567. *The Scope and Mechanism of Carbohydrate Osotriazole Formation. Part V.*[1] *Chloro- and Iodo-phenylosotriazoles.*

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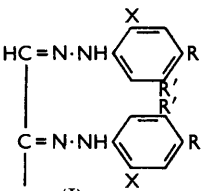
o-Chloro- and *o*-iodo-phenylosazones are dehalogenated when converted into osotriazoles by copper sulphate. Chlorine-water converts osazones into osotriazoles and chlorinates them in the 4-position (if free). Iodine converts osazones into osotriazoles but does not halogenate them. Halogen exchange occurs when iodophenylosazones are converted into triazoles with bromine but not with chlorine or iodine.

It has been shown [1] that copper precipitated during the conversion of osazones into osotriazoles, by means of copper sulphate, removed *o*-bromo-substituents. For a similar reaction with chloro- and iodo-derivatives, glucose *o*-chloro- (I; R = R′ = H, X = Cl) and *o*-iodo-phenylosazone (I; R = R′ = H, X = I) were prepared and refluxed with aqueous copper sulphate. Here, too, *ortho*-dehalogenation took place and glucose phenylosotriazole (II; R = R′ = H) was produced.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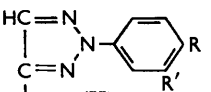
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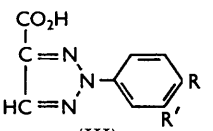
(III)

o-Halogenobenzoic acids were likewise dehalogenated by a refluxing aqueous suspension of copper powder. Apart from *o*-bromobenzoic acid investigated by Hurtley,[2] we found that *o*-chlorobenzoic acid yielded benzoic acid. The *o*-iodo-acid, on the other hand, lost its iodine rapidly, yielding biphenic acid by the Ullmann reaction. Dehalogenation of *o*-halogeno-phenylosotriazoles and -benzoic acids is probably due to location of the halogen atom *ortho* to an electron-attracting group which would facilitate the removal of the halogen cation, leaving a negative centre to be occupied by a hydrogen ion from the aqueous medium.

Chlorine water, like bromine water, converted osazones into osotriazoles and halogenated them in the 4-position. If this position was occupied, the osazones were merely converted into the osotriazoles. Thus, chlorine water converted glucose phenyl- (I; R = R′ = X = H) and *p*-chloro-phenylosazone (I; R = Cl, R′ = X = H) into the *p*-chlorophenylosotriazole (II; R = Cl, R′ = H) which was also obtained by the action of copper sulphate on glucose *p*-chlorophenylosazone. Glucose 3,4-dichloro- (II; R = R′ = Cl), 4-chloro-3-methyl- (II; R = Cl, R′ = Me), and 3-bromo-4-chloro-phenylosotriazole (II; R = Cl, R′ = Br) were also prepared by the action of chlorine-water on the *meta*-substituted osazones or by the action of copper sulphate on the disubstituted ones.

[1] Part IV, *J.*, 1960, 3993.
[2] Hurtley, *J.*, 1929, 1870.

Halogenation of triazoles in the 4-position is attributed to the electromeric effect of the approaching halogen cation which would cause a temporary shift of electrons from the triazole ring towards the *ortho*- and *para*-positions; owing to the steric effect of the triazole ring, substitution takes place in the *para*- and not in the *ortho*-position.

No halogen exchange took place when chloro- or bromo-phenylosazones were treated with bromine or chlorine respectively: glucose *p*-chlorophenylosazone yielded the *p*-chlorophenylosotriazole and the *meta*-isomer yielded the 4-bromo-3-chloro-phenylosotriazole (II; R = Br, R′ = Cl); glucose *p*-bromophenylosazone with chlorine yielded the *p*-bromophenylosotriazole, and the *meta*-isomer yielded the 3-bromo-4-chloro-phenylosotriazole (II; R = Cl, R′ = Br). In the case of iodophenylosazones, chlorine-water caused no exchange and glucose *p*-iodophenylosazone (I; R = I, R′ = X = H) yielded the corresponding *p*-iodophenylosotriazole (II; R = I, R′ = H); but when this osazone was treated with bromine water, an osotriazole was obtained which contained both iodine and bromine—it is probably a molecular compound. The *meta*-isomer also gave a product in which iodine was partially replaced by bromine.

Unlike chlorine and bromine, iodine in aqueous potassium iodide merely converted the osazones into osotriazoles without halogenating them. The reaction is also much slower, equiring 3 days for glucose *p*-methoxyphenylosazone, one week for glucose phenylosazone, and 2 and 3 weeks respectively for the *p*-iodo- and the *p*-bromo-phenyl derivative. Osazones having strong electron-attracting substituents such as nitro and carboxyl were unaffected by iodine. Also unaffected was glucose *p*-chlorophenylosazone, while the *meta*-isomer was only partially converted into the osotriazole after 3 weeks. This is in harmony with the view that triazole formation is inhibited by electron-attracting groups and facilitated by electron-donating ones.

Potassium permanganate readily converted glucose chloro- and iodo-phenylosotriazoles into chloro- and iodo-phenyl-1,2,3-triazole-4-carboxylic acid. As with bromine, 2-*m*-carboxyphenyl-1,2,3-triazole-4-carboxylic acid (III; R = H, R′ = CO_2H) resisted chlorination, probably because of $-I$ and $-T$ effects of the carboxyl group which render the 4-position deficient in electrons.

Treatment of 2-*m*-tolyl-1,2,3-triazole with potassium permanganate afforded 2-*m*-carboxyphenyl-1,2,3-triazole. The former was obtained by the action of copper sulphate on glyoxal bis-*m*-tolylhydrazone.

The ultraviolet absorption spectra of glucose *m*- and *p*-chloro- and *p*-iodo-phenylosotriazoles (II) and triazole-4-carboxylic acids (III) are characterised by a single peak between 272 and 278 mμ. On the other hand, osotriazoles and triazole-4-carboxylic acids having a 3-iodine substituent possess 2 peaks at 234—240 and 272—282 mμ. As with the osotriazoles and triazole-4-carboxylic acids studied earlier,[1] the peaks of the *para*-isomers are higher and shifted towards longer wavelengths. Similarly, the peaks for triazole-4-carboxylic acids are shifted more than for the corresponding osotriazoles. There is also a gradual shift towards longer wavelength for both the *meta*- and *para*-monosubstituted derivatives as we go from the chloro- through the bromo- to the iodo-substituents.

Experimental

Absorption spectra were determined for ethanolic solutions with a Unicam S.P. 500 spectrophotometer.

Glucose Osazones.—The osazones were prepared by adding an aqueous solution of glucose (10 g. in 100 ml.) to the calculated amount of the desired hydrazine hydrochloride and sodium acetate in water (300 ml.), followed by a few drops of acetic acid. The mixture was heated on the water-bath for the period shown and the *osazone* was filtered off (see Table 1). Unless otherwise stated, they were crystallised from dilute ethanol and were soluble in boiling ethanol or methanol and insoluble in water and ether.

Glucose Phenylosotriazole.—A solution of glucose *o*-chlorophenylosazone (5 g.) in dioxan (100 ml.) was refluxed with copper sulphate (5 g.) in water (100 ml.) for 4 hr., then filtered. To remove dioxan, the filtrate was distilled off until 100 ml. were collected. The residue was

TABLE 1. *Substituted glucose phenylosazones.*

Subst. in Ph	Time (hr.)	M. p. (decomp.)	Yield (%)	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
o-Cl	2	230—232°	50	51·0	4·8	13·2	$C_{18}H_{20}Cl_2N_4O_4$	50·6	4·7	13·1
m-Cl	2	208	62	50·7	4·8	12·9	$C_{18}H_{20}Cl_2N_4O_4$	50·6	4·7	13·1
p-Cl	3	211	75	50·3	4·6	13·1	$C_{18}H_{20}Cl_2N_4O_4$	50·6	4·7	13·1
4-Br-3-Cl ...	2	206—207	35	36·9	3·2	9·5	$C_{18}H_{18}Br_2Cl_2N_4O_4$	36·9	3·1	9·6
4-Cl-3-Me...	2	184	52	—	—	12·2	$C_{20}H_{24}Cl_2N_4O_4$	—	—	12·3
3,4-Cl_2	4	192	73	43·0	4·0	11·4	$C_{18}H_{18}Cl_4N_4O_4$	43·5	3·6	11·3
o-I	2	176	56	35·3	3·3	8·6	$C_{18}H_{20}I_2N_4O_4$	35·4	3·3	9·2
m-I	3	198	24	36·0	3·5	8·9	$C_{18}H_{20}I_2N_4O_4$	35·4	3·3	9·2
p-I	2	Amorphous	—	—	—	—	—	—	—	—

concentrated on the water-bath; the crystals that separated (2 g.) recrystallised from water in needles, m. p. 195—196° alone or mixed with glucose phenylosotriazole [3] (Found: C, 54·9; H, 5·5; N, 16·0. Calc. for $C_{12}H_{15}N_3O_4$: C, 54·3; H, 5·7; N, 15·8%).

Glucose *o*-iodophenylosazone (5 g.), similarly treated, gave the same product (1·2 g.), m. p. and mixed m. p. 195° (Found: C, 54·0; H, 5·6; N, 15·7%).

Action of Copper Powder on o-Halogenobenzoic Acids.—A suspension of *o*-chlorobenzoic acid (5 g.) in water (200 ml.) was refluxed with freshly prepared copper powder (15 g.) for 3—4 hr., filtered, and acidified. Benzoic acid separated (2·4 g.); recrystallised from water, it had m. p. and mixed m. p. 121°.

A suspension of *o*-bromobenzoic acid, similarly treated, afforded the same acid.

A suspension of *o*-iodobenzoic acid (6 g.) in water (300 ml.) was refluxed with copper powder (20 g.) for 15 min. and treated as above. Biphenic acid separated (2·5 g.) having m. p. and mixed m. p. 227° (from water).

Glucose m-*Chlorophenylosotriazole.*—Glucose *m*-chlorophenylosazone (10 g.) was treated with copper sulphate (10 g.) for 4 hr. The crystals (4 g.) that separated recrystallised from water–ethanol in needles, m. p. 206—208°, soluble in ethanol and methanol and insoluble in ether and water (Found: C, 47·9; H, 4·6; N, 14·2; Cl, 11·7. $C_{12}H_{14}ClN_3O_4$ requires C, 48·1; H, 4·7; N, 14·0; Cl, 11·9%).

Glucose 4-Bromo-3-chlorophenylosotriazole.—Glucose *m*-chlorophenylosazone (5 g.) in water (150 ml.) was treated in the cold with bromine (6 ml.), and the mixture kept overnight. The reddish-brown mass obtained was filtered off and washed with water and ethanol (2·5 g.). *Glucose 4-bromo-3-chlorophenylosotriazole* recrystallised from ethanol in needles, m. p. 223° (solubility as above) (Found: C, 38·6; H, 3·5; N, 11·3. $C_{12}H_{13}BrClN_3O_4$ requires C, 38·1; H, 3·4; N, 11·1%).

Glucose 4-bromo-3-chlorophenylosazone (5 g.) was treated with copper sulphate (5 g.) as before. The osotriazole that separated was filtered off (2·2 g.) and recrystallised from ethanol in needles, m. p. and mixed m. p. 223° (Found: C, 38·3; H, 3·4; N, 11·0%).

Glucose 4-Chloro-3-methylphenylosotriazole.—Chlorine was bubbled into a suspension of glucose *m*-tolylosazone (10 g.) in water (250 ml.) for 1·5 hr. and the mixture kept overnight. The mass obtained was filtered off and washed with water and ethanol (4·5 g.). *Glucose 4-chloro-3-methylphenylosotriazole* recrystallised from water–ethanol in needles, m. p. 218° (solubility as above) (Found: C, 49·5; H, 4·9; N, 13·1; Cl, 11·7. $C_{13}H_{16}ClN_3O_4$ requires C, 49·8; H, 5·1; N, 13·4; Cl, 11·3%).

A suspension of glucose 4-chloro-3-methylphenylosazone (7 g.), in dioxan (150 ml.) and 3·5% aqueous copper sulphate (200 ml.), was refluxed for 1·5 hr. and filtered hot. Dioxan was removed as before and the osotriazole separated (2 g.); it recrystallised from water–ethanol in needles, m. p. and mixed m. p. 218° (Found: C, 49·6; H, 5·5; N, 13·1; Cl, 10·8%).

Glucose 3,4-Dichlorophenylosotriazole.—Chlorine was bubled into a suspension of glucose *m*-chlorophenylosazone (7 g.) in water (250 ml.) for 2·5 hr. and the mixture treated as above. The osotriazole (2·5 g.) recrystallised from ethanol in needles, m. p. 216° (solubility as above) (Found: C, 43·3; H, 3·8; N, 12·3; Cl, 20·9. $C_{12}H_{13}Cl_2N_3O_4$ requires C, 43·1; H, 3·9; N, 12·6; Cl, 21·3%).

Glucose 3,4-dichlorophenylosazone (10 g.) was treated with copper sulphate (10 g.) as before. The product (3 g.) recrystallised from ethanol in needles, m. p. and mixed m. p. 216° (Found: C, 43·2; H, 4·1; N, 12·3; Cl, 21·0%).

Glucose p-*Chlorophenylosotriazole.*—(*a*) A hot solution of glucose *p*-chlorophenylosazone

(5 g.) in dioxan (150 ml.) was refluxed with copper sulphate (5 g.) in water (100 ml.) for 4 hr., then filtered. Dioxan was removed as before. The *osotriazole* that separated (2·5 g.) recrystallised from ethanol in needles, m. p. 220° (solubility as for other osotriazoles) (Found: C, 48·3; H, 4·6; N, 13·9. $C_{12}H_{14}ClN_3O_4$ requires C, 48·1; H, 4·7; N, 14·0; Cl, 11·9%).

(*b*) Glucose *p*-chlorophenylosazone (2 g.) in water (100 ml.) was treated in the cold with bromine (4 ml.) as before. The mass obtained was filtered off, washed (1 g.), and recrystallised from ethanol, forming needles, m. p. and mixed m. p. 220° (Found: C, 48·4; H, 4·8; N, 14·4; Cl, 11·4%).

(*c*) Chlorine was bubbled into a suspension of glucose phenylosazone (2 g.) in water (100 ml.) for 2 hr. The mass formed was filtered off (1·2 g.) and recrystallised from ethanol (m. p. and mixed m. p. 220°) (Found: C, 47·7; H, 4·7; N, 14·3; Cl, 11·7%).

(*d*) A suspension of glucose *p*-chlorophenylosazone (2 g.) was treated with chlorine. The osotriazole (1 g.), recrystallised from ethanol, had m. p. and mixed m. p. 220° (Found: C, 48·1; H, 5·1; N, 14·2; Cl, 11·7%).

Glucose p-*Chlorophenylosotriazole Tetra-acetate*.—A solution of the osotriazole in dry pyridine was treated with acetic anhydride; the *tetra-acetate* crystallised from methanol in needles, m. p. 108° (Found: C, 51·8 H, 4·9; N, 9·3. $C_{20}H_{22}ClN_3O_8$ requires C, 51·4; H, 4·7; N, 9·0%).

Glucose m-*Iodophenylosotriazole*.—A suspension of glucose *m*-iodophenylosazone (10 g.) in dioxan (200 ml.) was treated with 5% aqueous copper sulphate (200 ml.) as before. The *osotriazole* (1·5 g.) recrystallised from water–ethanol in needles, m. p. 223° (solubility as above) (Found: C, 36·9; H, 3·6; N, 10·8. $C_{12}H_{14}IN_3O_4$ requires C, 36·8; H, 3·6; N, 10·7%).

Glucose p-*Iodophenylosotriazole*.—Glucose *p*-iodophenylosazone (10 g.) was treated with copper sulphate (10 g.) as for the *meta*-isomer. On concentration, the *osotriazole* separated (2·5 g.); it recrystallised from dilute ethanol in needles, m. p. 240—242° (solubility as above) (Found: C, 37·0; H, 3·6; N, 10·4%).

A cold suspension of glucose *p*-iodophenylosazone (10 g.) was treated with chlorine as above. The osotriazole (4 g.) recrystallised from dilute ethanol in needles, m. p. and mixed m. p. 240—242° (Found: C, 37·2; H, 3·7; N, 10·2%).

Action of Bromine on Glucose p-*Iodophenylosazone*.—A cold suspension of glucose *p*-iodophenylosazone (10 g.) in water (150 ml.) was treated with bromine (5 ml.) as above. The mass formed was filtered off and washed with water and ethanol (6 g.). On crystallisation from ethanol, a mixed triazole was obtained (Found: C, 39·2; H, 3·6; N, 11·7; Br, 10·7; I, 17·7. Calc. for $C_{12}H_{14}BrN_3O_4$,$C_{12}H_{14}IN_3O_4$: C, 39·2; H, 3·8; N, 11·5; Br, 10·9; I, 17·3%).

Glucose 3-*Bromo*-4-*chlorophenylosotriazole*.—Glucose *m*-bromophenylosazone (4 g.), treated with chlorine as before, gave this *osotriazole* (1 g.), needles (from ethanol), m. p. 212° (Found: N, 11·2; Cl, 9·6; Br, 20·6. $C_{12}H_{13}BrClN_3O_4$ requires N, 11·1; Cl, 9·4; Br, 21·1%).

TABLE 2. *Formation of osotriazoles by iodine.*

Subst. in Ph of glucose phenyl-osotriazole	Time (days)	M. p. and mixed m. p.	Yield (%)	Found (%)				Calculated (%)		
				C	H	N	Formula	C	H	N
Unsubst.	7	195° [3]	67	54·6	5·7	15·9	$C_{12}H_{15}N_3O_4$	54·3	5·7	15·8
m-I	14	223	65	36·6	3·5	10·5	$C_{12}H_{14}IN_3O_4$	36·8	3·6	10·7
p-I	14	240—242	78	36·9	3·7	10·6	$C_{12}H_{14}IN_3O_4$	36·8	3·6	10·7
m-Me	10	195 [5]	70	55·6	6·1	15·5	$C_{13}H_{17}N_3O_4$	55·9	6·1	15·1
p-Me	7	207 [6]	64	55·7	6·0	15·0	$C_{13}H_{17}N_3O_4$	55·9	6·1	15·1
p-MeO	3	200 [1]	85	52·9	6·0	14·1	$C_{13}H_{17}N_3O_5$	52·9	5·7	14·2
m-Br	11	209—210 [5]	68	42·0	4·4	11·8	$C_{12}H_{14}BrN_3O_4$	41·9	4·1	12·2
p-Br.....	21	225—227 [4]	60	42·1	4·3	11·9	$C_{12}H_{14}BrN_3O_4$	41·9	4·1	12·2

Glucose p-*Bromophenylosotriazole*.—Glucose *p*-bromophenylosazone (3 g.) was treated with chlorine as before. The *p*-bromo-osotriazole was filtered off (1 g.) and recrystallised from ethanol in needles, m. p. and mixed m. p. 225—227° [4] (Found: C, 42·0; H, 4·2; N, 12·0; Br, 23·6. Calc. for $C_{12}H_{14}BrN_3O_4$: C, 41·9; H, 4·1; N, 12·2; Br, 23·3%).

Glucose p-*Carboxyphenylosotriazole*.—Glucose *p*-carboxyphenylosazone, similarly treated with chlorine, yielded glucose *p*-carboxyphenylosotriazole, m. p. and mixed m. p. 268° [1] (Found: C, 50·3; H, 4·9; N, 13·4. Calc. for $C_{13}H_{15}N_3O_6$: C, 50·5; H, 4·9; N, 13·6%).

[3] Hann and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 735.
[4] Hardegger, El Khadem, and Schreier, *Helv. Chim. Acta*, 1951, **34**, 253.
[5] El Khadem and El-Shafei, *J.*, 1959, 1655.
[6] Hardegger and El Khadem, *Helv. Chim. Acta*, 1947, **30**, 1478.

Formation of Osotriazoles by the action of Iodine.—The osazone (1 g.) was suspended in a solution of iodine (10 g.) in 10% aqueous potassium iodide (100 ml.) and left at room temperature for the period shown with occasional shaking. The osotriazole was filtered off and recrystallised from water–ethanol.

2-*Aryl*-1,2,3-*triazole*-4-*carboxylic Acids.*—A boiling suspension of the osotriazole (1—2 g.) in water (100—200 ml.) was treated with potassium permanganate (3—6 g.) until the pink colour persisted. The hot mixture was filtered, treated with sodium hydrogen sulphite, and acidified. The *acid* which separated recrystallised from water–ethanol; it was soluble in ethanol or methanol and insoluble in water (see Table 3).

Glyoxal Bis-m-*tolylhydrazone.*—Polymerised glyoxal [7] (25 g.) was thoroughly mixed with phosphorus pentoxide (15 g.) and heated with a flame. Monomeric glyoxal distilled and was collected in a trap cooled with solid carbon dioxide and acetone.[8] It was treated with a solution of *m*-tolylhydrazine (15 g.) in water (200 ml.) and acetic acid (10 ml.) and then heated at 40° for 10 min. The *bishydrazone* that separated (3 g.) recrystallised from dilute ethanol in yellow

TABLE 3. *Aryl*-1,2,3-*triazole*-4-*carboxylic acids.*

Subst. in Ph	M. p.	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
m-Cl	202—204°	54	48·6	2·6	19·2	$C_9H_6ClN_3O_2$	48·3	2·7	18·8
p-Cl	232	30	48·3	2·6	18·8	$C_9H_6ClN_3O_2$	48·3	2·7	18·8
3-Br-4-Cl	215	43	—	—	14·1	$C_9H_5BrClN_3O_2$ *	—	—	13·9
4-Br-3-Cl	222	62	36·0	1·7	13·8	$C_9H_5BrClN_3O_2$	35·7	1·7	13·9
3,4-Cl_2	216—217	54	42·2	2·0	15·7	$C_9H_5Cl_2N_3O_2$	41·9	1·9	16·3
m-I	201	50	34·2	2·0	13·6	$C_9H_6IN_3O_2$	34·3	1·9	13·3
p-I	265	55	34·4	2·0	13·0	$C_9H_6IN_3O_2$	34·3	1·9	13·3
4-Cl-3-CO_2H	273—274	58	45·1	2·3	15·6	$C_{10}H_6ClN_3O_4$	44·9	2·2	15·7

* Found: Cl, 12·0; Br, 26·6. Reqd.: Cl, 11·7; Br, 26·4%.

plates, m. p. 136° (decomp.), soluble in ethanol, methanol, and ether and insoluble in water (Found: C, 72·0; H, 6·7; N, 21·0. $C_{16}H_{18}N_4$ requires C, 72·2; H, 6·8; N, 21·0%).

2-m-*Tolyl*-1,2,3-*triazole.*—Glyoxal bis-*m*-tolylhydrazone (3 g.) was refluxed in a solution of copper sulphate (4 g.) in 20% aqueous dioxan (200 ml.) for 1·5 hr. The solution was then steam-distilled and the distillate (200 ml.) extracted with ether. The ethereal layer was washed with dilute hydrochloric acid and dried (Na_2SO_4). The triazole (1 g.) remaining after removal of the ether was used for the preparation of the corresponding acid without purification.

2-m-*Carboxyphenyl*-1,2,3-*triazole.*—To a boiling suspension of 2-*m*-tolyl-1,2,3-triazole (1 g.) in water (250 ml.), potassium permanganate (4·0 g.) was added and the mixture treated as before. The *acid* which separated (0·6 g.) recrystallised from water–ethanol in needles, m. p. 205—207° (Found: C, 57·2; H, 4·1; N, 22·0. $C_9H_7N_3O_2$ requires C, 57·1; H, 3·7; N, 22·2%).

Spectra.—These are recorded in Table 4.

TABLE 4. *Ultraviolet spectra.*

Osotriazole (II) R	R′	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{min.}$ (mμ)	log ε	Triazole (III) R	R′	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{min.}$ (mμ)	log ε
Cl	H	272—274	4·43	226	2·54	Cl	H	276	4·48	230	3·11
H	Cl	268—270	4·41	230	3·30	H	Cl	270	4·28	232—234	3·43
Br	H	276	4·46	225	2·97	Br	H	280	4·45	230	3·27
H	Br	268—271	4·25	236	3·40	H	Br	270	4·19	238	3·35
I	H	278	5·53	230—232	4·33	I	H	280	4·40	236—240	3·32
H	I	234—235	4·46	246	4·01	H	I	234—236	4·40	248	4·07
		270—272	4·48					272—274	4·44		
Cl	Cl	276	4·51	234	3·34	Cl	Cl	276—278	4·46	234—238	3·58
Br	Cl	274	4·24	236	2·67	Br	Cl	276	4·57	238	3·27
						Cl	Br	276	4·52	238—240	3·37
Br	Br	272	4·52	238	3·59	Br	Br	280	4·49	240	3·42
Cl	Me	274—276	4·31	230	2·67	Cl	CO_2H	266—268	4·53	242—244	3·96
Br	Me	274—276	4·49	230—232	3·09	Br	CO_2H	260—264	4·39	226—228	3·92

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[7] Ljubawin, *Ber.*, 1877, **10**, 1366.
[8] Harries and Temme, *Ber.*, 1907, **40**, 165.