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COMPETING CONCERTED AND RADICAL MECHANISMS I:
THE 2-ALKOXYQUINOLINE-N-OXIDE REARRANGEMENT

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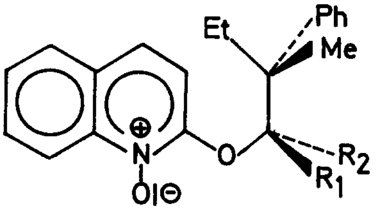
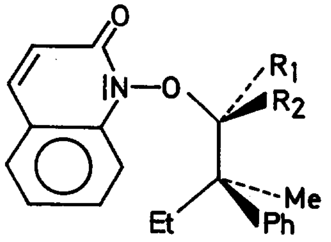
2-Benzyloxyquinoline-N-oxide has recently been shown to rearrange via both a sigmatropic (suprafacial) and a radical pair mechanism 1). We have investigated this rearrangement using 1,2-diphenyl-2-methylbutyl as the migrating group and CIDNP spectroscopy 2) as the detection method in order to determine the extent of the radical pair process.

The erythro (1a)*) and the threo (1b)*) isomer of 2-(1',2'-diphenyl-2'-methylbutoxy)-quinoline-N-oxide were prepared from 2-chloroquinoline-N-oxide and the potassium salts of erythro and threo-1,2-diphenyl-2-methylbutanol 3), respectively.



1 a R_1 = H, R_2 = Ph
b R_1 = Ph,R_2 = H



2 a R_1 = H, R_2 = Ph
b R_1 = Ph,R_2 = H

They were rearranged at 170° in hexachloroacetone yielding both erythro (2a)*) and threo-N-(1,2-diphenyl-2-methylbutoxy)-quinolone (2b)*) which differ sufficiently in the chemical shifts of their benzylic protons to permit

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*) Mixture of enantiomeres

NMR and CIDNP studies of the product ratio.

During the rearrangement of (1a) (Fig.1A, benzylic proton) the CIDNP-spectrum shown in Fig.1B was observed: emission [4)] of the benzylic protons of both (2a) ($\delta = 6.30$ ppm) and (2b) ($\delta = 6.36$ ppm), emission ratio $V_I = I_{2b}/I_{2a} \approx 1.25$; after complete rearrangement, the spectrum shown in Fig.1C was recorded indicating a product ratio $V_P = c_{2b}/c_{2a}$ of about 0.7 .

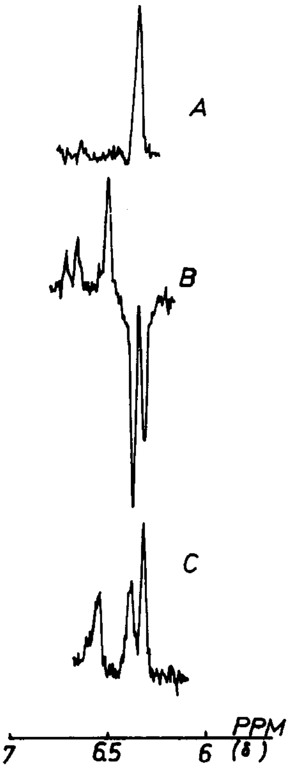

Fig. 1

From the product and the CIDNP-intensity ratios the extent of the radical pathway can be determined if the enhancement factors of (2a) and (2b) are assumed to be equal; in this case, the ratio 2b/2a produced by the radical reaction is identical with the ratio of CIDNP-intensities, V_I . The fractions of molecules undergoing concerted (x_c) and radical reactions (x_r) are then given by

$$R = x_c + x_r \cdot R_r \qquad \text{(eq. 1)}$$

where R_r and R are 'extents of retention' for the radical and for the over-all reaction, defined by $R_r = (1-V_I)/(1+V_I)$ and $R = (1-V_P)/(1+V_P)$, respectively, and $x_c + x_r = 1$. With eq.1 , $x_r = 0.75$, i.e., a 75% radical course is calculated for the rearrangement of (1a); the x_r value for the rearrangement of (1b), determined under the same conditions, was appreciably smaller (0.2 or 20% radical) indicating that the concerted mechanism seems to be more favorable for (1b) than for (1a) .

However, whether it is really justified to regard these values as the fraction of molecules which undergo radical processes is first of all dependent on the validity of the assumption of equal enhancement factors. This assumption seems to be justified only if there is in fact no difference between radical pairs yielding (2a) and those pairs yielding (2b), at least with respect to CIDNP. It can be shown that the latter will certainly be true if radical pairs generated from (1a) and (1b), respectively, give rise to the same CIDNP-intensity ratio. This condition, however, is apparently met in our system : whereas (2b) resulted in a product ratio V_P of about 10 , i.e., very different from that found in the rearrangement of (1a), there was no difference in V_I (≈ 1.25).

The finding that - with respect to CIDNP - identical radical pairs are generated from (1a) and (1b) also demonstrates the following: radical pairs giving rise to CIDNP apparently do not show any preference of retention of configuration, recombination of such radical pairs rather seems to be in accordance with Cram's rule (formation of (2b) more rapid than that of (2a)). Since this is not what is usually observed for radical rearrangements - e.g., (1,2)-shifts in ylides [5]- we suppose that it is necessary to account for 'inactive radical pairs' also, i.e., pairs which do not generate CIDNP (small distance of the radicals, short lifetimes) but give rise to more retention of configuration than the radical pair detected by CIDNP.
Thus, eq.1 should be replaced by

$$R = x_c + x_i \cdot \overline{R_i} + x_a \cdot R_a \qquad (\text{ eq.2 })$$

where x_i is the fraction of 'inactive' radical pairs, $\overline{R_i}$ their mean extent of retention ($1 \geq \overline{R_i} \geq R_a$), and x_a, R_a are the corresponding quantities for the 'active' species. x_r calculated from eq.1 is thus interrelated with x_i and x_a by

$$x_r = x_a + x_i \cdot \frac{1 - \overline{R_i}}{1 - R_a} \quad , \qquad (\text{ eq. 3})$$

i.e., x_r includes 'inactive' radical pairs as well, but only with a factor $(1-\bar{R}_i)/(1-R_a)$ which is always less than unity.

Thus, if for any system a contribution of 'inactive' radical pairs cannot be excluded for other reasons, x_r calculated from eq.1 should be regarded as the minimum fraction of molecules undergoing the radical pair reaction. Similar considerations apply for any other attempt to determine 'radical contributions' by means of a product-ratio/CIDNP combination 6); only minimum extents of radical reaction can be derived using these methods.

References

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4) Emission is in accordance with an intramolecular course of the radical reaction; intermolecular recombination should give rise to enhanced absorption.
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