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REACTIONS OF SODIUM NAPHTHALENIDE WITH AROMATIC AND ALIPHATIC ALDEHYDES AND KETONES

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Aromatic radical anions have been shown to function either as bases or reducing agents.[1] In this communication we wish to report the reactions of a variety of carbonyl compounds with sodium naphthalenide.

In the general procedure the carbonyl compound was added via syringe to a stirred, dry tetrahydrofuran (THF) solution containing an excess (usually two equivalents) of sodium naphthalenide (ca. 1M) under dry nitrogen. When significantly less than two equivalents of sodium naphthalenide were used, completion of the reaction was indicated by disappearance of the green color of the radical anion within a few seconds at room temperature. Addition of saturated, aqueous ammonium chloride after five minutes quenched the reaction. The products were directly analyzed by gas chromatography using authentic samples and/or isolated by distillation or column chromatography. Additional characterization was obtained by ir, nmr, mass spectroscopy, and elemental analysis. Our results are listed in Tables I and II.

Alcohol (Table I) is likely derived *via* the carbonyl dianion rather than disproportionation of the diol dianion (and/or the half-protonated quenching product) because the yield of alcohol is independent of reaction time and method of quenching. Reaction of p-chlorobenzaldehyde and cinnamaldehyde resulted in complete utilization of these aldehydes; however, only unidentified polymeric materials were isolated. Sodium naphthalenide is known to reduce aryl halides[2] and it is likely that reduction occurred at both the

Table I. Reaction of Sodium Naphthalenide with Aromatic Carbonyl Compounds

Compound	1,2-Diol (%)[a]	Alcohol[a]
benzaldehyde	1,2-diphenyl-1,2-ethanediol (88)	benzyl alcohol (7)
p-tolualdehyde	1,2-di(*p*-tolyl)-1,2-ethanediol (90)	*p*-methylbenzyl alcohol (1)
p-anisaldehyde	1,2-di(*p*-methoxyphenyl)-1,2-ethanediol (90)	*p*-methoxybenzyl alcohol (1)
p-chlorobenzaldehyde[b]	----	----
cinnamaldehyde[b]	----	----
benzophenone	tetraphenyl-1,2-ethanediol (7)	benzhydrol (90)
p-benzoquinone	----	hydroquinone (92)

[a] Yields are based on carbonyl compound.

[b] Polymeric products formed.

carbonyl and halogen functions. While benzaldehyde and benzophenone have nearly equal potentials for single electron reduction, the second reduction potential for benzophenone is well below that for benzaldehyde.[3] Thus, benzophenone forms the thermodynamically (and kinetically) more stable dianion which leads to the preponderance of alcohol. Kaplan et al., in a reaction between benzaldehyde and sodium biphenylide, reported significant yields of hydroxyalkylation products of the biphenyl moiety.[4] We found no evidence for similar adducts with sodium naphthalenide, though their formation cannot be entirely discounted.

The reactions of aliphatic carbonyl compounds with sodium naphthalenide (Table II) are in marked contrast to those of aromatic compounds. The low conversions in the cases of 3-pentanone and pentanal are attributable to proton abstraction, which is known to be fast.[5]

Table II. Reaction of Aliphatic Carbonyl Compounds with Sodium Naphthalenide

Carbonyl Compound	Reductive Coupling[a] (%)	Monohydroxy-alkylation[a] (%)	Dihydroxy-alkylation[a] (%)
3-pentanone[b]	----	1-(pentan-3-ol)-1,4-dihydronaphthalene (6)	1,4-bis(pentan-3-ol)-1,4-dihydronaphthalene (35)
pentanal[b]	5,6-decanediol (7)	1-(pentan-1-ol)-1,4-dihydronaphthalene (6)	1,4-bis(pentan-1-ol)-1,4-dihydronaphthalene (35)
2,2-dimethyl-propanal	----	1-(2,2-dimethylpropan-1-ol)-1,4-dihydronaphthalene (18)	1,4-bis(2,2-dimethyl-propan-1-ol)-1,4-dihydronaphthalene (65)

[a] Yields are based on carbonyl compounds.

[b] After quenching, the balance of the carbonyl compound was recovered as starting material.

A comparison of the data in Tables I and II demonstrates that while aromatic carbonyl compounds give reductive bimolecular coupling and monomeric reduction products, but little if any products of hydroxyalkylation, aliphatic carbonyl compounds yield significant quantities of hydroxyalkylation products.

Two mechanistic schemes are in accord with present data and a choice between these cannot presently be made. The essential difference between the two schemes focuses upon whether the bimolecular coupling products derived from aromatic carbonyl compounds result from the intermediacy of the carbonyl dianion.

Dianion Mechanism

Aliphatic Products (R = aliphatic)

$$\mathrm{R_2C{=}O} \quad + \quad \mathrm{Ar^{\cdot -}} \quad \longrightarrow \quad \mathrm{R_2\dot{C}{-}O^-} \quad + \quad \mathrm{Ar} \tag{1}$$

$$\mathrm{R_2\dot{C}{-}\bar{O}} \quad + \quad \mathrm{Ar^{\cdot -}} \quad \longrightarrow \quad \mathrm{A\bar{r}C(R)_2O^-} \quad + \quad \mathrm{Ar} \tag{2}$$

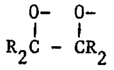
$$\mathrm{A\bar{r}C(R)_2O^-} \quad + \quad \mathrm{R_2C{=}O} \quad \longrightarrow \quad \mathrm{^-O(R)_2CArC(R)_2O^-} \tag{3}$$

Aromatic Products (R = aryl)

(1) followed by,

$$R_2\dot{C}-O^- \quad + \quad Ar^{\cdot -} \longrightarrow R_2\bar{C}-O^- \quad + \quad Ar \qquad (4)$$

$R_2\bar{C}-O^-$ + $R_2C{=}O$ ⟶



$$R_2\bar{C}-O^- + R_2C{=}O \longrightarrow R_2\overset{O^-}{\overset{|}{C}} - \overset{O^-}{\overset{|}{C}}R_2 \qquad (5)$$

Radical Mechanism

Aliphatic Products

$$R_2C{=}O \quad + \quad Ar^{\cdot -} \longrightarrow Ar\dot{C}(R)_2O^- \qquad (6)$$

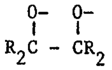
$$Ar\dot{C}(R)_2O^- \quad + \quad Ar^{\cdot -} \longrightarrow Ar\bar{C}(R)_2O^- \quad + \quad Ar \qquad (7)$$

then (3)

Aromatic Products

(1) followed by,

$2R_2\dot{C}-O^-$ ⟶



$$2R_2\dot{C}-O^- \longrightarrow R_2\overset{O^-}{\overset{|}{C}} - \overset{O^-}{\overset{|}{C}}R_2 \qquad (8)$$

Mechanistic studies are presently in progress in Professor John F. Garst's and our laboratories.

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