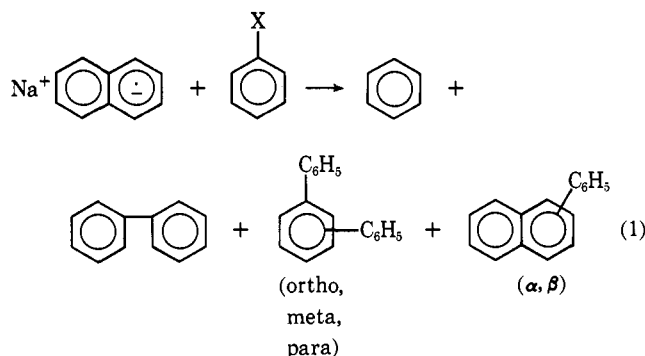


## Reaction of Sodium Naphthalene with Halobenzenes<sup>1</sup>

Sir:

The reaction of sodium naphthalene or biphenyl with alkyl halides has been reported previously by many authors.<sup>2-5</sup> It has been shown that all four alkyl halides (fluorides, chlorides, bromides, and iodides) with sodium naphthalene involve both alkyl radicals and alkyl anions as intermediates.<sup>6</sup> However, very little information has been reported concerning the reactions of sodium naphthalene with aryl halides.<sup>7,8</sup>

We have studied the reaction of sodium naphthalene with halobenzene (F, Cl, Br, and I) in THF with



where X = F, Cl, Br, and I.

**Table I.** Relative Amounts of Identified Products from the Reaction of Sodium Naphthalene with Halobenzene before Hydrolysis<sup>a</sup>

Type of X <sup>b</sup>	NaNp <sup>c</sup> X <sup>b</sup>	Temp, °C	% benzene	% bi- phenyl	% o- terphenyl	% m- terphenyl	% p- terphenyl	% α- phenyl Np	% β- phenyl Np
Bromobenzene	1/1	-60	86.9	8.7	1.1	0.1	0.1	1.4	0.9
Bromobenzene	2/1	-60	86.5	6.4	0.7	0.2	0.2	0.8	1.0
Bromobenzene	1/1	27	89.7	6.3	0.5	0.3	0.3	0.9	0.7
Bromobenzene	2/1	27	85.0	7.3	1.4	0.4	0.5	1.6	0.7
Fluorobenzene	1 1	-60	72.2	16.9	2.6			1.7	2.0
Chlorobenzene	2 1	-60	82.4	8.6	1.7	0.3	0.2	2.4	1.5
Iodobenzene	1 1	27	84.8	9.8	0.6	0.3	0.3	1.1	0.3

<sup>a</sup> Yields are based on halobenzene consumed. All variations were used with the fluoro-, chloro-, and iodobenzenes with no significant variations in the product distribution. <sup>b</sup> X = halobenzene (37.5 mmol/50 ml of THF). <sup>c</sup> NaNp = sodium naphthalene (75 mmol or 37.5 mmol/50 ml of THF); Np = naphthalene.

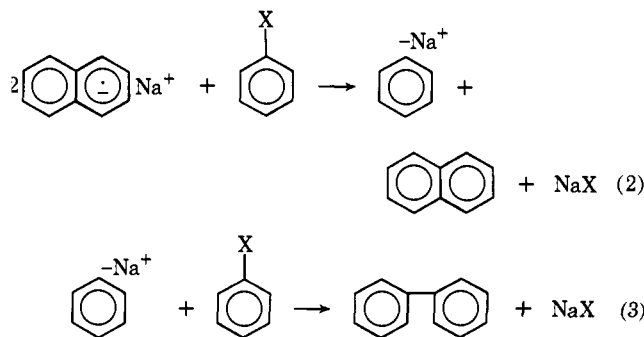
**Table II.** Relative Amounts of Identical Products from the Reaction of Sodium Naphthalene with Halobenzene after Hydrolysis<sup>a</sup>

Type of X <sup>b</sup>	NaNp <sup>c</sup> X <sup>b</sup>	Temp, °C	% benzene	% bi- phenyl	% o- terphenyl	% m- terphenyl	% p- terphenyl	% α- phenyl Np	% β- phenyl Np
Bromobenzene	1/1	-60	87.0	8.3	1.0	0.1	0.1	1.2	0.8
Bromobenzene	2/1	-60	86.6	6.3	0.4	0.1	0.1	0.6	0.5
Bromobenzene	1/1	27	89.2	6.3	0.5	0.3	0.4	0.8	0.7
Bromobenzene	2/1	27	85.3	8.0	1.2	0.4	0.5	1.6	9.7
Chlorobenzene	2/1	-60	81.4	8.7	1.5	0.3	0.2	2.1	1.4
Iodobenzene	1/1	27	86.3	9.3	0.6	0.3	0.2	0.9	0.3

<sup>a</sup> Yields are based on halobenzene consumed. <sup>b</sup> X = halobenzene (37.5 mmol/50 ml of THF). <sup>c</sup> NaNp = sodium naphthalene (75 mmol or 37.5 mmol/50 ml of THF); Np = naphthalene.

emphasis on product analysis. The reactions were carried out either at -60° or at room temperature (27°). The halobenzene was added slowly to the sodium naphthalene in THF solution by means of a hypodermic syringe. After hydrolysis with either heavy water or water at -60°, the reaction mixtures were analyzed by vapor-phase chromatography. Characterization of the products was obtained by comparison of gas-chromatographic retention times with those of authentic samples. The relative amounts of identified products from sodium naphthalene and halobenzene are shown in Table I. The major products of this reaction were as follows (eq 1)

The above reaction could proceed by an anionic, radical, or combination anionic-radical mechanism. The anionic and combination processes necessitate formation of a phenylsodium intermediate.



Strong evidence against the above mechanism involving aryl anions is provided by the absence of deuterated benzene of THF after treatment of the reaction mixture with D<sub>2</sub>O. We therefore feel that a radical mechanism is the most suitable one to explain our results. The following equations summarize this mechanism (eq 4-13). Furthermore, the radical mechanism is also supported by the following observations. (1) The product distribution is independent of the

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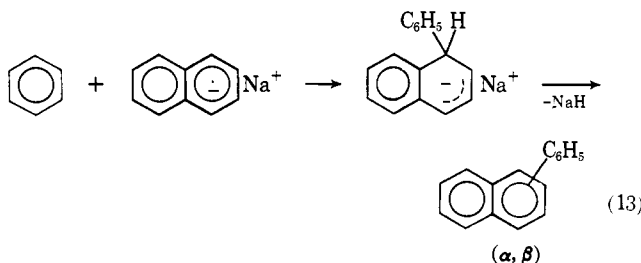
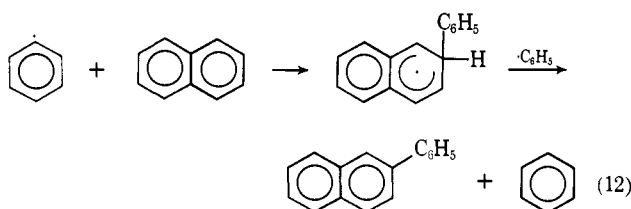
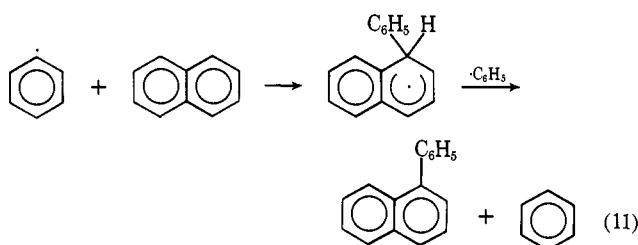
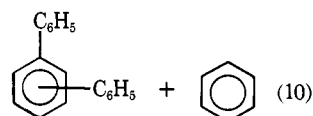
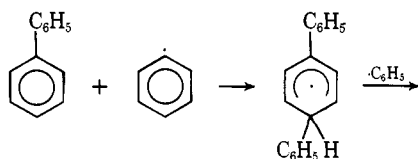
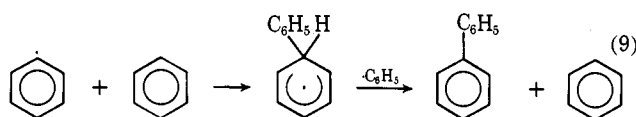
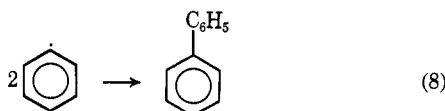
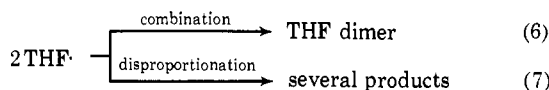
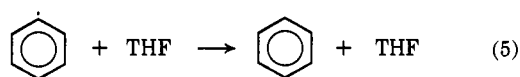
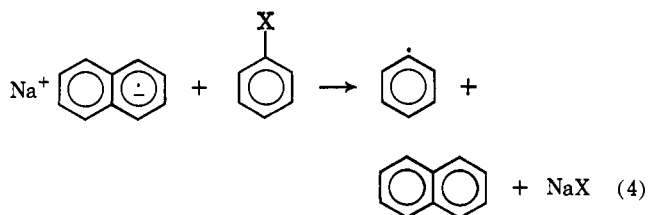
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concentration of sodium naphthalene in the range of 1–2. (2) A small amount of THF dimer was observed by mass spectrometry ( $m/e$  142) when sodium naphtha-

lene (37.5 mmol) reacted with chlorobenzene (18.75 mmol) at 27° in THF. (3) The product distribution before and after hydrolysis is identical (Tables I and II).

It thus appears that the reaction is proceeding by a radical mechanism. From our analysis of products from  $\text{D}_2\text{O}$  treatment, it would appear that any combination mechanism would have to be predominately of radical nature. This interpretation agrees with the data of Müller and Roscheisen on reactions of disodium tetraphenylethylene with bromobenzene.<sup>9</sup> Furthermore, our product distributions for the reaction of sodium naphthalene with either bromobenzene or iodobenzene were consistent with Hey and coworkers<sup>10</sup> who report that the isomer distributions for the reaction of benzoyl peroxides with biphenyl yielded 49% *o*-, 23% *m*-, and 29% *p*-terphenyl. We thus believe that a radical mechanism best explains the observed products. Others have generated phenyl radical in the presence of aromatic solvents and have observed the same product distributions that we have isolated (biphenyl, isomeric terphenyl).<sup>10–12</sup>

A two-step mechanism of the type shown in eq 9, 10, 11, and 12 has also been reported by several investigators.<sup>11,12</sup>

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### The Mechanism of Coenzyme B<sub>12</sub> Action in Dioldehydrase

Sir:

Recently,<sup>1</sup> a mechanism of action of coenzyme B<sub>12</sub> in dioldehydrase<sup>2</sup> was postulated on the basis of extensive model studies, in which the corrin Co(I) nucleophile derived from coenzyme B<sub>12</sub><sup>3</sup> functions as the actual catalytic intermediate. In this communication we demonstrate the validity of this mechanistic proposition on the basis of additional model reactions and parallel experiments with the reacting dioldehydrase holoenzyme of *Aerobacter aerogenes*.<sup>4</sup>

(1) G. N. Schrauzer and J. W. Sibert, *J. Amer. Chem. Soc.*, **92**, 1022 (1970).

(2) Dioldehydrase in DL-1,2-propanediol hydrolyase, E.C. 4.2.1.28.

(3) Coenzyme B<sub>12</sub> is  $\alpha$ -(5,6-dimethylbenzimidazolyl)-Co-5'-deoxyadenosylcobamide.

(4) Purified dioldehydrase was obtained from Dr. R. H. Abeles, Brandeis University, Waltham, Mass., or purchased from Calbiochem, Los Angeles, Calif. The activities of the enzyme from both sources differed, although their qualitative behavior was identical.