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ON THE MECHANISM OF DIMER FORMATION IN REACTION OF BENZYLIC HALIDES WITH SODIUM AND LITHIUM NAPHTHALENE(1)

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It has been reported by several groups that benzylic chlorides and bromides give very high yields of dimer on treatment with sodium or lithium naphthalene.(2) Considerable dimer formation (ca. 50%) has also been noted in reactions of simple alkyl iodides with sodium naphthalene in 1,2-dimethoxyethane.(3) In this latter case the mechanism of dimer formation was argued to be simple radical-radical combination (eq. 1),(3) though Garst has presented strong arguments that a

$$2R\cdot \longrightarrow R\text{-}R \qquad (1)$$

more likely pathway involves first reduction of initially formed alkyl radical to carbanion by naphthalene anion radical (eq. 2), a process known to occur at, or near, the diffusion controlled limit,(4) followed by an electron-transfer reaction between carbanion and alkyl iodide to generate a radical pair which collapses to dimer (eq. 3).(5) Zieger and coworkers (2a) have accepted

$$R\cdot + C_{10}H_8^{\dot{-}} \longrightarrow R^- + C_{10}H_8 \qquad (2)$$

$$R^- + R\text{-}I \longrightarrow 2R^\cdot + I^- \longrightarrow R\text{-}R + I^- \qquad (3)$$

Garst's mechanism for dimer formation from benzylic chlorides and bromides under conditions where naphthalene anion radical concentration is high, but favored eq. 1 (simple radical combination) under conditions where anion radical concentration is low, e.g., slow addition of lithium naphthalene to a THF solution of benzhydryl chloride. We would like to present evidence that indicates nearly all the dimer formed from benzyl and benzhydryl chloride on reaction with naphthalene anion radical in THF under conditions of either high or low anion radical concentration involves a carbanion precursor and probably is formed by Garst's mechanism (eq. 3 and 4). With benzyl bromide at least 90% of the bibenzyl must also be formed in this manner, and with benzyl iodide, at least 80%.

The approach was simply to compare the amount of dimer produced in the presence and absence of an efficient carbanion trap. From simple competition experiments(6) it was determined that tert-butyl alcohol reacts with sodium naphthalene in THF at a rate only about one-third as fast as benzyl chloride and at about one-quarter the rate of benzhydryl chloride. (The other halides studied are even more reactive.) Thus, it was possible to completely reduce any of the halides in the presence of the butyl alcohol by adding sodium naphthalene solution (ca. 0.5 M) to a solution of the halide (ca. 0.5 M) containing excess alcohol (2.5 M). While much of the alcohol will react with the anion radical, the difference in reactivity would guarantee a considerable amount still present by the time all of the halide is consumed. Control experiments showed that the dimers, bibenzyl and sym-tetraphenylethane, were not affected by the butyl alcohol-sodium naphthalene combination and an experiment in which benzhydryl chloride was reduced by sodium naphthalene in the presence of tert-butyl alcohol O-D (90% D) yielded diphenylmethane containing (by nmr) 80±10% of one deuterium in the benzylic position. The rather striking results, shown in Table I, also indicate that the butyl alcohol must be a quite efficient carbanion trap.

Thus, within experimental error, the presence of a relatively acidic proton source completely suppresses dimer formation in the reaction of benzylic chlorides with sodium naphthalene and very nearly so with lithium naphthalene. Surprisingly, even inverse addition (see Table I for details) does not result in dimer formation. Also of note is the fact that while inverse addition of benzhydryl chloride to sodium naphthalene in the absence of alcohol does result in a 75% reduction in yield of dimer, such an effect is not seen with any of the benzyl halides. This implies that the benzyl anion must be superior to sodium naphthalene in its reactivity toward benzyl halide.

As noted above, dimer formation from benzyl bromide or iodide could not be completely suppressed by 2.5 M alcohol. In the case of benzyl iodide, reduction with sodium naphthalene in 50% alcohol - 50% THF, or in pure alcohol solution gave results that are almost within experimental error of those obtained in the more dilute alcohol-THF mixture. We feel that this strongly implies that this residual dimer does not arise from a carbanion precursor but rather by either radical coupling (eq. 1) or through radical attack on neutral iodide, yielding bibenzyl in the manner discussed by Drury and Kaplan for similar intramolecular situations (eq. 4).(7)

(4)

The effect of added tert.-butyl alcohol on the reaction of n-heptyl iodide was briefly examined. Here the reaction is complicated by production of a relatively large fraction of coupling product formed by eq. 5,(8) (benzylic radicals yield only traces of such products), and probably by further reaction of the alkyldihydronaphthalene anion with alkyl iodide (eq. 6). As shown in Table

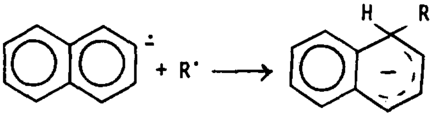
Table I

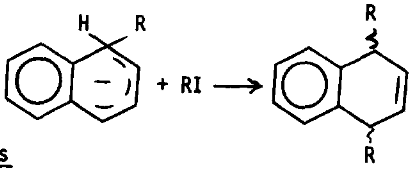
Reaction of Organic Halides with Sodium and Lithium Naphthalene in Tetrahydrofuran(a)

Halide	Mode of Addition(b)	Without $(CH_3)_3COH$		With $(CH_3)_3COH$(c)	
		%R-R	%RH	%R-R	%RH
Benzhydryl Chloride	normal	85 (70)	11 (26)	2.5 (3)	100 (97)
" "	inverse	21	63	<1	100
Benzyl Chloride	normal	86 (84)	9 (6)	<1 (4)	100 (96)
" "	inverse	82	15	<1	99
Benzyl Bromide	normal	83	8	8	94
" "	inverse	75	19	9	90
Benzyl Iodide	normal	78 (78)	7 (6)	17 (15)	74 (62)
" "	inverse	88	8	22	82
" "	normal	-	-	16(d)	77(d)
" "	"	-	-	13(e)	79(e)
n-Heptyl Iodide	normal(f)	13 (38)	17 (17)	9 (16)	38 (65)
" "	" (f)	28 (50)	12 (15)	8 (14)	38 (59)

(a)Analyses were performed by gas chromatography, using internal standards, and are averages of 2 or more experiments unless otherwise noted. Reproducibility of g.c. measurements is *ca.* ± 3%. Data in parentheses are for lithium naphthalene. (b)Normal addition: 0.5 M anion radical solution (in THF) added dropwise with stirring at 25° to 2 ml of 0.5 M halide in THF under N_2 until green color persisted. Reaction mixture was then quenched with a drop of water and analyzed. Inverse addition: 2 ml of 0.5 M halide added rapidly with vigorous stirring at 25° to 7 to 10 ml of 0.5 M anion radical solution under N_2. (c)Halide solution was 2.5 M in *tert*-butyl alcohol unless otherwise noted. (d)Halide dissolved in 1 ml THF plus 1 ml of alcohol. (e)Halide dissolved in 2 ml of alcohol. (f)Separate experiments.

I, the yields of heptane and tetradecane are quite variable in the absence of alcohol and apparently are rather sensitive to the rate of addition of anion radical. In the presence of 2.5 M alcohol the results are more reproducible (probably through elimination of eq. 6), the yield of heptane is increased and that of dimer decreased. Again, however, a modest amount of dimer remains. Interestingly, these results parallel very closely those observed by Bank and Bank on reaction of an alkyl iodide with sodium naphthalene in the presence of $MgBr_2$.(9) The $MgBr_2$ was also argued to be an efficient carbanion trap.(9) Again, it appears that this residual dimer may well arise by a non-carbanion route.


(5)


(6)

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(6) From partial (ca. 10%) reaction of a solution 0.25 *M* in each halide and 2.5 *M* in alcohol and measurement of the yields of dihydronaphthalenes, toluene, and diphenylmethane the following relative reactivities were estimated: *tert*.-butyl alcohol = 1, benzyl chloride = 2.7, benzhydryl chloride = 3.6. It should be emphasized that these relative rates have only qualitative significance since the absolute rates are probably on the order of $10^4 M^{-1} sec^{-1}$ (See S. Arai, E. L. Tremba, J. R. Brandom, and L. Dorfman, *Can. J. Chem.* *45*, 1119 (1967) for absolute rates of alcohol-anion radical reactions) and local depletion of the more reactive species in the vicinity of the added anion radical almost certainly obtains. This should result in a leveling effect, making the alcohol appear more reactive than it actually is.

(7) (a) R. F. Drury and L. Kaplan, *J. Amer. Chem. Soc.*, *95*, 2217 (1973). (b) An alternative possibility is that the effective acidity of the alcohol is drastically decreased at higher concentrations due to hydrogen bonding, though increasing solvent polarity normally *increases* acidity.

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(9) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969).