Selectivity of Intramolecular Hydrogen Transfer in the Free Amido-radical

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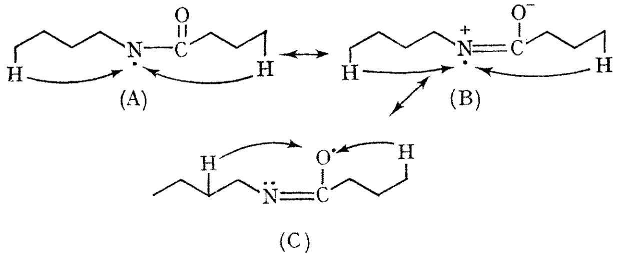
IRRADIATION of *N*-halogenoamides[1,2] results in inter- and intra-molecular halogen–hydrogen exchange reactions through the photolytic cleavage of the N–halogen bond. The intramolecular photorearrangement[1] results from the transfer of the δ-hydrogen atom in the acyl side-chain of the amido-radical. This is in accord with the favoured transition state proposed.[1,3]



In theory an amido-radical can be represented by three resonance structures A, B, and C, from which intramolecular hydrogen transfers do not necessarily give rise to the same product. We have therefore determined (i) whether the hydrogen transfer occurs to the oxygen-(C) as well as to the nitrogen-atom (A,B) and (ii) whether the hydrogen atom transfers† preferentially from the alkyl or acyl side chain.[4]

On irradiation (>280 nm.) of (1) and (4) (benzene, under N_2), the rearrangements readily occur to give clean products (n.m.r.). The *N*-bromoamides (4a) and (4b) yielded (5a) and (5b) exclusively. These products were further dehydrobrominated (Bu^tOK) to give (6a) and (6b). The *N*-bromide (1) gave (3), upon the usual working up, presumably due to ring closure of (2). In contrast to the good yields of (3) and (5) (Table), irradiation of (7a) and (7b) gave nearly quantitative yields of t-butylacetamide. We detected (8) (< 2%) in the photolysate from (7b) from the n.m.r. signal at τ 6·23 corresponding to CH_2–O. The structure of compounds (3), (5), and (6) were confirmed from their i.r., n.m.r., mass spectral and analysis data.

Photolysis of N-*halogeno-amides*

Reaction	Yield (%)[a]	ϕ^b	Relative ϕ	Concn. × 10^2 (mole/l.)[b]
(1) → (2)	>90	33·9	3·5	1·74
(4a) → (5a)	85	131	13·5	1·40
(4b) → (5b)	93	—	—	—
(7a) → (8)	0	9·7	1	1·44
(7b) → (8)	<2	—[c]	—[c]	1·20

[a] Isolated yields in the preparative runs.

[b] The quantum yield (ϕ) was determined with degassed benzene solutions in the concentrations as indicated and the remaining *N*-bromo-amides were analysed by iodometry. The light source was a GE-FC8T9/BL and the light intensity was $6{\cdot}9 \times 10^{-10}$ Einstein/sec.

[c] The value of ϕ was too low to be significant.

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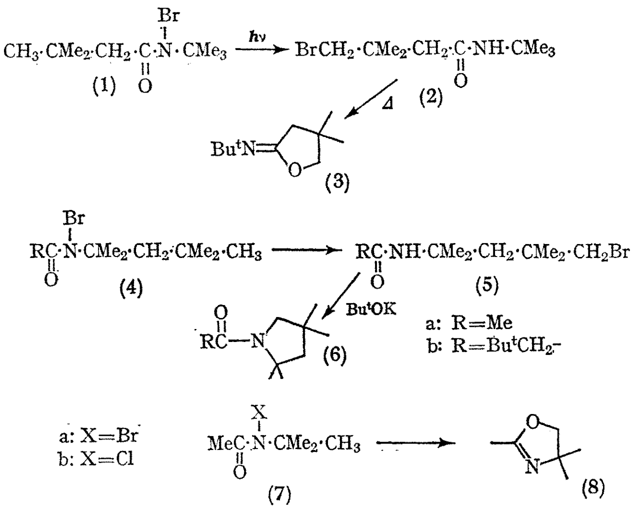
† In contrast to the results reported in refs. 1 and 2, transfer of δ-hydrogen of the acyl chain does not occur in the amidyl radicals derived from the photolysis of nitrosamides (ref. 4).

Further (3) was hydrolysed to 4,4-dimethylbutyrolactone and both (6a) and (6b) reduced ($LiAlH_4$) to the corresponding pyrrolidines.

The results confirm (i) that the intramolecular hydrogen transfer to the oxygen-atom C is virtually nil and (ii) that if a δ-hydrogen is available in the alkyl side-chain it is this hydrogen that transfers in the amido-radical. The quantum yields of (1), (4a), and (7a) (Table), which measure the efficiency of chain propagation in the photorearrangement, proportionally reflect the stereo-accessibility of the abstractable hydrogen. Assuming the intramolecular hydrogen transfer is the rate determining step, the stereochemical requirements in the transition state[1,3,4] must be viewed as the dominant factor controlling the reaction. The trace yield of (8) resulting from photolysis of (7b) in our work and the reported higher yield from similar experiments in a Vycor vessel (1b) suggest a secondary reaction being responsible for the formation of (8). In view of the well established mechanism for the intermolecular halogen–hydrogen exchange reaction,[2] it is very likely that the halogen atom is the chain carrier‡ in the photolysis of (7).

We thank the National Research Council of Canada for financial assistance.



(*Received, March 3rd,* 1969; *Com.* 301.)

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‡ Professor F. D. Greene has kindly informed us that he has reached the same conclusion using different amide systems.

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