

REACTIVITY OF COMPOUNDS OF DIPHENYLMETHANE SERIES. VI.\*  
 HYDROLYSIS OF BENZHYDRYL BROMIDES IN 80% ACETONE;  
 CUMULATIVE EFFECT OF SUBSTITUENTS

J. MINDL and M. VEČEŘA

*Department of Organic Chemistry,  
 Institute of Chemical Technology, 532 10 Pardubice*

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The substituents contributions have been found to be not additive in hydrolysis of disubstituted benzhydryl bromides in 80% acetone. Whereas electronegative substituents in 3,3'-positions slightly diminish the reactivity, the same ones in 3,5-positions increase the reactivity more than it was presumed. These deviations were expressed by  $\iota$  values and compared with literature data. On the basis of isokinetic relation the hydrolysis mechanism has been predicted to be the same for all compounds of the series investigated.

The previous study<sup>1</sup> of protonation equilibria of 3,4'- and 4,4'-disubstituted benzhydrols showed that the contributions of substituents were not additive in shifting the equilibria. The deviations from additive values were proportional to the product of the both substituent constants (Eq. (1)).

$$\Delta pK_R^+ = (\sigma_X^+ + \sigma_Y^+ + \iota\sigma_X^+\sigma_Y^+) \quad (1)$$

Similar deviations were found in the case of reactions taking place at the  $\alpha$ -carbon atom of aryl-alkyl derivatives and characterized by carbonium ion formation<sup>2-5</sup>. In all the cases the real reactivity was different from that corresponding to the sum of contributions of the both substituents.

The non-additivity found in the benzhydryl system substituted at 3,4'- and 4,4'-positions led to questions as to how the influence from other positions would make itself felt and by what the deviations were caused. Therefore, series of benzhydryl bromides substituted at 3,3'- and 3,5-positions were chosen and submitted to hydrolyses in 80% acetone. The titration and conductometric methods described in our previous report<sup>6</sup> were used for determination of rate constants.

## EXPERIMENTAL

### Reagents

The benzhydryl bromides were prepared from the corresponding benzhydrols by reaction with phosphorus tribromide, methoxybenzhydryl bromides were prepared by reaction with

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phosphorus tribromide in the presence of pyridine as it is given in ref.<sup>6</sup>. Physical properties of the benzhydryl bromides and results of elemental analyses are given in Table I.

*Benzhydrols* were synthesized from the corresponding benzophenones by reduction with sodium borohydride in methanol. After about 40 minutes boiling the mixture was mixed with a large amount of acidified water, and the product was isolated by extraction with ether, distilled

TABLE I  
Physical Constants and Elemental Analyses of Benzhydryl Bromides

No	Substituents	B. p., °C/Torr $n_D^{20}$	Formula m. w.	% Br <sup>a</sup>	
				Calc./Found	
1	3-Br, 3'-NO <sub>2</sub>	—	C <sub>13</sub> H <sub>9</sub> Br <sub>2</sub> NO <sub>2</sub> 371.0	21.54	
		1.6563		21.08	
2	3-Br, 5-NO <sub>2</sub>	—	C <sub>13</sub> H <sub>9</sub> Br <sub>2</sub> NO <sub>2</sub> 371.0	21.54	
		1.6540 <sup>b</sup>		21.17	
3	3,3'-Br <sub>2</sub>	178—80/0.25	C <sub>13</sub> H <sub>9</sub> Br <sub>3</sub> 404.9	19.74	
		1.6609		19.49	
4	3,5-Br <sub>2</sub>	193—195/1	C <sub>13</sub> H <sub>9</sub> Br <sub>3</sub> 404.9	19.74	
		1.6590		19.33	
5	3,5-(OC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	—	C <sub>25</sub> H <sub>19</sub> BrO <sub>2</sub> 431.3	18.53	
		—		18.40	
6	3,3'-(NO <sub>2</sub> ) <sub>2</sub>	143—145 <sup>c</sup>	C <sub>13</sub> H <sub>9</sub> BrN <sub>2</sub> O <sub>4</sub> 337.1	23.71	
		—		23.30	
7	3,5-(NO <sub>2</sub> ) <sub>2</sub>	—	C <sub>13</sub> H <sub>9</sub> BrN <sub>2</sub> O <sub>4</sub> 337.1	23.71	
		1.6052		23.65	
8	3-NO <sub>2</sub> , 4'-OCH <sub>3</sub>	—	C <sub>13</sub> H <sub>12</sub> BrNO <sub>3</sub> 322.2	24.80	
		1.6150		24.44	
9	3-Br, 5-NO <sub>2</sub> , 4'-OCH <sub>3</sub>	—	C <sub>14</sub> H <sub>11</sub> Br <sub>2</sub> NO <sub>3</sub> 401.1	19.77	
		—		19.61	
10	3,5-(NO <sub>2</sub> ) <sub>2</sub> , 4'-OCH <sub>3</sub>	—	C <sub>14</sub> H <sub>11</sub> BrN <sub>2</sub> O <sub>5</sub> 367.2	21.76	
		1.5652 <sup>b</sup>		21.65	
11	3,3'-(CF <sub>3</sub> ) <sub>2</sub>	124—126/2	C <sub>15</sub> H <sub>9</sub> BrF <sub>6</sub> 383.1	20.86	
		1.5067		20.48	
12	3,3'-(CH <sub>3</sub> ) <sub>2</sub>	120—122/2	C <sub>15</sub> H <sub>15</sub> Br 275.2	29.04	
		1.5799		28.95	
13	3,5-(CH <sub>3</sub> ) <sub>2</sub>	122—125/2	C <sub>15</sub> H <sub>15</sub> Br 275.2	29.04	
		1.6112		29.10	
14	3-CF <sub>3</sub>	142—143/8	C <sub>14</sub> H <sub>10</sub> BrF <sub>3</sub> 315.2	25.36	
		1.5475		15.26	

<sup>a</sup> The data involves only the bromine bound to aliphatic CH group. Its content was determined alkalimetrically after hydrolysis in 50% aqueous acetone in a sealed ampoule at 150°C during 5 days reaction. <sup>b</sup> Determined at 25°C. <sup>c</sup> M.p., °C.

in vacuum or crystallized from *n*-heptane. 3-Trifluoromethylbenzhydrol was prepared by the Grignard reaction from 3-trifluoromethylphenylmagnesium bromide and benzaldehyde. M.p. 62–63.5°C, ref.<sup>7</sup> gives m.p. 63.5–65°C. 3,3'-Bis(trifluoromethyl)benzhydrol was prepared similarly by the reaction of 3-trifluoromethylphenylmagnesium bromide with ethyl formate. M.p. 48–49.5°C, ref.<sup>7</sup> gives m.p. 48–49.5°C. 3,3'-Dimethyl- and 3,5-dimethylbenzhydrols were prepared by a procedure similar to that described by Nishida<sup>2</sup>. Physical constants and elemental analyses of the benzhydrols are given in Table II.

**Benzophenones.** 3-Nitro-3'-bromobenzophenone was prepared by heating 22.7 g *m*-nitrobenzophenone, 5.2 ml bromine, 0.25 g iodine and 2 ml water in a glass ampoule at 160°C for five hours. After cooling, the product was extracted with benzene. The benzene layer was successively washed with 20% sodium hydroxide, water, 10% sodium dithionite and water. After evaporation of benzene, the product was crystallized from ethanol. Yield 24 g (78.2%), m.p. 121–122°C; for C<sub>13</sub>H<sub>8</sub>BrNO<sub>3</sub> (306.1) calculated: 51.01% C, 2.63% H, 4.57% N; found: 51.22% C, 2.67% H,

TABLE II  
Physical Constants and Elemental Analyses of Benzhydrols

Substituents	M.p., °C <i>n</i> <sub>D</sub> <sup>20</sup>	Formula m.w.	Calculated/Found		
			% C	% H	% N
3-Br, 3'-NO <sub>2</sub>	—	C <sub>13</sub> H <sub>10</sub> BrNO <sub>3</sub>	50.67	3.27	4.55
	1.6250	308.1	50.64	3.89	4.84
3-Br, 5-NO <sub>2</sub>	75–77	C <sub>13</sub> H <sub>10</sub> BrNO <sub>3</sub>	50.67	3.27	4.55
	—	308.1	50.54	3.55	4.87
3,3'-Br <sub>2</sub>	181–185/2 <sup>a</sup>	C <sub>13</sub> H <sub>10</sub> Br <sub>2</sub> O	45.65	2.95	—
	1.6145	342.0	46.01	3.02	—
3,5-Br <sub>2</sub>	71–72	C <sub>13</sub> H <sub>10</sub> Br <sub>2</sub> O	45.65	2.95	—
	—	342.0	45.87	3.00	—
3,5-(OC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	245–248/2 <sup>a</sup>	C <sub>25</sub> H <sub>20</sub> O <sub>3</sub>	81.50	5.47	—
	1.6190	368.4	82.22	5.31	—
3,3'-(NO <sub>2</sub> ) <sub>2</sub>	105.5–106.5	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub>	56.94	3.67	10.22
	—	274.2	57.26	4.01	10.49
3,5-(NO <sub>2</sub> ) <sub>2</sub>	79–80.5	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub>	56.94	3.67	10.22
	—	274.2	57.04	3.78	10.53
3-NO <sub>2</sub> , 4'-OCH <sub>3</sub>	87–88.5	C <sub>14</sub> H <sub>13</sub> NO <sub>4</sub>	64.86	5.05	5.40
	—	259.3	65.08	5.27	5.15
3-Br, 5-NO <sub>2</sub> , 4'-OCH <sub>3</sub>	—	C <sub>14</sub> H <sub>12</sub> BrNO <sub>4</sub>	49.73	3.59	4.17
	1.5954	338.2	49.57	3.10	4.11
3,5-(NO <sub>2</sub> ) <sub>2</sub> , 4'-OCH <sub>3</sub>	—	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>6</sub>	55.26	3.98	9.21
	—	304.3	55.58	3.63	9.20

<sup>a</sup> B.p., °C/Torr.

4.87% N. 3-Bromo-5-nitrobenzophenone was prepared by the Friedel-Crafts reaction of 3-bromo-5-nitrobenzoyl chloride with benzene. The raw product was crystallized from ethanol. M.p. 98.5–99°C; for  $C_{13}H_8BrNO_3$  (306.1) calculated: 51.01% C, 2.63% H, 4.57% N; found: 51.09% C, 2.74% H, 4.77% N. 3,5-Dibromobenzophenone was prepared similarly, m.p. 71–72°C; for  $C_{13}H_8Br_2O$  (340.0) calculated: 45.92% C, 2.37% H; found: 46.25% C, 2.28% H. 3,5-Diphenoxybenzophenone was prepared from 3,5-dibromobenzophenone by melting with potassium phenolate in the presence of copper (*cf.* our preparation of 3-phenoxybenzophenone<sup>8</sup>); pale yellow viscous oil, b.p. 240–244°C/1 Torr,  $n_D^{20}$  1.6358; for  $C_{25}H_{18}O_3$  (366.4) calculated: 81.95% C, 4.95% H; found: 81.61% C, 5.06% H. 3,5-Dinitro-4'-methoxybenzophenone was prepared by reaction of 3,5-dinitrobenzoyl chloride with anisol in the presence of  $AlCl_3$ . The raw product was isolated, washed with water and 10% sodium hydroxide and crystallized from ethanol; m.p. 118.5–119.5°C; for  $C_{14}H_{10}N_2O_6$  (302.2) calculated: 55.63% C, 3.34% H, 9.27% N; found: 55.96% C, 3.65% H, 9.20% N. The abovementioned reaction also gave 3,5-dinitro-4'-hydroxybenzophenone, m.p. 176–177°C; for  $C_{13}H_8N_2O_5$  (290.2) calculated: 9.65% N; found: 10.00% N. The hydroxybenzophenone was methylated with dimethyl sulphate in alkaline medium to give the corresponding methoxybenzophenone. 3-Bromo-5-nitro-4'-methoxybenzophenone was prepared similarly by reaction of 3-bromo-5-nitrobenzoyl chloride with anisol; m.p. 95.5–96.5°C; for  $C_{14}H_{10}BrNO_4$  (336.2) calculated: 50.02% C, 2.99% H, 4.16% N; found: 50.42% C, 3.34% H, 4.16% N.

3-Bromo-5-nitrobenzoyl chloride, b.p. 189–192°C/20 Torr,  $n_D^{20}$  1.6151, was prepared by reaction of thionyl chloride with 3-bromo-5-nitrobenzoic acid. This acid (m.p. 160–161°C) was synthesized by hydrolysis of its methyl ester.

*Methyl 3-bromo-5-nitrobenzoate.* A mixture of 122 g methyl 3-nitrobenzoate, 100 g silver sulphate and 750 ml conc. sulphuric acid was stirred and heated at 90°C in a flask equipped with a stirrer, reflux condenser and separatory funnel. 37 ml bromine was added drop by drop to this mixture during 2 hours. The reaction mixture was stirred at the mentioned temperature for another 2 hours. After cooling the precipitated silver bromide was filtered off, and the filtrate was mixed with 2 l water and 1 kg crushed ice. The product precipitated was collected by suction and washed with water to yield 167 g (93%) raw material; after crystallization from methanol it melted<sup>9</sup> at 70–71°C.

### Kinetic Measurements

With respect to the stability of the carbonium ion it was necessary to take into account the reversibility of its formation. The way of determination and calculation of  $k_1^0$  values was similar to that given in our previous report<sup>6</sup> where the respective references are included, too. The reactions having half-lives  $t_{1/2} < 2$  minutes were followed only by means of a conductometer Radelkis OK-102/1 connected with a recorder.

## RESULTS AND DISCUSSION

Table III gives the hydrolysis rate constants of nineteen mono- and polysubstituted benzhydryl bromides in 80% aqueous acetone at various temperatures. For the sake of discussion, the whole set was divided into four groups: monosubstituted, 3,5-disubstituted, 3,3'-disubstituted and 3'-methoxy-3,5-trisubstituted benzhydryl bromides. The first group was supplemented by 3-trifluoromethylbenzhydryl bromide. The  $\sigma^+$  value 0.52 given by Brown<sup>10</sup> stands in accord with that found by us for  $CF_3$

TABLE III  
Hydrolysis Rate Constants  $k_1^0$  ( $s^{-1}$ ) of Mono- and Polysubstituted Benzhydryl Bromides in 80% Aqueous Acetone

Compound <sup>a</sup>	$t, ^\circ C$	$k_1^0 \cdot 10^4$	$\log(k/k_0)_{exp}$	$\log(k^{exp}/k^{add})$
1	75.0	0.215	-3.672	-0.052
	85.0	0.564		
	95.0	1.87		
2	65.0	0.485	-2.925	0.694
	75.0	1.20		
	85.0	3.29		
3	65.0	0.810	-2.672	0.004
	75.0	2.15		
	85.0	6.07		
4	55.0	0.408	-2.410	0.266
	65.0	1.52		
	75.0	3.93		
5	45.0	5.46	-1.172	0.072
	55.0	12.1		
	75.0	67.9		
6	85.0	0.051	-4.794 <sup>b</sup>	-0.231
	95.0	0.208		
	105.0	0.564		
7	75.0	0.986	-3.052	1.511
	65.0	0.352		
	85.0	2.68		
8	-5.0	74.2	-2.434 <sup>c</sup>	
	5.0	170.0		
	15.0	355		
9	5.0	33.6	-3.845 <sup>c</sup>	0.717
	15.0	71.7		
	25.0	161.4		
10	15.0	35.5	-4.868 <sup>c</sup>	1.289
	25.0	53.4		
	35.0	161.4		
11	75.0	0.314	-3.507	-0.135
	85.0	0.937		
	95.0	2.29		
12	15.0	37.6	-	-
	35.0	174		
	55.0	790		

TABLE III  
(Continued)

Compound <sup>a</sup>	<i>t</i> , °C	<i>k</i> <sub>1</sub> <sup>0</sup> · 10 <sup>4</sup>	log ( <i>k</i> / <i>k</i> <sub>0</sub> ) <sub>exp</sub>	log ( <i>k</i> <sup>exp</sup> / <i>k</i> <sup>add</sup> )
13	15.0	41.9		
	35.0	174		
	55.0	798	0.524	0.001
14	25.0	0.156	-2.108	—
	45.0	1.34		
	75.0	20.8	-1.686	—
15	55.0	239		
	65.0	498		
	75.0	1 010	0	—
16	45.0	200		
	55.0	437	0.262	
17	75.0	241	-0.622	—
18	65.0	18.1		
	75.0	46.4	-1.686	—
19	75.0	5.28	-2.282	—

<sup>a</sup> For numbers see Table I. Substituents in the compound 15 H, 16 3-CH<sub>3</sub>, 17 3-OC<sub>6</sub>H<sub>5</sub>, 18 3-Br, and 19 3-NO<sub>2</sub>. <sup>b</sup> Extrapolated for 75°C. <sup>c</sup> Experimental value of *k* compared to the value *k*<sub>0</sub> = = *k*<sub>4'-OCH<sub>3</sub></sub> (Fig. 1) for the temperature 15°C.

substituent (0.49). We tried to determine the rate constants of all the substances in the narrowest possible temperature range to enable the comparison with the disubstituted derivatives and exclude the errors due to extrapolation using the Arrhenius relation. Fig. 1 gives the hydrolysis rate constants of benzhydryl bromides measured at 75°C plotted against the sum of substituent constants. The set involves the both disubstituted series and is supplemented by the rate constants of necessary monosubstituted benzhydryl bromides. The straight line *a* drawn through the points corresponds to the hydrolysis of the benzhydryl bromides carrying a constant substituent 4'-OCH<sub>3</sub> (at 15°C), the straight line *b* corresponds to the hydrolysis of the mono- and disubstituted benzhydryl bromides not carrying this substituent (at 75°C). Full circles correspond to monosubstituted benzhydryl bromides, halved circles correspond to 3,5-disubstituted (resp. 4'-methoxy-3,5-disubstituted) ones, and empty circles correspond to 3,3'- (resp. 3,4'-OCH<sub>3</sub>) disubstituted ones. The values of the substances 6, 12, 13, 15, 16 were extrapolated from the values obtained at different temperatures. The rate constant value of the substance 20, which corresponds to 4-methoxybenzhydryl bromide, was determined by extrapolation of the data given

in our previous report<sup>6</sup> ( $\log k_{4-\text{OCH}_3} \approx 0.99$ ). The point 21 corresponds to the value of 3-bromo-4'-methoxybenzhydryl bromide obtained by extrapolation ( $\log k_{3-\text{Br}-4'-\text{OCH}_3} \approx -0.43$ ).

From this picture it is obvious that the reactivity of the 3,3'-disubstituted series is practically additive (corresponding to the sum of the respective substituent constants) or slightly lower, whereas it is considerably higher for 3,5-disubstituted derivatives. Fig. 2 gives a graphical comparison of derivatives having various combinations of substituents.

$$\log(k_{XY}^{\text{exp}}/k_0) = \log(k_{XY}^{\text{add}}/k_0) + \nu\sigma_X^+ \log(k_Y^{\text{exp}}/k_0) \quad (2)$$

As the Eq. (1) can be transformed into Eq. (2), the parameters of individual axes (Fig. 2) were chosen in such a way that angular coefficients of the straight lines drawn through the points express the  $\nu$  values of individual combinations of substituent positions. For the sake of comparison the same Fig. gives literature data

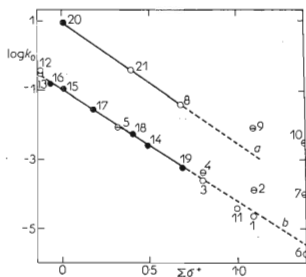


FIG. 1

Correlation of Logarithms of Hydrolysis Rate Constants  $k_1^0$  of Substituted Benzhydryl Bromides in 80% Aqueous Acetone with Sum of Substituent Constants  $\sigma^+$

For numbers see Table III, for description of the straight lines and points see text (p. 3501).

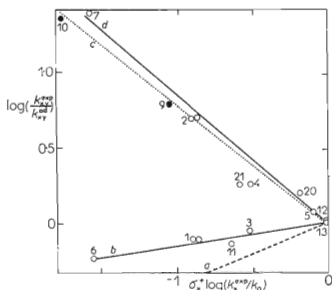


FIG. 2

$\nu$  Values Found for Substituent Combinations in 4,4'-Positions (a), 3,3'-Positions (b), 4'-OCH<sub>3</sub>-3,5-Positions (c), and 3,5-Positions (d)

The values were obtained from the hydrolysis rate constants of benzhydryl bromides. For numbers see Tables I and II. The point 20 corresponds to the hydrolysis of 3,5-dichlorobenzyl chloride in 50% ethanol at 60°C (ref. 1<sup>3</sup>); the point 21 corresponds to ethanolysis of 3,5-dichlorobenzhydryl chloride<sup>2</sup> at 25°C.

(processed in the same way) of solvolysis of benzhydryl chlorides<sup>2,3</sup> and those of protonation equilibria of 4,4'-disubstituted benzhydrols<sup>1</sup>. (The experimental points are not given to avoid confusion.) The dependence given in Fig. 2 shows a marked quantitative difference between the reactivity of the derivatives disubstituted at one or both nuclei ( $t_{3,3'} = 0.18$ ;  $t_{4,4'} = 0.40$ ;  $t_{3,5'} = -0.85$ ).

Physical interpretation of the  $t$  constant giving the direction and magnitude of the deviation from additivity is not simple. It can involve direct interactions between substituents or interactions through the reaction centre or changes of molecular geometry caused by a further substituent or eventually combinations of these effects. Using a similar model, Bergmann and Dubois found deviations from additivity in the case of electrophilic addition of bromine to 3,4'- and 4,4'-disubstituted 1,1-diarylethylenes<sup>4</sup>. The authors explain the non-additivity by a change of position of the planes of both nuclei caused by introduction of a further substituent. By processing their experimental data we found that the extent of non-additivity is the same

TABLE IV

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

Compound <sup>a</sup>	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>		$-\Delta S^\ddagger$ , cal grad <sup>-1</sup> mol <sup>-1</sup>	
	<i>b</i>	<i>c</i>	<i>b</i>	<i>c</i>
1	26.8	25.7	3.31	6.31
2	22.3	23.6	12.5	8.7
3	23.5	23.0	8.0	9.5
4	25.0	22.4	2.3	10.1
5	17.9	18.9	17.2	14.3
6	31.6	28.6	5.3	2.9
7	23.7	24.0	9.2	8.4
8	11.5	12.5	25.3	21.7
9	12.3	13.8	25.4	20.1
10	14.3	14.8	20.6	18.9
11	24.6	25.3	8.7	6.8
12	13.7	14.5	22.1	19.4
13	13.2	14.5	23.6	19.5
14	19.5	20.3	14.9	12.6
15	15.8	15.8	17.9	17.8
16	15.4	15.2	17.9	18.5
17	16.4	17.3	18.9	16.1
18	21.2	19.3	7.8	13.8
19	22.4	21.9	9.4	10.7

<sup>a</sup> For numbers see Tables I and II. <sup>b</sup> Non-isokinetic values. <sup>c</sup> Isokinetic values ( $\beta$  571°C).



for these combinations of substituents, as it is in the series of the disubstituted benzhydrols. The reactivity change of these compounds corresponds well to Eq. (1) using the value  $\iota = 0.4$ . As far as the change of the angle of deviation of nuclear planes is connected predominantly with the resonance effects of substituents, the deviations should not attain such extent as those of 3,4'- and 4,4'-disubstituted derivatives, but their direction should be retained. From Fig. 2 it is obvious that this presumption could explain the deviations found. However, it is not excluded that there are further possible explanations.

The effect of interactions between substituents acting from 3- and 5-positions of the same nucleus differs in magnitude and direction, as it is shown in Fig. 2 ( $\iota_{3,5} = -0.85$ ). Comparison of the additivity of substituent effects of the individual reaction series of the substituted benzhydryl bromides necessitates both the same reaction conditions and the same hydrolysis mechanism for all the model substances involved. *E.g.* it is known that a similar hydrolysis of electropositively substituted benzyl chlorides takes the  $S_N1$  course, whereas 4-nitrobenzyl chloride reacts by both  $S_N1$  and  $S_N2$  mechanisms under the same conditions<sup>11</sup>. The presumption of uniform mechanism was supported by verification of validity of the isokinetic relation, *i.e.* processing the kinetic data of various temperatures with the use of a computer<sup>12</sup>. The isokinetic temperature  $\beta = 571 \pm 59^\circ\text{C}$  was calculated from hydrolysis rate constants of nineteen mono- and polysubstituted benzhydryl bromides given in the present paper and from those of nine further monosubstituted derivatives given in the previous report<sup>6</sup>. Table IV presents the activation parameters of hydrolysis

TABLE V  
Dependence of Reaction Constant  $\rho$  of Hydrolysis of Benzhydryl Bromides on Temperature

Constant substituent	$t, ^\circ\text{C}$	$-\rho^a$	$-\rho^b$
H	0	4.8 <sup>c</sup>	—
	25	4.3 <sup>c</sup>	—
	75	2.9	—
3-Br	65	2.5	3.4
	75	2.5	3.3
3-NO <sub>2</sub>	75	1.4	3.5
	85	1.4	3.6
	95	—	3.2
3-NO <sub>2</sub> , 4'-OCH <sub>3</sub>	15	1.4	—

<sup>a</sup> Changing substituents at the 5-position. <sup>b</sup> Changing substituents at the 3'-position. <sup>c</sup> The values taken from ref. <sup>6</sup>.

of the substituted benzhydryl bromides compared to the analogous values calculated on the basis of the  $\beta$  value (isokinetic parameters). A further support of the uniform  $S_N1$  mechanism was directed to the series disubstituted at 3- and 5-positions. The polysubstituted benzhydryl bromides carrying 4'-methoxy group (compounds 8–10 in Table I) were synthesized for this purpose and tested kinetically in analogous way. Table III gives the hydrolysis rate constants  $k_1^0$  of these compounds in 80% aqueous acetone at various temperatures. From the experiments it follows that the hydrolysis of the 3,5-disubstituted benzhydryl bromides proceeds by  $S_N1$  mechanism probably in the whole series. The following observations lead to this conclusion: character of the deviations of the 3,5-disubstituted and 4'-methoxy-3,5-trisubstituted benzhydryl bromides is approximatively the same, as it can be seen in Fig. 2 (comparison of angular coefficients of the straight lines *c* and *d*). A change of the  $S_N1$  mechanism by introduction of 4'-methoxy group is considered not to be very likely. So far we have not enough data for explanation of the magnitude and direction of the  $\iota$  constant.

Table V shows the influence of temperature on the magnitude of hydrolysis rate constant of benzhydryl bromides. From the comparison of the individual values it follows that this influence can only be studied in a sufficiently broad temperature range ( $\rho$  value is  $-4.8$  and  $-2.9$  at  $0^\circ\text{C}$  and  $75^\circ\text{C}$ , respectively). The Table also shows the influence of a constant substituent on the magnitude of the reaction constant. Electronegative substituents at 3'-position increase the  $\rho$  value, whereas the same ones at 5-position decrease this value. The change of the reaction constant  $\rho$  caused by a further substituent follows from the  $\iota$  value of the corresponding combination of substituents. Similar deviations were found in our study of influence of constant substituents in a series of disubstituted benzhydrols<sup>1</sup>.

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