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REACTION OF SODIUM NAPHTHALENE WITH HALOBENZENES: AN ALTERNATE MECHANISTIC VIEW

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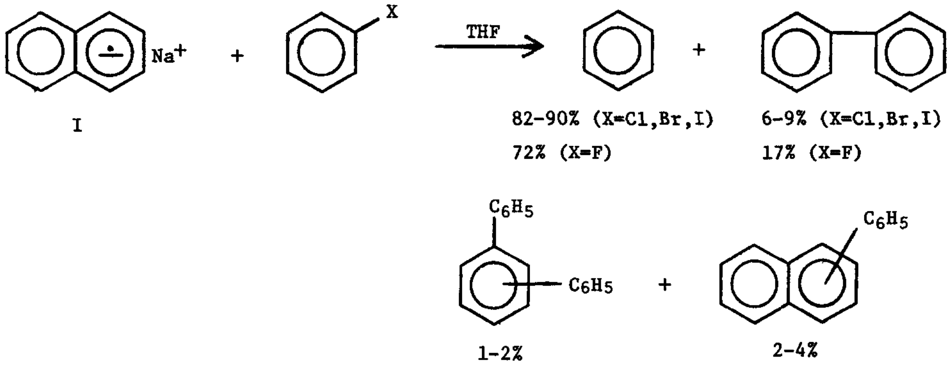
Our continuing interest in the reactions of sodium naphthalene with alkyl[1] and vinyl[2] halides led us to consider in some detail the recent report of an investigation[3] of the reaction of this radical anion with aryl halides. The results reported in that communication may be summarized as follows:



I

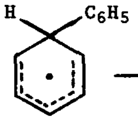
(1)

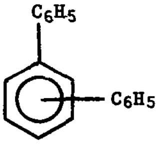
After consideration of both radical and anionic mechanisms, the authors concluded that the radical mechanism outlined below best accommodates their experimental observations.

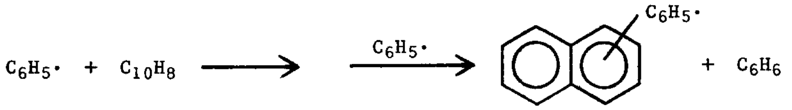
$$\text{I} + C_6H_5X \longrightarrow C_6H_5\cdot + X^- + C_{10}H_8 \qquad (2)$$

$$C_6H_5\cdot + \text{THF} \longrightarrow C_6H_6 + (\text{THF})\cdot \qquad (3)$$

$$2\ C_6H_5\cdot \longrightarrow C_6H_5{-}C_6H_5 \qquad (4)$$

$C_6H_5\cdot + C_6H_5 \longrightarrow$  $\xrightarrow{C_6H_5\cdot} C_6H_5{-}C_6H_5 + C_6H_6$ (5)

$C_6H_5\cdot + C_6H_5{-}C_6H_5 \longrightarrow \xrightarrow{C_6H_5\cdot}$  $+ C_6H_6$ (6)



(7)

Since this scheme (eq. 2-7) is at variance both with the mechanism previously proposed[2] and now firmly established[4] for the sodium naphthalene promoted reduction of 3-chloro-3-hexene to 3-hexene, and with the well documented mechanism for reaction of alkyl halides with sodium naphthalene,[1,5] we were prompted to examine it with some care. On so doing we find it to be inconsistent either internally or with precedent established in other laboratories on at least four counts.

1. Abstraction of hydrogen from tetrahydrofuran (THF) by the 5-hexenyl radical does not compete with reduction of that radical by sodium naphthalene to the corresponding anion.[6] A more directly analogous radical, the sp^2-hybridized, 3-hexen-3-yl radical, is reduced by sodium naphthalene to a configurationally more stable anion more rapidly than it can extract hydrogen atoms from THF. This conclusion follows unequivocally from the observation that the extent to which the radical equilibrates with its C-3 epimer is unaffected by conducting the reaction in perdeuterated solvent, even though the product distribution from a reaction carried out in mixed perprotonated-perdeuterated solvent shows k_H/k_D = *ca.* 8 for incorporation of hydrogen (deuterium) at C-3.[4] These precedents are in conflict with the principal postulated source of benzene from the reaction of sodium naphthalene with the halobenzenes (eq. 3).

2. Extensive "dimer" formation ($2RX \xrightarrow{I} R-R$) results from reaction of alkyl halides and sodium naphthalene only when iodides are employed. Alkyl chlorides and fluorides yield no "dimer".[1,5] This observation has been rationalized[1] on the grounds that the diminished reduction potentials of iodides relative to chlorides result in such rapid production of free radicals that an instantaneous concentration of radicals is achieved sufficient to permit dimerization, a process second-order in radical concentration, to compete with processes first-order in radical, *i.e.* reduction by, and coupling with, sodium naphthalene. Theoretical considerations and what quantitative data are available suggest chlorobenzene should generate radicals less rapidly than alkyl chlorides.[7] On this basis the significant yield of biphenyl from the reaction of chlorobenzene, and especially the *enhanced* yield from fluorobenzene, appear difficult to rationalize by eq. 4. Indeed, the suggestion that "dimers" are ever produced by coupling of two radicals independently generated by reaction of two molecules of alkyl halide with two molecules of I, even in the case of alkyl iodides, has been cogently questioned by Garst.[8]

3. Equation 5 cannot possibly correctly depict the primary process for biphenyl formation. The benzene required for this process can only be generated by initial reaction of a halobenzene molecule with a molecule of I, a reaction which concomitantly yields a molecule of naphthalene. Consequently, the concentration of naphthalene available for reaction with a phenyl radical (eq. 7) must always equal or exceed the concentration of benzene available for this purpose (eq. 5). Since the relative "phenyl affinities" of naphthalene and benzene are on the order of 24:1,[9] equations 5 and 7 would predict the yield of phenyl naphthalene should vastly exceed that of biphenyl. The experimental result is just the opposite.

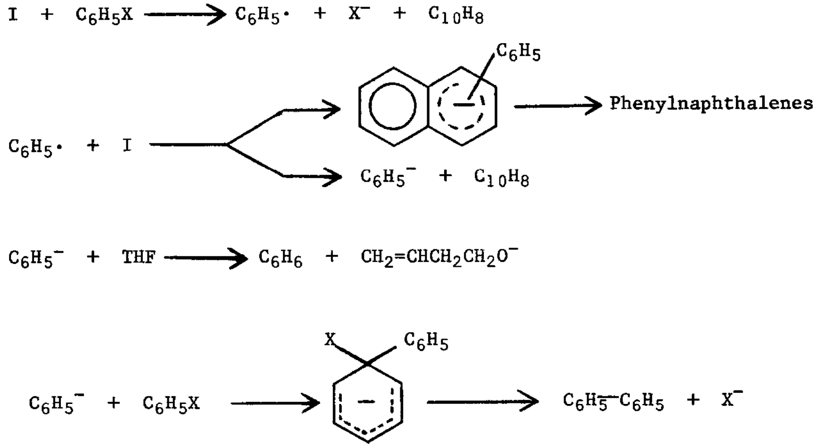
4. Alkylation of naphthalene always accompanies reaction of alkyl halides with sodium naphthalene. This reaction has been explicitly demonstrated *not* to involve radical addition to

naphthalene,[1] but rather to result from alkyl radical-radical anion coupling. There would seem to be no *a priori* reason for phenyl radicals to behave differently (eq. 7).

We have carried out the following preliminary experiments to test our conclusion that equations 3-5 and 7 cannot possibly govern the formation of products from reaction of sodium naphthalene with the halobenzenes. Taken together, equations 3 and 5 imply that the relative yield of benzene and biphenyl is governed, at least in part, by solvent and benzene competing for phenyl radicals. This implies that the absolute yield of biphenyl should increase if the concentration of benzene is artificially enhanced. Experimentally, no significant difference in the absolute yield of biphenyl is observed when the reaction is carried out in 40-60 volume percent benzene-THF as opposed to 100% THF as solvent.

Equation 5 implies that if the reaction were carried out in the presence of a large concentration of toluene, significant yields of methylbiphenyls should result. Reaction of bromobenzene with I in 40-60 volume percent toluene-THF, in fact, results in no detectable yield of *p*-methylbiphenyl, even though the *para* "phenyl affinity" of toluene relative to benzene is 1.4.[10] A significant yield of biphenyl is obtained, however. Similarly reaction of *p*-chlorotoluene with I in 40-60 volume percent benzene-THF yields some *p*,*p*'-dimethylbiphenyl, but no detectable *p*-methylbiphenyl. Significantly, a mixture of bromobenzene and *p*-chlorotoluene on reaction with I in THF yields detectable quantities of biphenyl, *p*-methylbiphenyl, and *p*,*p*'-dimethylbiphenyl.[11]

These results, while inconsistent with the previously proposed radical mechanism, are readily accommodated by the alternate mechanism outlined below.



$$\text{I} + C_6H_5X \longrightarrow C_6H_5\cdot + X^- + C_{10}H_8$$

$$C_6H_5\cdot + \text{I} \longrightarrow C_6H_5^- + C_{10}H_8$$

$$C_6H_5^- + \text{THF} \longrightarrow C_6H_6 + CH_2{=}CHCH_2CH_2O^-$$

$$C_6H_5^- + C_6H_5X \longrightarrow C_6H_5{-}C_6H_5 + X^-$$

This mechanism is fully consonant with that currently accepted for reaction of alkyl halides with sodium naphthalene. The high ratio of benzene to phenylnaphthalenes is anticipated by this mechanism, since the greater electronegativity of the sp^2 hybridized phenyl radical, as contrasted with an sp^3 hybridized alkyl radical, should favor electron transfer from, as opposed to coupling with, the naphthalene radical anion.

The postulated mechanism for "dimer" formation, nucleophilic aromatic substitution, is consistent with, if not uniquely demanded by, the enhanced yield of "dimer" when fluorobenzene is employed and by the apparent site specificity of the dimeric structures. Further experiments designed to test the validity of this mechanism are in progress and will be reported in detail subsequently.

NOTES AND REFERENCES

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(9) D. H. Hey and G. H. Williams, *J. Chem. Phys.*, 23, 757 (1955).

(10) D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 6 (1955).

(11) While by no means yet totally definitive, all our results to date suggest that the interannular bond of the biphenyl formed in these reactions joins only those carbon atoms which originally bear halogen substituents, *i.e.*, that "dimer" formation is site specific.