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DOE/PC/90038-T3

CONTRACT TITLE AND NUMBER:
Synthesis of a Naphthalene-Hydroxynaphthalene Polymer Model Compound
DE-AC22-90PC90038

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Report No. SRI-ORG-90-983-7126-IX
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DOE/PC/90038--T3

DE93 006128

CONTRACT PERIOD: 6/13/90-6/12/91

1. CONTRACT OBJECTIVE: To synthesize a new naphthalene-hydroxynaphthalene polymer model compound for use in coal combustion studies. This effort will also require the development of a synthetic procedure to synthesize this compound since it is unreported.

2. TECHNICAL APPROACH CHANGES: No major change to the technical approach.

3. CONTRACT (By Reporting Element)

1 -- Plan Development and Project Organization. Much of the early part of the quarter was directed primarily toward this phase of the project. Therefore, during this quarter, we prepared and submitted a Management Plan, a Milestone Schedule, a Cost Plan, a Notice of Energy RD&D, and a potential environmental impact questionnaire. During this time, we also directed our efforts toward project organization, the reevaluation of our proposed schemes, and the procurement of materials.

2 -- Sample Characterization. As a result of our synthesis efforts, a number of potential precursors and intermediates were prepared and submitted to the Organic Chemistry Research Area's Analytical Section for characterization and identification.

3 -- Monomer Synthesis Development. The synthesis of the pre-Bakelite intermediate has been identified as being key to the evaluation of our synthetic approach to the target compound. During this quarter, we have been reevaluating our synthetic approach while we have begun trying to synthesize this compound. As a result of our reevaluation, we also have been considering slightly modified target compounds which might be obtained by more direct routes or from commercially available materials. We also targeted simplified intermediates which would expedite our evaluation of the feasibility of the Bakelite process for the final polymerization, the key step of our suggested scheme. The results of our simplified model compound will also provide data to help us determine any modifications that will be required.

4 -- Monomer Synthesis Scale-up. Projected work in this phase of the project has not begun, because thus far, we have been unable to develop suitable procedures for the preparation of either the monomer or the simplified target compound.

4. QUARTERLY REPORT SUMMARY STATUS ASSESSMENT AND FORECAST:

In our original approach (**Scheme** I), we targeted an intermediate containing a 1-*O*- and 4-*C*-dinaphthylmethylated 1,8-dihydroxynaphthalene. We have since been considering a slightly modified target compound in which the dihydroxynaphthalene moiety is a 1-*O*- and 4-*C*-dinaphthylmethylated 1,5-dihydroxynaphthalene since a potential precursor to this target, 1,5-dihydroxynaphthalene is a commercially available compound. We have not formally notified Dr. Rao of this change since the actual position of the second hydroxyl was not specified in the target compound and since this modification has not been finalized. Our preliminary efforts toward this modified target have indicated that 1,5-dihydroxynaphthalene cannot be selectively nor cleanly 4-alkylated with 1-chloromethylnaphthalene nor can it be selectively 4-acylated with 1-naphthoic acid or ethyl 1-naphthoate. Therefore, we realize that this approach may not provide an easier route

to a potential target intermediate. Any further pursuit of this modification will probably require *O*-blocking of one or both of the hydroxyls and the 4-halogenation of dihydroxynaphthalene so that we will have a functional group that may direct the desired alkylation, by a route such as its conversion to a Grignard reagent. However, before any other modifications to the dihydroxynaphthalene were seriously pursued, we decided that it would be best to try to simplify the target intermediate further, by substituting naphthol for the dihydroxynaphthalene. We felt that this intermediate would be easier to obtain, and that it would be allow us to evaluate the key step of our suggested scheme, the Bakelite process for the final polymerization. Our approaches to the synthesis of the simplified pre-Bakelite reaction intermediate are given in the following schemes. As shown in **Scheme II**, our first approach *O*-alkylated the commercially available compound, 4-chloro-1-naphthol (**8**) with 1-chloromethylnaphthalene to give ether (**9**). The desired intermediate (**10**) should then have been obtainable by generating the corresponding Grignard reagent of (**9**) and alkylating with 1-naphthaldehyde. However, our attempts to generate the Grignard reagent of **9** were not successful, even after using a variety of solvents (diethyl ether, THF, and DME) with catalytic amounts of iodine and ethyl bromide, and after refluxing for more than 3 days. An attempt to generate the Grignard reagent *in situ* with the naphthaldehyde already mixed into the solution (refluxed in DME with iodine for 3+ days) also was unsuccessful in generating any of the desired product. In the near future, we will be trying to generate the Grignard reagent from molecular magnesium generated by the reduction of $MgCl_2$ with potassium in THF. The results of this effort will be given in the next monthly report.

We have also pursued the Friedel-Crafts acylation of 1-naphthol as another approach to the desired target intermediate. As shown in **Scheme III**, this approach would give **13** with the required *C-C* linkage required for the target intermediate. Therefore, 1-naphthol **11** was treated with 1-naphthoyl chloride **12** and aluminum chloride in ether at room temperature, and this resulted in the formation of a mixture consisting of naphthoic acid as well as another product which appears to be 1-(1-naphthol)naphthoate (**14**) according to TLC. We will be repeating this reaction in other solvents as well as at different temperatures to try to determine if any better reaction conditions can be found.

At the same time, we tried to determine if prior blocking of the naphthol hydroxy would be beneficial since 2-acylation was anticipated to occur competitively. Therefore, as is shown in **Scheme IV**, we synthesized 1-naphthol naphthoate from 1-naphthol and 1-naphthoyl chloride, and we then attempted to further acylate it with additional naphthoyl chloride and aluminum chloride in ether at reflux. Preliminarily, the mass spectral data indicates that some acylation has occurred with this attempt, but the TLC of the major component of the product mixture corresponds to that of 1-naphthol naphthoate (**14**). We are awaiting more conclusive spectral data for this effort. We have also synthesized the naphthylmethyl ether of naphthol as shown in **Scheme V**. The refluxing of naphthol with 1-chloromethylnaphthalene in acetone with potassium carbonate gave ether **15**. An attempt to acylate this ether with 1-naphthoyl chloride and aluminum chloride has resulted in the formation of a mixture of products which may be difficult to separate. However, mass spectral data shows that this mixture contains a component with the desired molecular weight. Therefore, we will be investigating this reaction in other solvents and at different temperatures to try to determine if we will be able to control this reaction.

Because of the difficulty of controlling the site of alkylation or acylation, we are also considering other non-Friedel Crafts approaches to the desired intermediate. Among these are the approaches shown in **Schemes VI and VII**, Grignard or Wittig reactions (with either 1-naphthylmethylmagnesium chloride or triphenylnaphthylmethylphosphonium chloride, respectively) with 1,4-naphthoquinone. Preliminarily with the Wittig approach, the ylide generated from triphenylnaphthylmethyl chloride (synthesized from 1-chloromethylnaphthalene and triphenylphosphine) was not nucleophilic enough to attack the naphthoquinone carbonyl. This has been assumed to be the case since only the ylide was isolated. As for the Grignard reaction, we have been having difficulty generating 1-naphthylmethylmagnesium chloride from 1-chloromethylnaphthalene, and therefore, no results for this approach can be reported before the next monthly report.

Attachments: Schemes I-VII

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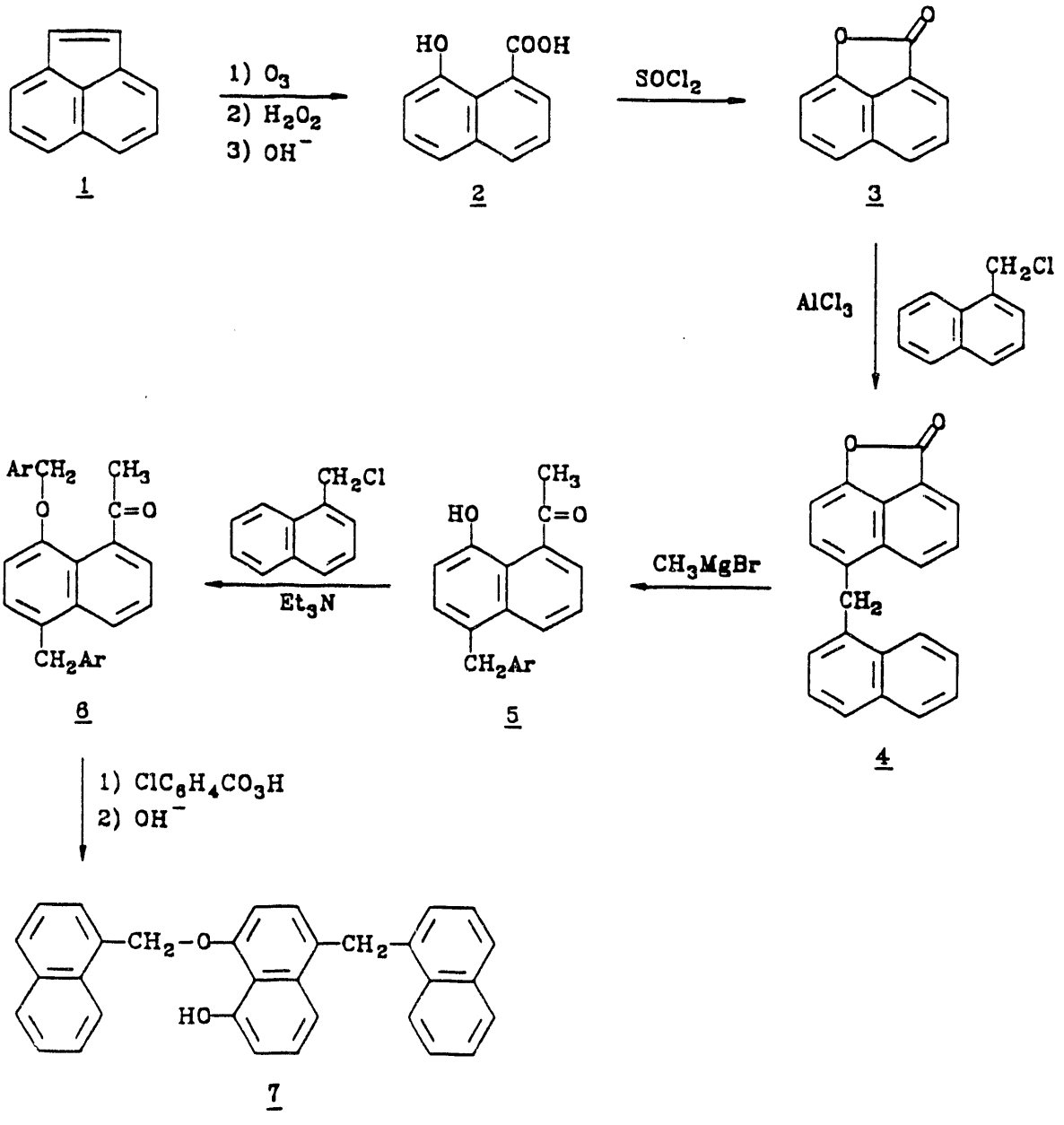
Scheme I



1 2 3 4 5 6 7

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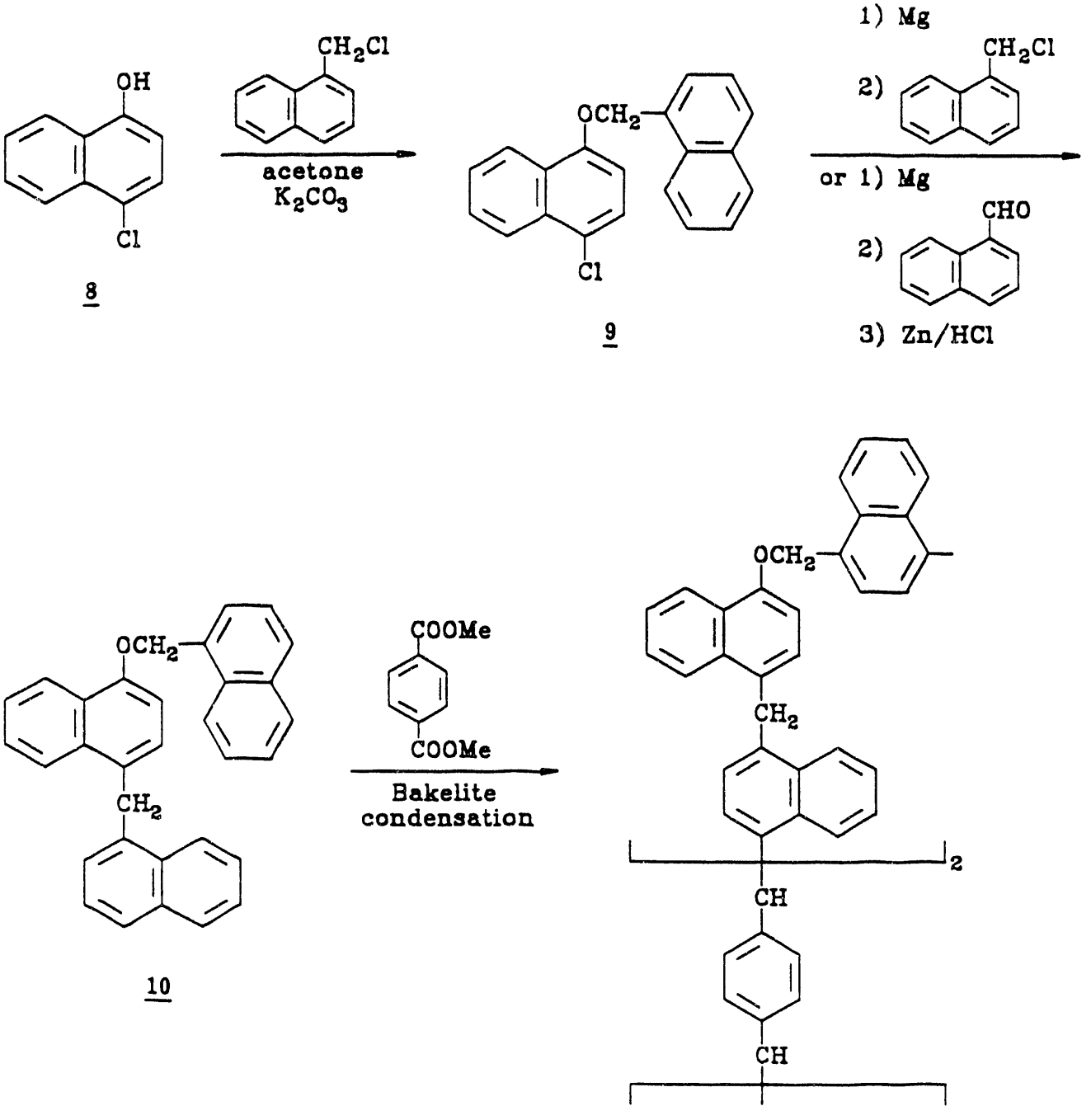
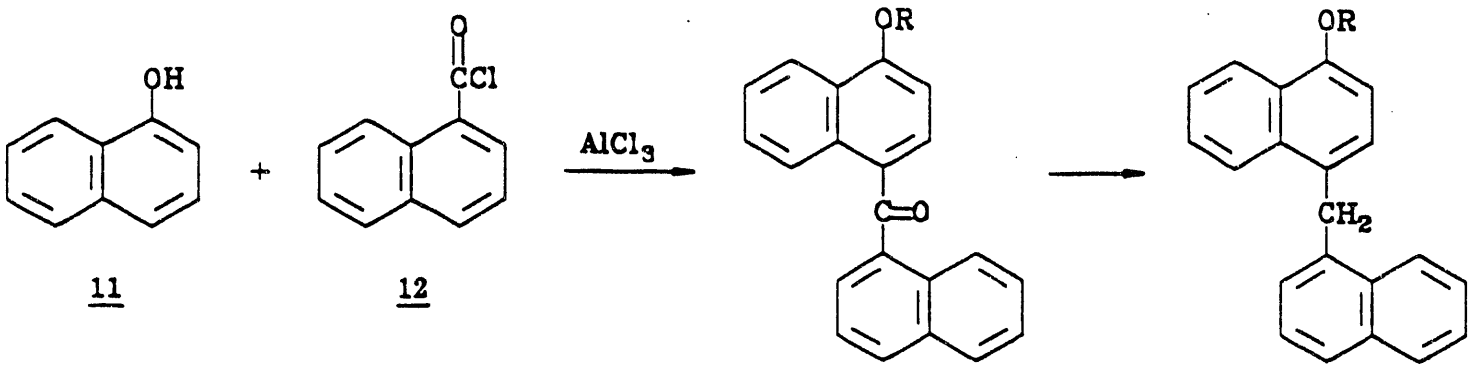
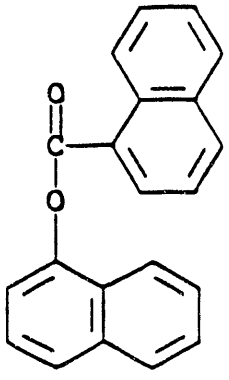
Scheme II


OH
Cl
8
CH2Cl
acetone
K2CO3
OCH2
Cl
9
1) Mg
2)
CH2Cl
or 1) Mg
2)
CHO
3) Zn/HCl
OCH2
CH2
10
COOMe
COOMe
Bakelite
condensation
OCH2
CH2
2
CH
CH

Scheme III



11 12 13



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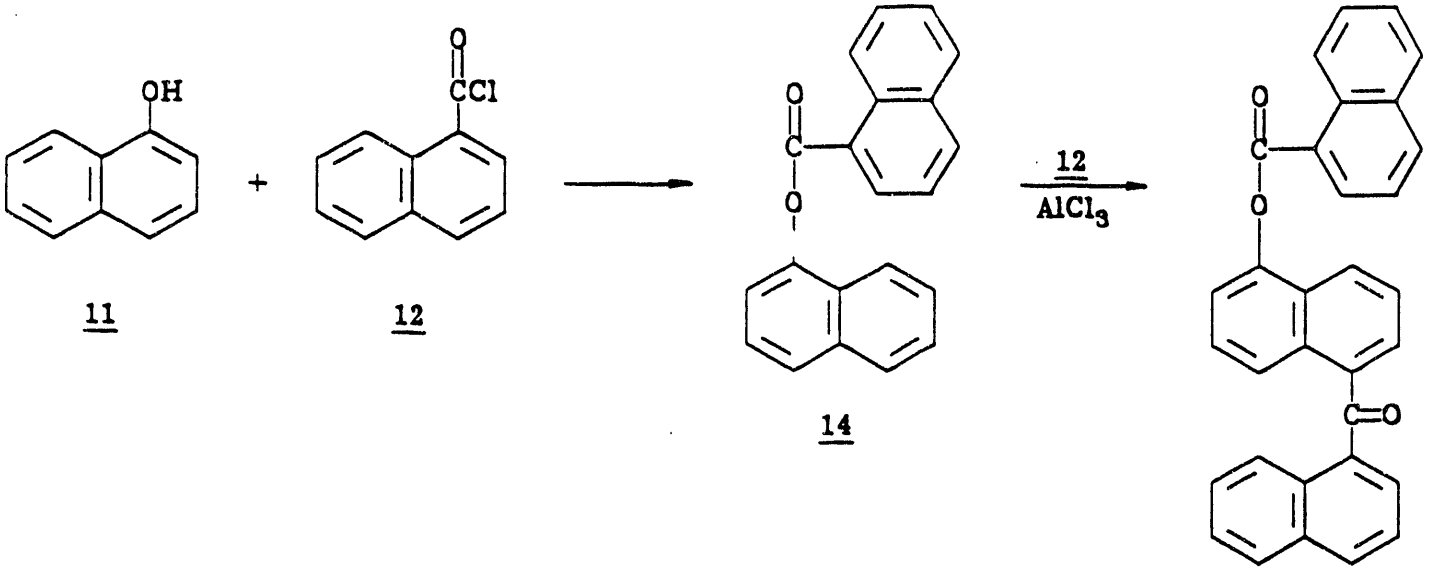
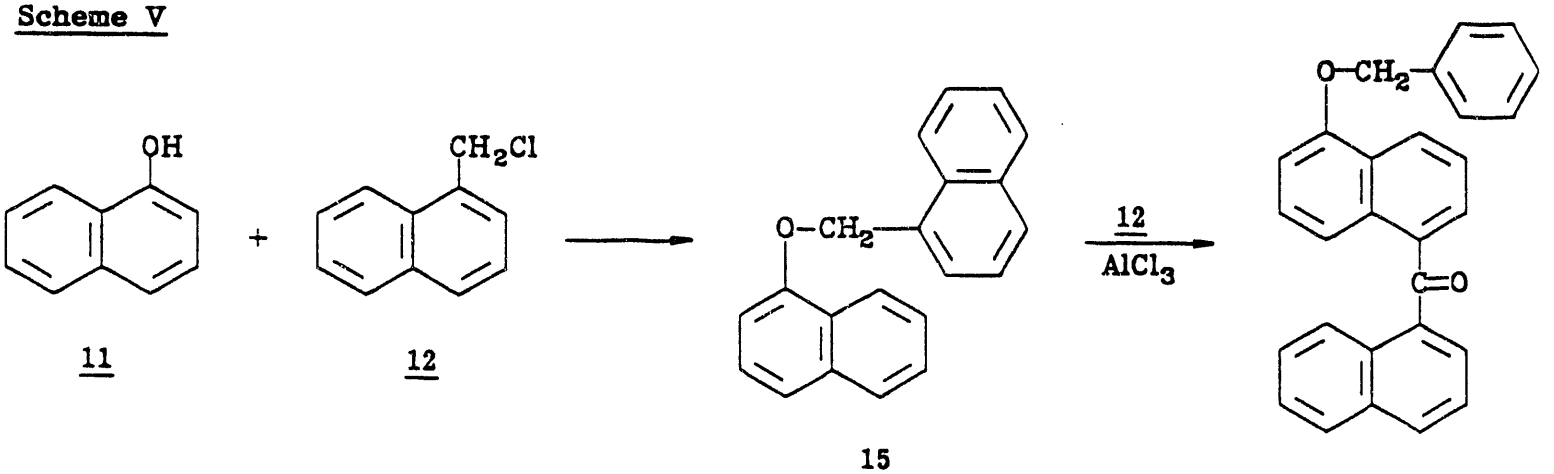
Scheme IV



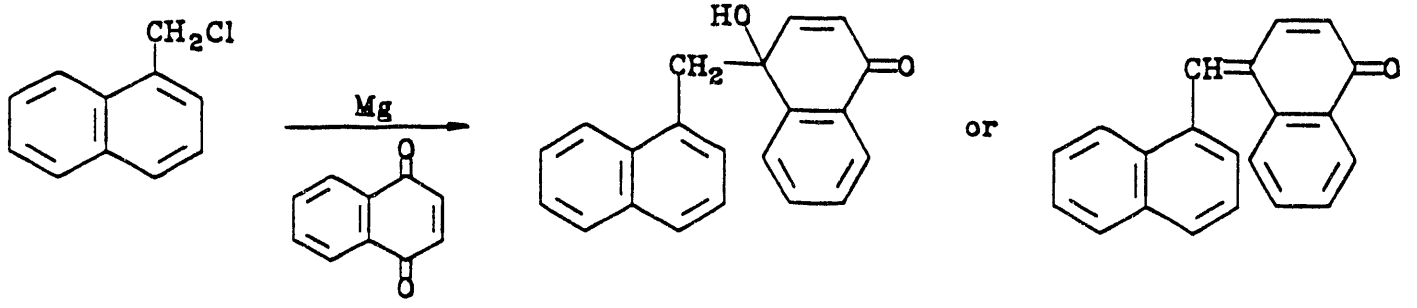
11 12 14

Scheme V

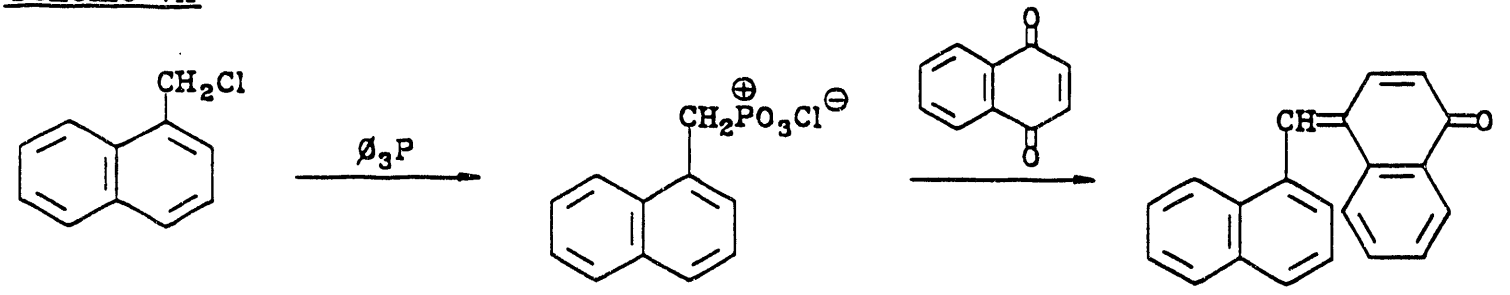


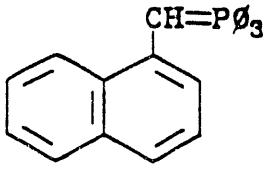
11 12 15

Scheme VI



Scheme VII





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