DOE/PC/90038 - T5

QUARTERLY REPORT

CONTRACT TITLE AND NUMBER:

Synthesis of a Naphthalene-Hydroxynaphthalene Polymer Model Compound
DE-AC22-90PC90038

Report No. S
Reporting

DOE/PC/90038--T5

DE93 006130

CONTRACTOR NAME:

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

1. CONTRACT OBJECTIVE: The objective of this contract is the synthesis of a new naphthalene-hydroxynaphthalene polymer model compound for coal combustion studies. This effort also requires the development of a synthetic procedure for this compound since it has not been reported before.

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

3. CONTRACT (By Reporting Element)

1 -- Plan Development and Project Organization. Although no new work has been directed toward this phase of the project, we have been in contact with Dr. Rao to alert him of our difficulties in synthesizing the targeted polymer and intermediates. As a result, we are also designing alternative targets and intermediates that may worth pursuing, and we will be submitting a request for an extension that will allow us to pursue these compounds for as long as project funds will allow.

2 -- Sample Characterization. During this quarter, 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. As with previous quarters, this quarter's were focused on the synthesis of the pre-Bakelite intermediate. We continued to pursue the modified and simplified intermediate that we targeted earlier. We have also continued to search for alternative routes to this intermediate, since thus far, we have been unsuccessful in our efforts.

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, the funds for monomer synthesis development are exhausted; therefore, we have begun to apply our unused funds for these phases toward the development of a suitable monomer synthesis procedure.

4. QUARTERLY REPORT SUMMARY STATUS ASSESSMENT AND FORECAST:

We initially targeted 1-*O*- and 4-*C*-dinaphthylmethylated 1,8-dihydroxynaphthalene as the key intermediate and then later modified the target compound to one based on 1,5-dihydroxynaphthalene since 1,5-dihydroxynaphthalene is a commercially available compound. Our preliminary efforts toward this modified target showed that we could not cleanly alkylate or acylate 1,5-dihydroxynaphthalene with 1-chloromethylnaphthalene or 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

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED dihydroxynaphthalene. We hoped that this intermediate would be easier to obtain, and that it would facilitate our evaluation of the key Bakelite polymerization step.

Our approaches to the synthesis of the simplified pre-Bakelite reaction intermediate are given in the following schemes. **Scheme I** shows that our first approach *O*-alkylated the commercially available compound, 4-chloro-1-naphthol (1) with 1-chloromethylnaphthalene to give ether **2**. We hoped to prepare intermediate 3 by treating 1-chloromethylnaphthalene with the corresponding Grignard reagent of **2**. Alternatively, we hoped to treat the Grignard reagent of 2 with 1-naphthaldehyde and then reduce the resulting hydroxyl to get 3. Unfortunately, neither of these approaches were successful since we were unable to generate the Grignard reagent of 2 by any of a number of methods including: using a variety of solvents (diethyl ether, THF, and DME) with catalytic amounts of iodine and ethyl bromide; refluxing for more than 3 days, with and without naphthaldehyde in the reaction mixture; and refluxing in DME with iodine for >3 days. We also generated the Grignard reagent from molecular magnesium generated by the reduction of $MgCl_2$ with potassium in THF. Preliminary data (mass spectral) from this last approach showed that the product mixture contained a product with the correct molecular ion. However, reaction monitoring by TLC indicated that conversion to the desired product was very limited, and subsequent efforts to improve the % conversion were unsuccessful. Another attempted variation was the lithiation of 2 in THF. Again, the preliminary analysis of the reaction mixture showed that one of the components in the reaction mixture was potentially the desired compound 3. Unfortunately, our efforts to isolate the potential desired product by column chromatography showed that none of the major compound was the desired compound.

During this time, we also pursued the Friedel-Crafts acylation of 1-naphthol as another approach to the desired target intermediate. As shown in **Scheme II**, we hoped that 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 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 a number of different 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 obtained complex mixtures of products.

Since literature reported that 4-acylations of 1-methoxynaphthalene with benzoyl chloride occurred selectively and in high yields, we attempted the analogous 4-acylation of 1-methoxynaphthalene with 1-naphthoyl chloride, as shown in **Scheme III**. Initially, we found that this reaction proceeded slowly at room temperature to give a product mixture containing the desired 4-acylated compound **6**. At this time, we thought that if a sufficient quantity of **6** could be isolated, this compound could then be reduced to 7, demethylated, and alkylated with 1-chloromethylnaphthalene to 3. Unfortunately, when we tried to repeat this work, we were unable to isolate any of the desired compound **5** from the product mixture, and therefore, we have not pursued Friedel-Crafts acylations any more.

Our consistent lack of success with our many approaches to the simplified pre-polymerization intermediate has led us to speculate that our targeted hydroxy- and alkoxynaphthalenes are too reactive or that they may be oxidized very easily or are light-sensitive. This conclusion is supported by the complex product mixtures (by layer chromatography) that we have routinely obtained in all of the reactions tried. Therefore, we have more recently pursued a new prepolymerization intermediate by a scheme in which the inclusion of the hydroxy- or alkoxynaphthalene moiety would not occur until the last, polymerization step. As shown in **Scheme IV**, we wanted to alkylate either terephthaldicarboxyaldehyde or terepththaloyl chloride with Grignard reagent **10** to give adduct **11**. Grignard reagent **10** would be prepared from *O*-blocked 5-bromo-1-naphthylmethanol **9**.

In pursuit of this new route, both 1-naphthaldehyde or 1-naphthoic acid were 5-brominated and then reduced to alcohol **15**, as shown in **Scheme V**. This alcohol was then treated with dihydropyran to give tetrahydropyranyl ether **9**.

We also treated 5-bromo-1-naphthaldehyde with ethylene glycol and *p*-toluene sulfonic acid to obtain acetal **16**, as shown in **Scheme VI**. We planned to treat this intermediate with magnesium to provide another potential Grignard reagent to be reacted with the previously mentioned substrates (terepththaloyl chloride and terephthaldicarboxaldehyde).

Next, we attempted to prepare the Grignard reagent with elemental magnesium generated from $MgCl_2$ and potassium metal. A mixture of products was obtained which was separated by column chromatography. Mass spectroscopy showed no molecular ion peaks corresponding to any of the major components of the product mixture. Therefore, we next attempted to generate Grignard reagent using reported standard method of adding magnesium to an ether solution of the aryl halide and catalyzing the reaction with iodine. As a control, we also simultaneously attempted to generate naphthylmagnesium bromide from 1-bromonaphthalene with the same procedure. In both of these cases, we found the generation of the Grignard reagent to be very sluggish at best. The physical appearance of the solution seemed to indicate that some Grignard reagent may have formed (clouding of the solution, color change, formation of a salt/precipitate, disappearance of some of the magnesium metal). However, a mass spectrometric analysis of the product mixture after addition of terephthaldicarboxaldehyde did not show any of the desired adducts molecular ions.

Therefore, we can only report that we are still unable to provide the target polymer or even any of the key intermediates leading to this target. Dr. Rao has been informed of our progress (or lack of progress), and he has suggested that we begin to design other alternative compounds which contain the functionalities required by the target compound. In response to this suggestion, we have quickly designed the potential targets shown in **Scheme VII**. We are currently evaluating the schemes further and we will continue designing routes to the other analogous compounds.

Cecil D. Kwong /JDavis

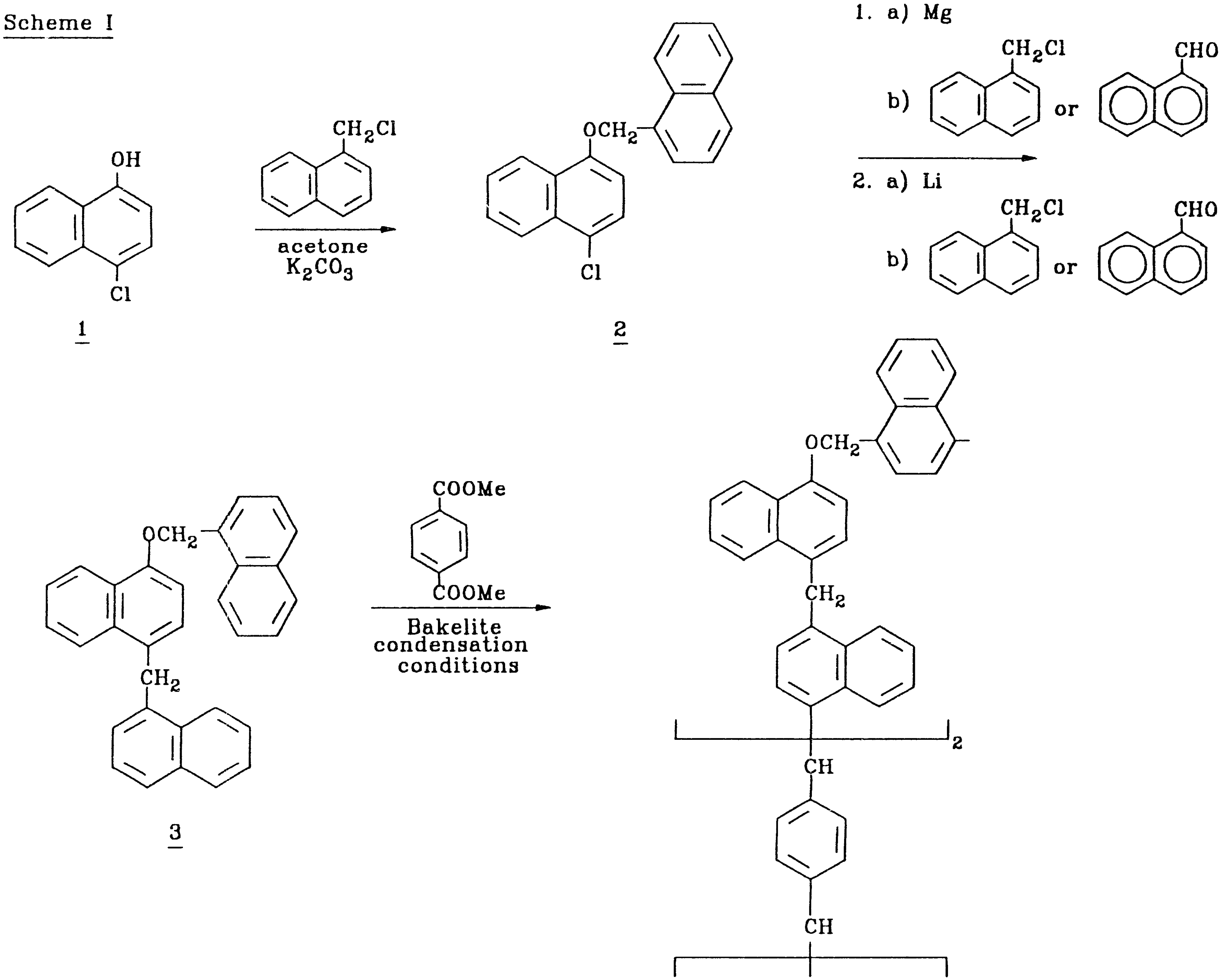
Cecil D. Kwong, Project Manager
Organic Chemistry Research Area

CDK/jed

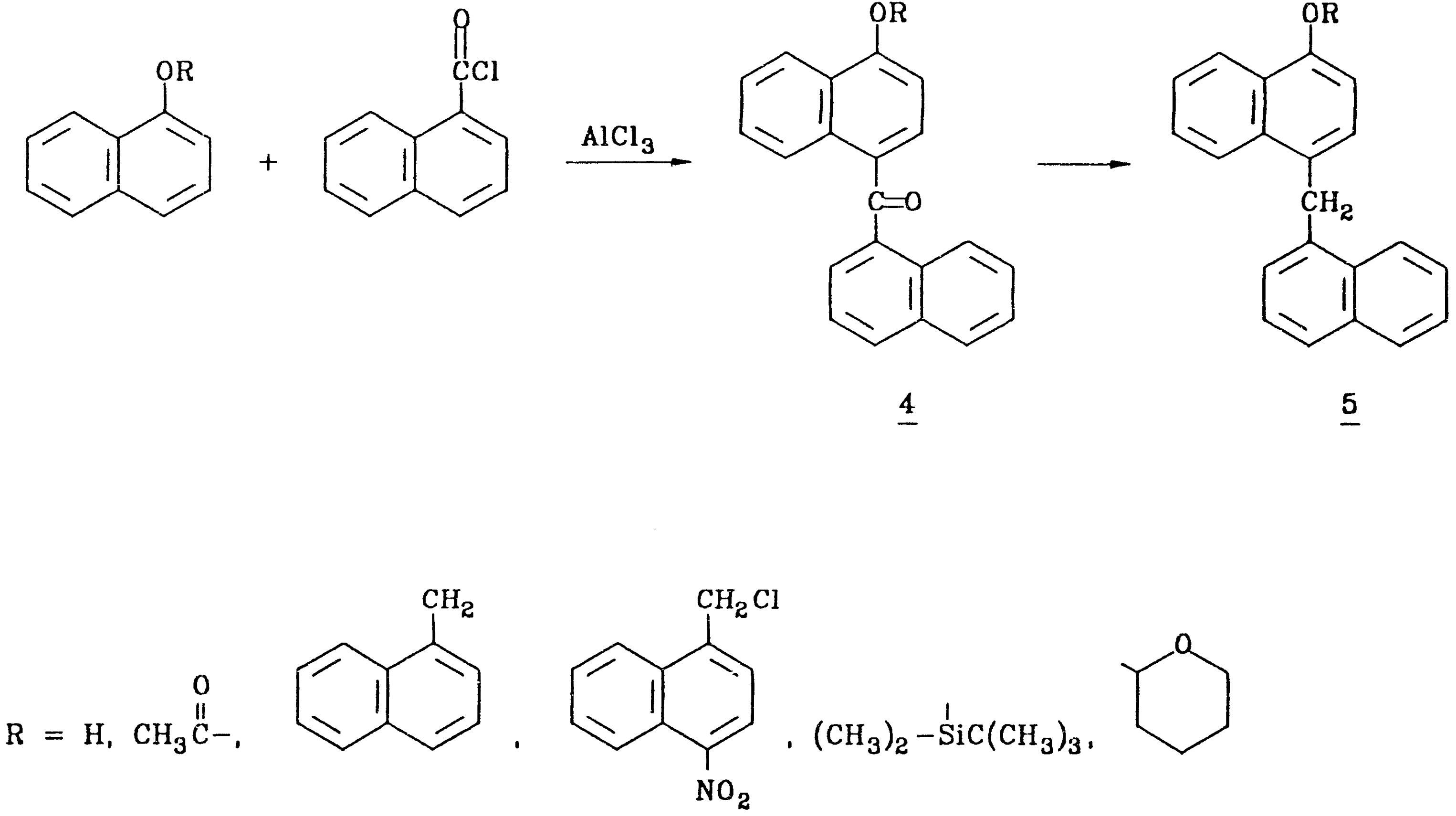
Attachments:
- Milestone Status Report
- Cost Management Report
- Schemes I-IX
- KPSR

DISCLAIMER

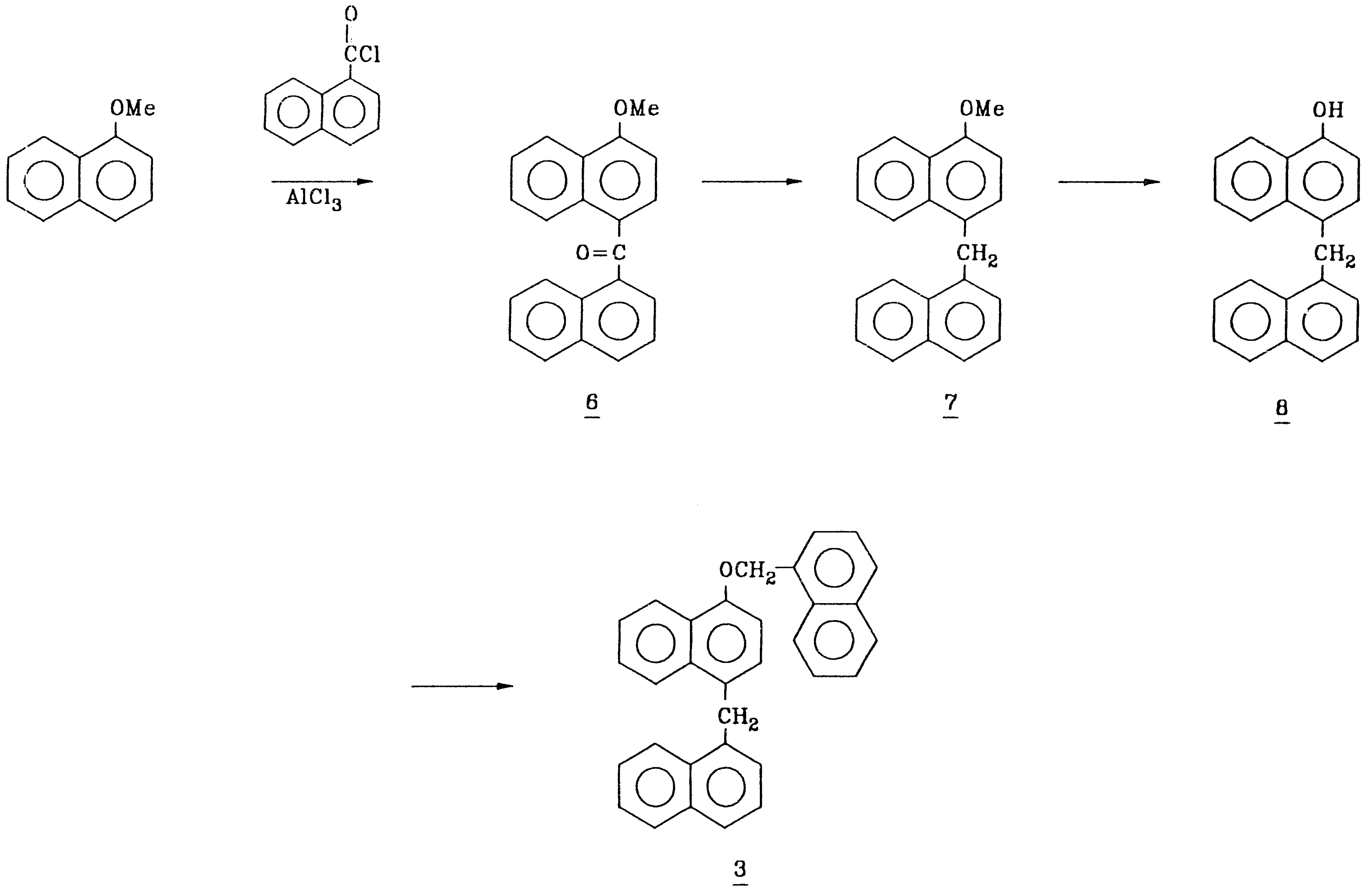
Scheme I


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
conditions
OCH$_2$
CH$_2$
2
CH
CH

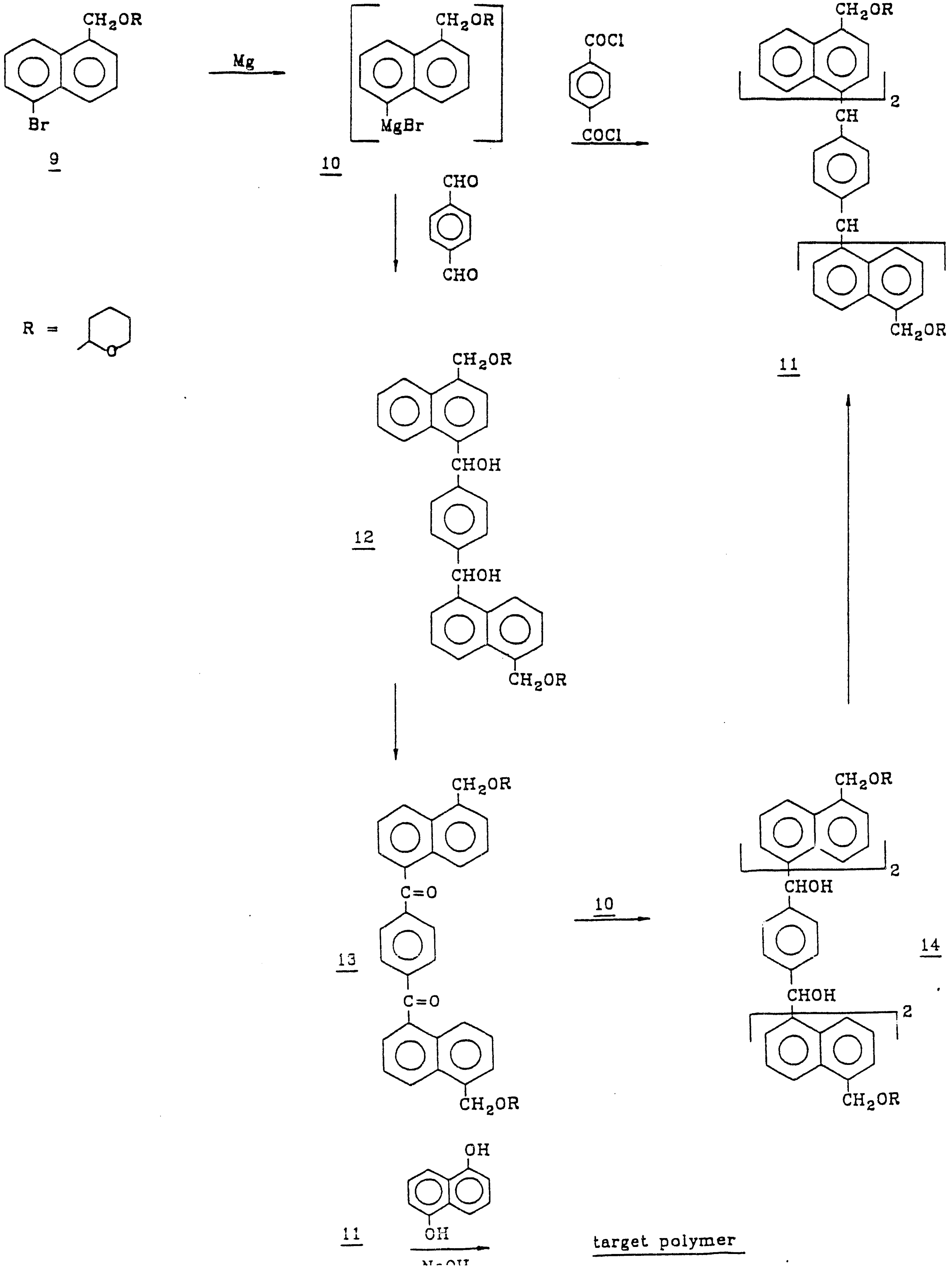
Scheme II


OR
$\overset{O}{\overset{\|}{C}}Cl$
+
$AlCl_3$
OR
C=O
OR
CH_2
4
5
R = H, $CH_3\overset{O}{\overset{\|}{C}}-$,
CH_2
CH_2Cl
NO_2
$(CH_3)_2-SiC(CH_3)_3$,
O

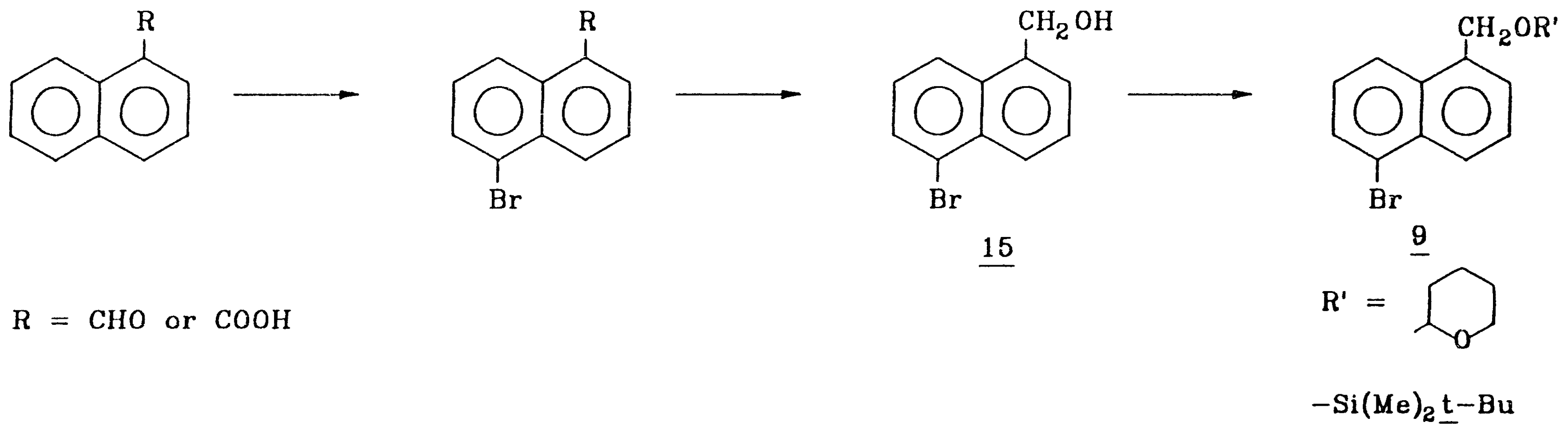
Scheme III



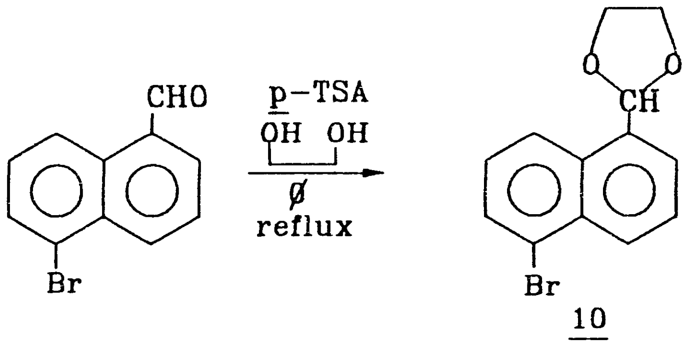
Scheme IV


CH2OR
Br
9
Mg
CH2OR
MgBr
10
COCl
COCl
CH2OR
2
CH
CH
CH2OR
11
CHO
CHO
R =
O
CH2OR
CHOH
12
CHOH
CH2OR
CH2OR
C=O
13
C=O
CH2OR
10
CH2OR
2
CHOH
14
CHOH
2
CH2OR
OH
OH
11
target polymer

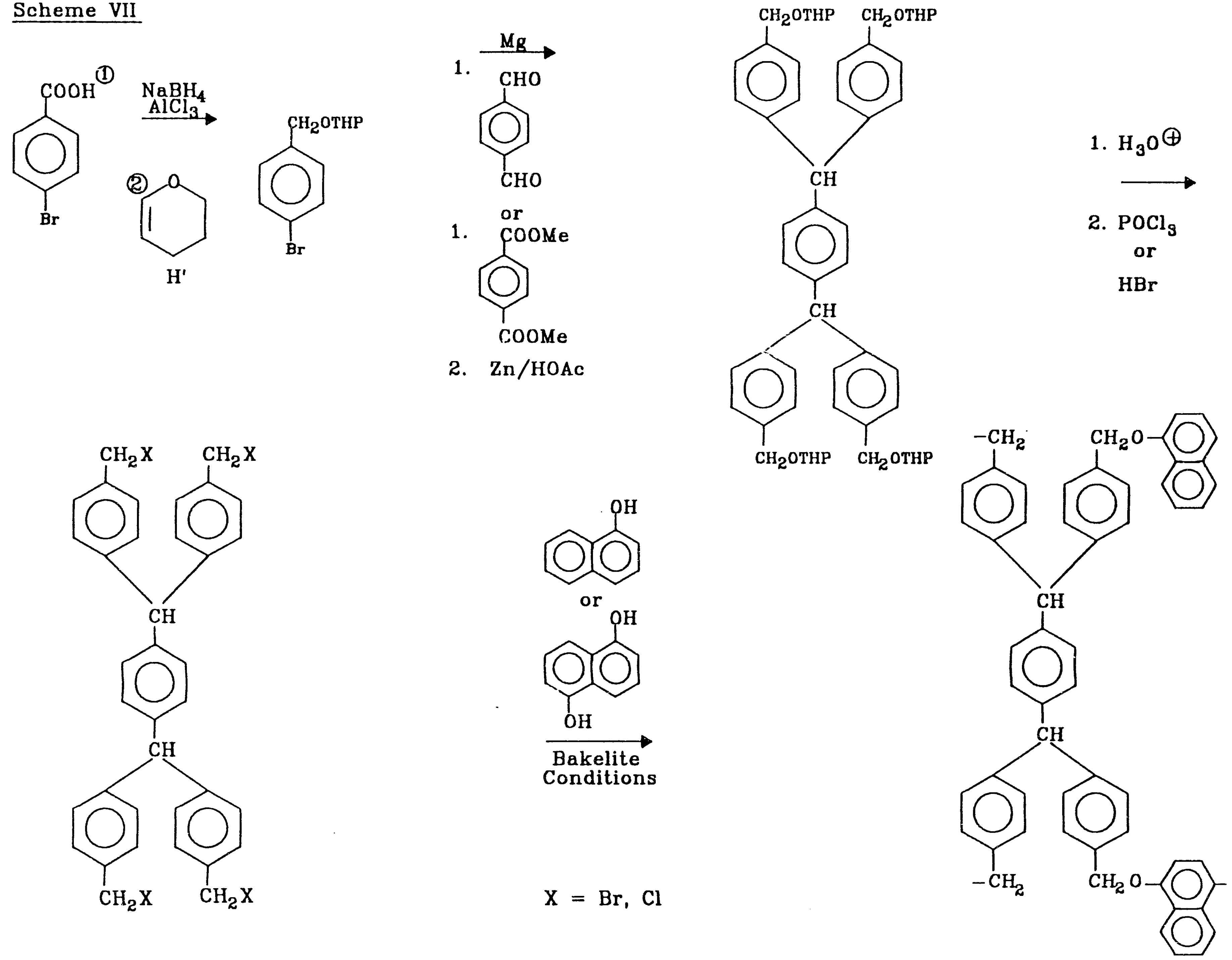
Scheme V



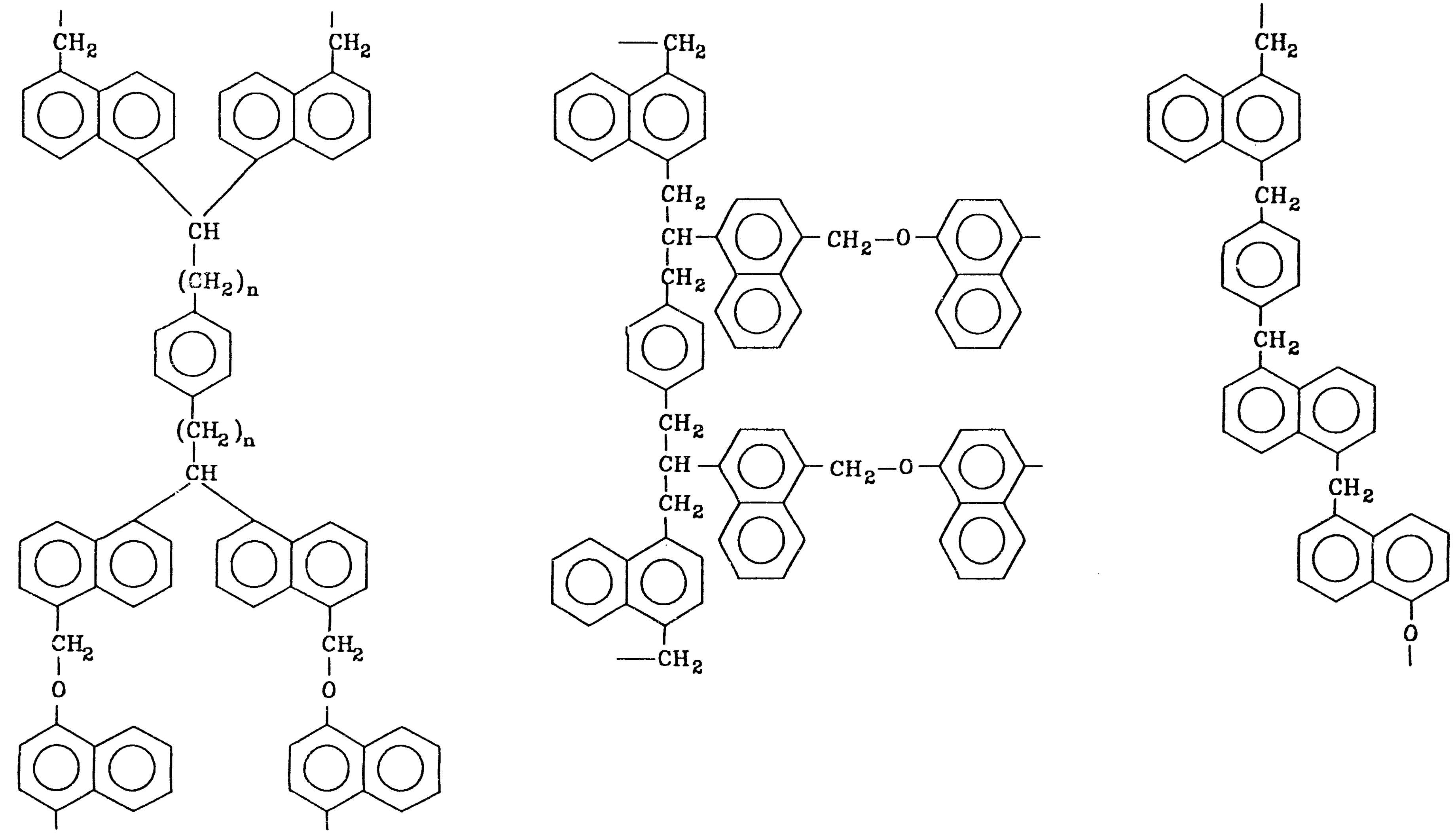
Scheme VI



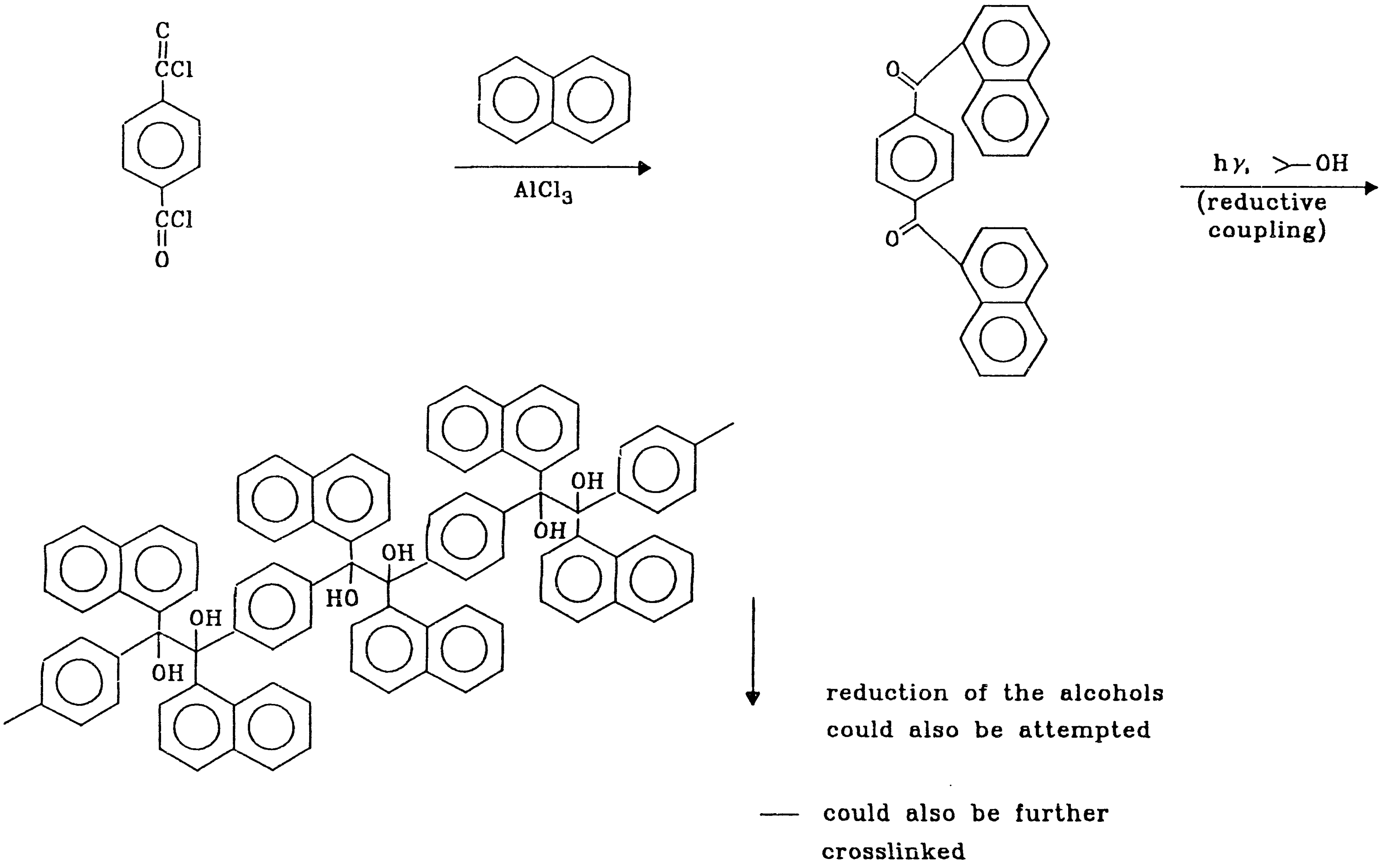
Scheme VII


COOH ①
Br
NaBH$_4$
AlCl$_3$
②
O
H'
CH$_2$OTHP
Br
1. Mg
CHO
CHO
or
1. COOMe
COOMe
2. Zn/HOAc
CH$_2$OTHP
CH$_2$OTHP
CH
CH
CH$_2$OTHP
CH$_2$OTHP
1. H$_3$O$^\oplus$
2. POCl$_3$
or
HBr
CH$_2$X
CH$_2$X
CH
CH
CH$_2$X
CH$_2$X
OH
or
OH
OH
Bakelite Conditions
X = Br, Cl
–CH$_2$
CH$_2$O
CH
CH
–CH$_2$
CH$_2$O

Scheme VIII


CH2
CH2
CH
(CH2)n
(CH2)n
CH
CH2
O
CH2
O
CH2
CH2
CH
CH2
CH2-O
CH2
CH
CH2
CH2-O
CH2
CH2
CH2
CH2
CH2
O

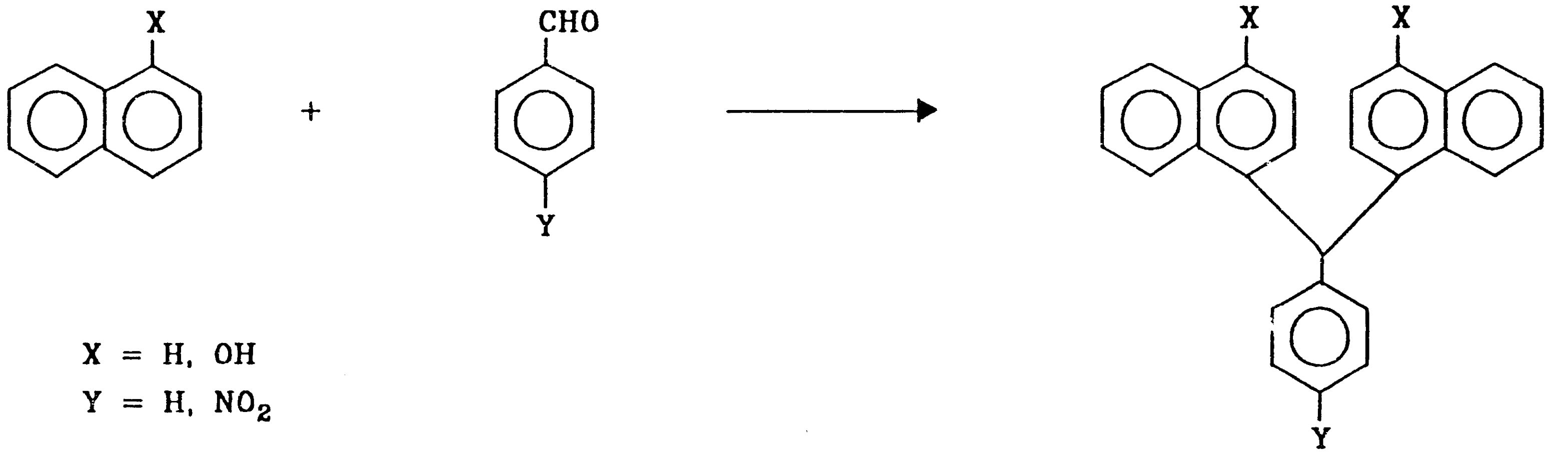
Scheme IX



reduction of the alcohols could also be attempted

— could also be further crosslinked

Scheme X



X = H, OH

Y = H, NO_2

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2 / 5 / 93