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REDUCTION OF SOME 2,3-DIARYL CYCLOHEXANONES AND THEIR OXIMES.

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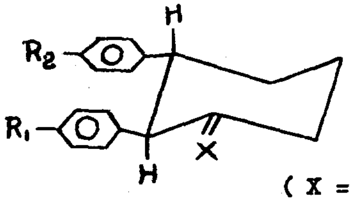
The reduction of 2,3-diaryl cyclohexanone oximes yielded exclusively a single amine with an equatorial NH_2, but the reduction of the corresponding ketones yielded a mixture of epimeric cyclohexanols.(Table) The 2,3-diaryl cyclohexanones were prepared by the conjugate addition of arylmagnesium bromides to 2-aryl-cyclohex-2-en-1-ones and were proved to be diequatorial by NMR spectra.[1]



I : R_1 = R_2 = H
II : R_1 = H, R_2 = CH_3
III : R_1 = R_2 = CH_3

(X = NOH, Oximes; X = O, Ketones)

The reduction of oximes, analogous to the corresponding ketones, is expected to follow the same stereochemical course[2]. Sodium-alcohol reduction of the oximes I to III gave a single amine as proved by the TLC of the crude products. TLC of crude benzoates also revealed the presence of a single entity only. The NH_2 group in these bases was shown to be equatorial on the basis of its reaction with nitrous acid[2] and by the IR and NMR spectra of the benzoyl derivatives[1].

In distinct contrast to the LAH reduction of the ketones, which gave a mixture of the two epimeric cyclohexanols, the corresponding oximes on similar reduction yielded the cyclohexylamines with equatorial NH_2 in 89 to 94% yield. Careful chromatography and TLC of the crude amine obtained in the reduction did not reveal the presence of any other entity. Similar observations were made on the crude benzoates also. The results are listed in the Table. The formation of a single amine in these reductions is unexpected[3]. On the basis of similarity of the keto and oximino groups, the axial amine also should be formed in comparable amounts in the LAH reduction of the oximes. The results of the reduction of 2,3-diaryl cyclohexanones and their oximes indicate that the controlling factors in the reduction of oximes and ketones may not be the same. The product stability appears to be a more important factor for oxime reductions. The results obtained can be explained on the basis of conformational free energy differences, for the NH_2 group has a larger ΔG value (1.2 k.cal./mole)[4] than OH (0.7 k.cal./mole)[5].

TABLE*

Product composition in the reduction of cyclohexanones and their oximes.

Compound reduced	X = O % yield of the epimeric cyclohexanols Equatorial	 Axial	X = NOH % yield of the equatorial cyclohexylamines
	Sodium and alcohol reduction		
I	74 (101°C)	26 (74°C)	92 (193°C)
II	76 (93°C)	24 (71°C)	91 (169°C)
III	80 (127°C)	20 (97°C)	89 (180-182°C)
	Lithium aluminium hydride reduction		
I	60	40	91
II	63	37	94
III	59	41	90

* The yield of the epimeric cyclohexanols were determined by chromatography on alumina. Melting points are given in brackets. The m.p.s under amines refer to the benzoates. IR and NMR spectra have confirmed the configurational assignments.

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