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# Stability and Reactivity of Cationic Polyelectrolytes in Alkaline Conditions

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## I. Introduction

Ionic polymers have found utility as components of fuel cells, where they are used as ion-transporting membranes. Cationic polymers bearing ammonium or phosphonium units, for example, have recently proven beneficial for use in alkaline fuel cells. One of the problems associated with such cationic polymers is that many organic polymers and functional groups undergo potentially undesirable decomposition reactions in the presence of hydroxide ions due to hydroxide's identity as a strong base and a good nucleophile. In this contribution, the decomposition pathways that we have observed for phosphonium polyelectrolytes will be discussed. The influence of structure on the decomposition pathway and rate of decomposition will also be discussed with the aim of elucidating design principles that could improve the stability of these polymers for use in alkaline environments.

## II. Benzyl Phosphonium Polymers

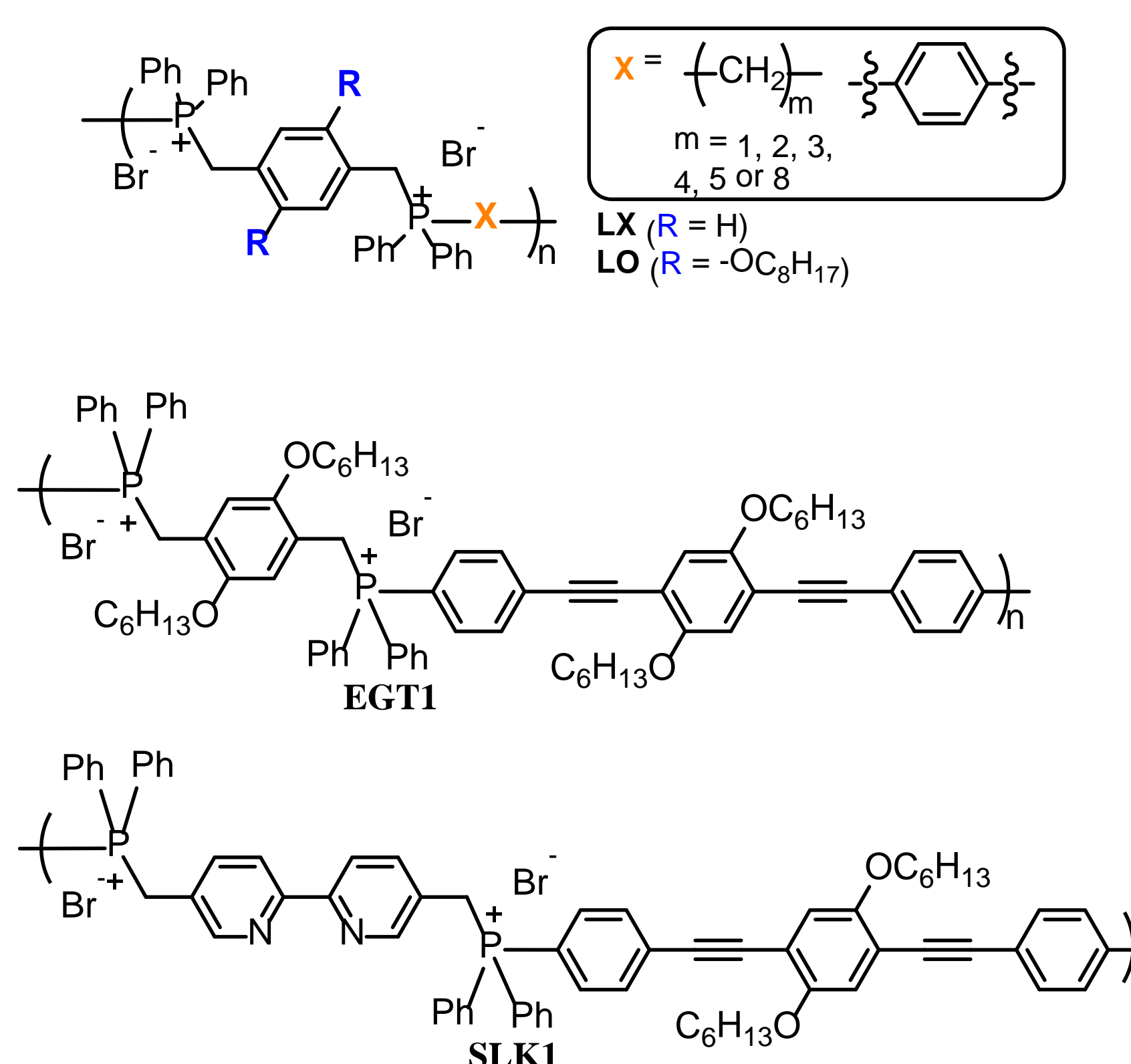


Figure 1. Structures of LX, LO, EGT1, and SLK1 polymers.

## III. Polymer Synthesis & Structure

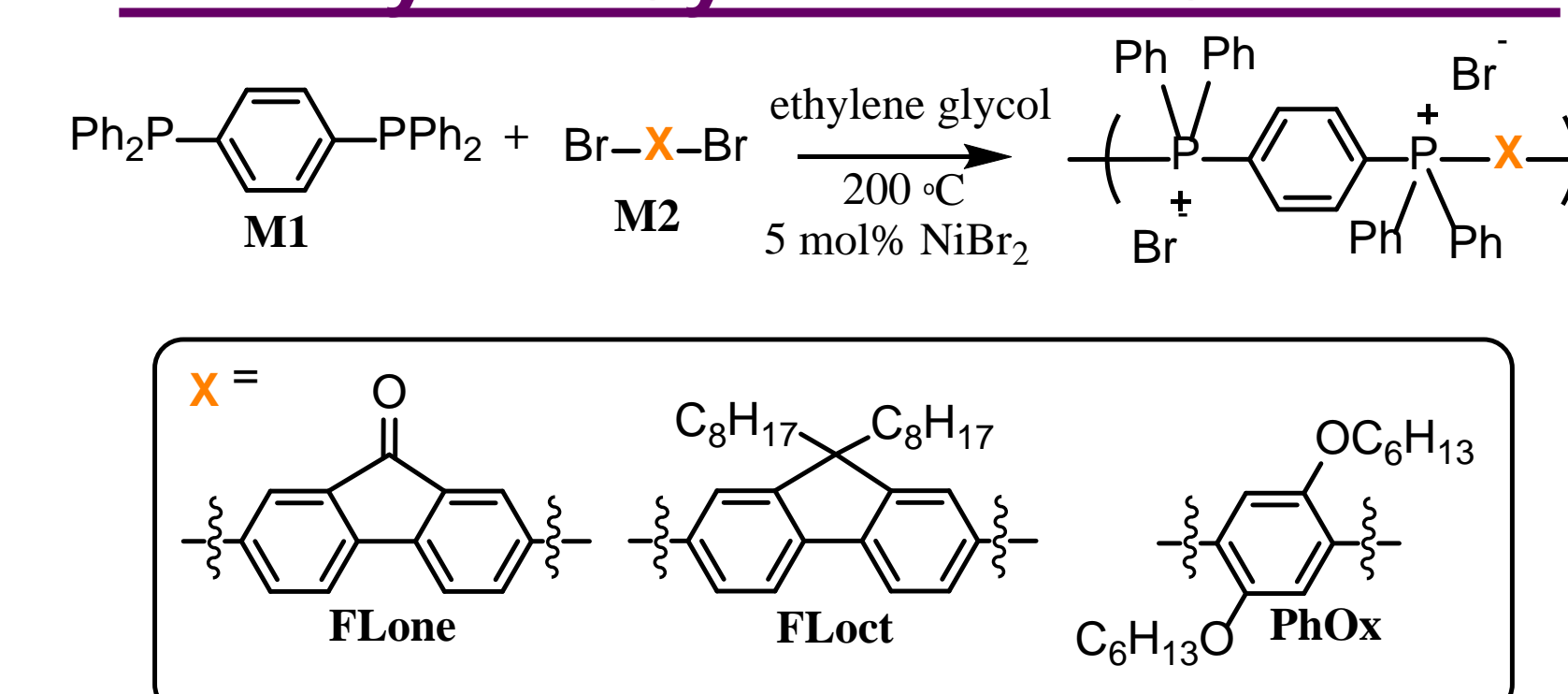


Figure 2. Synthesis reaction to form FLone, FLoct, and PhOx polymers.

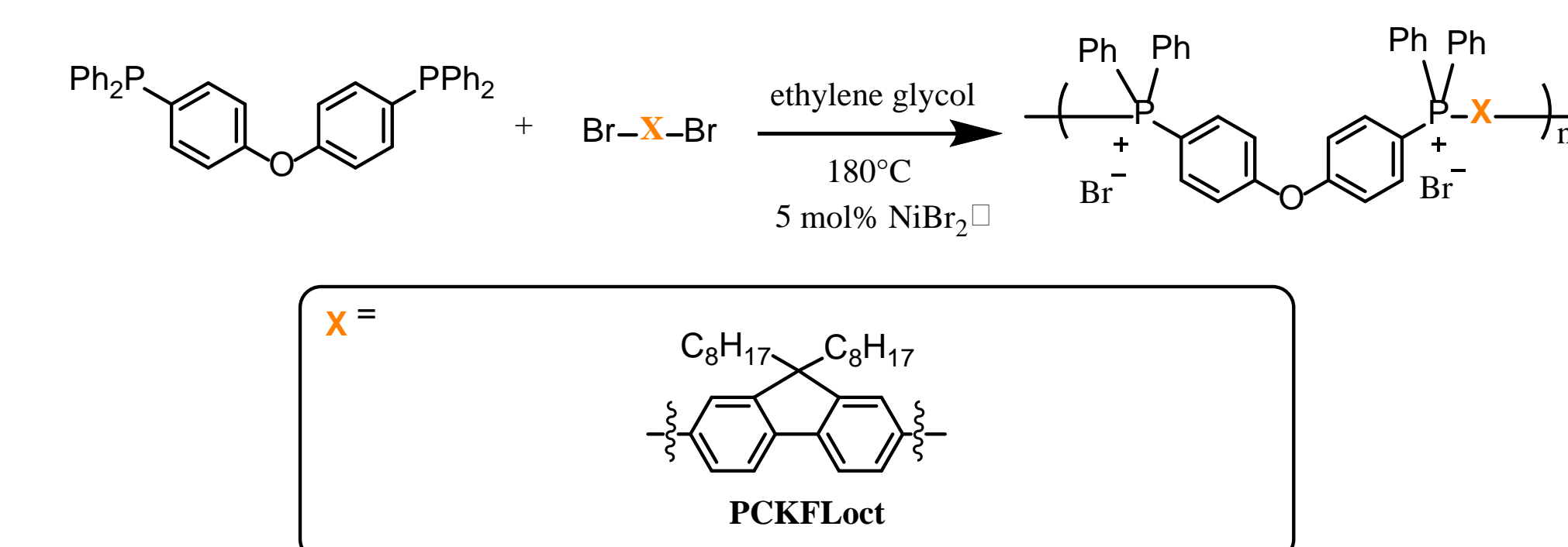


Figure 3. Synthesis reaction to form polymer with improved stability (PCKFLoct).

## IV. Polymer Characterization

|       | UV-Vis $\lambda_{\text{max}}$ (nm) |          | Solution Fluorescence $\lambda_{\text{em}}$ (nm) | Decomposition Temperature- $T_d$ (°C) | $^{31}\text{P}$ NMR (ppm) |
|-------|------------------------------------|----------|--|---------------------------------------|---------------------------|
|       | Solution                           | Film     |  |                                       |                           |
| FLoct | 304.952                            | 534.9901 | 357  | 220                                   | 23.8                      |
| FLone | 299.939                            | 439.9391 | 358  | 198                                   | 28.6                      |
| Phox  | 324.976                            | ~300     | 328  | 172                                   | 22.7                      |

Table 1. Polymer characterization of FLoct, FLone, and PhOx polymers.

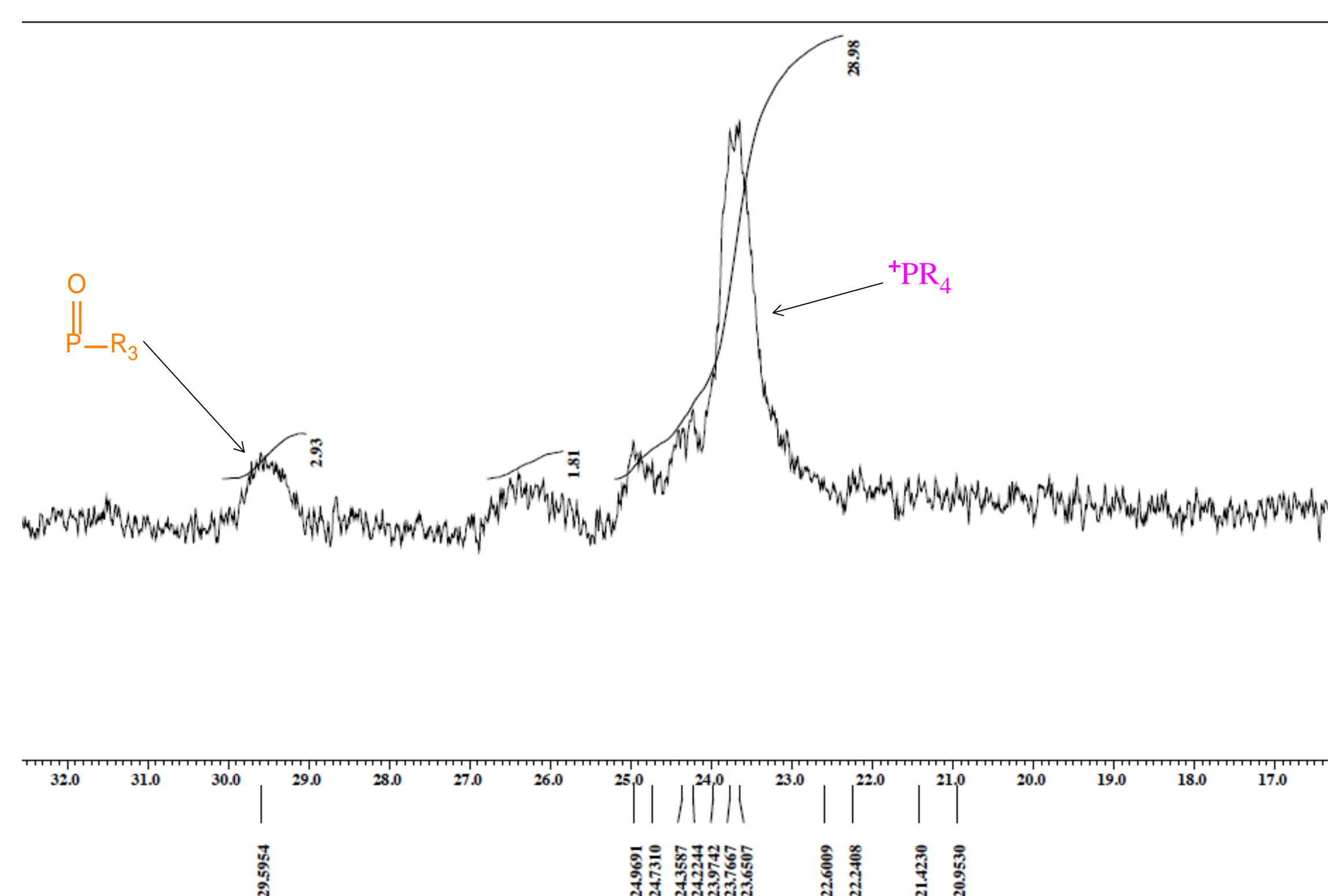


Figure 4. Representative phosphorous NMR spectrum for the polymer PCKFLoct.

## V. Possible Decomposition Pathways

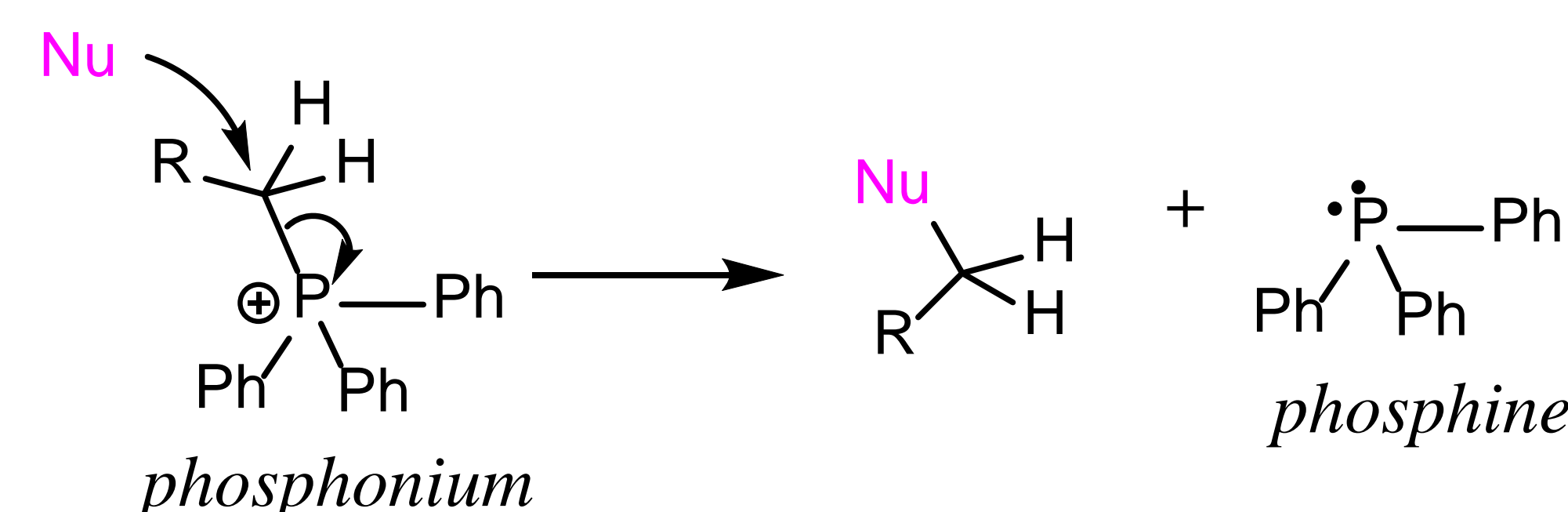


Figure 5. Nucleophilic substitution

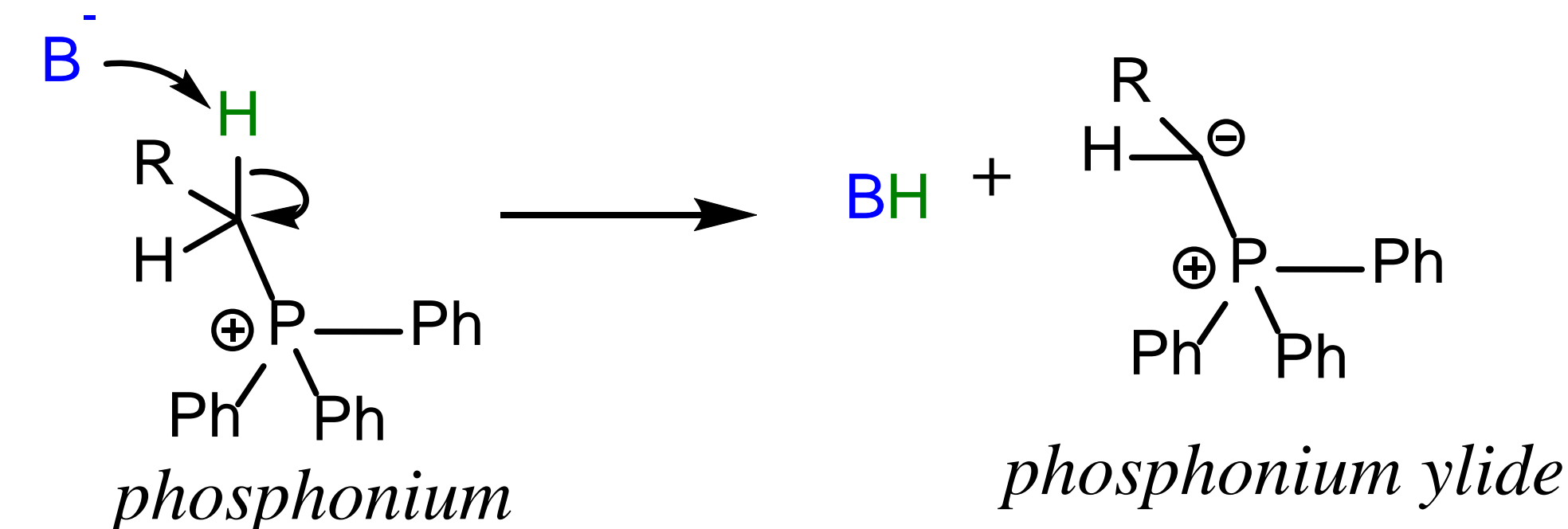


Figure 6. Deprotonation

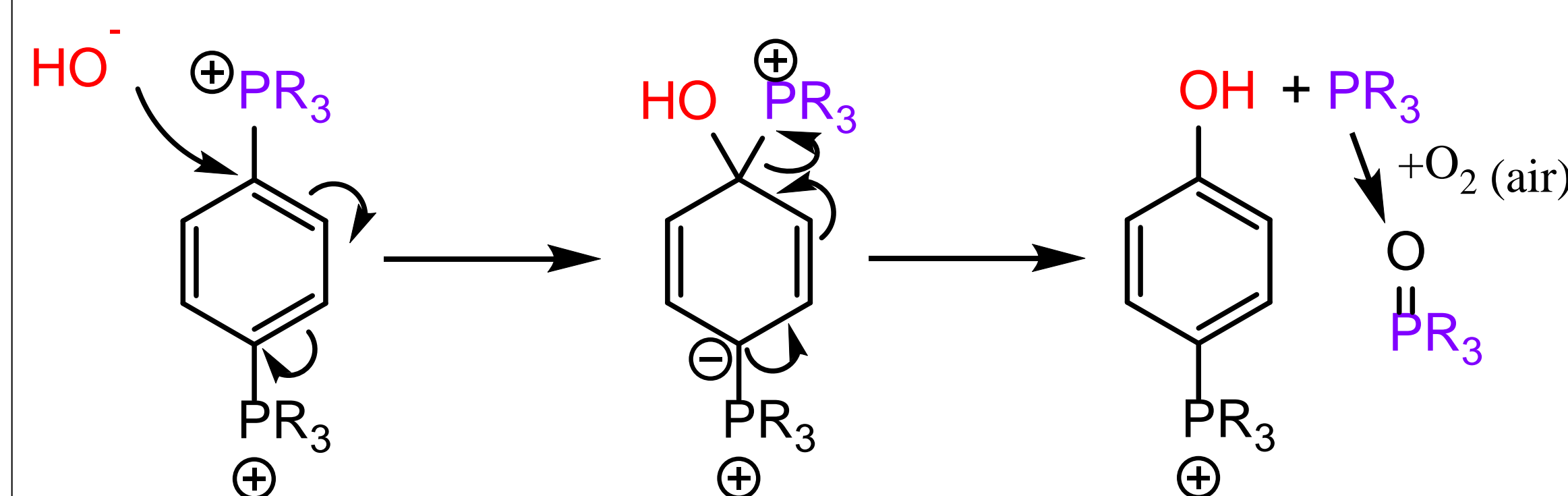


Figure 7. Nucleophilic aromatic substitution

## VI. Conclusions

The various phosphonium electrolytes tested all exhibited signs of degradation upon exposure to alkaline conditions. The benzyl phosphonium polymers underwent deprotonation to form phosphonium ylides when subjected to a non-nucleophilic strong base. The polymers FLone, FLoct, PhOx, and PCKFLoct all decomposed when heated with the nucleophilic base NaOH. FLone, FLoct, and PhOx appear to have decomposed via the nucleophilic aromatic substitution pathway while PCKFLoct appears to have decomposed via nucleophilic substitution. Incorporating functional groups that make the polymers less susceptible to the three different decomposition pathways possible in alkaline environments would improve the stability of the phosphonium polymers.

## VII. Acknowledgements and References

### Research Team



**Caitlin E. Keen**  
 Caitlin Keen is a junior chemistry major at Clemson University. She has been working with the Smith group for two years.

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### References

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