

CCXCV.—*The Isomerism of the Oximes. Part XXXVI.*
The Methylation of Aldoximes and Ketoximes.

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THE work of Brady and Goldstein (J., 1926, 2403) on the quantitative methylation of aldoximes has been continued and extended to the ketoximes. The conclusion previously reached was that the

O-ether was formed by an ionic, and the *N*-ether by a molecular, reaction, the α -aldoxime by reason of its higher dissociation constant giving less of the *N*-ether than the β -aldoxime; for example, α -*m*-nitrobenzaldoxime ($K_a = 7.1 \times 10^{-11}$) gave 22% of *N*-ether, and β -*m*-nitrobenzaldoxime ($K_a = 1.8 \times 10^{-11}$) more than 62% of *N*-ether.

The oximes previously studied showed a marked difference between the dissociation constants of the two isomerides. A strong confirmation of the views expressed would be forthcoming if, from two isomeric oximes differing but slightly in their dissociation constants, approximately the same amounts of *O*- and *N*-ether were formed on alkylation. This has been found to occur, and Table I gives the results of the quantitative methylation of three such pairs of oximes.

TABLE I.

	<i>N</i> -Ether/ <i>O</i> -Ether.	$K_a \times 10^{11}$.
α -Furfuraldoxime	1 : 0.95	1.5
β -Furfuraldoxime	1 : 0.85	1.4
α - <i>p</i> -Nitrobenzophenoneoxime	1 : 1.15	1.4
β - <i>p</i> -Nitrobenzophenoneoxime	1 : 2.55	3.4
α -Phenyl- <i>p</i> -tolylketoxime	1 : 2.97	—
β -Phenyl- <i>p</i> -tolylketoxime	1 : 2.16	—

Attempts have been made to measure the dissociation constants of α - and β -phenyl-*p*-tolylketoximes without success (Brady and Chokshi, this vol., p. 946), but from qualitative experience there is every reason to suppose that both isomerides have dissociation constants of about the same order.

α -Furfuraldoxime is of interest, as it gives more *N*- than *O*-ether on methylation, and the qualitative observation that α -2-methoxy-1-naphthaldoxime gives more *N*- than *O*-ether (Brady and Goldstein, J., 1927, 1960) has been confirmed quantitatively, the ratio being 1 : 0.96. These are the first examples of α -aldoximes giving more *N*- than *O*-ether and demonstrate still further the unsoundness of drawing inferences of the constitution of parent substances from the structure of their methylation products.

Acetophenoneoxime ($K_a = 0.33 \times 10^{-11}$) and benzophenoneoxime ($K_a = 0.50 \times 10^{-11}$) give 1 : 1.43 and 1 : 1.16 of *N*- and *O*-ethers, respectively. The amount of *N*-ether formed is less than would be expected from the low dissociation constants of these oximes, but the quantity found must be regarded as a minimum. The *N*-ethers of the ketoximes are much more readily hydrolysed in alkaline solution than those of the aldoximes and are consequently decomposed to some extent during the methylation process, with the formation of ketone and *N*-methylhydroxylamine; chloroform would remove the former with *N*-ether and *O*-ether, but not the

latter. Loss of *N*-methylhydroxylamine would decrease the amount of *N*-ether found, and the presence of ketone increase the *O*-ether. In addition the oximes, being feeble acids, would be partly extracted by the chloroform from the alkaline solution, again increasing the apparent amount of *O*-ether formed. The amount of *N*-ether formed from the phenyl-*p*-tolylketoximes (Table I) is probably also too small for the same reasons.

EXPERIMENTAL.

Quantitative Methylation.—The method employed was similar to that of Brady and Goldstein (*loc. cit.*). The strength of the sodium oximate solution was 2*N*, a slight excess of sodium hydroxide was present (0.032 mol. to 0.030 mol. of oxime), and one molecular equivalent of methyl sulphate was used. The methylation was carried out at room temperature.

The following points call for special mention. The sodium salts of α -2-methoxy-1-naphthaldoxime, α -*p*-nitrobenzophenoneoxime, and α - and β -phenyl-*p*-tolylketoximes were sparingly soluble in water and in such cases from 25% to 50% of the water was replaced by methyl alcohol to ensure complete solution; the effect of this upon the ionisation of the salt was not considered to be sufficiently great to vitiate the comparisons (compare Brady and Goldstein, *loc. cit.*). Owing to decomposition of the *N*-ether at the higher temperature, benzophenoneoxime was methylated at 0° for 2 hours with mechanical stirring. The results are in Table II, where *W* = weight of oxime used, *w* = weight of oxime unacted upon, *N* = weight of *N*-ether formed, *T* = total weight of *O*- and *N*-ethers formed, all in grams, and *N* : (*T* - *N*) is the ratio of *N*- to *O*-ether.

TABLE II.

Oxime.		<i>W</i> .	<i>w</i> .	<i>N</i> .	<i>T</i> .	<i>N</i> : (<i>T</i> - <i>N</i>).
α -Furfuraldoxime	(1)	3.30	0.19	1.85	3.57	0.95
	(2)	3.41	0.29	1.89	3.64	0.94
β -Furfuraldoxime	(1)	3.12	0.18	1.82	3.37	0.85
	(2)	3.40	0.20	1.89	3.65	0.84
α -2-Methoxy-1-naphthaldoxime	(1)	3.20	0.00	1.75	3.42	0.95
	(2)	2.62	0.00	1.35	2.78	0.98
α - <i>p</i> -Nitrobenzophenoneoxime		2.62	0.08	1.24	2.67	1.15
β - <i>p</i> -Nitrobenzophenoneoxime	(1)	3.01	0.02	0.88	3.17	2.61
	(2)	2.11	0.00	0.65	2.24	2.50
α -Phenyl- <i>p</i> -tolylketoxime	(1)	1.77	0.00	0.47	1.89	3.05
	(2)	1.34	0.00	0.37	1.43	2.89
β -Phenyl- <i>p</i> -tolylketoxime	(1)	0.80	0.00	0.26	0.86	2.20
	(2)	1.74	0.00	0.60	1.86	2.13
Acetophenoneoxime		1.75	0.01	0.80	1.92	1.43
Benzophenoneoxime		4.65	0.13	2.23	4.83	1.16

*Action of Ultra-violet Light on α -*p*-Nitrobenzophenoneoxime.*—When the oxime (2 g.) in benzene (50 c.c.) was exposed in a quartz flask

to the light of a quartz mercury lamp for 72 hours, some *p*-nitrobenzophenone was formed, but most of the oxime was recovered unchanged. It seems that this method, often useful for obtaining β -aldoximes (Brady and McHugh, J., 1924, **125**, 547), is not applicable for preparing unstable ketoximes.

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