Tetrahedron Letters No.46, pp. 4087-4088, 1969. Pergamon Press. Printed in Great Britain.

EVIDENCE FOR RADICAL MECHANISM AND A CAGE EFFECT IN THE THERMAL REARRANGEMENT OF N-BENZYL-N-METHYLANILINE N-OXIDE

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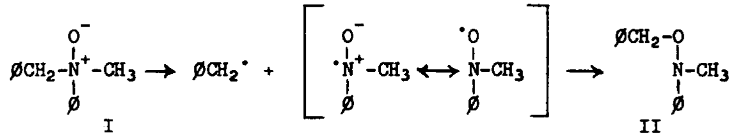
(Received in USA 26 May 1969; received in UK for publication 16 June 1969)

We wish to report direct evidence for a homolytic scission-recombination mechanism in the thermal "Meisenheimer" rearrangement[2] of the title compound, I, to the hydroxylamine, II (equation I). This mechanism was apparently first proposed by Schöllkopf,[3] who adduced threefold



$$\phi CH_2-\overset{O^-}{\underset{\phi}{N^+}}-CH_3 \longrightarrow \phi CH_2^{\bullet} + \left[{}^{\bullet}\overset{O^-}{\underset{\phi}{N^+}}-CH_3 \longleftrightarrow \overset{{}^{\bullet}O}{\underset{\phi}{N}}-CH_3 \right] \longrightarrow \overset{\phi CH_2-O}{\underset{\phi}{N}}-CH_3 \qquad (1)$$

I

II

evidence in its support: (1) optically active α-deuterobenzyl suffers 61-78% racemisation;[4] (2) for benzyl ring substitution, $\rho = +1.2$, too small for a carbanion mechanism, although of the correct algebraic sign; (3) methylphenylnitroxide radical may be detected during photolysis at -5°C. The third fact is not directly applicable to the thermal reaction.

We have observed that bubbling air or oxygen through a solution of I greatly reduces the yield of II, compared to the yield under nitrogen. I, prepared[5] as its crystalline hydrochloride, I-HCl, and liberated *in situ* with dilute sodium hydroxide, was allowed to rearrange in 80% ethanol-20% water (by volume) at 70.3°C for 13 hours. Solutions (or aliquots at time intervals) were quenched in ice water, extracted with pentane, and the pentane removed by distillation. The yield of II was determined by nmr using weighed amounts of anisole as integration reference. Under nitrogen the yield of II was 89%; under air this fell to 41%, and under pure oxygen, to 33% (averages of duplicate experiments.) Under all conditions, however, the rate constant was the same within the observed precision, 6.2 ± 0.4 X 10^{-3} min^{-1}.

Toluene was produced in only 0.7% yield under nitrogen, and less than 0.1% under air or oxygen. Benzaldehyde was not detected under nitrogen, but was formed in trace amount under air and 4% yield under oxygen.

These results support a homolytic scission mechanism accompanied by a cage effect. A 33% yield of II arises from "caged" radicals which cannot be trapped by oxygen (c. 0.002 M at 1 atm); we reckon the % cage effect as (33/89) x 100 = 37%. The remainder of radicals escape the cage and either re-encounter one another (under nitrogen, coupling to II), or are trapped by oxygen. The yield of toluene from attack on ethanol is expected to be low since benzylic radicals are known[6] to be unreactive in H-atom abstraction. The first order rate constant does not change because the same rate-determining transition state precedes both cage and non-cage pathways.

A carbanion mechanism, in contrast, predicts a high toluene yield via rapid neutralization of all benzyl anions escaping the cage. The role of oxygen would be to reduce the yield of toluene, but not the yield of II.

It is interesting that our efficiency of radical production, 63%, corresponds with Schöllkopf's value of 61-78% racemisation in α-deuterobenzyl. Since free radicals must become racemic, it is evident that caged radicals couple predominantly with retention of configuration.

Acknowledgements: We are grateful for financial support from The National Science Foundation (for purchase of the Varian A-60 nmr spectrometer), the Graduate School of Boston University, and the Army Research Office-Durham.

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