and 4b was obtained. The product was collected at 430-439 K/103.0 kPa.

2-Isopropoxy-3-methyl-1-butene and isomer (5a and 5b). A catalytic amount of toluene-p-sulfonic acid was added to a mixture of 2 - methoxy - 3 - methyl - 1 butene¹ 1a (10 cm^3) and isopropyl alcohol (200 cm^3). After standing overnight, the mixture was distilled under acid conditions to remove the liberated methanol and the excess of isopropyl alcohol. An about 25% yield of the desired vinyl ethers was collected at 385-395 K/101.0 kPa.

2-s-Butoxy-3-methyl-1-butene and isomer (6a and 6b). Equimolar amounts of 1a and s-butyl alcohol were mixed, a small amount of toluene-p-sulfonic acid was added, and the mixture was fractionated. A 60% yield of the desired compounds could be collected at 415-423 K/100·3 kPa.

2-(3-Pentoxy)-3-methyl-1-butene and isomer (7a and 7b). These compounds were prepared as described above for 5a and 5b but using 3-pentanol instead of s-butyl alcohol. The product, obtained in about 40% yield, boiled at 431-436 K/100·1 kPa.

2-Phenoxy-3-methyl-1-butene and isomer (8a and 8b). Tolueneppsulfonic acid was added to an equimolar mixture of 4a and phenol and the mixture was subjected to fractional distillation at reduced pressure. A 40% yield of a product boiling at 386-390 K/1.6 kPa was obtained. The product contained ca 99.5% of 9b.

Prior to the equilibrations, the vinyl ethers were purified by preparative gas chromatography using a column containing 20% Carbowax 20 M on Chromosorb G.

Determination of normal boiling points. The normal boiling points of the compounds studied, which were used for the estimation of ΔH_{wap}° and ΔS_{wap}° at 298-15 K, were determined by the gas chromatographic method described previously.4 The following compounds were used as the reference compounds (compound, normal boiling point): isobutyl vinyl ether (R1), 356-2 K; isobutylidene ethyl ether (R2), 366-7 K; 1-methoxycyclopentene (R3), 387.0 K; 1-ethoxycyclopentene (R4), 409·0 K; 1methoxycyclohexene (R5), 417.1 K; 1-ethoxycyclohexene (R6), 435-0 K: 1-(1-propoxy)cyclohexene (R7), 455-9 K: 1cyclopentoxycyclopentene (R8), 479.7 K. The boiling points of 2a and 2a were determined by means of the following reference curve (reference compound, relative retention time): R1, 0.0262; R2, 0.312; R3, 0.513; R4, 0.787; R5, 1.000. The relative retention times of 2a and 2b were 0.360 and 0.518 leading to normal bps of 362.5 and 391.8 K, respectively. 3a, 3b, 4a and 4b; reference

curve: R2, 0·149; R3, 0·266; R5, 0·411; R6, 0·604; R7, 1·000. The relative retention times of **3a**, **3b**, **4a** and **4b** were 0·454, 0·661, 0·494 and 0·740 corresponding to normal bps of 422·2, 439·2, 425·8 and 443·9 K, respectively. **5a**, **5b**, **7a** and **7b**; reference curve: R2, 0·175; R3, 0·261; R5, 0·449; R6, 0·632; R7, 1·000. The relative retention times of **5a**, **5b**, **7a** and **7b** were 0·231, 0·318, 0·522 and 0·780, in the above order, leading to normal bps of 381·2, 398·4, 425·2 and 444·9 K, respectively. **6a** and **6b**; reference curve : R1, 0·223; R3, 0·411; R5, 0·709; R6, 1·000. The relative retention times of **6a** (0·541) and **6b** (0·792) led to normal bps of 402·2 and 423·0 K, respectively. **8a** and **8b**; reference curve: R5, 0·343; R6, 0·425; R7, 0·600; R8, 1·000. The relative retention times of **8a** and **8b** were 0·775 and 1·000 leading to normal bps of 467·7 and 479·7 K, respectively.

Procedure. The practical performance of the equilibrations has been described in detail elsewhere.¹⁴ Cyclohexane was used as solvent and iodine as catalyst. During the equilibrations the only noteworthy side reaction was the formation of a small amount of the corresponding acetal and the ketone, which was due to the presence of traces of water in the solvent and/or substrate $i-PrC(OR)=CH_2 + H_2O \rightarrow i-PrCOCH_1 + ROH; i-PrC(OR)=CH_2 + H_2O \rightarrow i-PrCOCH_2 + H_2O \rightarrow$ $ROH \rightarrow i-Pr(CH_3)C(OR)_2$]. In many cases the position of equilibrium was approached from both directions and the results of such experiments were in nice agreement. If only a single starting mixture was used in the equilibrations, the progress of isomerization was followed over sufficiently extended periods of time (several times the time necessary for the isomer ratio to become constant) to be sure that the true thermodynamic equilibrium had been reached. The behavior of 3a and 3b was surprising in that equilibrations ran smoothly and without significant loss of material if 3b was used as the starting compound, but extensive polymerization could not be avoided if the equilibrations were started from 3a. The equilibration times varied from ca 10 min at the highest temperatures used to a few weeks at the lowest temperatures. The columns used in the gas chromatographic analyses were 4 m columns containing 10% of either Carbowax 1500 or SE-30 on Chromosorb G. The peaks were eluted in alphabetical order and peak separation was good. Peak areas, which were considered to be proportional to the molar amounts of the isomeric vinyl ethers,' were integrated by means of a Hewlett-Packard 3370 B integrator, or by the cut-and-weigh method.

Because of the low concentration (ca 0.5 mol%) of **8a** in the synthetic product, it could be identified solely on the basis of its retention time and its behavior in the equilibrations. Besides the peak of **8b**, only one significant peak could be detected in the chromatogram, and the retention time suited well for **8a**. The experimental difference in the boiling points of **8a** and **8b** (see determination of normal boiling points) was also reasonable.

Acknowledgement—The author is indebted to Mr. Kari Jokila for some experimental aid and to Dr Nils Cleve for the computer program.

REFERENCES

- ¹E. Taskinen, J. Chem. Thermodyn. 5, 783 (1973)
- ²E. Taskinen and P. Liukas, Acta Chem. Scand. B28, 114 (1974)
- ³E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.* 62, 539 (1966)
- ⁴E. Taskinen, J. Chem. Thermodyn. 6, 271 (1974)
- ⁵D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, p. 317. Wiley, New York (1969)
- ⁶C. T. Mortimer, *Reaction Heats and Bond Strengths*, Ch. 3. Pergamon Press, Oxford (1962)

- ⁷R. W. Taft, Steric Effects in Organic Chemistry, (Edited by M. S. Newman), Ch. 13. Wiley, New York (1956)
 ⁸E. S. Gould, Mechanism and Structure in Organic Chemistry, p.
- 212. Henry Holt and Co., New York (1959)
- ^{*}Y. Mikawa, Bull. Chem. Soc. Japan 29, 110 (1956) ¹⁰Yu. L. Frolov, A. K. Filippova, A. V. Kalabina, L. K. Pogodaeva
- and N. A. Tyukavkina, *Zhur. Strukt. Khim.* 3, 676 (1962) ¹¹H. O. House and V. Kramar, *J. Org. Chem.* 28, 3362 (1963)