Evidence Against Alkyl Dimer Formation through S_N2 Processes in Wurtz Reactions of Alkyl Iodides with Sodium in 1,2-Dimethoxyethane: Bineopentyl from Neopentyl Iodide

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Summary In reactions of alkyl iodides in 1,2-dimethoxyethane with sodium at *ca.* 22°, alkyl dimer formation through conventional S_N2 processes is ruled out by the finding that there is no discrimination against the formation of bineopentyl from neopentyl iodide.

IT is thought that nucleophilic (S_N2) displacements of alkylsodiums on alkyl halides lead to the dimers formed in Wurtz reactions using sodium.[1]† Abundant evidence documents a free-radical course (equation 1) for the corresponding reactions of simple (saturated) alkyllithiums

$$RM + RX \rightarrow MX + 2\,R\cdot \rightarrow R_2 \text{ (or RH + olefin)} \qquad (1)$$

with simple alkyl halides,[3] but since lithium is often peculiar among the alkali metals, this is not necessarily inconsistent with an S_N2 view of alkylsodium reactions.

As a test of the S_N2 mechanism for reactions of alkyl iodides in 1,2-dimethoxyethane (DME) with sodium mirrors at *ca.* 22° we have examined the reaction of neopentyl iodide.

Neopentyl iodide (0·098 M in DME) gave bineopentyl in 80% yield (neopentane, 20%; balance of neopentyl groups, 95%). This is an even higher dimer yield than that (67%) from the similar reaction of pentyl iodide (0·101 M), although when the yield of the other bimolecular reduction process (2 RI + 2 Na → RH + olefin + 2 NaI) is added to that of decane, the net yield of bimolecular reduction products is also 80% (balance of pentyl groups, 99%). Partitioning between monomolecular reduction (to RH and solvent-derived products, methanol and methyl vinyl ether) and bimolecular reduction is insensitive to whether R is pentyl or neopentyl.

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† Largely, this view is based on results of stereochemical studies of allylic and benzylic systems.[2]

Even more striking is the similar insensitivity for dimer formation from mixtures of pentyl and neopentyl iodides. When each is 0·050 M initially, the three possible dimers, decane, 2,2-dimethyloctane, and bineopentyl, are formed in ratios 1·2 : 1·7 : 1·1, respectively. These ratios are trivially different from statistical (1 : 2 : 1), implying almost no selectivity among alkyl groups.

Neopentyl halides are notoriously slow in conventional S_N2 reactions, typical reactivities being *ca.* 10^{-4} relative to primary alkyl halides like pentyl.[4] The steric factors to which this is attributed would be greatly compounded if the attacking nucleophile were the neopentyl anion (neopentylsodium). Either the alkyl dimers are not formed in reactions of alkylsodiums with alkyl iodides or such reactions are not conventional S_N2 processes. Free-radical combination according to (1) is mechanistically attractive,‡ and (1) has been suggested as the mechanism of formation of alkyl dimers in reactions of alkyl iodides with sodium dihydronaphthylide in DME.[6] However, other pathways (*e.g.*, unconventional nucleophilic displacements, dimerizations of radicals formed at the sodium surfaces§) have not been ruled out. The details of the coupling mechanism remain obscure where sodium is involved.

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‡ Sauer and Braig have found evidence for S_N2 coupling in allylic alkyllithium-alkyl halide reactions, but free radical coupling in corresponding simple systems.[5]

§ The CIDNP from reactions of alkyl iodides in DME with sodium has a phase consistent with this pathway, but not clearly consistent with reaction (1).[7]

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