

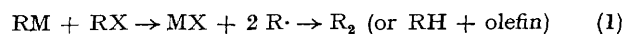
Evidence Against Alkyl Dimer Formation through S_N2 Processes in Wurtz Reactions of Alkyl Iodides with Sodium in 1,2-Dimethoxyethane: Bineopentyl from Neopentyl Iodide

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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) alkylolithiums



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 ($2 RI + 2 Na \rightarrow RH + \text{olefin} + 2 NaI$) 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.

† 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 (neopentyl-sodium). Either the alkyl dimers are not formed in reactions of alkylsodiums with alkyl iodides or such re-

actions 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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