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THE IRRADIATION OF ARYL ALDOXIMES[1]

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THE irradiative conversion of oximes into their geometrical isomers was first observed by Ciamician and Silber for aldehydes in 1903 (1). Similar observations with regards to ketones were reported by Stoermer (2) in 1911, and since then this irradiative interconversion of oximes has been the subject of sporadic study (3,4).

We have now found that the irradiation of aryl aldoximes in a variety of solvents leads, aside from geometrical isomerisation, to the formation of amides with apparent migration of oxygen and hydrogen; benzaldoxime, for instance, gives benzamide.

The irradiations were performed in a quartz immersion apparatus at <u>ca</u> 10° using an 80W Hanovia CH3 lamp. The solutions were 0.5% in oxime, about 200 ml being contained by the apparatus. The results of the irradiation of α-(syn)-benzaldoxime are given in Table 1. No amide was obtained on irradiation of the syn oxime acetate.

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[1] Photochemical Syntheses, Part 7.

TABLE 1

	SOLVENT	TIME(hours)	YIELD[2]
1.	Cyclohexane	30	12
2.	Cyclohexane + 0.5 eq. NEt_3	26	trace
3.	Cyclohexane + 0.5 eq. HOAc	24	19
4.	Cyclohexane + 0.5 eq. CF_3COOH	8	22
5.	Cyclohexane + 2.0 eq. CF_3COOH	6	32
6.	Benzene	32	ca 2
7.	MeOH[3]	9	12
8.	HOAc[3,4]	3	41
9.	Dioxan	37	6

Under conditions Nos. 1, 3-5, 7-9 irradiation was continued until the rate of change in ultraviolet absorption spectrum was very slow, and until the amount of amide, as determined by the extinction of the carbonyl band near 6μ, ceased to increase. In methanol (No.7) reaction, as far as oxime disappearance was concerned, was quite fast, but little amide was formed. In benzene (No.6) reaction was slow and appeared to result in general destruction. Under conditions shown under 2 the oxime was destroy-

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[2] Isolation yields. These are not maximal but should have relative significance.

[3] The infrared of the crude product suggested that formation of the aldehyde, and, in the case of acetic acid acetylation to the oxime acetate, could compete.

[4] Neither the syn nor the anti oxime gave any amide in the absence of light.

ed, but only traces of amide formed. The products were not investigated further. Benzamide is itself very slowly destroyed by irradiation in cyclohexane solution.

Although the addition of acetic acid and trifluoroacetic acid to cyclohexane increases the rate and yield of amide the difference between the acids is less than might be anticipated on the basis of acid strength. It is not clear, therefore, if the overall reaction is acid-catalysed; a correlation with ionising power (5) of the solvent may also exist.

A number of other aryl aldoximes have been briefly studied in acetic acid. The results are given in Table 2.

TABLE 2

OXIME OF -	YIELD[2]	m.p.	m.p.(lit.)	TIME(hrs.)
Benzaldehyde	41	123-6°	127°	3
p-Tolualdehyde	30	153-5°	155°	4
p-Chlorobenzaldehyde	26[5]	177-8°	179°	2
Anisaldehyde	11	160-3°	163°	5
α-Naphthaldehyde	45	203-4°	202°	3

However, under conditions approximating to these not all aromatic aldoximes rearranged. No amide was obtained in less than 8 hours from the oximes of *m*- and *p*-nitrobenzaldehyde [although these have been reported to undergo geometrical inversion in benzene suspension (1)], *p*-fluorobenzaldehyde, isonicotinic aldehyde and *p*-cyanobenzaldehyde.

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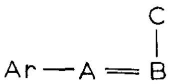
[5] About 5.0% in cyclohexane. Prior conversion to the anti oxime was noted. Anti oximes were obtained in good yield (in cyclohexane) from the first four oximes in Table 2.

The observation of Beckmann or Beckmann-like rearrangements in nitrones has been recorded previously (6-9) and in one of these at least (7) the intermediacy of an oxazirane has been demonstrated. It is possible that a similar intermediate may be involved in the present rearrangement.[6] The nature of the solvent effect would suggest that significant charge separation occurs in the amide formation.

The effect of the substituent groups may be interpreted in (at least) two ways, decision between which is not presently possible. Either the substituent modifies the nature of the excited state, as observed in the photo-reduction of substituted benzophenones, (11), or else the substituent affects the stability of an intermediate. In the latter case this could be by either accelerating the non-photochemical return of an intermediate to the starting oxime,[7] or by stabilising such an intermediate so as to permit it to undergo more general photolytic decomposition. A detailed mechanistic study in this general area is in progress.

A survey of the literature suggests that the system (I), or its vinylogue, may be generally susceptible to photochemical rearrangement, with the overall transfer of C from B to A (or vinylogue). The oxime rearrangement here reported falls into this class, as does that of the nitrones.



$$\mathrm{Ar{-}A{=}\overset{\overset{\displaystyle C}{|}}{B}}$$

(I)

Other examples available of what may be termed, in the present

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[6] The intermediacy of the oxazirane in the formation of benzamide from o-benzylhydroxylamine has been suggested (10).

[7] The reversal of more heavily substituted oxaziranes to nitrones has been recorded on several occasions; see, for instance, (7).

instance, oxygen-transfer rearrangements are the photochemical conversion of quinoxaline oxide (A = CH; B = $\overset{\oplus}{N}$-C; C = $\overset{\ominus}{O}$) to 2-hydroxyquinoxaline (12), of azoxybenzenes (A = N; B = $\overset{\oplus}{N}$-C; C = $\overset{\ominus}{O}$) to hydroxyazobenzenes (13) and of the oxythiobenzoyl chlorides (A = C-Cl; B = $\overset{\oplus}{S}$; C = $\overset{\ominus}{O}$) to benzoyl chloride (14).

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