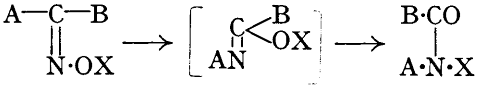
108. *Studies of the Beckmann Change. Part IV. Some Effects of Substitution on the Rate of Rearrangement of Ketoxime Picryl Ethers. A Suggested Mechanism of the Transformation.*

By ARTHUR W. CHAPMAN and FREDERICK A. FIDLER.

IN previous papers of this series (J., **1933**, 806; **1934**, 1550; **1935**, 1223) it has been shown that certain esters and ethers derived from ketoximes undergo a spontaneous Beckmann transformation at room temperature or when heated, and that this rearrangement consists of an intramolecular exchange of positions by one of the hydrocarbon radicals (A) attached to the central carbon atom of the ester molecule (I) and the acyloxy or related group OX.



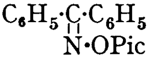
$$\begin{array}{c}\text{A—C—B}\\ \|\\ \text{N·OX}\end{array} \longrightarrow \left[\begin{array}{c}\text{C}{<}^{\text{B}}_{\text{OX}}\\ \|\\ \text{AN}\end{array}\right] \longrightarrow \begin{array}{c}\text{B·CO}\\ |\\ \text{A·N·X}\end{array}$$

(I.) (II.) (III.)

Ketoximes themselves are only transformed in the presence of a reagent, the function of which appears to be the formation with the oxime of an ester-like substance capable of undergoing the spontaneous change. This applies, not only to reagents such as phosphorus pentachloride or benzenesulphonyl chloride, but also to the more complex course of the rearrangement under the influence of hydrogen chloride.

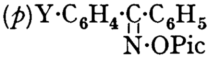
Whilst, however, the general character of the rearrangement and the function of the reagent had become clear, more precise knowledge was lacking as to the means by which the groups A and OX exchange places within the molecule, and it seemed possible that some light might be thrown upon this internal mechanism by an investigation of the effects of substitution upon the rate of transformation and upon the energy of activation of the rearrangement.

Three complete series of oxime picryl ethers (V)—(VII) (Y = Cl, NO_2, and Me) and one further disubstituted compound (VII; Y = OMe) were therefore prepared and studied. In addition, two other ethers derived from benzophenoneoxime (IV; with 2 : 4 : 6-trinitro-*m*-tolyl and 2 : 4-dinitrophenyl in place of picryl) were examined.



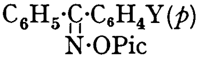
$$\begin{array}{c}C_6H_5{\cdot}C{\cdot}C_6H_5\\ \|\\ \text{N·OPic}\end{array}$$

(IV.)



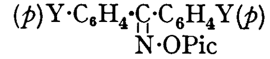
$$\begin{array}{r}(p)Y{\cdot}C_6H_4{\cdot}C{\cdot}C_6H_5\\ \|\\ \text{N·OPic}\end{array}$$

(V.)



$$\begin{array}{l}C_6H_5{\cdot}C{\cdot}C_6H_4Y(p)\\ \|\\ \text{N·OPic}\end{array}$$

(VI.)



$$\begin{array}{c}(p)Y{\cdot}C_6H_4{\cdot}C{\cdot}C_6H_4Y(p)\\ \|\\ \text{N·OPic}\end{array}$$

(VII.)

The velocities of rearrangement of the chloro- and methyl-substituted compounds into the corresponding anilides (III) were measured in carbon tetrachloride solutions of two or three different concentrations at several temperatures. The values at each temperature were extrapolated to give the velocity at infinite dilution (k_0), and from these values the energy of activation of the rearrangement as brought about by collision with molecules of carbon tetrachloride was calculated (cf. Part II, *loc. cit.*, p. 1551). Measurements of the rates of rearrangement of benzophenoneoxime picryl ether have already been published (Parts I and II), but a number of these were repeated and substantially confirmed, with a small correction for the value of E.

The results of the measurements on two complete series of oxime picryl ethers are in the following tables (t = temperature; k_0 calculated with time in seconds and Napierian logarithms, and E derived from the slope of the line obtained by plotting log k_0/η against $1/T$).

From these observations certain conclusions immediately emerge. The introduction of the electron-attracting chlorine atom into either phenyl group of the ketoxime retards the transformation, whereas the electron-repelling methyl group accelerates it. Moreover, the introduction of a substituent into the migrating nucleus has a much greater effect on the rate of transformation than a similar substitution in the stationary nucleus. The influence of the polar character of the substituent on the ease of rearrangement was demonstrated even more strikingly by the behaviour of the remaining compounds. The picryl ether of *p*-nitrobenzophenone-α-oxime (VI; Y = NO_2) was isomerised much less readily

Picryl ether of :	Benzophenone-oxime.		*p*-Chlorobenzophenone				Di-*p*-chloro-benzophenone-oxime.	
			α-Oxime.		β-Oxime.			
Hydrocarbon group { migrating	C_6H_5		C_6H_5		p-C_6H_4Cl		p-C_6H_4Cl	
Hydrocarbon group { stationary	C_6H_5		p-C_6H_4Cl		C_6H_5		p-C_6H_4Cl	
	t.	$k_0 \times 10^5$.	*t.*	$k_0 \times 10^5$.	*t.*	$k_0 \times 10^5$.	*t.*	$k_0 \times 10^5$.
	70·4°	1·55						
	80·5	4·65	85·8°	3·6	90·8°	2·8		
	90·7	13·2	95·0	9·45			90·8°	1·32
	100·45	36·4	99·8	15·4	100·8	7·74	100·0	3·24
	(cf. also Part II)		105·3	29·7	104·5	11·4		
					110·6	20·6	110·3	11·4
					115·3	31·5	115·5	17·7
E (cals./g.-mol.)	29,200		30,800		30,200		31,500	

Picryl ether of :	Phenyl *p*-tolyl ketone				Di-*p*-tolyl ketoxime.	
	α-Oxime.		β-Oxime.			
Hydrocarbon group { migrating	C_6H_5		p-C_6H_4Me		p-C_6H_4Me	
Hydrocarbon group { stationary	p-C_6H_4Me		C_6H_5		p-C_6H_4Me	
	t.	$k_0 \times 10^5$.	*t.*	$k_0 \times 10^5$.	*t.*	$k_0 \times 10^5$.
					44·7°	3·0
					50·3	6·25
			55·5°	2·20	60·4	17·1
	65·2°	2·50	65·0	7·94	70·3	55·1
	75·6	7·47	75·3	19·5		
	85·6	18·0	80·4	37·2		
	90·9	32·4				
E (cals./g.-mol.)	26,500		28,300		25,800	

than any of the chloro-compounds, but was converted into p-*nitrobenz*-N-*picrylanilide* (phenyl migrating) by 6 hours' heating at 100° in ethylene dichloride solution. The picryl ethers of the β-oxime and of the dinitro-compound (V and VII) were, however, both recovered unchanged after 6—7 hours' heating at 100° in the same solvent. On the other hand, when attempts were made to prepare di-*p*-anisyl ketoxime picryl ether (VII; Y = OMe) from the oxime, the only product that could be isolated was *p*-anisoyl-*p*-anisidide; rearrangement had evidently occurred at room temperature.

The energies of activation obtained from the measurements of the rates of change vary considerably from the fastest to the slowest transformation. There are minor anomalies in the values of *E* for the α- and the β-oximes of both monosubstituted ketones, but the general trend is clearly for an increase in velocity of rearrangement to be accompanied by a decrease in *E*. The variations in *E* are of the order to be expected if the differences in velocity of rearrangement arise essentially from differences in critical increment.

Over the range of temperatures investigated, the effects of chloro-substitution on the velocity of change were, as shown in the following table, strictly additive (cf. somewhat similar additive effects in a different reaction, Bradfield and B. Jones, J., **1928**, 1006; B. Jones, J., **1935**, 1831, 1835). In the methyl series the additivity was not so apparent, but the values for these substances are (for reasons discussed in the experimental section) probably less accurate than those for the chloro-compounds. (The values of k_0 used below were read off from the graphs of log k_0 and $1/T$.)

Chloro-compounds.

$10^4/T$	26	27	28
$A = \frac{k_0 \text{ (unsubs.)}}{k_0\ (\alpha\text{-chloro-})}$	1·90	2·04	2·45
$B = \frac{k_0 \text{ (unsubs.)}}{k_0\ (\beta\text{-chloro-})}$	4·57	4·68	5·00
$A \times B$	8·71	9·55	11·7
$C = \frac{k_0 \text{ (unsubs.)}}{k_0 \text{ (dichloro-)}}$	8·51	9·55	11·5

Methyl compounds.

$10^4/T$	28	29	30
$A = \frac{k_0 \text{ (unsubs.)}}{k_0\ (\alpha\text{-methyl-})}$ ...	0·41	0·36	0·32
$B = \frac{k_0 \text{ (unsubs.)}}{k_0\ (\beta\text{-methyl-})}$ ...	0·13	0·12	0·12
$A \times B$	0·051	0·045	0·038
$C = \frac{k_0 \text{ (unsubs.)}}{k_0 \text{ (dimethyl-)}}$	0·036	0·031	0·026

The effects of substitution in the picryl group were less easy to determine, since suitable materials were less readily accessible. The rate of rearrangement of benzophenoneoxime 2 : 4 : 6-trinitro-*m*-tolyl ether was measured in the same way as for the other compounds with the following results :

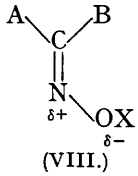
	2 : 4 : 6-*Trinitro*-m-*tolyl ether*.		*Picryl ether*.	
	t.	$k_0 \times 10^5$.	*t*.	$k_0 \times 10^5$.
			80·5°	4·65
	89·4°	2·40*	90·7	13·2
	92·1	3·79		
	95·0	5·10		
	102·8	12·0	100·45	36·4
	104·8	17·0*		
	108·7	22·2 †		
	111·2	34·3 †		
E (cals./g.-mol.)	32,100		29,200	

* 1% Solution. † 0·5% Solution.

The introduction of the electron-repelling methyl group into the picryl radical retarded the transformation, and the retardation was accompanied by an increase in *E* approximately equivalent to the change in rate of rearrangement. This retarding effect of a diminution in the electron-attraction of the picryl group was confirmed by an examination of the 2 : 4-dinitrophenyl ether of benzophenoneoxime which did not rearrange even in nitromethane at 100°.

From these and previous observations it is possible to construct a somewhat more detailed picture of the transformation. The oximes by themselves do not undergo the Beckmann rearrangement, and the activity of the reagents employed to bring about the change can be traced to the formation of compounds of Type (I) where X is an acyl or related group. Such compounds undergo spontaneous isomeric change to (II) and (III) at appropriate temperatures, but only if the group —OX is one having a strong attraction for electrons, as in the esters derived from strong acids. Esters derived from weak acids, like the oximes themselves, can be heated to the temperature of decomposition without rearrangement.

In an oxime ester derived from a strong acid, the attraction for electrons exerted by —OX creates a dipole at —N—O with its positive end at the nitrogen atom (VIII). In consequence of the structure of the oxime ester molecule, the field of the dipole is so oriented that an attraction is set up between the nitrogen atom and those electrons (of the bond A—C) which unite the central carbon atom to the group (A) situated on that side of the molecule away from —OX. If the molecule acquires sufficient energy, this attraction results in the nitrogen atom becoming attached to group A, and the balance of charges is corrected by the migration of —OX to the central carbon atom. The fact that the product of the rearrangement is determined solely by the spatial configuration of the oxime is thus accounted for. The process, whilst requiring —OX to exert a powerful attraction for electrons, should be facilitated by any factor, such as an electron-repelling group on A or B, tending to increase the concentration of electrons at A—C and *vice versa*, and it might also be expected that such substitution should be more effective on A, which participates in the bond A—C, than on the more remote group B. These are precisely the effects that have been observed.



(VIII.)

Such a formulation of the transformation can only be regarded as provisional, but it appears to agree with all the facts available regarding the rearrangement of the ketoximes. It bears a close resemblance to the picture drawn by Mills (British Association Address, *Chem. and Ind.*, 1932, **10**, 755) and differs from it mainly in assigning to the union of the nitrogen atom with group A a more important share in the determination of the ease of rearrangement. Were the rate of change determined solely by the polarisation of the N—O bond or the attraction of —OX for the central carbon atom, it would be expected that the effects of substitution in the two groups A and B would be nearly equal instead of being markedly different.

As a result of the work described in this series of papers certain definite general conclusions have been reached regarding the nature of the Beckmann change of ketoximes, and these are now summarised.

1. The rearrangement of oxime esters and related compounds first described by Kuhara is, indeed, a spontaneous transformation brought about by heat alone and not requiring an external reagent, though its velocity depends upon the polar character of the solvent, if any, in which it takes place.
2. There is no evidence that this spontaneous transformation involves any actual dissociation into free ions. Such a dissociation appears inherently improbable, and the change is best regarded as truly intramolecular.
3. The activity of the majority of reagents employed to bring about the Beckmann change in ketoximes can readily be explained by the intermediate formation of an ester-like compound capable of undergoing spontaneous rearrangement. Study of the outstanding example of a reagent that did not appear to fall into this category showed that it, too, acted in the same way, which therefore appears to be the one general mode of transformation.
4. A more detailed mechanism of the change has been suggested which takes into account both the effects of substitution on the ease of rearrangement and the spatial factor which determines the nature of the product of transformation of an unsymmetrical ketoxime.

EXPERIMENTAL.

(Analyses are micro-determinations by Dr. A. Schoeller.)

The picryl ethers of the various oximes were prepared by the method described in Part I. The purity of each of the unsymmetrical oxime derivatives was checked by converting it into the corresponding *N*-picrylanilide, and purification was continued until this could be obtained free from any appreciable trace of isomeride.

Separation of the Stereoisomeric Oximes.—More convenient methods than those in the literature were found for the separation of the two isomeric oximes of *p*-chloro- and *p*-methylbenzophenone. The mixture of *p*-chlorobenzophenoneoximes was crystallised twice from alcohol, and the main yield of α-oxime obtained (m. p. 163—164°). The filtrates were diluted with water, the precipitate being rich in β-oxime. After drying, this was extracted with cold alcohol, which left behind most of the remaining α-oxime. The β-oxime was again precipitated by water, and was recrystallised from light petroleum (b. p. 60—80°). The material so obtained (m. p. 92—95°) was used for preparation of the picryl ether.

The two phenyl tolyl ketoximes had been separated by Hantzsch (*Ber.*, 1890, **23**, 2325) by fractional precipitation with water from solution in glacial acetic acid, but this method is unsatisfactory when the isomerides are required in considerable quantities. It was found that the α-oxime is sparingly soluble in acetone but the β-compound readily so. The isomerides were therefore separated by extraction with acetone, which left a residue of almost pure α-oxime (m. p. after recrystallisation from alcohol 153—156°). The acetone solution was diluted with water, and the extraction and precipitation repeated on the crude β-oxime so obtained. The final precipitate of β-oxime was further purified by crystallisation from light petroleum (m. p. 114—116°). It decomposed even on standing in the open air, and was converted into the picryl ether as soon as purified.

The two oximes of *p*-nitrobenzophenone were obtained by Sutton and Taylor's modification (J., 1931, 2190) of Brady and Mehta's method (J., 1924, **125**, 2297).

The following compounds have not been previously described.

Phenyl p-*tolyl α-ketoxime picryl ether*, colourless minute needles from chloroform and methyl alcohol, m. p. 103° (Found : C, 56·85; H, 3·5. $C_{20}H_{14}O_7N_4$ requires C, 56·85; H, 3·35%). It yielded p-*toluoyl*-N-*picrylanilide*, pale yellow crystals from acetone and alcohol, m. p. 209° (Found : C, 56·7; H, 3·4%), when heated in carbon tetrachloride solution, and this was also prepared from *p*-toluanilide imidochloride and sodium picrate (cf. Mumm, Hesse, and Volquartz, *Ber.*, 1915, **48**, 379).

Phenyl p-*tolyl β-ketoxime picryl ether*, yellowish-brown crystalline powder from acetone and alcohol, m. p. 83° (Found : C, 56·2; H, 3·3%), was converted into *benz*-N-*picryl*-p-*toluidide*, bright yellow crystals, m. p. 180—185° (Found : C, 56·9; H, 3·45%), which was also synthesised from benz-*p*-toluidide imidochloride and sodium picrate. The preparation and crystallisation from chloroform and alcohol of di-*p*-tolyl ketoxime picryl ether, m. p. 95°, were best conducted in a freezing mixture (cf. Part I).

p-*Nitrobenzophenone-α-oxime picryl ether*, pale yellow crystals from acetone and alcohol, m. p. 134° (Found : C, 50·45; H, 2·65. $C_{19}H_{11}O_9N_5$ requires C, 50·3; H, 2·45%), yielded, on hydrolysis with cold alcoholic potash, *p*-nitrobenzophenone-α-oxime (m. p. and mixed m. p.

154—156°). It was converted into p-*nitrobenz*-N-*picrylanilide*, pale yellow plates from acetone and alcohol, m. p. 214—215° (Found : C, 50·45; H, 2·35%), when heated in ethylene dichloride solution (2 g. in 25 c.c.) in a sealed tube at 100° for 5 hours.

p-*Nitrobenzophenone*-β-*oxime picryl ether*, pale brown crystalline powder from acetone and alcohol, m. p. 154—155° (decomp.) (Found : C, 50·65; H, 2·55%), gave the β-oxime (m. p. and mixed m. p. 135—138°) on hydrolysis with cold alcoholic potash. After 6 hours' heating at 100° in ethylene dichloride solution, evaporation of the solvent yielded only unchanged picryl ether (m. p. 140—145°, mixed m. p. 146—148°, m. p. and mixed m. p. after recrystallisation 154—155°).

pp'-*Dinitrobenzophenoneoxime*, almost colourless needles from alcohol, m. p. 195° (decomp.), was obtained by boiling the ketone (10 g.) with hydroxylamine hydrochloride (5 g. in 10 c.c. of water) and alcohol (40 c.c.) for 2 hours (Found : C, 54·3; H, 3·3. $C_{13}H_9O_5N_3$ requires C, 54·3; H, 3·15%).

pp'-*Dinitrobenzophenoneoxime picryl ether*, almost colourless, fine needles from acetone and alcohol, m. p. 189° (decomp.) (Found : C, 45·9; H, 2·1. $C_{19}H_{10}O_{11}N_6$ requires C, 45·8; H, 2·0%). It yielded the oxime (m. p. 189—192°, mixed m. p. 192—193°) when hydrolysed with cold alcoholic sodium hydroxide, but was recovered unchanged after 7 hours' heating at 100° in ethylene dichloride solution (m. p. and mixed m. p. 186°).

Benzophenoneoxime 2 : 4-*dinitrophenyl ether*, colourless fine needles (m. p. 173—174°) from acetone (Found : C, 62·7; H, 3·6. $C_{19}H_{13}O_5N_3$ requires C, 62·8; H, 3·6%), gave benzophenoneoxime on hydrolysis (m. p. and mixed m. p. 143—144°). It was recovered unchanged (m. p. 167—169°) after 7 hours' heating at 100° in ethylene dichloride or in nitromethane solution. The isomeric *benz*-N-2 : 4-*dinitrophenylanilide*, bright yellow crystals from acetone and alcohol, m. p. 155—156° (Found : C, 62·7; H, 3·75%), was obtained from benzanilide imidochloride and sodium 2 : 4-dinitrophenoxide.

p-Chlorobenzophenone-β-oxime picryl ether had m. p. 116—118° (given in Part I as m. p. 109—110°).

When attempts were made to prepare di-*p*-anisyl ketoxime picryl ether from the oxime and picryl chloride, the only substance that could be isolated, even when the reaction was carried out in a freezing mixture, formed colourless plates, m. p. 202—203°, from alcohol, and proved to be *p*-anisoyl-*p*-anisidide (Found : C, 70·0; H, 5·95. Calc. for $C_{15}H_{15}O_3N$: C, 70·0; H, 5·9%), as shown by mixed m. p. with an authentic specimen.

Velocity Determinations.—The method described in Part I for carbon tetrachloride solutions was employed in all measurements except those on the picryl ethers of phenyl tolyl β-ketoxime and di-*p*-tolyl ketoxime, the change products of which were too soluble in this solvent. For these two compounds a somewhat more complicated and less accurate method was adopted as follows : after removal from the thermostat and chilling in ice, each reaction tube was opened and 25 c.c. of the solution were transferred to a 50-c.c. graduated flask and made up to 50 c.c. with ice-cold light petroleum (b. p. 60—80°). The solution was seeded with the appropriate change product, kept in ice for 3 hours with occasional shaking, and then filtered and evaporated as already described.

The results of the measurements are given in the tables below, each value being the mean of six observations. (Concentrations, *c*, are in g.-mol./litre at the particular temperature employed; time in seconds, Napierian logarithms.)

Conversion of benzophenoneoxime picryl ether into benz-N-*picrylanilide*
(values additional to those of Part II).

Temp.					Temp.				
70·4°	c		0·0228		90·7°	c	0·0111	0·0222	0·0333
	$k \times 10^5$		1·80			$k \times 10^5$	15·2	16·8	19·1
80·5	c	0·0112	0·0225	0·0338	100·45	c	0·0109	0·0219	0·0328
	$k \times 10^5$	5·30	6·18	6·48		$k \times 10^5$	40·3	45·1	48·4

Conversion of p-*chlorobenzophenone*-α-*oxime picryl ether into* p-*chlorobenz*-N-*picrylanilide.*

Temp.					
85·8°	c		0·0104	0·0139	0·0208
	$k \times 10^5$		3·88	3·84	3·95
95·0	c	0·0068		0·0136	0·0204
	$k \times 10^5$	9·60		10·4	9·94
99·8	c	0·0067		0·0135	0·0202
	$k \times 10^5$	15·9		17·0	17·3
105·3	c	0·0067	0·0100	0·0134	
	$k \times 10^5$	31·1	31·5	32·3	

Conversion of p-*chlorobenzophenone*-β-*oxime picryl ether into benz*-N-*picryl*-p-*chloroanilide.*

Temp.					Temp.				
90·8°	c		0·0137		104·55°	c	0·0067	0·0134	0·0201
	$k \times 10^5$		2·88			$k \times 10^5$	12·0	12·7	13·2
100·85	c	0·0067	0·0134	0·0202	110·6	c	0·0066	0·0132	0·0199
	$k \times 10^5$	8·41	8·83	9·67		$k \times 10^5$	22·2	23·4	25·0

Conversion of pp′-*dichlorobenzophenoneoxime picryl ether into* p-*chlorobenz*-N-*picryl*-p-*chloroanilide.*

Temp.					
90·8°	c			0·0190	
	$k \times 10^5$			1·56	
100·0	c		0·0094	0·0188	0·0282
	$k \times 10^5$		3·72	4·07	4·58
110·3	c	0·0062	0·0093	0·0185	0·0278
	$k \times 10^5$	12·0	12·7	13·1	13·4
115·5	c		0·0092	0·0183	0·0275
	$k \times 10^5$		19·5	20·8	22·7

Conversion of phenyl p-*tolyl* α-*ketoxime picryl ether into* p-*toluoyl*-N-*picrylanilide.*

Temp.				Temp.			
65·2°	c	0·0074	0·0148	85·6°	c	0·0072	0·0144
	$k \times 10^5$	2·55	2·46		$k \times 10^5$	22·5	27·0
75·6	c	0·0073	0·0146	90·9	c	0·0071	0·0143
	$k \times 10^5$	7·91	8·35		$k \times 10^5$	39·5	46·7

Conversion of phenyl p-*tolyl* β-*ketoxime picryl ether into benz*-N-*picryl*-p-*toluidide.*

Temp.				Temp.			
55·5°	c	0·0090	0·0180	75·3°	c	0·0088	0·0176
	$k \times 10^5$	2·2	2·2		$k \times 10^5$	21	23
65·0	c	0·0089	0·0178	80 4	c	0·0087	0·0174
	$k \times 10^5$	8·6	7·3		$k \times 10^5$	41	45

Conversion of di-p-*tolyl ketoxime picryl ether into* p-*toluoyl*-N-*picryl*-p-*toluidide.*

Temp.					Temp.				
44·7°	c		0·0147		64·6°	c		0·0143	
	$k \times 10^5$		3·0			$k \times 10^5$		32·4	
50·3	c	0·0073	0·0146		70·3	c	0·0071		0·0214
	$k \times 10^5$	7·4	6·2			$k \times 10^5$	59		66
60·4	c	0·0072	0·0144	0·0217					
	$k \times 10^5$	18·1	19·6	19·1					

Conversion of benzophenoneoxime 2 : 4 : 6-*trinitro*-m-*tolyl ether into benz*-N-2 : 4 : 6-*trinitro*-m-*tolylanilide.*

Temp.				Temp.			
89·4°	c		0·0215	102·8°	c	0·0106	0·0211
	$k \times 10^5$		2·40		$k \times 10^5$	12·1	12·2
92·1	c	0·0107	0·0214	104·8	c	0·0105	0·0210
	$k \times 10^5$	3·9	3·95		$k \times 10^5$	15·3	17·0
95·0	c	0·0107	0·0213	108·7	c	0·0105	
	$k \times 10^5$	5·4	5·72		$k \times 10^5$	22·2	
100·1	c	0·0106	0·0212	111·2	c	0·0104	
	$k \times 10^5$	6·80	8·25		$k \times 10^5$	34·3	

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