# Single-electron Transfer to Iodides from Sodium Naphthalide and Butyl-lithium

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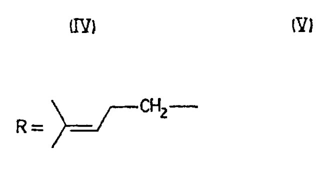
*Summary* A non-concerted single-electron transfer pathway has been established for the reductive elimination of α-iodo epoxides to allylic alcohols with sodium naphthalide; the exchange reaction between BuLi and RI must proceed exclusively by single-electron transfer to account for identity of rates of reaction between BuLi and epimeric 3-iodo-4β,5β-epoxycholestanes.

EXCLUSIVE formation of linalo-ol [protonated (V)] by the addition of sodium naphthalide, $C_{10}H_8^{\cdot-}$, to a mixture of *cis*-and *trans*-1-iodo-2,3-epoxy-3,7-dimethyloct-6-ene (I) was briefly reported earlier.[1] There is evidence that this reagent reacts with iodides to give radicals,[2] but the above finding did not allow a choice between paths *a* and *b* (Scheme). It is also possible that a non-radical concerted pathway was involved. Previous observations[2] that the radical R· produced from RX and $C_{10}H_8^{\cdot-}$ undergoes two simultaneous reactions with the $C_{10}H_8^{\cdot-}$ present, to give either $R^-$ *via* electron transfer, or $C_{10}H_8R^-$ *via* combination, leading to alkylnaphthalenes, have now been used to distinguish between the paths *a* and *b*. The alkylnaphthalenes are produced irrespective of the mode of addition but their formation in substantial quantities is favoured by drop-wise addition of the iodide to the radical-ion. Hence the above iodo-epoxide mixture in dimethoxyethane (DME) was added drop-wise to a concentrated solution of sodium naphthalide in DME. Linalo-ol was obtained in quantitative yield to the total exclusion of alkylnaphthalenes thereby ruling out path *a*. In order to disprove a concerted mechanism for the reaction stereoisomeric iodo-epoxides in the steroid series were prepared.

5β-Hydroxycholest-3-ene (VI)[3] on treatment with *N*-iodosuccinimide (NIS) gave 3α-iodo-4β,5β-epoxycholestane (VII) which was converted into the more stable *cis*-epimer, 3β-iodo-4β,5β-epoxycholestane (VIII)† by NaI in acetone. Compounds (VII) and (VIII) on treatment with sodium naphthalide both gave exclusively (VI). In order to establish the relative rates of these reactions a 1 : 1 mixture of (VII) and (VIII) was treated with enough sodium naphthalide in DME to react with 75% of the iodides. Analysis of the product by n.m.r. spectroscopy showed that unchanged iodides were still present in a 1 : 1 ratio. Identi-



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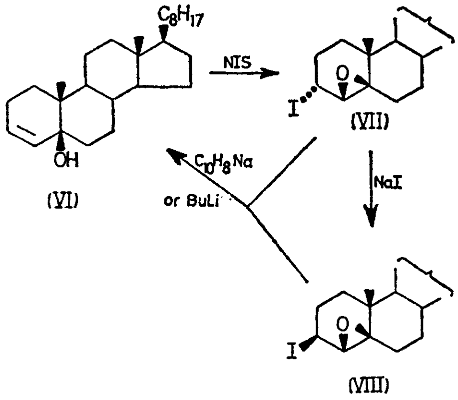
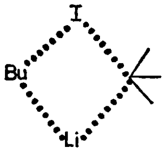
† All compounds were satisfactorily characterized: compound (VII), δ 4·37 (3H, t), and 3·3 (4H, s); compound (VIII), δ 4·55 (3H, q) and 3·0 (4H, d).

cal rates of reaction observed here would not have been expected if a concerted mechanism was operative since there would have been a preference for either ***anti*** or ***syn*** elimination.‡ Identity of rates are consistent with an earlier report that rates of reaction of sodium naphthalide with n-propyl and isopropyl iodides are equal.[4] It appears that in these radical-producing reactions the transition state closely resembles the starting materials.





(IX)

Thus the epoxy-iodides react by a single-electron transfer leading to a radical which rearranges quickly to the allyloxyl radical prior to reduction with more sodium naphthalide.§

The extremely fast irreversible opening of the epoxide adjacent to a radical suggests that it possible to use this system for investigating the exchange reactions between butyl-lithium and alkyl iodides which are believed to produce radicals.[5] The e.s.r. and CIDNP results, however, do not exclude the possibility of a simultaneous non-radical pathway for much of the exchange.

Butyl-lithium in ether reacted with (VII) and (VIII) to give exclusively (VI). When a 1:1 mixture of (VII) and (VIII) was treated with insufficient quantity of the reagent, the unchanged iodides were found to be present in the same ratio, *i.e.* the rates of reaction for the two iodides were the same.

This observation cannot be rationalized on the basis of the accepted non-radical mechanisms for the BuLi–RI exchange reaction.[6] Thus if the reaction were to proceed by a non-carbanionic $S_Ei$ mechanism involving the four-membered transition state (IX), then the transition states corresponding to the reaction of the $\beta$-iodide (equatorial-quasi equatorial) and the $\alpha$-iodide (axial-quasi axial) would encounter steric hindrance of sufficiently different magnitudes relative to the starting materials that identity of rates¶ would not be expected. (The stereochemistry of the starting iodides is based on n.m.r. analysis† and their relative stabilities which indicate that they do not *both* adopt conformations in which the iodide is quasi equatorial.) The $S_E2$ transition state also requiring a pyramidal carbon, and the lithium carbanide ion-pair mechanism can also be rejected on similar grounds. On the other hand, the similarity between rates of reaction in single-electron transfer to the stereoisomeric iodides is not exceptional in view of the reaction with sodium naphthalide.

This leads to the conclusion that the exchange reaction between BuLi and RI proceeds exclusively by a single-electron transfer to produce alkyl radicals which subsequently collapse to carbanions. With the epoxy iodides and BuLi a similar collapse to carbanion, followed by opening of epoxide,[7] has not been ruled out but the opening to allyloxyl radicals seems more likely.

(*Received, 4th February* 1975; *Com.* 127.)

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‡ Unless both occur at diffusion controlled rates. This is considered unlikely as the rate with RI has been estimated[2] to be $10^8$ l mol$^{-1}$ s$^{-1}$.

§ In view of the observation by Garst[2] concerning the rates of rearrangement relative to reduction of the hex-5-enyl radicals, this rate must be $> 10^7$ s$^{-1}$.

¶ The two epoxy iodides do not react at identical rates with $LiAlH_4$ or with Zn though these reactions also give (VI) exclusively.

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[7] H. J. Fabris, *J. Org. Chem.*, 1967, **32**, 2031.