

REACTIVITY OF COMPOUNDS OF DIPHENYLMETHANE SERIES. V.*
KINETICS OF HYDROLYSIS OF MONOSUBSTITUTED
DIPHENYLMETHYL BROMIDES AND ESTERS IN 80% AQUEOUS ACETONE

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Received July 13th, 1971

The influences of substituents and leaving groups on hydrolysis rate have been studied using the model of benzhydryl esters in 80% aqueous acetone medium at various temperatures. The influence of temperature has been found to be approximately the same for the series of fourteen monosubstituted benzhydryl bromides and that of six benzhydryl esters. By comparison with literature data it has been found that the ρ constant value does not depend on the leaving group (Cl or Br) under the same experimental conditions.

The results of studies of the influence of substituents on solvolysis rate of arylmethyl esters of mineral or organic acids show that the sensitivity towards the substitution of the nucleus of the given substrate is a function of temperature¹, nucleophilic and solvation abilities of solvent and leaving group²⁻⁷. The empirical relations of Brown⁸ or Yukawa and Tsuno⁹ can be used for quantitative evaluation of the substituent effects. The influences of leaving groups were compared by Lohmann⁷ using the empirical relation (I):

$$\log k^X/k^{\text{Br}} = \gamma L. \quad (I)$$

This equation expresses the relative ability of various leaving groups to leave the carbon atom during solvolyses. The constant L , characteristic for the leaving group, was determined by comparison of the rates of alkaline methanolysis of methyl esters and methyl bromides in methanol. The constant γ represents the reacting system, and it equals unity for the reaction given. Simultaneous influence of temperature and leaving group has not been given sufficient attention so far.

The aim of this paper was to follow the influence of substituents, temperature and leaving group in a series of diphenylmethane derivatives during hydrolysis in 80% aqueous acetone. The influence of temperature was followed in a series of the benzhydryl bromides monosubstituted at positions 3 or 4. The influence of leaving group was studied in a series of six benzhydryl esters. The substituents and leaving groups were chosen to cover sufficiently broad ranges of scales of σ^+ and L constants respectively. The choice of 80% aqueous acetone as solvent followed from both the optimum measurable range of the rate constants under the experimental conditions adopted

* Part IV: This Journal 37, 1143 (1972).

by us and the possibility of comparison of the values measured with the literature data¹⁰⁻¹⁵. The present results form a basis for a study of polysubstitution in diphenylmethane series.

EXPERIMENTAL

Reagents. The benzhydryl bromides were prepared from the respective benzhydrols¹⁶. The less reactive benzhydryl bromides 8-14 (Table I) were prepared by reaction of the corresponding benzhydrols with phosphorus tribromide according to the general procedure given by Claisen¹⁷. 3-Methoxybenzhydryl bromide was prepared in an analogous way to that of tetrahydrofurfuryl bromide¹⁸. The compounds 1-6 (Table I) were prepared by introducing dry hydrogen bromide into a suspension of anhydrous sodium sulphate and 10% solution of the substituted benzhydryl in tetrachloromethane under intensive stirring. After 15 minutes of the reaction, the hydrated sodium sulphate was replaced by a fresh portion. The saturation with hydrogen bromide was continued for another one hour. After removing the sodium sulphate by filtration, the respective benzhydryl bromide was isolated by vacuum distillation. The yields of the benzhydryl bromides were about 70%. Their melting and boiling points are given in Table I together with literature data and results of elemental analyses. Benzhydryl chloride¹⁹, acetate²⁰ and trifluoroacetate²¹ were prepared according to the literature. Benzhydryl 3,5-dinitrobenzoate was prepared in a similar way as benzhydryl 4-nitrobenzoate²², m.p. 142-143°C (ref.²³ gives m.p. 142°C).

Benzhydryl fluoride. 0.12M liquid hydrogen fluoride was added at once to a solution of 0.1M diphenyldiazomethane in 150 ml light petroleum at -50°C under intensive stirring. The reaction was finished in 2 minutes which was manifested by decolorization of the original redish purple colouration of diphenyldiazomethane. After this time, 5 ml pyridine was added under stirring, and the reaction mixture was left to reach the room temperature. The benzhydryl fluoride was isolated by vacuum distillation at 105-108°C/2 Torr. Yield 32%. n_D^{20} 1.5658. For C₁₃H₁₁F (186.2) calculated: 83.84% C, 5.96% H; found: 83.64% C, 5.51% H. The bromine content of the benzhydryl bromides was determined as the hydrogen bromide evolved on hydrolysis with 60% aqueous acetone by means of alkalimetric analysis with the Tashiro indicator.

Kinetic measurements. The hydrolyses in 80% aqueous acetone medium proceeded as S_N1 reactions. The constants k_1^0 were determined by extrapolation of the dependence of the rate constants k_1 on time²⁴ to $t = 0$. The hydrolysis rate was followed by titrimetric as well as conductometric methods. The titrimetric method of determination using the samples withdrawal was adopted for the compounds 2-9 (Table I) up to the temperature 25°C. For the higher temperatures (35.0-140.0°C) the samples were closed in sealed glass ampoules. At definite time intervals 5 ml samples of the reaction mixture were withdrawn (0.02M benzhydryl bromide in 80% (by vol.) aqueous acetone thermostated in a flask or ampoule). The samples were diluted with 100 ml acetone and titrated under nitrogen using the Tashiro indicator in the case of the hydrolyses of benzhydryl bromide, chloride and trifluoroacetate. Benzhydryl acetate and 3,5-dinitrobenzoate were titrated on phenolphthalein. The conductometric method was used in most cases simultaneously with the titrimetric determination. A thermostated pressure conductometric cell was used for higher temperatures. The conductivity was measured by means of a Konduktoskop apparatus (Laboratorní potřeby). The results of measurements of the rate constants by the both methods (titrimetry and conductometry) are presented in Table II. Only the conductometric method was used in the case of hydrolysis measurements of benzhydryl fluoride and 4-phenoxybenzhydryl bromide.

TABLE I
Physical Properties and Analyses of Monosubstituted Benzhydryl Bromides

Compound	Substituent	B.p., °C (Torr)	Formula m. w.	% Br calculated/found
1	4-OC ₆ H ₅	208 — 11 (1)	C ₁₉ H ₁₅ OBr 338.3	23.06 22.72
2	4-CH ₃	142 — 5 (2) ^a	C ₁₄ H ₁₃ Br 261.2	30.59 30.76
3	4-t-C ₄ H ₉	37,5—38,5 ^b	C ₁₇ H ₁₉ Br 303.3	26.35 26.14
4	4-F	163 — 5 (3)	C ₁₃ H ₁₀ BrF 265.1	30.14 30.48
5	3-CH ₃	174 — 6 (7)	C ₁₄ H ₁₃ Br 261.2	30.59 30.67
6	H	44,0—45,0 ^{b,d}	— —	—
7	3-OCH ₃	194 — 8 (17)	C ₁₄ H ₁₃ BrO 277.2	28.83 28.71
8	4-Cl	170 — 4 (5) ^e	C ₁₃ H ₁₀ BrCl 281.6	28.37 28.29
9	4-Br	208 — 11 (20)	C ₁₃ H ₁₀ Br ₂ 326.1	49.02 48.82
10	3-OC ₆ H ₅	214 — 16 (3)	C ₁₉ H ₁₅ OBr 338.3	23.06 23.16
11	3-Br	40,0—41,5 ^b	C ₁₃ H ₁₀ Br ₂ 326.1	49.02 48.82
12	3-Cl	165 — 9 (2)	C ₁₃ H ₁₀ BrCl 281.6	28.37 28.35
13	3-CN	171 — 4 (5)	C ₁₄ H ₁₀ BrN 272.1	29.36 29.27
14	3-NO ₂	183 — 6 (5)	C ₁₃ H ₁₀ BrNO ₂ 292.1	27.35 27.24

^aRef.²⁸ gives b.p. 140—145°C/1 Torr; ^b m.p.; ^c ref.¹⁰ gives b.p. 176—178°C/14 Torr; ^d ref.¹⁷ gives b.p. 45°C; ^e ref.²⁹ gives b.p. 39—40°C.

RESULTS AND DISCUSSION

The rate constants k_1^0 of hydrolyses of fourteen monosubstituted benzhydryl bromides in 80% aqueous acetone at various temperatures are presented in Table II. Fig. 1 shows the dependence of $\log k_1^0$ on the Brown's σ^+ constants at 0–50°C, and it can be seen that the correlation is well fulfilled for the monosubstituted benzhydryl bromides. 4-Fluoro derivative is an exception (the statistical treatment in Table III); in 80% aqueous acetone at the three temperature chosen (0, 15, 25°C) it hydrolyzes 1.3 times more rapidly than it should hydrolyze according to the respective Brown's σ^+ constant⁸. When studying the protonation behaviour of 4-fluorobenzophenone²⁵ and 4-fluorobenzhydrol¹⁶, we did not find any deviation. It must, however, be pointed out that similar changes of solvolysis rate were observed in the case of several 4-fluoro-substituted arylalkyl chlorides, too¹⁰.

Due to experimental reasons we could not determine the hydrolysis rates of 3-nitro-, 3-cyano-, 3-bromo- and 4-phenoxybenzhydryl bromides with sufficient accuracy at 25°C, and, therefore, in Fig. 1 we give the values extrapolated from the data obtained at other temperatures. This enabled us to include all the fourteen members of the series in the correlation, and the value $\rho = -4.32$ calculated (Table III) has the maximum statistical significance. For the purpose of further study it was necessary to include 3-phenoxybenzhydryl bromide in the set, too. The σ^+ value of 3-phenoxy substituent was not known. From our measurements it follows $\sigma^+(3\text{-OC}_6\text{H}_5) = 0.16$. From Table III and Fig. 1 it follows that the value of the reaction constant ρ decreases with increasing temperature in hydrolysis of monosubstituted benzhydryl bromides.

The dependence of the activation enthalpy ΔH^\ddagger on the activation entropy ΔS^\ddagger is expressed by the isokinetic relation (2):

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (2)$$

We verified the validity of the isokinetic relation in the hydrolysis of this series of compounds by linear regression of the dependence $\log k = f(T^{-1})$ of each member of the series of benzhydryl bromides and by determination of the coordinate of intersection of the regression lines (in the way minimizing the sum of squares of deviations of experimental values from this point)²⁶. In this way the parameter β was determined which expressed the dependence of the constant on temperature according to Eq. (3):

$$\rho\sigma^+ = \Delta H^\ddagger(1 - \beta/T)/2.3\beta R \quad (3)$$

We found the value $\beta_{(\rho)} = 2000 \pm 29\text{K}$ for the series of monosubstituted benzhydryl bromides in 80% aqueous acetone. In Table IV the values of isokinetic and non-isokinetic parameters are compared for the hydrolysis of the series of fourteen monosubstituted benzhydryl bromides in aqueous acetone. The present knowledge about isokinetic values does not allow drawing any conclusion as to the value of the β constant with respect to the type of reaction or equilibrium. The reason for this is both the lack of suitable experimental data and their incorrect statistical treatment. The study of hydrolyses of benzhydryl bromide, chloride, fluoride, acetate, trifluoroacetate and 3,5-dinitrobenzoate (Table V) enables us to calculate the value β for this series, too.

TABLE II

Rate Constants of Hydrolysis of Monosubstituted Benzhydryl Bromides in 80% Aqueous Acetone

Compound ^a	°C	$(k_1^0 \pm s_{k_1}) \cdot 10^5$ _{s⁻¹}		k/k_H^c
1	-24.7	327 ^b	11	—
	-18.2	612 ^b	10	—
		592 ^b	15	—
	-11.0	1 238 ^b	46	—
		1 210 ^b	34	—
0.0	3 520 ^b	111	235	
2	-5.0	240	4	—
	0.0	475 ^b	12	30.6
		443 ^b	19	—
		742	10	—
	15.0	1 517	12	—
		1 870 ^b	61	24.3
		1 970 ^b	44	—
25.0	5 050 ^b	134	24.7	
	4 870 ^b	98	—	
3	0.0	242	8	16.1
	15.0	1 090	84	14.7
	25.0	2 590 ^b	104	13.4
		2 800 ^b	115	—
4	0.0	43.6	1.9	2.91
	15.0	200	4.7	2.70
	25.0	525 ^b	33	2.52
5	0.0	22.7	0.5	1.97
		36.5 ^b	1.8	—
	15.0	156	2	2.11
		158 ^b	6	—
		164 ^b	4	—
	25.0	419	4	1.97
372		15	—	
6	0.0	14.4	0.2	1
		15.5 ^b	0.3	—
6	15.0	76.2	0.9	1
		68.3 ^b	1.1	—
		77.9 ^b	1.9	—
	25.0	202.0	3	1
		200 ^b	6	—
35.0	197 ^b	2	—	
	503 ^b	12	1	

TABLE II
(Continued)

Compound ^a	°C	$(k_1^0 \pm s_{k_1}) \cdot 10^5$	k/k_H^c
7	15.0	44.9	0.5
	25.0	136	1
	35.0	338	5
8	15.0	23.5	0.3
	25.0	71.3	0.4
		63.3 ^b	1.1
	35.0	181	3
9	15.0	16.3	0.8
	25.0	47.5 ^b	4.0
		42.7 ^b	0.2
	35.0	124	2
10	15.0	13.8	0.9
	25.0	39.7 ^b	2.1
		40.0	1.3
	35.0	111	7
11	35.0	12.1	0.6
	45.0	36.8	1.8
	55.0	106	4
12	25.0	4.42	0.08
	35.0	11.2	0.2
13	45.0	8.95	0.31
	55.0	24.1	1.0
14	45.0	2.52	0.05
	55.0	6.84	0.25

^aNumbers of benzhydryl bromides agree with Table I; ^bconductometric measurements; ^cdetermined for the mean values.

We have found $\beta_{(\gamma)} = 1951 \pm 63\text{K}$ which coincided with $\beta_{(\epsilon)}$ value (hydrolysis of monosubstituted benzhydryl bromides) within experimental error. As this type of studies was not carried out with other substrates, it cannot be estimated to what extent the coincidence of isokinetic temperature of the both dependences has general validity.

Fig. 2 presents the dependence of the reactivity of benzhydryl esters on the Lohmann's constant L . This correlation is treated statistically in Table III. We chose four leaving groups (bromide, chloride, fluoride and acetate) covering a relatively broad

region of the Lohmann's scale of L values⁷. We recalculated the hydrolysis rate constants of these compounds in 80% aqueous acetone for the temperature 25°C and presented them in Table V along with the thermodynamic parameters. The series of esters was extended by benzhydryl trifluoroacetate and 3,5-dinitrobenzoate whose L values are not known. From our experimental data these values could be determined approximatively: $L = -4.40$ and -1.72 for 3,5-dinitrobenzoyloxy and trifluoroacetoxy groups respectively.

The papers on relations between the reactivity and type of leaving groups are not frequent so far. Rather more attention has been paid to reactions of S_N2 type. If we compare the value of the reaction constant (γ 1.445 of the leaving groups of our system) with that of methanolysis of tert-butyl esters^{6,7} (γ 1.585) which proceeds by S_N1 mechanism, too, we may state that substrate is more sensitive to the influence of leaving group in S_N1 reactions as compared to the reactions proceeding by S_N2 mechanism for which the value of the constant approaches unity⁷. The correlation of the dependence of $\log k^X$ of the hydrolysis of benzhydryl esters on the constants L is quite satisfactory (r 0.986; Fig. 2). With respect to the small number of the members of the series, however, this result cannot be given much significance. We presume that the L constants found on the basis of S_N2 reactions of compounds of the type CH_3X with sodium methoxide will depend on the solvating medium.

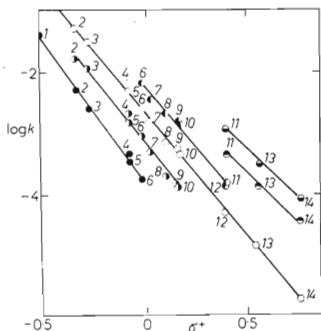


FIG. 1

Dependence of $\log k$ on σ^+ for Hydrolysis of Benzhydryl Bromides at Various Temperatures

Temperature 55°C (◼), 45°C (●), 35°C (○), 25°C (◻), 15°C (◊), 0°C (●); for numbers see Table II.

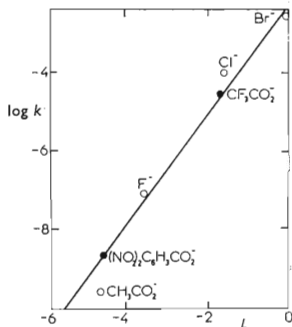


FIG. 2

Dependence of $\log k$ of Hydrolysis of Benzhydryl Esters on Lohmann's L Constants (empty circles)

Full circles denote the L values determined in the present paper.

TABLE III
Statistical Characteristics of LFER of Hydrolysis of Benzhydryl Esters

Relation	°C	$(-\rho \pm s_\rho)$	$s_{1/2}^a$	r^b	ψ^c	n^d	Note
$\log(k/k_H) = \rho\sigma^+$	0.0	4.769 ± 0.032	0.041	1.000	0.015	6	<i>e</i>
	15.0	4.554 ± 0.057	0.034	0.999	0.033	9	<i>e, k</i>
	25.0	4.322 ± 0.045	0.055	0.999	0.037	14	<i>e, g, k</i>
	35.0	4.062 ± 0.040	0.032	1.000	0.024	6	<i>e</i>
	0.0	4.784 ± 0.126	0.109	0.997	0.091	10	<i>f, l</i>
	0.0	4.873 ± 0.267	0.255	0.980	—	8	<i>f, h</i>
	25.0	4.360 ± 0.177	0.098	0.997	0.090	5	<i>f, l</i>
$\frac{\log(k/k_H)^{Cl}}{\log(k/k_H)^{Br}} = Q$	—	1.013 ± 0.020	—	0.998	—	15	<i>i, l</i>
$\log(k/k^{Br}) = \gamma L$	25.0	1.445 ± 0.174	0.197	0.986	0.238	4	<i>j</i>

^aStandard deviation from the regression line; ^bcorrelation coefficient; ^cExner test²⁷; ^dnumber of members of the series; ^ebenzhydryl bromides; ^fbenzhydryl chlorides; ^gextrapolated values of the substituents 4-OC₆H₅, 3-Br, 3-CN and 3-NO₂ were included in this series, too; ^hhydrolysis in 85% aqueous acetone, ref¹¹; ⁱstatistical angular coefficient, Fig. 3; ^jthe value of γ constant was determined for -Br, -Cl, -F and -OCOCH₃ as leaving groups; ^kthe correlation is not substantially improved by using the Yukawa-Tsuno equation⁹; ^lthe series of benzhydryl chlorides from Fig. 3.

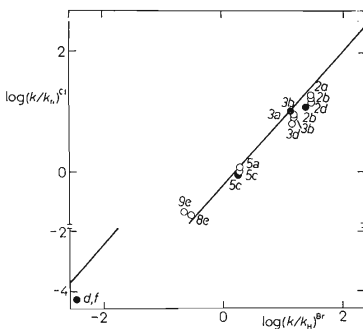


FIG. 3

Relative Reactivities of Monosubstituted Benzhydryl Chlorides and Bromides during Hydrolysis in 80% Aqueous Acetone

For numbers see Table I. The values $\log(k/k_H)^{Cl}$ were taken from literature and are marked with letters *a* (ref.¹²); *b* (ref.¹³); *c* (ref.¹⁴); *d* hydrolysis in 85% aqueous acetone (ref.¹¹); *e* (ref.¹⁰); *f* an extrapolated value from ref.¹⁵ was taken for 4-NO₂ substituent. Full and empty circles represent the hydrolysis at 0°C and 25°C, respectively.

There remains a separate problem *viz.* in what way the leaving group can affect the value of the reaction constant ρ . In Fig. 3 we have compared the values of logarithms of relative hydrolysis rates of monosubstituted benzhydryl bromides with those of benzhydryl chlorides in 80% aqueous acetone; the latter values were taken from ref.¹⁰⁻¹⁵. Table III presents the statistical characteristics of the LFFR of benzhydryl chlorides at 0 and 25°C for the members given in Fig. 3. We have also compared the values of hydrolysis rate constants in 85% aqueous acetone² with our results for benzhydryl bromides, because the relative reaction rates remain practically unchanged by such a small change of solvent structure⁵. From Table III and Fig. 3 it follows that, under corresponding conditions, the reaction constants are identical within experimental error. This agreement was confirmed statistically in other way (Table III; $Q \approx 1$). From several papers it follows that the reaction constant ρ depends on the leaving group. *E.g.* Buckson and Smith² gave the values $\rho = -4.64$ and -2.90 for ethanolyse of cumyl chlorides and thionbenzoates respectively. Hoffmann³ found $k_1 = 24.6 \cdot 10^{-5} \text{ s}^{-1}$ for ethanolyse (at 75°C) of 4-nitrobenzyl tosylate and bromide $k_1 = 1.2 \cdot 10^{-5} \text{ s}^{-1}$ respectively ($k^{0\text{Tos}}/k^{\text{Br}} \approx 20$), and $k_1 = 41.0 \cdot 10^{-5} \text{ s}^{-1}$ and $0.184 \cdot 10^{-5} \text{ s}^{-1}$ for ethanolyse (at 25°C) of 4-methylbenzyl tosylate and bromide respectively ($k^{0\text{Tos}}/k^{\text{Br}} \approx 223$). These results of studies

TABLE IV

Activation Parameters of Hydrolysis of Monosubstituted Benzhydryl Bromides in 80% Aqueous Acetone

Compound ^a	ΔH^\ddagger , kcal/mol		$-\Delta S^\ddagger$, cal grad ⁻¹ mol ⁻¹	
	<i>b</i>	<i>c</i>	<i>b</i>	<i>c</i>
1	12.5	13.2	19.2	16.7
2	14.9	14.5	14.6	16.2
3	15.0	14.8	15.3	16.0
4	15.5	15.9	16.9	15.4
5	16.4	16.1	14.4	15.4
6	16.2	16.6	16.5	15.1
7	17.2	16.9	13.9	15.0
8	17.4	17.3	14.6	14.8
9	17.3	17.6	15.8	14.7
10	17.8	17.7	14.4	14.6
11	21.2	19.2	7.8	14.0
12	16.4	19.3	23.5	13.9
13	19.9	20.3	14.6	13.5
14	20.1	21.2	16.6	13.0

^aFor numbers see Table I; ^bnon-isokinetic values; ^cisokinetic values.

TABLE V
Rate Constants and Activation Parameters of Hydrolysis of Benzhydryl Esters in 80% Aqueous Acetone Medium

Leaving group	$(k_1 \pm s_{k_1}) \cdot 10^5, s^{-1}$	$t, ^\circ C$	$\log k_1^a$	$\Delta H^\ddagger \pm s_{\Delta H^\ddagger}$ (kcal/mol)	$-\Delta S^\ddagger \pm s_{\Delta S^\ddagger}$ (e. u.)	L^b	pK_a^b
Chloride	7.30 ± 0.28	25.0	-4.137	20.9 ± 0.3	7.5 ± 0.9	-1.61	-4.14
	22.22 ± 0.41	35.0					
	71.15 ± 0.86	45.0					
Trifluoroacetate	2.04 ± 0.01	25.0	-4.691	21.3 ± 0.2	8.5 ± 0.5	-1.72 ^d	0.23 ^c
	6.18 ± 0.01	35.0					
	20.88 ± 0.42	45.0					
Fluoride	2.03 ± 0.03	70.0	-7.078	25.4 ± 0.4	6.5 ± 1.1	-3.60	3.14
	6.45 ± 0.04	80.0					
	16.60 ± 0.83	90.0					
3,5-Dinitrobenzoate	0.678 ± 0.033	100.0	-8.578	28.2 ± 0.2	8.1 ± 0.6	-4.40 ^d	2.82 ^c
	1.93 ± 0.17	110.0					
	4.81 ± 0.02	120.0					
Acetate	0.988 ± 0.007	120.0	-9.528	26.2 ± 0.2	15.8 ± 0.6	-4.68	4.72
	2.21 ± 0.05	130.0					
	5.21 ± 0.03	140.0					

^aExtrapolated to the temperature 25°C; ^btaken from ref.⁶; ^ctaken from ref.³⁰; ^dcalculated from our experimental values according to Eq. (1).

of the reactions proceeding by S_N1 mechanism would suggest a dependence of ρ constant on leaving group. On the contrary, from our measurements of hydrolysis rate of benzhydryl bromides and from literature data on benzhydryl chlorides it follows that the both reaction constants are identical (Table III) even though the hydrolysis rate of benzhydryl bromides is about 30 times greater.

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Translated by J. Panchartek.