109. *The Polarimetric Study of Intramolecular Rearrangement in Inactive Substances. Part VIII. α- and β-Furfuraldoximes and Some Other Aldoximes.*

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On repetition of some earlier work it has been found that, in confirmation of former results, there is no change detectable by our method of α-benzaldoxime or α-piperonaldoxime into the β-forms, in ethyl tartrate solution; but that there is a slight change, formerly overlooked, of α-anisaldoxime into the β-form.

The α- and the β-form of furfuraldoxime have now also been examined. They seem to be quite stable at room temperature, but at 70° both undergo transformation to yield an equilibrium mixture containing approximately 55% of the α- and 45% of the β-oxime.

IN earlier parts of this series (see Part VII, J., 1929, 1895), experiments were described in which the change of certain β-oximes into the α-forms was followed quantitatively, by observing the alteration undergone by the rotation of certain optically active indicators in which the oximes were dissolved. A marked diminution of rotation occurred as the change, β-oxime to α-oxime, proceeded, whereas change in the opposite direction was not observed. This point was referred to specifically in the case of α-benzaldoxime (m. p. 35°) (see J., 1907, **91**, 510, 513), where, with the means at our disposal, no alteration in rotation was detected; the change appeared to be irreversible Similarly a solution of α-anisaldoxime gave a rotation agreeing with the end rotation for the β-oxime (*loc. cit.*, p. 516) and a similar observation was made for β-*m*-nitrobenzaldoxime (*Ber.*, 1907, **40**, 2572). Without any very definite discussion of the point, it was at the time tacitly assumed, on the evidence available, that if there was an equilibrium in the oximes then examined, it lay so far to the side of the α-oxime as to be undetectable by our method. Recently, however, Theilacker and Chou (*Annalen*, 1936, **523**, 143) have examined anisaldoxime, one of those used by Patterson and McMillan (J., 1907, **91**, 504); and, by a melting-point method, found that on melting β(or α?)-anisaldoxime, or on allowing it to stand for 38 hours in ethyl *d*-tartrate, an equilibrium mixture of oximes was obtained containing about 7% of the β-oxime. From this, and from experiments with 2 : 6-dichloro-3-nitrobenzaldoxime, they conclude that the transformations between all stereoisomeric aromatic aldoximes lead to equilibrium mixtures, although in many cases the equilibrium may be greatly displaced towards one form or the other.

In view of this we have recently repeated some of the earlier polarimetric work on this subject, and have made some additional observations.

EXPERIMENTAL.

β-Benzaldoxime (m. p. 126°) was re-examined in ethyl tartrate (the apparatus used being that described in J., 1908, **93**, 1041) and gave the following data:

p (relative to ethyl tartrate) = 95·5.

t (mins.)	0	40	80	105	350	1200	1370	∞
$\alpha^{20^\circ}_{5461}$ (100 mm.)	14·7°	14·6°	14·54°	14·5°	14·1°	13·1°	12·99°	12·00°

For comparison, two solutions of the isomeric α-benzaldoxime (b. p. 121°/19 mm.; m. p. 35°) were prepared and gave the following results:

	I, *p* = 95·52.			II, *p* = 95·03.		
t (mins.)	60	500	1590	100	605	1485
$\alpha^{20^\circ}_{5461}$ (100 mm.)	12·02°	12·02°	12·02°	11·98°	11·98°	11·98°

These data agree quite closely with those formerly found; the end rotation for the β-oxime solution is, within the limits of experimental error, identical with that given by the α-oxime solution, and in addition the rotation of the α-oxime solutions does not alter with lapse of time.

We re-examined also piperonaldoxime in similar fashion. At 20° the β-oxime (m. p. 144—145°) gave these results:

$p = 95{\cdot}02$; $a = 1{\cdot}25^\circ$.

t (mins.)	0	15	60	105	135	450	∞
$\alpha^{20^\circ}_{5461}$ (100 mm.)	13·69°	13·66°	13·50°	13·38°	13·30°	12·77°	12·44°

On the other hand the α-form (m. p. 110°) gave:

$p = 95{\cdot}01$.

t (mins.)	60	145	6940
$\alpha^{20^\circ}_{5461}$ (100 mm.)	12·44°	12·44°	12·44°

The rotation of the solution containing the α-oxime thus showed no change of rotation with lapse of time, and its value was the same as that ultimately exhibited by the solution of the β-oxime.

In this case also it appears, either that the α-oxime does not change into the β-oxime under these conditions, or that the change is too slight to be detected by our method.

When the rotation of the β-oxime solution had reached a definite end-point, the oxime was precipitated from solution by water. The substance thus obtained had m. p. 111°, mixed m. p. with pure piperonaldoxime (m. p. 110°) 109°. This also indicates almost complete conversion of the β- into the α-oxime.

With β-anisaldoxime (m. p. 133°) the following data were obtained:

$p = 94{\cdot}97$.

t (mins.)	0	30	95	130	270	330
$\alpha^{20^\circ}_{5461}$ (100 mm.)	+15·54°	15·47°	15·35°	15·27°	14·94°	14·50°
t (mins.)	405	630	1405	1650	4980	∞
$\alpha^{20^\circ}_{5461}$ (100 mm.)	+14·67°	14·35°	13·62°	13·49°	12·86°	12·79°

These agree closely with the results recorded in J., 1907, **91**, 516.

The isomeric α-anisaldoxime (m. p. 65°), however, yielded these figures:

$p = 94{\cdot}99$.

t (mins.)	0	60	200	405	780	1185	2955	4740	∞
$\alpha^{20^\circ}_{5461}$ (100 mm.)	+12·55°	12·56°	12·58°	12·61°	12·65°	12·68°	12·74°	12·77°	12·78°

There is in the last case a slight upward change in rotation amounting in all to 0·23°, and it takes place so slowly as to amount to only 0·03° after 200 minutes, a fact which, especially since the other oximes examined had shown no change, may account for its having been overlooked previously. A very slight change of temperature would produce an equal effect. Theilacker and Chou estimate from their experiments that equilibrium between the two anisaldoximes occurs in a mixture of 93% of the lower- and 7% of the higher-melting oxime. According to our present experiments, where the initial rotation in the β-oxime solution was + 15·54° and in the α-oxime solution + 12·55°, there is a total difference of 2·99°. On the assumption—which may not be strictly correct, but is not likely to be seriously in error—that the change in rotation of the ethyl tartrate is directly proportional to the relative quantities of the oximes present, the change in rotation (0·23°) indicates a rearrangement of 8% of the α- into β-oxime; that is, equilibrium is attained in ethyl tartrate solution at 20° when there are 8% of β- and 92% of α-oxime. This agrees quite closely therefore with Theilacker and Chou's value.

We have now extended our experiments to the furfuraldoximes, samples of which, m. p.'s 89° and 73°,* were prepared for us by Miss J. M. Murdoch (Mrs. A. H. Lamberton), to whom we express our thanks. Solutions of these in ethyl tartrate were examined at 20°, with the following results:

β-Furfuraldoxime (m. p. 89°), $p = 95{\cdot}1$.

t (mins.)	30	95	260	1170
$\alpha^{20^\circ}_{5461}$ (100 mm.)	15·27°	15·27°	15·27°	15·27°

α-Furfuraldoxime (m. p. 73°), $p = 95$.

t (mins.)	30	120	1260
$\alpha^{20^\circ}_{5461}$ (100 mm.)	13·95°	13·95°	13·95°

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* Brady and Goldstein (J., 1927, 1961) record higher m. p.'s, *viz.*, 91—92° and 75—76°. Mr. John Robertson has confirmed this in this laboratory, but our polarimetric experiments having been made before we became aware of Brady's paper, we thought it unnecessary to repeat them with these slightly better specimens.

It thus appears that, at room temperature, (1) there is a difference (2·32°) in the effects of these two oximes on the rotation of ethyl tartrate at the concentration used, and that the oxime with the higher m. p. has the greater solvent influence, just as is the case with most, if not all, other pairs of oximes; (2) the rotation of either solution does not alter with lapse of time. Both oximes seem to be quite stable at room temperature in these circumstances.

At a higher temperature (70°), however, interconversion was observed, as is shown by the following data (in this experiment a longer polarimeter tube was used):

β-Furfuraldoxime (m. p. 89°); $p = 97·5$, $a = 0·66°$.

t (mins.)	0	15	45	75	105	145	200	325	∞	
$\alpha_{5461}^{70°}$ (160 mm.)	27·29°	27·25°	27·16°	27·06°	27·01°	26·94°	26·85°	26·73°	26·63°	
$1000k$	—	4·16	5·23	5·97	4·11	5·09	4·96	6·30	—	(mean) 5·118

k is calculated from the equation $k_2[1/(t_2 - t_1)] \log_e (a - x_1)/(a - x_2)$, where a is the total change of rotation, and x_1 and x_2 are respectively the changes of rotation after times t_1 and t_2,

α-Furfuraldoxime (m. p. 73°); $p = 97·51$.

t (mins.)	0	30	55	120	165	200	240	285	330	∞
$\alpha_{5461}^{70°}$ (160 mm.)	+26·1°	26·15°	26·20°	26·27°	26·32°	26·36°	26·39°	26·42°	26·45°	26·63°
$1000k$	—	3·31	4·39	2·73	3·32	3·38	3·84	3·95	3·42	—

Here the two forms of this oxime appear to reach a definite equilibrium value, and since the total change of rotation is 1·19° (from 27·29° to 26·10°) and the change of rotation due to conversion of β-oxime into equilibrium mixture is 0·66° and the similar change in the α-oxime is 0·53°, the proportions in the equilibrium mixture would be about 55% of α-oxime and 45% of β-oxime.

We also carried out some experiments with 2 : 6-dichloro-3-nitrobenzaldoxime, which, however, was so insoluble in ethyl tartrate that results worth recording could not be obtained.

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