ON THE MECHANISM OF ALKYL DIMER FORMATION IN REACTIONS OF ALKYL IODIDES WITH
SODIUM NAPHTHALENE. EVIDENCE FROM REACTIONS OF 1,4-DIIODOBUTANE.

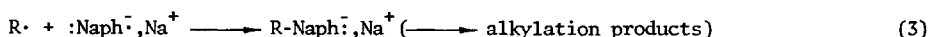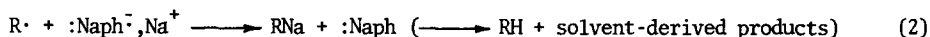John F. Garst and John T. Barbas

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Recent studies indicate that the initial reactions of alkyl halides with sodium naphtha-
lene in DME are best regarded as dissociative electron-transfer reactions, with no significant
competition from nucleophilic displacement reactions (Eq. 1) (1,2a). The initially-formed

$$RX + :Naph^{-},Na^{+} \longrightarrow R\cdot + :Naph + NaX \tag{1}$$

radicals are scavenged by sodium naphthalene in competitive electron-transfer and radical com-
bination steps (Eq. 2 and 3), leading to reduction products (RH) and alkylation products

$$R\cdot + :Naph^{-},Na^{+} \longrightarrow RNa + :Naph \; (\longrightarrow RH + \text{solvent-derived products}) \tag{2}$$

$$R\cdot + :Naph^{-},Na^{+} \longrightarrow R\text{-Naph}^{-},Na^{+} (\longrightarrow \text{alkylation products}) \tag{3}$$

(alkyl- and dialkyldihydronaphthalenes, alkyl naphthalenes), respectively. Reactions 2 and 3
represent the exclusive fates of initially-formed radicals when the alkyl halide reactant is
an alkyl fluoride or chloride, but the presence of alkyl dimers among the products of reac-
tions of alkyl bromides and iodides implies the possibility that reaction 4 may be significant
in these cases.

$$2 R\cdot \longrightarrow R_2 \text{ (or RH + olefin)} \tag{4}$$

In fact, the product distributions obtained in reactions of alkyl iodides with sodium
naphthalene clearly indicate that the alkyl dimers are not formed in S_N2 reactions of alkyl-
sodiums with alkyl iodides (2). These product distributions are, however, consistent with
radical coupling-disproportionation reactions. On this basis, the reaction sequence 1-4 has
been proposed as the mechanism of alkyl dimer formation (2b). The considerations presented
here reopen the question of the mechanism of alkyl dimer formation in these reactions.

Many recent reports document reactions of alkyllithiums with alkyl halides, including
iodides, which proceed by dissociative electron-transfer processes (Eq. 5) (3). The fates of

$$RLi + RI \longrightarrow [2 R\cdot, LiI] \longrightarrow \text{products} \tag{5}$$

the radicals so formed may be varied, with metal-halogen interchange being accomplished fre-

quently, but the ultimate products are radical coupling-disproportionation products.

In view of these studies, the reaction sequence 1-2-6 should be considered a viable can-

$$RNa + RI \longrightarrow [2 \ R\cdot, \ NaI] \longrightarrow R_2 \ (or \ RH + olefin) \tag{6}$$
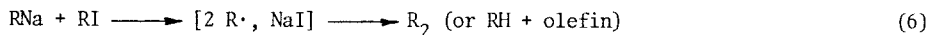
didate for the mechanism of alkyl dimer formation in reactions of alkyl iodides with sodium naphthalene. Inasmuch as it prescribes dimer formation in radical coupling reactions, it is as consistent as the sequence 1-4 with the product distributions mentioned previously (2).

When the reaction of 1,4-diiodobutane with sodium naphthalene is carried out under conditions which should suppress coupling and other reactions among the initially-formed 4-iodo-butyl radicals, the distribution between reduction products (cyclobutane, 51%) and alkylation products (4) (44%, perhaps slightly more) is identical, within experimental error, with that observed for simple primary alkyl halides (e.g., 5-hexenyl and cyclopentylmethyl halides) (1, 5). We have previously reported our conclusions that the 4-iodobutyl radicals formed in these reactions do not react unimolecularly to give cyclobutane and that they do not have cyclic bridged structures (5). Instead, they behave "classically," insofar as the balance of the competition between reactions 2 and 3 (R = 4-iodobutyl) is concerned.

If the reaction sequence 1-4 were applicable to reactions of 1,4-diiodobutane in DME carried out under conditions which lead to alkyl dimers from simple alkyl iodides, the product distribution would be affected by the occurrence of reaction 7 (analogous to reaction 4).

$$2 \ I(CH_2)_3CH_2\cdot \longrightarrow I(CH_2)_8I \ or \ other \ products \tag{7}$$
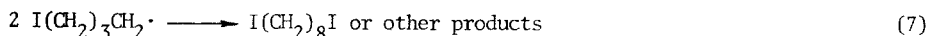
We have performed these experiments. In addition to the "evaporation" method used earlier (1,5), two "injection" procedures were employed. In the "diiodobutane injection" experiments, 1,4-diiodobutane was injected by means of a syringe into preformed solutions of sodium naphthalene (ca. 0.1 M) in DME. In the "sodium naphthalene injection" experiments, small amounts of solutions of sodium naphthalene (ca. 0.1 M) in DME were injected successively into solutions of 1,4-diiodobutane (ca. 0.1 M initially) in DME. Both injection methods lead to 30-50% yields of alkyl dimers when they are applied to simple primary alkyl iodides (1,2).

When applied to 1,4-diiodobutane, the injection experiments gave the same product distributions as the evaporation experiments! The yields of cyclobutane (in moles per mole of 1,4-diiodobutane) from these experiments were: evaporation (0.53, 0.49, 0.50) (5): diiodobutane injection (0.54, 0.52, 0.54, 0.51, 0.50); sodium naphthalene injection (0.51, 0.50). The vpc traces of these reaction mixtures were identical over their entireties, including the region

of alkylation products. No C_8 hydrocarbons were detected in any experiments. Cyclobutane was the only significant C_4 hydrocarbon product in each case (6).

Thus, it is clear that initially-formed 4-iodobutyl radicals do not couple or otherwise react among themselves in these reactions. Unless the balance of the competition between reaction 7 and reactions 2 and 3 (R = 4-iodobutyl) is very different from the balance of the competition between reaction 4 and reactions 2 and 3 (R = primary alkyl radicals), the mechanism of alkyl dimer formation from simple primary alkyl iodides cannot be the sequence 1-4. There is no reason to expect such a difference in the balance of these competitions.

On the other hand, if the sequence 1-2-6 applies to both simple alkyl iodides and 1,4-diiodobutane, the experimental data are readily accounted for. The cyclobutane is then viewed as arising from 4-iodobutylsodium, presumably through a reaction analogous to 6. The absence

$$I(CH_2)_3CH_2I \longrightarrow [\cdot CH_2(CH_2)_2CH_2\cdot,NaI] \longrightarrow \text{cyclobutane} \qquad (8)$$
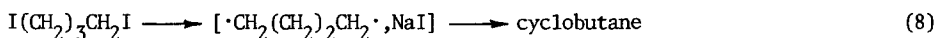
of C_8 and higher alkanes and related products is attributed to reaction 8 being much faster than reaction 9. That 8 should be much faster than 9 is entirely reasonable for a unimolecu-

$$I(CH_2)_3CH_2Na + I(CH_2)_4I \longrightarrow \longrightarrow I(CH_2)_8I \qquad (9)$$
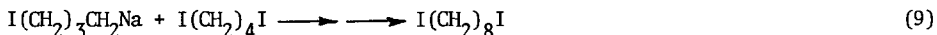
lar version (Eq. 8) of a bimolecular reaction (Eq. 9).

The bearing of this work on mechanisms of Wurtz reactions is obvious, but space does not permit discussion of relevant earlier studies. Many leading references to these are given in the articles which comprise Ref. 3. Suffice it to state that some of the results of such studies of reactions of alkylsodiums with alkyl iodides are not easily reconciled with reaction 6 (3e). On the other hand, there seem to be no data which definitively eliminate reaction 6 as the mechanism of such reactions under the conditions employed in the present work.

Thus, the question of the mechanism of alkyl dimer formation in reactions of alkyl iodides with sodium naphthalene is reopened. The present evidence favors the reaction sequence 1-2-6 over the sequence 1-4. The reactions described herein may provide a new procedure for the generation and investigation of diradicals in solution.

REFERENCES

1. J. F. Garst, J. T. Barbas, and F. E. Barton, II, J. Amer. Chem. Soc., 90, 7159 (1968). Results of "evaporation" experiments are reported. In such experiments, alkyl halides are slowly evaporated into stirred solutions of sodium naphthalene. These experiments are designed to suppress alkyl dimer formation through any mechanism.

2. (a) G. D. Sargent and G. A. Lux, J. Amer. Chem. Soc., 90, 7160 (1968); (b) G. D. Sargent, J. N. Cron, and S. Bank, J. Amer. Chem. Soc., 88, 5363 (1966).

3. (a) G. A. Russell and D. W. Lamson, Abstracts, 157th ACS National Meeting, Division of Organic Chemistry, paper 115 (1969); (b) H. R. Ward, J. Amer. Chem. Soc., 89, 5517 (1967); H. R. Ward and R. G. Lawler, J. Amer. Chem. Soc., 89, 5518 (1967); R. G. Lawler, J. Amer. Chem. Soc., 89, 5519 (1967); H. R. Ward, R. G. Lawler, and R. A. Cooper, J. Amer. Chem. Soc., 91, 746 (1969); (c) A. R. Lepley, J. Amer. Chem. Soc., 90, 2710 (1968); J. Amer. Chem. Soc., 91, 749 (1969); Chem. Comm., 64 (1969); A. R. Lepley and R. L. Landau, J. Amer. Chem. Soc., 91, 748 (1969); (d) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. Bieber, J. Amer. Chem. Soc., 88, 78 (1966); (e) D. Bryce-Smith, J. Chem. Soc., 1603 (1956); Bull. Soc. Chim. Fr., 1418 (1963); (f) F. S. D'yachkovskii and A. E. Shilov, J. Gen. Chem. USSR, 33, 400 (1963); Russ. Chem. Rev., 35, 300 (1966).

4. D. Lipkin, G. J. Divis, and R. W. Jordan, Preprints, Div. Petrol. Chem. 13, D60 (1968).

5. J. F. Garst and J. T. Barbas, J. Amer. Chem. Soc., 91, 3385 (1969). Reactions of 1,4-diiodobutane with sodium naphthalene using the "evaporation" method (Ref. 1) are described.

6. Analyses were based on vpc, using internal standards. Mass spectra and nmr spectra were employed for the identification of materials giving rise to peaks in vpc traces. These were taken on materials obtained from vpc runs by trapping or leading into a spectrometer. Further details are given in Ref. 5.