

Letter

# Selective mono-allylation of diphenyl ether with allyl bromide catalyzed by lead halo composite ( $\text{Pb}_3\text{BrF}_5/\text{Pb}_3\text{ClF}_5$ )

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## Abstract

Allylation of diphenyl ether (DPO) with allyl bromide (ABr) was catalyzed by lead halo composite of the general formula  $\text{Pb}_3\text{XF}_5$  (where X = Br or Cl) at 80°C. The reaction was carried out in a stirred glass reactor at atmospheric pressure with ABr and DPO (molar ratio of ABr:DPO = 1:5) which gave mainly *para*-allyl DPO. Side reactions like isomerization of the double bond and cyclization of allylic functional groups were observed when allyl bromide was taken in excess. These products were *p*-1-propenyl DPO 'oxepane', *ortho*- and *para*-monoallyl DPO's and *p,p'*-diallyl DPO. However, under the optimized reaction conditions, the allylation was more selective for *para*-allyl DPO. This implies that functional selectivity which is difficult to achieve in most cases, could be easily achieved with solid lead halo composite catalysts. © 2000 Published by Elsevier Science B.V.

**Keywords:** Allylation; Diphenyl ether (DPO); Allyl bromide (ABr); Lead halo composite; Oxepane

## 1. Introduction

Direct allylations of polynuclear aromatic compounds by electrophilic aromatic substitution using allyl halides or alcohols are usually difficult to perform due to the instability of the products under the reaction conditions employed. Since the allyl derivatives of polynuclear aromatics such as biphenyl, naphthalene and diphenyl ether (DPO) are potential precursors for making monomers of high quality polymeric materi-

als, the preparation of allylated derivatives of these is of great importance from a commercial viewpoint.

Ochiai et al. have reported that the combinations of allylsilane and allylgermane, or allylsilane and thallium(II) trifluoroacetate, gave allylated products in good yields in allylation of aromatic compound [1]. Kodomari et al. [2] have carried out selective monoallylation using a combination of solid acid and solid base like  $\text{ZnCl}_2\text{-SiO}_2$  and  $\text{K}_2\text{CO}_3\text{-Al}_2\text{O}_3$ . Here it was observed that the solid base acts as a scavenger for the hydrogen halide liberated during the course of the reaction. Solid acids, such as acidic zeolites and clays, have also been used for the selective allylation with allylic alcohols [3]. Clark et al. [4] have reported that zinc chloride supported on montmorillonite K10

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clay was an useful alternative to traditionally used allylation catalysts such as  $\text{AlCl}_3$  and HF. But the clay catalyst showed poor activities and selectivities in allylation of aromatic compounds.

It has been reported by Yamaguchi et al. [5] that tin(II) bromide acts as a good allylation catalyst in the allylation of anisole with allyl bromide. Here, higher temperatures were required for the reaction to take place which would lead to side reactions. Alkylation and benzylation reactions have also been reported to take place using  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$  as catalyst [6]. Espeel et al. [7] have reported the formation of allylbenzene, toluene and anisole over zeolites by electrophilic substitution with allyl alcohols. Because of the acidic nature of zeolites, these catalysts favored side reactions and gave poor selectivities to the desired products. Allylation of naphthalene with allylic alcohols employing Pd catalysts in the presence of molecular sieves 4A has also been reported [8]. In this case, the products formed were mono-, di- and tri-allyl naphthols. Most of the catalyst systems reported for allylation were tested for their reactivity in allylation of DPO with allyl bromide and we found that the above catalyst systems did not give any significant results.

Recently, it has been reported that a combination of lead fluoride and sodium halide (where halide is either bromide or chloride) gave lead halo composite of the general formula  $\text{Pb}_3\text{XF}_5$  (where X = Br or Cl) and that this composite could be used efficiently for the monoallylation of aromatics [9,10]. Hence, we decided to investigate the role of lead halo composite as catalyst in allylation of DPO with allyl bromide as an allylating agent. We report in this communication our observations made with lead halo composite-catalyzed allylation of DPO by allyl bromide (ABr) at  $80^\circ\text{C}$  and atmospheric pressure.

## 2. Experimental

### 2.1. Materials

The DPO was procured from M/s. S.D. Fine Chemicals Ltd., Mumbai, and allyl bromide from M/s. Loba Chemie (P) Ltd., Mumbai, and both were used as received in the experiments. Lead fluoride (purity >98%) was obtained from M/s. Reidel. Sodium chloride and

sodium bromide were procured from local chemical suppliers, Pune.

### 2.2. Preparation of lead halo composites

To a solution of sodium bromide (4.2 g) or sodium chloride (2.4 g) in distilled water (50 ml) was added powdered lead fluoride (30 g) and the mixture was stirred well for 1 h at room temperature till a white slurry was obtained. This slurry was separated by filtration and the residue was collected and dried in an oven at  $90^\circ\text{C}$  overnight. The dried material is powdered and characterized by XRD and other physico-chemical techniques to determine its composition and structural properties. It was found that the molecular compositions of the composites were  $\text{Pb}_3\text{BrF}_5$  and  $\text{Pb}_3\text{ClF}_5$ , respectively.

### 2.3. Catalyst activation

The lead halo composites were activated by stirring in an acetonitrile solvent at  $90^\circ\text{C}$  for 24 h, after which the acetonitrile was filtered off. The residues thus obtained were dried in an oven at  $90^\circ\text{C}$  overnight and were used as catalysts in allylation experiments.

### 2.4. Characterization of the catalysts

The catalysts were characterized by powder X-ray diffraction technique (Rigaku Model D/MAXIII VC, Japan). The analysis showed that the lead halo composite is not just a physical mixture of known lead compounds:  $\text{PbF}_2$ ,  $\text{PbBrF}$ ,  $\text{PbClF}$ ,  $\text{PbBr}_2$  or  $\text{PbCl}_2$ , but the formation of a new lead composite material. This suggested that chemical interaction between the two solids,  $\text{PbF}_2$  and NaBr or  $\text{PbF}_2$  and NaCl has taken place, resulting in lead halo composites of the composition  $\text{Pb}_3\text{BrF}_5$  and  $\text{Pb}_3\text{ClF}_5$ , respectively. The detailed investigation of the composite material is in progress for further experiments.

### 2.5. Analysis of reaction products

The products of allylation of DPO were analyzed by a HP-5890 gas chromatograph fitted with a fused megabore column SE-52, HP-5 (cross-linked 5% PhMe silicone), 30 m length, 0.53 mm i.d., 0.3  $\mu\text{m}$

film thickness and a FID detector. The gas chromatograph was programmed with an initial temperature of 40°C (held for 3 min) followed by 20°C min<sup>-1</sup> heating rate up to 220°C, and a total run time of 20 min. Conversions were calculated based on the allyl bromide consumed, using pentadecane as an internal standard in the reaction mixture. The allylated products obtained were confirmed by GCMS (Shimadzu QP 5000) and GC-IR (Shimadzu-FTIR) and also by comparing the retention times with their standards.

### 2.6. Experimental procedure

The experiments on allylation of DPO with allyl bromide and lead halo composite catalyst were carried out in a stirred glass reactor maintained at 80°C by a thermostatic oil bath in an inert atmosphere (fitted with nitrogen balloon) and water condenser fixed on the top. After a contact time of 5.0 h, the reaction mixture was cooled to room temperature and a sample was withdrawn and centrifuged to get a clear solution. This solution was analyzed by gas chromatography for DPO, ABr and allylated products. The solid catalyst was separated at the end of reaction by filtration and treated with acetone to leach out the adsorbed reaction products. The desorbed products were analyzed and accounted for the total mass balance of the allylation reaction.

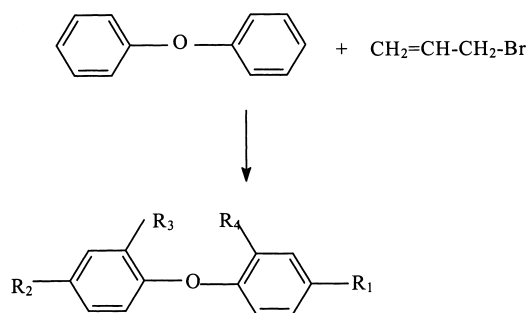
### 2.7. Regeneration of catalyst

The lead halo composites once used were found to contain the adsorbed product materials and HBr. In order to remove the adsorbed species, the used catalysts were washed with 5 ml of acetone each time and centrifuged. After the filtrate was discarded, the solids were collected and dried at 90°C in an oven overnight and were used in fresh allylation experiments.

## 3. Results and discussion

The allylation of DPO by ABr catalyzed by lead halo composite to give allylated DPO products is as shown in Fig. 1.

The kinetics study of allylation of DPO by allyl bromide at 80°C catalyzed by lead halo composite were



Where, R = - Allylic group

If, R=R<sub>1</sub>, or R<sub>2</sub>, and R<sub>3</sub>=R<sub>4</sub>=H, *para*-allyl DPO

R=R<sub>4</sub> or R<sub>3</sub>, and R<sub>1</sub>=R<sub>2</sub>=H, *ortho*-allyl DPO

R= R<sub>3</sub> & R<sub>4</sub>, and R<sub>1</sub>=R<sub>2</sub>=H, *o,o'*-diallyl DPO

R=R<sub>1</sub> & R<sub>2</sub>, *p,p'*-diallyl DPO

Fig. 1. Reaction scheme.

carried out by varying the concentrations of reactants, the rate of allylation with respect to the concentrations varied is presented in Table 1.

The results presented in Table 1 indicated that the allylation of DPO by ABr gave mainly *ortho*- and *para*-allyl DPO's as the main products. The other minor products were *o,o'*- and *p,p'*-diallyl DPO's and side products such as, 10-methyl-10 H, 11 H-dibenzo (b, f) oxepane and *p*-1-propenyl DPO. These side products are shown in Fig. 2. Among the monoallyl DPO's, the *para*-isomer yield was more than *ortho*-isomer. Since DPO was taken in excess, it also acts as a solvent and favors the forward reaction by allowing the dissolution of products formed in the reaction mixture. When excess of ABr was taken (ABr:DPO = 5:1), it was found that diallylation of DPO occurred to give *o,o'*- and *p,p'*-diallyl DPO and small amounts of side products 'oxepane' and *p*-1-propenyl DPO. Under these conditions also, the selectivity was higher for *p,p'*-diallyl DPO than *o,o'*-DPO. In general, the allylation of DPO catalyzed by lead halo composite has been found to be *para*-selective to give *para*-, *mono*- or *di*-allylated DPO's.

Two types of lead halo composites of the general formula Pb<sub>3</sub>XF<sub>5</sub> (where X = Cl or Br) have been tested in the allylation of DPO reaction. Catalyst Pb<sub>3</sub>BrF<sub>5</sub> and Pb<sub>3</sub>ClF<sub>5</sub> showed similar activities in allylation of DPO.

Table 1  
Allylation of DPO by ABr<sup>a</sup>

Run no.	Catalyst	DPO (mmol)	ABr:DPO (mol ratio)	Conversion with respect to ABr	Selectivity (%)			Others
					mono-allyl DPO		di-allyl DPO	
					<i>ortho</i> -	<i>para</i> -	<i>p,p'</i> -	
1	Pb <sub>3</sub> BrF <sub>5</sub>	100	1:20	65	31	69	–	–
2	Pb <sub>3</sub> BrF <sub>5</sub>	75	1:15	69	26	74	–	–
3 <sup>b</sup>	Pb <sub>3</sub> BrF <sub>5</sub>	75	1:15	50	34	66	–	–
4	Pb <sub>3</sub> BrF <sub>5</sub>	50	1:10	67	31	69	–	–
5	Pb <sub>3</sub> ClF <sub>5</sub>	75	1:15	67	37	63	–	–
6	Pb <sub>3</sub> BrF <sub>5</sub>	25	1:5	80	30	70	–	–
7 <sup>c</sup>	Pb <sub>3</sub> BrF <sub>5</sub>	25	1:5	83	30	70	–	–
8 <sup>d</sup>	Pb <sub>3</sub> BrF <sub>5</sub>	25	1:5	94	35	65	–	–
9	Pb <sub>3</sub> BrF <sub>5</sub>	10	1:2	87	25	75	–	–
10	Pb <sub>3</sub> BrF <sub>5</sub>	2.5	2:1	59 <sup>e</sup>	24	61	4	11
11	Pb <sub>3</sub> BrF <sub>5</sub>	1	5:1	70 <sup>e</sup>	22	62	5	9

<sup>a</sup> Conditions: catalyst concentration = 2.5 mmol, ABr = 5.0 mmol, temperature = 80°C and time = 5.0 h.

<sup>b</sup> Regenerated.

<sup>c</sup> Activated.

<sup>d</sup> Catalyst concentration = 5.0 mmol.

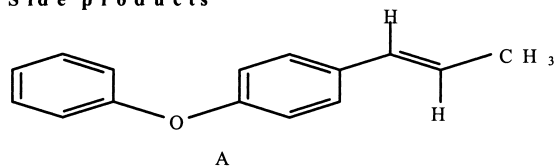
<sup>e</sup> Conversion of DPO.

### 3.1. Effect of reactant concentrations on the rates of allylation of DPO

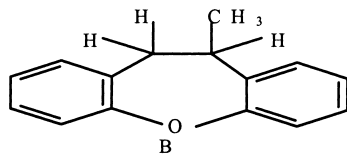
When the concentration of the catalyst was increased, the rates of allylation were also increased. The graph of catalyst concentration versus conversion (%) ABr is shown in Fig. 3. It was found that the conversion of ABr changed exponentially with the catalyst concentration. However, complete conversion

of DPO was not achieved in our study. The effect of ABr concentrations on the rates of allylation of DPO indicated that higher concentrations of ABr favored the formation of diallylated DPO's (ABr:DPO = 5:1) and at lower concentration only monoallylated DPO's are formed. The effect of temperature on the rates of allylation of DPO studied in the temperature range (80–120°C) indicated that there were no significant changes in the conversions of ABr and, in fact, the

#### Side products



A = p-1-propenyl DPO



B = 10-methyl-10H,11H-dibenzo(b,f)oxepane

Fig. 2. Side products of allylation of DPO by ABr.

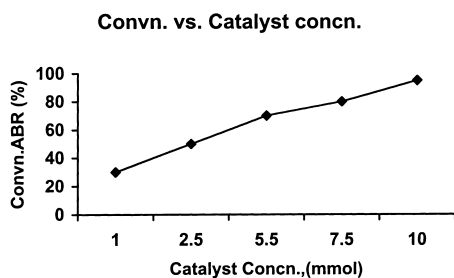


Fig. 3. Effect of catalyst concentration.

concentrations of side products like oxepane and *p*-1-propenyl DPO increased at higher temperature. Hence, it was inferred that the optimum reaction temperature for the allylation of DPO was 80°C to get selectively monoallylated DPO's. Among these *para*-selectivity was the highest.

From the above data, we conclude that the lead halo composites of the general formula  $Pb_3XF_5$  (where X = Br or Cl) were efficient catalyst systems in promoting allylation of DPO. The optimum reaction conditions to give *p*-monoallyl or di-allyl DPO's were ABr:DPO mol ratio = 1:5, at a conversion of 94 (wt.%) with respect to ABr in 5 h of reaction time.

#### 4. Conclusions

The allylation of aromatic substrates like DPO with ABr was found to be catalyzed with lead halo composite catalyst at 80°C and at atmospheric pressure. Under the optimized reaction conditions, the catalyst system gave higher selectivities for monoallylated

DPO's. Among the monoallylated, the selectivity for *para*-allyl DPO was found to be higher under the reaction conditions. Such a functional selectivity is rarely possible to achieve where HBr is liberated as the primary product, and this will favor the consecutive reactions leading to the formation of side products. Hence, HBr should be removed from the reaction mixture, and this is possible only if the allylation is carried out in a flow reactor under vapor phase conditions. This would ensure the constant removal of HBr under flow conditions and would prevent the formation of by-products. Some work in this direction is in progress at our group and will be published later.

#### References

- [1] M. Dechiali, M. Arimoto, E. Fujita, *Tetrahedron Lett.* 22 (1981) 4491.
- [2] M. Kodomari, S. Nawa, T. Miyoshi, *J. Chem. Soc. Chem. Commun.* (1995) 1895.
- [3] K. Smith, G.M. Pollaced, *J. Chem. Soc., Perkin Trans. 1* (1994) 3519.
- [4] J.H. Clark, A.P. Kylett, D.J. Macquarrie, S.J. Barlow, P. Landon, *J. Chem. Soc., Chem. Commun.* (1989) 1353.
- [5] J.-I. Yamaguchi, Y. Takagi, A. Nakayama, T. Fujiwara, T. Takeda, *Chem. Lett.* 1 (1991) 133.
- [6] A.A. Gevorkyan, A.S. Arakelyan, A.A. Dzhaniyan, *Arm. Khim. Zh.* 43 (8) (1990) 523.
- [7] P.H. Espeel, B. Janssens, P.A. Jacobs, *J. Org. Chem.* 58 (1993) 7688.
- [8] Y. Tada, A. Satake, I. Shimizu, A. Yamamoto, *Chem. Lett.* (1996) 1021.
- [9] J. Ichihara, T. Hanafusa, Y. Takai, Y. Ito, *Chem. Lett.* (1992) 1161.
- [10] J. Ichihara, *Chem. Commun.* (1997) 1921.