ADAMANTANE COMPOUNDS. IV.*

β-(1-ADAMANTYLCARBONYL)-β-HALOGENOACRYLIC ACIDS AND THEIR ESTERS

M.KUCHAŘ and B.KAKÁČ

Research Institute of Pharmacy and Biochemistry, Prague 3

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Esters of β-(1-adamantylcarbonyl)-β-chloro(bromo)acrylic acids were prepared by Wittig reaction of triphenyl-(1-adamantylcarbonyl)-chloro(bromo)methylenephosphorane with the ethyl ester of glyoxylic acid. The IR spectroscopy of the reaction products showed that the presence of halogens in the above phosphoranes is practically without effect on the ratio of *cis-trans* isomers in the reaction product. Acidolysis of these esters yielded the corresponding γ-(1-adamantyl)-γ-hydroxy-β-chloro(bromo)-$\Delta^{\alpha,\beta}$-crotonolactones, accompanied in the crude state by mere traces of the isomeric linear acids. The effects of halogens on lactonization is discussed.

In connection with the synthesis of adamantane analogues of β-acylacrylic acids we prepared esters of β-halogen-β-(1-adamantylcarbonyl)acrylic acids and, by an acidolysis, their β-halogeno-γ-lactonols *IVb,c*. For the preparation of esters *IIIb,c* we have selected Wittig's reaction, similarly to previous cases[1,2]. (equation A) It represents the only direct synthesis of aliphatic analogues since the other direct methods are based on Friedel-Crafts' reactions of the anhydride of bromomaleic acid[3] or of mucochloric or mucobromic acid[4,5] and they are applicable only in the aromatic series. The possibility of synthesis of aliphatic compounds of this type is indicated by the recently described reaction of mucobromic acid with alkylmagnesium halogenides which yields γ-alkyl-α,β-dibromo-$\Delta^{\alpha,\beta}$-crotonolactones[6].

Halogenophosphoranes *Ib,c* – the starting compounds for Wittig's reaction, were obtained by halogenation of phosphorane *Ia*, analogously to Denney and Ross[7]. Their pK_a values – 5·75 for *Ib* and 6·75 for *Ic* – support the general finding that[8] the halogen at the α-carbon in resonance-stabilized alkylidene-phosphoranes decreases through its $-I$ effect their basicity as compared with the corresponding nonhalogenated phosphorane (pK_a of *Ia* was 7·25).

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Reaction of phosphoranes *Ib,c* with ethyl glyoxylate yielded esters of β-halogeno acids *IIIb,c*; reaction of the nonhalogenated phosphorane *Ia* yielded the ester of β-(1-adamantylcarbonyl)acrylic acid (*IIIa*) (ref.[1]). Treatment of the reaction mixture by evaporation of benzene, extraction of the residue with light petroleum and condensation, yielded the crude esters *IIIb,c* which were subjected to chromatography on a column of silica gel, eluting with a mixture of light petroleum and ether (8 : 1). In these products, we determined the total content of ester *IIIb* and *IIIc* (irrespective of the geometric arrangement of the substituents at the double bond), proceeding from the UV spectrum with a maximum at 211 nm and 226 nm, respectively, and from the halogen content (*cf.* Table I). In this way the reaction yield was calculated. Preparative chromatography of the esters thus obtained on a thin layer of Kieselgel KGF_{254} resulted in the isolation of pairs of substances with close values of R_F, the IR spectra of which corresponded to the assumed structure (see Table III) and differed only in the wavenumber $\nu = 1150\ cm^{-1}$ for *IIIb* and $\nu = 1160\ cm^{-1}$ for *IIIc*; in both cases the isomer present in greater amount showed the maximum at this wavenumber. These maxima were ascribed to the *trans* configuration of substituents at the double bond —CX=CH— because Wittig's reaction of resonance-stabilized alkylidenephosphoranes generally yields reaction products with prevalent *trans*-isomers[9-11] and because the literature contains several cases when the wavenumber for the =C—H bond at the carbon double bond is shifted to the region of $1150\ cm^{-1}$ (ref.[12,13]).

The determination of the *cis-trans* ratio could not be done on the basis of IR spectra of products after chromatography on a column of silica gel. The products thus obtained are not pure since thin-layer chromatography revealed traces of im-

TABLE I

Preparation of Esters $1\text{-}C_{10}H_{15}COCX{=}CHCOOC_2H_5$

X	Yield[a] %	Content of ester[b], % according to UV	Content of ester[b], % according to estimation of X	Content of *cis*[c] %	K[d]
H	74·8	87·2	87·5[e]	5·7 ± 2·0	2·50 (2·36)
Cl	70·1	85·7	87·9	11·3 ± 2·0	1·85 (1·64)
Br	82·2	90·3	87·4	9·5 ± 2·0	1·59 (1·44)

[a] The yield was determined from the content of the ester in the crude product. [b] In the crude product. [c] The content of the *cis* isomer referred to the pure product. [d] $K = \varepsilon_{ester}/\varepsilon_{trans}$, the values in parentheses correspond to the *trans*-isomer. [e] The content was determined by titration after alkaline saponification.

purities which could not be identified but which probably interfere with the wavenumber characteristic for the ester group (about 1720 cm^{-1}). Therefore, the esters after column chromatography were purified by preparative chromatography on a thin layer of Kieselgel KGF_{254}. To determine the ratio of *cis-trans* isomers, chloroform was applied to the extraction of both spots corresponding to the isomeric esters. On the basis of IR spectra, the *cis-trans* ratio was determined in analogy to the esters of β-(1-adamantylcarbonyl)-α-halogenacrylic acids[2], *i.e.* by comparing the ratio of absorbances of the wavenumber corresponding to the ester group (1726 and 1718 cm^{-1}, respectively) and the *trans*-configuration of the substituents at the double bond (1150 and 1160 cm^{-1}, respectively) of the mixture and of the *trans*-isomer standard. In view of the fact that the maxima characteristic for the *trans*-configuration are shifted into a region in which absorption due to chloroform may play a role we used for the calculation of the above ratio the values of absorbances not corrected by the method of the basal line. Pure *trans*-isomers were prepared by crystallization of the first two chromatographic fractions in which the *cis*-isomer was detected only in traces.

Analogously, the nonhalogenated ester *IIIa* was isolated. The total content of the *IIIa* ester was determined from the UV spectrum (λ = 226 nm) and by titration after alkaline saponification. After preparative chromatography on a thin layer of Kieselgel KGF_{254}, the IR spectrum of the product thus obtained was used for calculating the *cis-trans* ratio from absorbances at 1726 and 984 cm^{-1} by the same procedure as used in a previous communication[2].

It follows from Table I that in all three products *IIIa,b,c* the *cis-trans* ratio of isomers differs only insignificantly and that the content of the *trans*-isomer varies between 89 and 94%. This is a difference as compared with the reaction of 1-ada-

TABLE II

Acidolysis of Esters 1-$C_{10}H_{15}COCX{=}CHCOOC_2H_5$

Starting ester		Duration of acidolysis h	Content of *IV*[a] %	Content of *III*, %	
X	content of *trans*, %			according to NMR	according to IR
Cl	88·7	1	72·7	17·0	20·1
Cl	88·7	2	83·9	10·0	8·5
Br	90·5	1	98·7[c]	—	—
Br	100	1[b]	99·0[c]	—	—

[a] From the IR spectrum. [b] The same result even after 2 h of acidolysis. [c] The content corresponds to the content of bromine.

mantylglyoxal with ethoxycarbonylmethylenephosphorane and its halogen derivatives where the introduction of the halogen increased stereoselectivity in favour of the trans isomer. In the case of the halogenophosphoranes *Ib,c* the opposite tendency is at least suggested since the introduction of the halogen is reflected in a slight decrease of stereoselectivity of Wittig's reaction.

The esters *IIIb,c* were subjected to acidolysis with a mixture of acetic and hydrohalogenic acid. For the determination of cyclic γ-hydroxy-$\Delta^{\alpha,\beta}$-crotonolactones *IVb,c* and of corresponding linear acids we used IR spectra. The content of γ-lactonols *IVb,c* in the crude products after acidolysis could be calculated directly from the absorbance of the characteristic wavenumber $\nu = 1767\ cm^{-1}$ since the standard

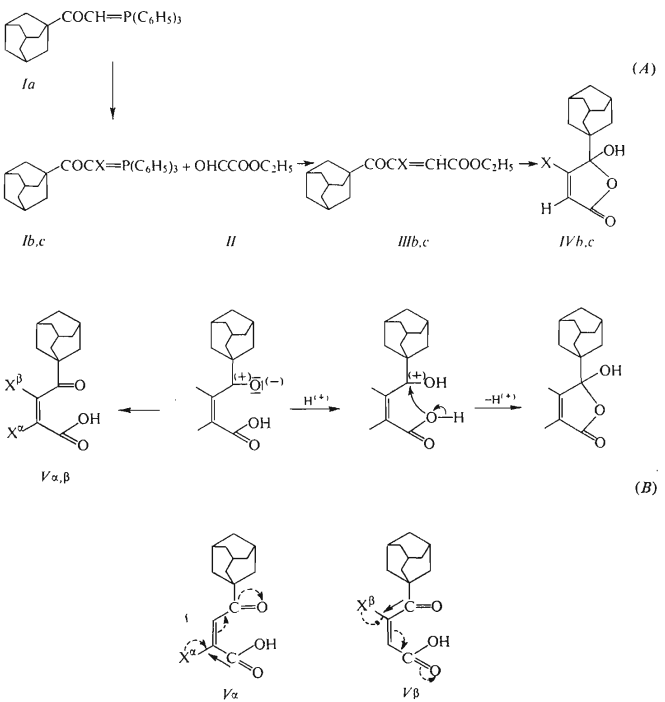


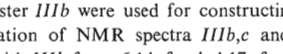
TABLE III

Properties of Esters of β-Halogeno-β-(1-adamantylcarbonyl)acrylic Acids and of β-Halogeno-γ-(1-adamantyl)-γ-hydroxy-$\Delta^{\alpha,\beta}$-crotonolactones

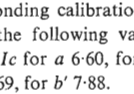
Compound	M. p. °C	R_F		pK_a
		S_1	S_2	
trans-IIIb	45—46·5	—	0·51 (0·47)[a]	
trans-IIIc	78·5—79·5	—	0·47 (0·43)[a]	
IVb	170·5—171·5	0·51	0·72	6·40
IVc	172·5—174	0·51	0·72	5·90

[a] The R_F value corresponding to the *cis*-isomer.

samples of γ-lactonols were available upon two-fold crystallization of the crude products from benzene. In the region about 1 700 cm^{-1} in which a maximum of the linear acid may be expected just as that of a linear ester, the IR spectra of crude *IVb* and *IVc* differed. Crude *IVb* displayed a maximum in this region, the absorbance of which dropped with increased reaction time of acidolysis (see Table II). This fact assumes either the presence of a nonreacted ester or a change of equilibrium between the two isomeric forms with the duration of acidolysis. The presence of the ester could not be demonstrated in a preparative manner since even the pure lactonol *IVb* was not sufficiently soluble in 1M-Na_2CO_3. Therefore, we used for the identification of ester *IIIb* as well as for its quantitative content determination the NMR spectra, employing the integration of the area of the proton band at the double bond at 6·14 and a triplet at 1·25 p.p.m. and a comparison with the *trans*-ester *IIIb* standard. It was found that the content of the nonreacted ester after 1 hour of acidolysis was about 17·0%, after 2 hours of acidolysis about 10·0%. An almost identical result was obtained from the IR spectrum of crude γ-lactonol after acidolysis where pure γ-lactonol *IVb* and the ester *IIIb* were used for constructing the corresponding calibration curve. Determination of NMR spectra *IIIb,c* and *IVb,c* gave the following values (in p.p.m.): with *IIIb* for *a* 6·14, for *b* 4·17, for *c* 1·25; with *IIIc* for *a* 6·60, for *b* 4·14, for *c* 1·21; with *IVb* for *a'* 6·14, for *b'* 3·92; with *IVc* for *a'* 6·69, for *b'* 7·88.



III b, c



IV b, c

TABLE III
(Continued)

λ_{max} nm	ε	ν_{max}, cm^{-1}	
		KBr-tablet	chloroform
211	11 400	1 035, 1 172, 1 280, 1 623, 1 710 i, 1 730	1 022, 1 150, 1 324, 1 617, 1 695 i, 1 726
226	12 829	1 020, 1 163, 1 270, 1 626, 1 700, 1 722	1 026, 1 160, 1 230, 1 623, 1 700, 1 718
210	10 801	1 059, 1 609, 1 750, 3 368	1 075, 1 628, 1 767, 3 545
210	12 330	1 040, 1 608, 1 758, 3 410	1 033, 1 600, 1 768, 3 550

Crude γ-lactonol *IVc* obtained by acidolysis of the ester *IIIc* had in the IR spectrum a very low maximum at about 1 700 cm^{-1} and its absorbance did not change with the duration of acidolysis. Since with the aid of NMR spectra no presence of the ester *IIIc* could be demonstrated, the maximum seems to correspond to the linear acid. Its amount could not be determined from the difference between the content of the γ-lactonol obtained from the IR spectrum and the total amount calculated from the bromine content. These values differ only within the limits of experimental error of the two determinations (about 2·0%). During acidolysis of two of the esters *IIIb,c* the result is independent of their stereochemical composition and, in the products, cyclic γ-lactonol *IVb,c* predominates unequivocally, irrespective of whether pure *trans*-esters or their mixtures with the *cis*-isomer were used. The preference of the cyclic form is supported also by the behaviour of γ-lactonols *IVb,c* in a mixture of hydrochloric or hydrobromic acid and of acetic acid. After an hour of boiling under acidolysis conditions, γ-lactonols were isolated, accompanied in the case of *IVc* by the linear isomer, the amount of which lies again within the range of experimental error of measuring the content on the basis of IR spectra and of bromine content.*

If these results are compared with the acidolysis of esters of β-(1-adamantylcarbobyl)-α-halogenoacrylic acids[2] it may be seen that with β-halogeno derivatives, cyclic γ-lactonol is more preferred in an acidolysis medium. This means that the

* When using a hydrohalogenic acid with a halogen different from that in the γ-lactonol *IVb,c*, no exchange reaction takes place because, in contrast with α-halogenoacrylic acids[2], it cannot proceed *via* a 1,4-enolization addition.

lactonization of the corresponding linear acid $V(\alpha,\beta)$ is supported more pronouncedly by the halogen in position β rather than in position α. We assume that this fact might be explained first of all by the different electron effect of halogen on the carbonyl or carboxyl, depending on its position with respect to these groups[14]. Halogen in the α-position with respect to carboxyl makes it possible, through its positive mesomeric effect, for a tautomeric form favouring lactonization to be formed. Through its negative induction effect it decreases the electron density in the carboxyl and hence makes lactonization more difficult. In the β-position with respect to carboxyl, the halogen exerts an induction effect on carbonyl and hence supports lactonization by a decrease of the electron density at the C-cation of the enolized carbonyl. The carboxyl is affected by the halogen through its positive mesomeric effect which increases the disposition of the carboxyl toward lactonization due to an increase of electron density (equation *B*).

It is probable that the effect on carbonyl or carboxyl of a positive mesomeric effect is accompanied by an induction effect of opposite sense, the influence of which against the mesomeric effect is roughly the same in both cases and need not be considered when comparing the effect of halogens in the two positions on the course of lactonization. The mutual effects are apparent from a comparison of pK_a of nonhalogenated γ-lactonol (7·65) and the halogen derivatives (5·50 for α-chlorine, 5·70 for α-bromine, 6·40 for β-chlorine and 5·90 for β-bromine). It is of importance that in the case of the β-halogeno derivatives the two above effects facilitate lactonization while with the α-halogeno derivatives lactonization is supported only by the mesomeric effect. This fact is apparently the main cause underlying the different extent of lactonization of the above-mentioned α- and β-halogenoacrylic acids.

EXPERIMENTAL

Methods

Esters of β-halogenoacrylic acids *IIIb,c*, the nonhalogenated derivative *IIIa* and β-halogeno-γ-lactonols *IVb,c* were determined after a chromatographic separation on the basis of extinction of the spot with the light of a low-pressure mercury discharge tube of the Chromatolite type. For esters we used a thin layer of Kieselgel GF_{254} in benzene; for γ-lactonols we used Whatman No 4 paper impregnated with 40% ethanolic formamide and phosphoric acid in benzene–cyclohexane 1 : 1 (S_1) or benzene (S_2). The UV absorption spectra in the region of 200—400 nm were determined on an Optica Milano CF-4R spectrophotometer in a 1 cm silica cuvette. As solvent we used 50% aqueous methanol, with γ-lactonols *IVb,c* the solvent contained hydrochloric acid at a concentration of 0·1M. The IR absorption spectra in the region of 400—4000 cm^{-1} were recorded on a Zeiss (Jena) UR-10 spectrophotometer, either in a KBr tablet or in chloroform in a 0·1 mm NaCl cuvette. The quantitative determinations of the esters and γ-lactonols were done in 1% chloroform solution. The NMR spectra were recorded in a ZKR 60 apparatus (Zeiss, Jena) in the form of a 6% solution in deuteriochloroform. As internal standard we used hexamethyldisiloxane and the values obtained were referred to tetramethylsilane. The pK_a values of lactonols *IVb,c* were measured in 80% 2-methoxyethanol, those of halogenophosphoranes

Ib,c in methanol using a potentiometer of the Titrigraph (Radiometer) type SBR 2c. The halogen content in esters *IIIb,c*, and in γ-lactonols *IVb,c* was determined argentometrically using potentiometric indication on a Metrohm potentiograph. The ester *IIIa* was evaluated by titration after previous saponification with excess potassium hydroxide in isopropyl alcohol–water (2 : 1).

Triphenyl(1-adamantylcarbonyl)chloromethylenephosphorane (*Ib*)

A solution of 1·7 g (24·0 mmol) chlorine in 20 ml tetrachloromethane was added slowly under stirring to a solution of 8·85 g (20·0 mmol) 1-adamantylcarbonylmethylenephosphorane[1] in 220 ml dichloromethane at −65 to −70°C. The reaction mixture remained at this temperature for 30 min and, after spontaneous warming to the room temperature, the light-yellow solution was evaporated to 50 ml and diluted with 250 ml light petroleum. An oily phosphonium salt precipitated and crystallized in the refrigerator overnight. It was then dissolved in 100 ml of a mixture of acetone and water (4 : 1) and the solution after filtration with charcoal was made alkaline with 1M-NaOH to a positive reaction to phenolphthalein. The crude phosphorane thus obtained (*Ib*) was crystallized from acetone to yield 5·2 g (55·0%) product with a m.p. of 187–189°C; pK_a 5·75; λ_{max} (KBr) 1108, 1362, 1479 cm^{-1}. For $C_{30}H_{30}ClOP$ (473·0) calculated: 76·20% C, 6·39% H, 7·50% Cl; found: 76·20% C, 6·67% H, 7·46% Cl.

Triphenyl(1-adamantylcarbonyl)bromomethylenephosphorane (*Ic*)

It was prepared in the same way as *Ib* from 8·85 g *Ia* in 60 ml dichloromethane and 3·36 g (21·0 mmol) bromine in 20 ml tetrachloromethane with the difference that the phosphonium salt was isolated by evaporation to dryness and the crystalline residue was dissolved in 200 ml of a mixture of ethanol and water (5 : 1). After alkalinization to phenolphthalein the crude phosphorane *Ic* was twice crystallized from acetone and a product obtained (5·05 g, 48·8%) melting at 190 to 191°C; pK_a 6·75; λ_{max} (KBr) 1108, 1356, 1478 cm^{-1}. For $C_{30}H_{30}BrOP$ (517·4) calculated: 69·70% C, 5·77% H, 15·44% Br; found: 69·53% C, 5·63% H, 15·25% Br.

Ethyl Ester of β-(1-Adamantylcarbonyl)acrylic Acid (*IIIa*)

A suspension of 8·85 g (20·0 mmol) *Ia* in 150 ml benzene was added to a solution of 2·04 g (20·0 mmol) *II* (refs[15,16]) in 30 ml benzene and the reaction mixture was boiled for 5 h in an atmosphere of nitrogen. On the following day the clear solution was evaporated *in vacuo* to dryness and the residue was extracted with 100 ml light petroleum (b.p. 60–65°C). After separation of the insoluble product the filtrate was concentrated *in vacuo* and the residue was eluted without separation on a column of 90 g silica gel (diameter 30 mm) with a mixture of light petroleum and ether (9 : 1). By evaporation to dryness the solution yielded a crystalline residue containing 87% ester *IIIa* (4·5 g, 74·8%). Crystallization of this product from ethanol yielded a fraction (2·4 g) melting at 63–65°C which, upon further two-fold crystallization from ethanol, yielded the pure *trans*-isomer (1·7 g, m.p. 64–65°C). Its $K = \varepsilon_{ester}/\varepsilon_{trans}$ did not change upon further crystalization. For $C_{16}H_{22}O_3$ (262·3) calculated: 73·50% C, 8·46% H; found: 73·50% C, 8·50% H.

Ethyl Esters of β-(1-Adamantylcarbonyl)-β-halogenoacrylic Acids (*IIIb,c*)

These were prepared in the same way as *IIIa*, with the only difference that for chromatographic elution we used a mixture of light petroleum and ether (8 : 1). After evaporation, crude esters were isolated from the solution – *IIIb* as an oil containing 86·0% of the ester in a yield of 70·1%, *IIIc* as a partly crystalline compound containing 90·0% of the ester in a yield of 82·2%. These

crude products were used for the preparation of pure esters of *trans*-acids and of the corresponding γ-lactonols *IVb,c*. The pure *trans*-isomers were prepared by fractional chromatography on a column of silica gel using elution with benzene. The first two fractions of 50 ml each, in which only traces of the *cis*-isomer were detected, were combined and the product obtained from them by evaporation *in vacuo* was twice crystallized from ethanol. In this way, *trans-IIIb* was isolated in a yield of 28·0% melting at 45—46·5°C; for $C_{16}H_{21}ClO_3$ (296·8) calculated: 64·98% C, 7·12% H, 11·93% Cl; found: 64·73% C, 7·26% H, 12·06% Cl. *trans-IIIc* was obtained in a yield of 42·5%, m.p. 78·5—79·5°C; for $C_{16}H_{21}BrO_3$ (341·2) calculated: 56·40% C, 6·69% H, 23·41% Br; found: 56·52% C, 6·41% H, 23·20% Br.

Determination of the *cis-trans* Ratio of Isomers in *IIIa,b,c*

5 mg of the product obtained after column chromatography and evaporation of the solvent were placed in a strip on a thin layer of Kieselgel KGF_{254} and eluted with benzene to reach the end (15 cm). After volatilization of benzene in a stream of air at room temperature the chromatogram was developed under UV light and both bands corresponding to the *cis* and *trans* isomers of the esters were together extracted with chloroform. After its evaporation the IR spectrum in a 1% solution in chloroform was measured and compared with a *trans*-ester standard.

γ-(1-Adamantyl)-γ-hydroxy-β-chloro-$\Delta^{\alpha,\beta}$-crotonolactone (*IVb*)

3·7 g of a crude ester which contained 3·2 g (10·8 mol) of a mixture of *cis* and *trans* isomers *IIIb* were boiled in 75 ml of a mixture of acetic acid and hydrochloric acid (5 : 1). After 1 h a sample was withdrawn and, after cooling to room temperature, poured into 50 ml water; the precipitate was cooled to 0°C, filtered and, after drying in the dark in a desiccator, the content of γ-lactonol *IVb* and of the nonreacted ester *IIIb* in the product was determined. The main portion of the reaction mixture was boiled for another hour and then poured into 400 ml water and the crude product then isolated (3·0 g). Its content of γ-lactonol and ester was then determined. Two-fold crystallization from benzene yielded pure *IVb* (1·4 g, 50·0%), m.p. 170·5—171·5°C. For $C_{14}H_{17}ClO_3$ (268·7) calculated: 62·50% C, 6·37% H, 13·18% Cl; found: 62·48% C, 6·28% H, 13·31% Cl.

γ(1-Adamantyl)-γ-hydroxy-β-bromo-$\Delta^{\alpha,\beta}$-crotonolactone (*IVc*)

2·0 g (5·9 mmol) pure *trans-IIIc* was boiled for 1 h in 40 ml of a mixture of acetic and hydrobromic acids (5 : 1). After treating the reaction mixture in the same way as in the case of *IVb*, a crude product was isolated (1·5 g, 81·1%), m.p. 170—173·5°C in which the content of γ-lactonol *IVc* and of bromine was determined. Two-fold crystallization from benzene yielded pure *IVc* (0·87 g, 47·0%), m.p. 172·5—174°C. For $C_{14}H_{17}BrO_3$ (313·2) calculated: 53·75% C, 5·47% H, 25·55% Br; found: 53·77% C, 5·60% H, 25·67% Br.

Behaviour of β-Halogeno-γ-lactonols *IVb,c* in a Mixture of Acetic and Hydrochloric Acids

0·2 g of *IV* was boiled for 1 h in 10 ml of a mixture of acetic and hydrohalogenic acid (5 : 1). The clear reaction mixtures was cooled and poured into 25 ml water. After 24 h of standing the precipitate was filtered and washed with water to a negative reaction to halogenide ions. In this way, the original γ-lactonol was isolated; in the case of *IVc* it was accompanied by a linear isomer, the amount of which was not greater than 1%.

The analyses were done at the microanalytical department of the Research Institute of Pharmacy and Biochemistry (headed by Dr J. Körbl) and in the analytical department of the same institute

under the direction of Dr F. Jančík. The IR absorption spectra were measured by Mrs P. Vejdělková, the UV spectra by Mr V. Malý, the pK_a values by Mr E. Kraus and the chromatographic estimations were done by Mrs M. Jelínková.

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