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QUARTERLY REPORT

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

CONTRACTOR NAME: SOUTHERN RESEARCH INSTITUTE
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Birmingham, AL 35255-5305

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. No new work has been directed toward this phase of the project.

2 -- Sample Characterization. Our synthesis efforts have resulted in the preparation of a number of potential precursors and intermediates. These compounds were 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 continued to be the focus of our efforts. We first modified the target intermediate slightly to allow this compound to be obtained by a more direct route, using commercially available materials. Since then, we have further simplified intermediate to expedite our evaluation of the feasibility of the Bakelite process for the final polymerization, the key step of our suggested scheme.

4, 5, & 6 -- Monomer Synthesis Scale-up, Polymer Synthesis Development, and Polymer Synthesis Scale-up. Projected work in these phases of the project has not begun, because we have been unable to develop suitable procedures for the preparation of either the monomer or the simplified target compound. However, since the funds for the monomer synthesis development are almost exhausted, we will now begin applying the unused funds for these phases toward the development of a suitable monomer synthesis procedure.

4. QUARTERLY REPORT SUMMARY STATUS ASSESSMENT AND FORECAST:

In our original approach, we targeted 1-*O*- and 4-*C*-dinaphthylmethylated 1,8-dihydroxynaphthalene as the key intermediate. We later modified the target compound to one based on 1,5-dihydroxynaphthalene, since 1,5-dihydroxynaphthalene is a commercially available compound. Unfortunately, our preliminary efforts toward this modified target showed that 1,5-dihydroxynaphthalene could not be selectively nor cleanly 4-alkylated with 1-chloromethylnaphthalene. It also could not be selectively 4-acylated with 1-naphthoic acid or ethyl 1-naphthoate. Therefore, we further simplified the target and removed one of the activating (OH/OMe groups) by substituting naphthol for dihydroxynaphthalene. We hoped that this intermediate would be easier to obtain, and that it would facilitate our evaluation of the key Bakelite polymerization.

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Our approaches to the synthesis of the simplified pre-Bakelite reaction intermediate are given in the following schemes. As shown in **Scheme I**, our first approach *O*-alkylated the commercially available compound, 4-chloro-1-naphthol (**1**) with 1-chloromethylnaphthalene to give ether **2**. The desired intermediate **3** should then have been obtainable by generating the corresponding Grignard reagent of **2** and alkylating with 1-chloromethylnaphthalene (or 1-naphthaldehyde followed by reduction of the resulting hydroxyl). However, our attempts to generate the Grignard reagent of **2** were not successful, even after using a variety of solvents (diethyl ether, THF, and DME) with catalytic amounts of iodine and ethyl bromide, after refluxing for more than 3 days, or with naphthaldehyde in the reaction mixture and refluxing in DME with iodine for 3+ days. We also tried to generate the Grignard reagent from molecular magnesium generated by the reduction of $MgCl_2$ with potassium in THF. Preliminary data (mass spectral) from this approach showed that a product with the correct molecular ion was forming. However, reaction monitoring by TLC indicated that conversion to the desired product was very limited, and subsequent efforts to improve the yield were unsuccessful. We have recently tried the lithiation of **2** in THF, and thus far, a preliminary analysis of the reaction mixture shows that, after the addition of 1-chloromethylnaphthalene a mixture of products containing the desired compound **3** is forming. We are currently isolating the components of this mixture to identify compound **3**. We will also be investigating ways to improve this reaction, since TLC monitoring of the reaction showed that this reaction was not proceeding to 100 % completion, and that it was accompanied by the formation of many side products.

We have also pursued the Friedel-Crafts acylation of 1-naphthol as another approach to the desired target intermediate. As shown in **Scheme II**, this approach would give **4** with the required *C-C* linkage required for the target intermediate. Therefore, 1-naphthol was treated with 1-naphthoyl chloride 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 (**4**) according to MS and TLC. Repeating this reaction in other solvents as well as at different temperatures also did not improve the results of this reaction. We then attempted to 4-acylate the 1-naphthylmethyl ether of 1-naphthol and 1-naphthyl 1-naphthoate to determine if blocking the *OH* might be beneficial to this reaction, but again, we consistently obtained complex mixtures of products. These results greatly diminished our enthusiasm for this reaction, but before the Friedel Crafts acylation approach was abandoned, we reinspected the literature and found that 4-acylations of 1-methoxynaphthalene with benzoyl chloride were reported to occur selectively and in high yields. Therefore, we have renewed our interest in Friedel-Crafts acylations, and we have been investigating the 4-acylation of 1-methoxynaphthalene with 1-naphthoyl chloride, as shown in **Scheme III**. Thus far, we have found that this reaction proceeds slowly at room temperature to give a product mixture that appears to contain the desired 4-acylated compound **6**. Our plans are for this compound to be isolated, reduced to **7**, demethylated, and alkylated with 1-chloromethylnaphthalene to **3**.

Another possible approach to intermediate **7** is shown in **Scheme IV**. 4-Methoxynaphthaldehyde will be reacted with naphthylmagnesium bromide, and the resulting alcohol **9** will be reduced to **7**.

Other unrelated approaches that we have pursued are the reaction of 1,4-naphthoquinone with the Grignard and Wittig reagents of 1-chloromethylnaphthalene (1-naphthylmethylmagnesium chloride or triphenylnaphthylmethylphosphonium chloride), as shown in **Schemes V and VI**. Our repeated attempts with both of these reactions showed that 1,4-naphthoquinone is not reactive to either of these nucleophiles, and therefore these approaches has been terminated. Finally, we also attempted one other approach which was a completely different route to the desired target intermediate. As shown in **Scheme VII**, we treated naphthalene with bromine in carbon tetrachloride to obtain 1,2,3,4-tetrabromo-1,2,3,4-tetrahydronaphthalene (**10**). A preliminary treatment of **10** with naphthylmethanol at ~150 °C resulted in the formation of a viscous, dark purple product, accompanied by the production of hydrogen bromide. This product could not be fully characterized as **11**, even though the IR spectrum for this product showed no evidence of *-OH* absorption while showing evidence of the formation of the ether linkage (-CH_2O-), aromatic substitution, aromatic -CH, and -CBr. Furthermore, an attempt to treat 1,2,3,4-tetrabromo-1,2,3,4-tetrahydronaphthalene (**10**) with sodium naphthylmethoxide (from NaH and naphthylmethanol) resulted in the formation of 1,4-

dibromonaphthalene (12), thus showing that the benzylic protons are very acidic and easily abstracted. Therefore, we have decided to terminate our pursuit of this approach.

As previously stated, we are guardedly optimistic with our recent success with the first lithiation and Friedel Crafts approaches discussed above, and most of our efforts are being directed toward these approaches. However, we are continuing to search for alternate approaches to the simplified intermediate. Any new approaches will be presented in future reports.

Cecil D Kwong

Cecil D. Kwong, Project Manager
Organic Chemistry Research Area

Attachments:
- Milestone Status Report
- Cost Management Report
- Schemes I-VII
- KPSR

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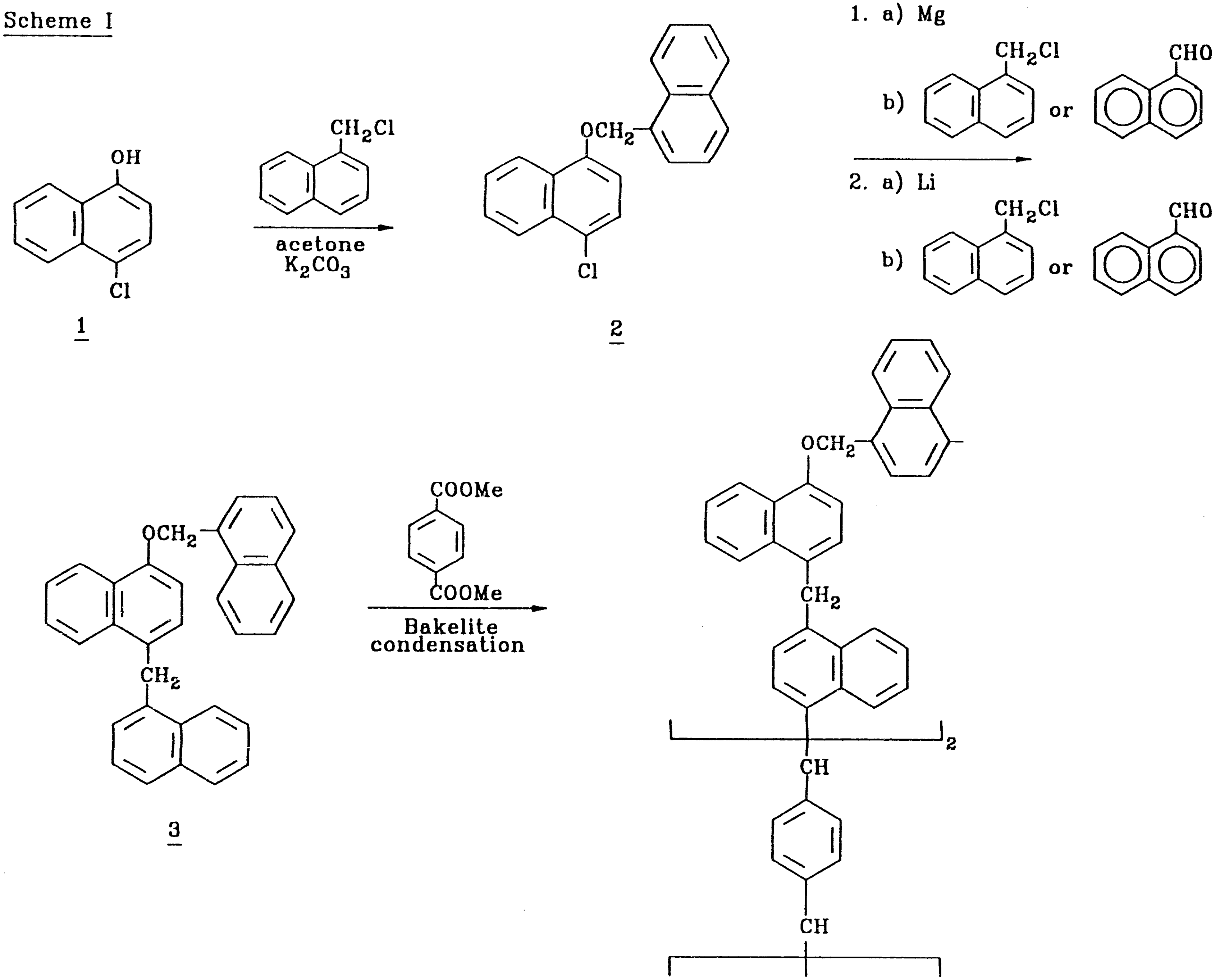
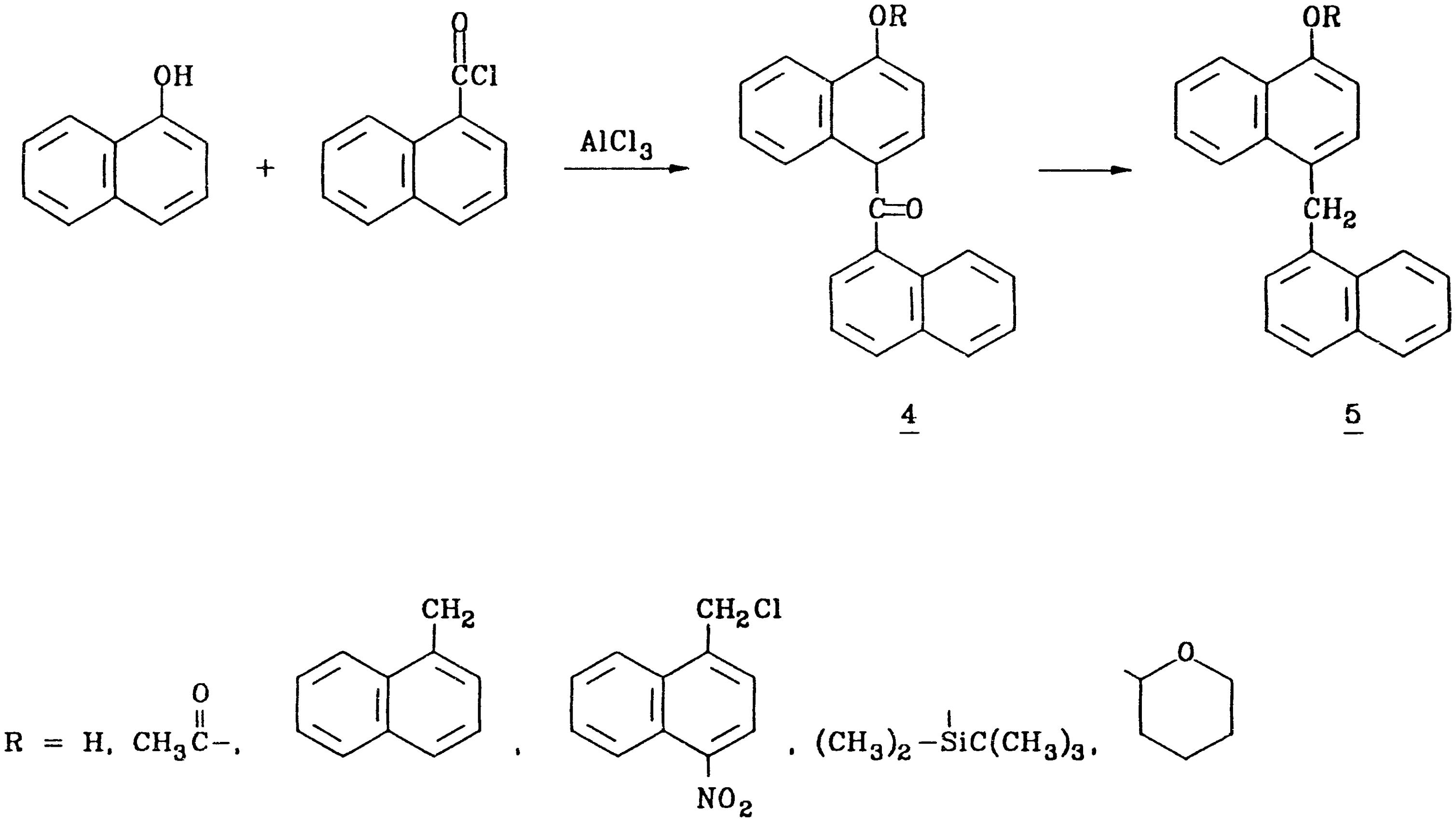
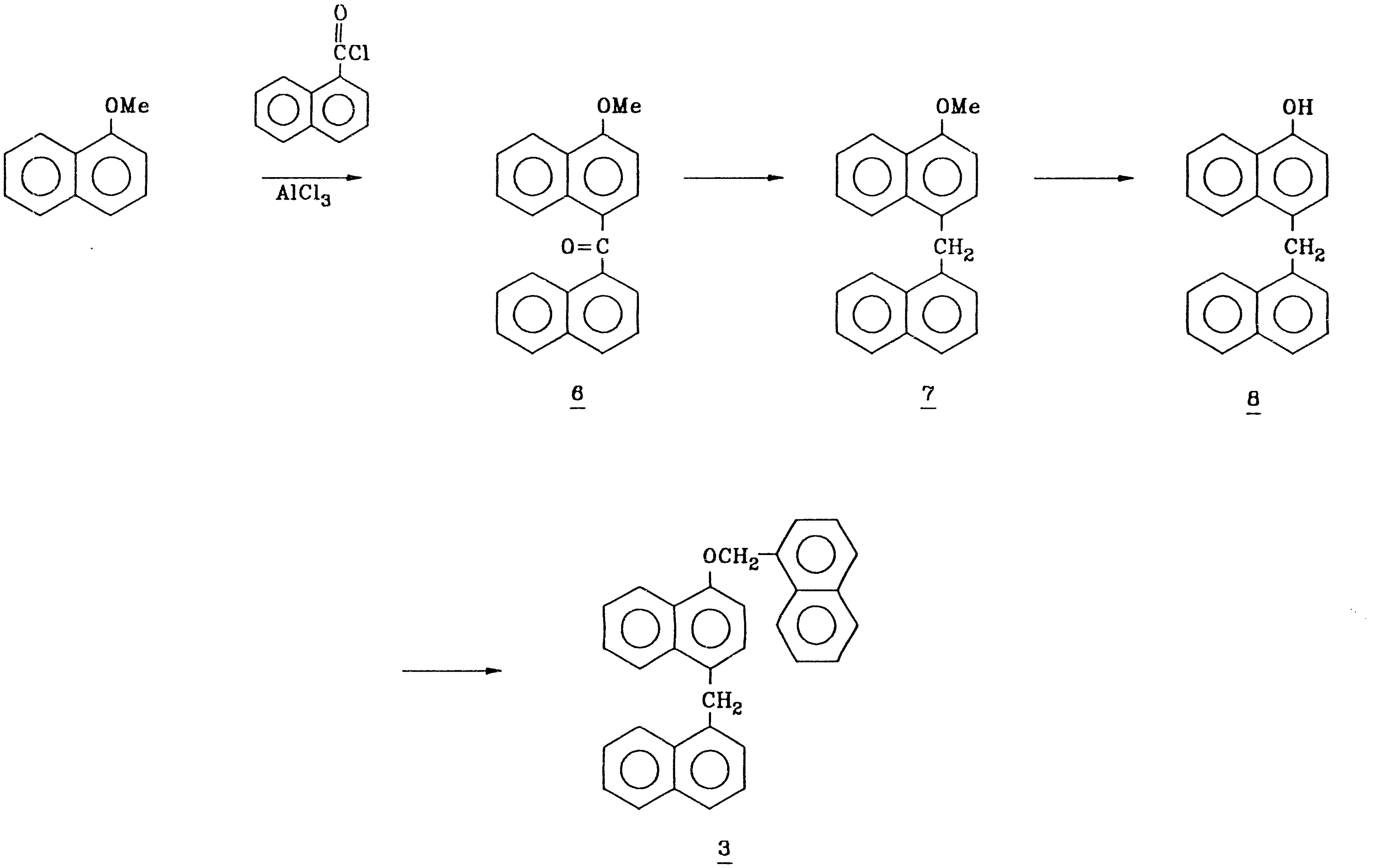
Scheme I


OH
Cl
1
CH$_2$Cl
acetone
K$_2$CO$_3$
OCH$_2$
Cl
2
1. a) Mg
b) CH$_2$Cl or CHO
2. a) Li
b) CH$_2$Cl or CHO
OCH$_2$
CH$_2$
3
COOMe
COOMe
Bakelite condensation
OCH$_2$
CH$_2$
2
CH
CH

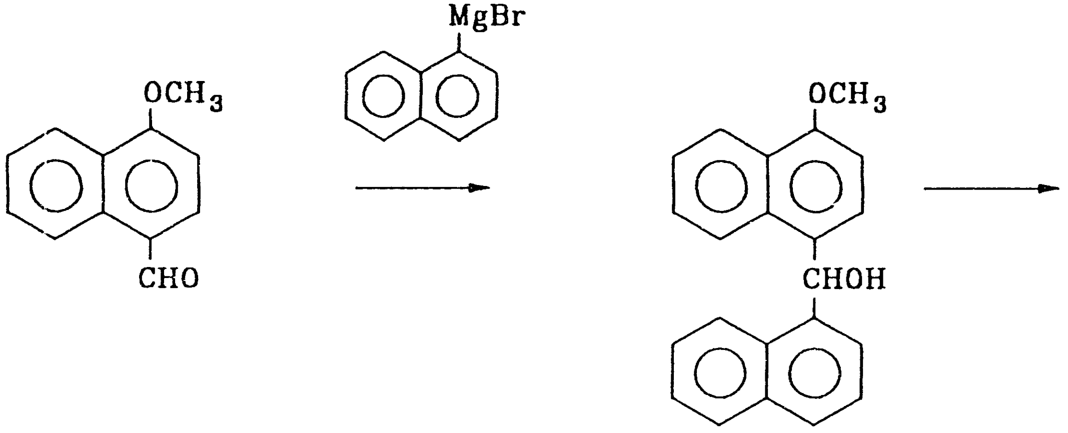
Scheme II


OH
O
CCl
+
AlCl$_3$
OR
C=O
4
OR
CH$_2$
5
R = H, CH$_3$C(=O)−,
CH$_2$
CH$_2$Cl
NO$_2$
(CH$_3$)$_2$−SiC(CH$_3$)$_3$,
O

Scheme III



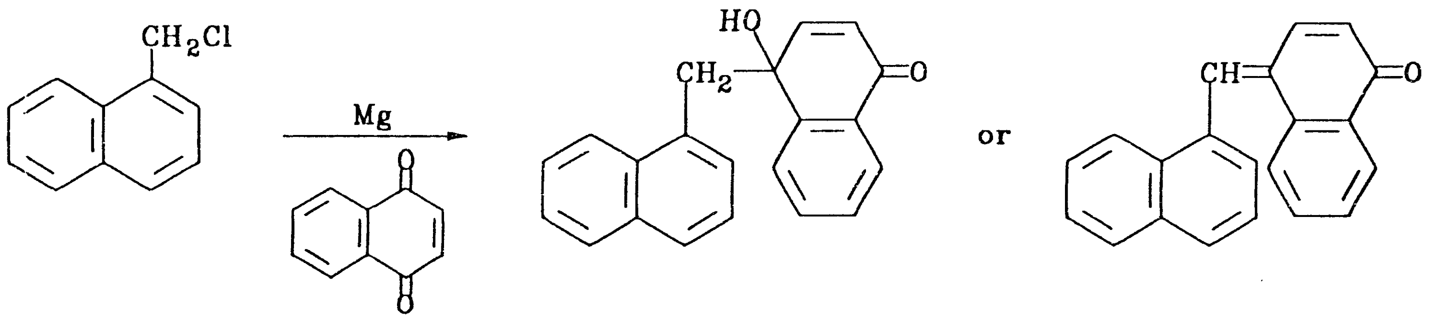
Scheme IV



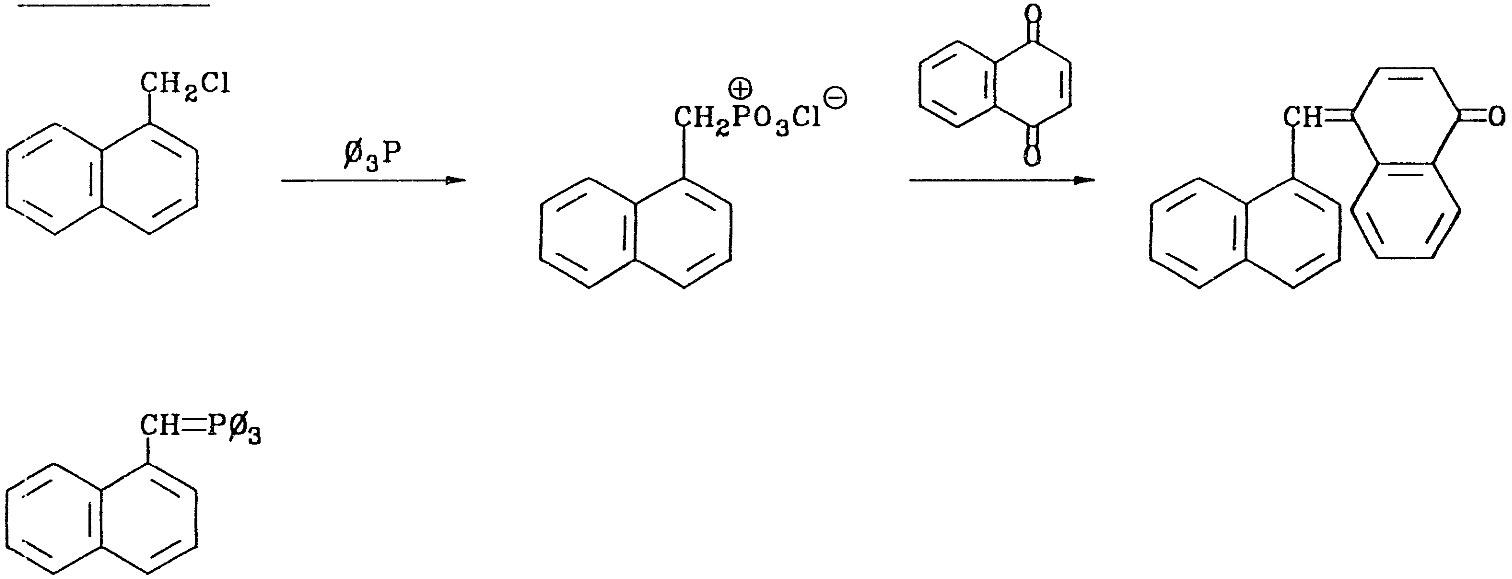
9

7

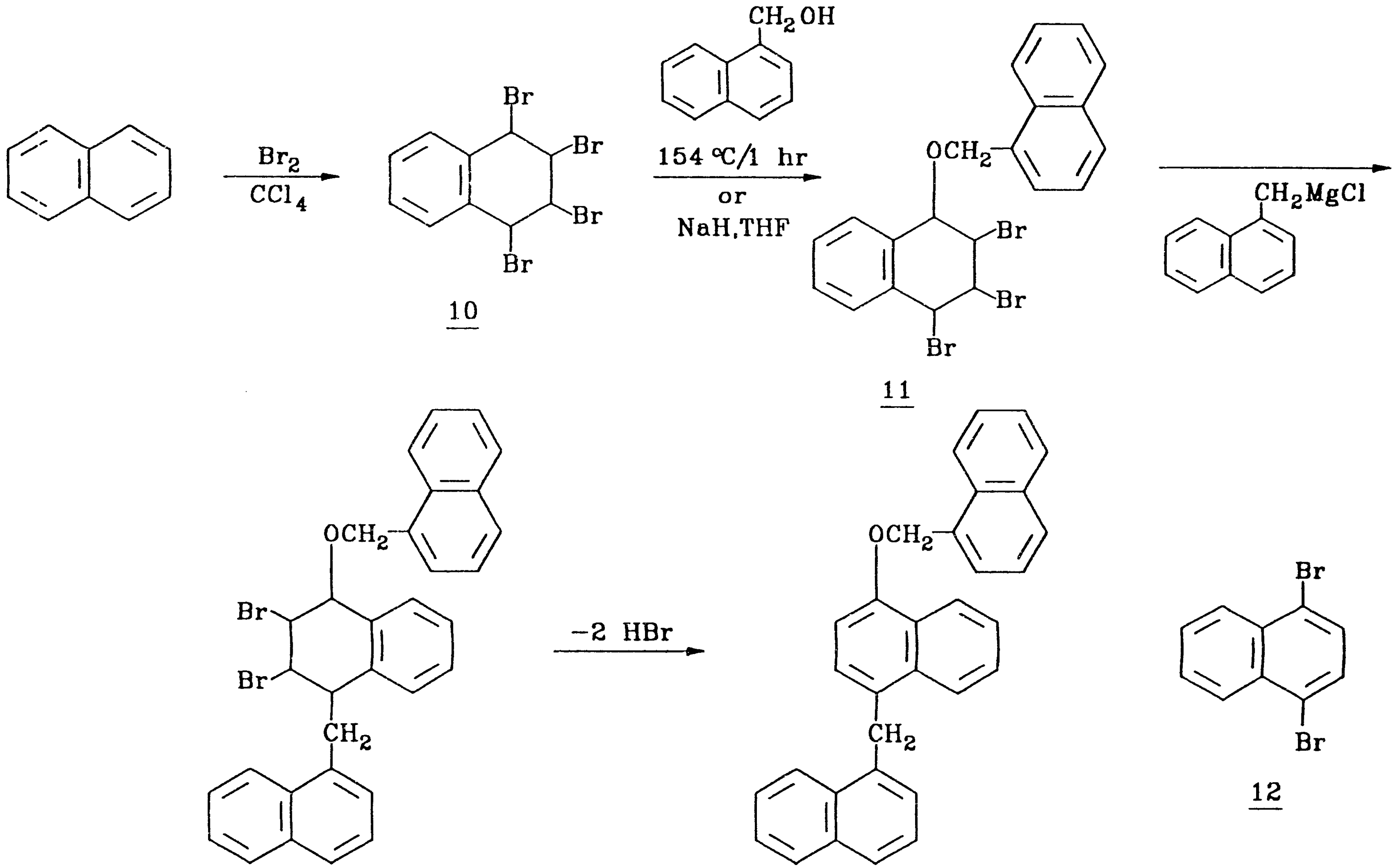
Scheme V



Scheme VI



Scheme VII


Br2
CCl4
Br
Br
Br
Br
10
CH2OH
154 °C/1 hr
or
NaH,THF
OCH2
Br
Br
Br
11
CH2MgCl
OCH2
Br
Br
CH2
−2 HBr
OCH2
CH2
Br
Br
12

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