

Classroom



In this section of *Resonance*, we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. "Classroom" is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

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An Appreciation of Free Radical Chemistry 6. Experiments Involving Free Radicals

Part 1. Introduction, *Resonance*, Vol.10, No.2, pp.72-78, 2005.
Part 2. Free Radical Reactions in Industry, *Resonance*, Vol.10, No.3, pp.71-79, 2005.
Part 3. Free Radicals in Diseases and Health, *Resonance*, Vol.10, No.4, pp.65-74, 2005.
Part 4. Free Radicals in Atmospheric Chemistry, *Resonance*, Vol.10, No.7, pp.61-72, 2005.
Part 5. Free Radicals in Organic Synthesis, *Resonance*, Vol.10, No.8, pp.80-90, 2005.

Keywords

Allylic bromination, Sandmeyer reaction, phenolic/coupling benzopinacol, NBS, FeCl₃ and CuCl in radical reactions.

In the previous five parts, we have seen how the ubiquitous free radicals touch our lives in many ways. In this part, four experiments involving free radical intermediates are described. They are very simple, economical and practical, and can be easily carried out in laboratories with meagre resources. They can, therefore, be adapted for MSc chemistry practicals as part of free radical chemistry course.

Experiment 1. Free Radical Substitution

Allylic bromination using NBS – Bromination of Cyclohexene to 3-Bromocyclohexene

Place 7.98 g (0.04 mol) of N-bromosuccinimide, 9.84 g (0.12 mol) of cyclohexene, and 30 ml of carbon tetrachloride in a 100 ml round-bottomed flask. Add about 100 mg of benzoyl peroxide. Connect the flask to a water-cooled condenser. Within a few minutes, the reaction commences and the flask becomes warm. When the reaction has slightly subsided, reflux the mixture on a water-bath for about one hour. During the reaction, the heavy,



yellowish NBS is converted to lighter, colourless succinimide suspension. Cool the flask, filter the reaction mixture with suction, and wash the solid with 2-3 ml of carbon tetrachloride. Distil off the solvent (b.p. 77 °C) and the unreacted cyclohexene (b.p. 83 °C) on a water-bath carefully. Distil the residue under water-pump vacuum. Collect the early fraction containing the remaining solvent and cyclohexene separately and then 3-bromocyclohexene boiling at 66-67 °C / 20 torr.

Experiment 2. Oxidative Free Radical Coupling of 2-naphthol
Metal Salt for Radical Generation by Electron Acceptance – Preparation of bis-2-naphthol (binaphthol)

Method A: Place 1.44 g (0.01 mol) of 2-naphthol (m.p. 123 °C) and 60 ml of water in a 250 ml two-necked round-bottomed flask connected to a reflux condenser and a dropping funnel. Heat the contents to boiling with fast stirring (magnetic stirrer) and add a solution of 2.8 g (0.01 mol) of crystallised FeCl₃ in about 10 ml of water. The oily emulsion of 2-naphthol disappears and bis-2-naphthol flakes form. Boil for 5-10 minutes more and filter quickly through a warm Buchner funnel. Wash the solid with 20 ml of boiling water and dry in the air. Recrystallise from toluene, to get about 0.8-0.9 g of pure product, m.p. 218 °C.

Method B: Grind a mixture of 2.88 g (0.02 mol) of 2-naphthol and 7.0 g (0.025 mol) with 1-2 drops of water in an agate (or porcelain) mortar and pestle for about 20 minutes. Allow the mixture to stand for about 2 hours with a little grinding now and then. Wash the mixture with 40 ml of water into a 100 ml beaker, boil for 10-15 minutes, filter, wash the solid with 10 ml of boiling water, dry, and recrystallise from toluene. Yield by this method can be greater than 90%.

Experiment 3. Light-induced Free Radical Coupling

Preparation of Benzopinacol from Benzophenone

Prepare a solution of 3.0 g (0.0165 mol) of benzophenone in 35 ml of 2-propanol in a 100 ml conical flask (pyrex glass). Add a



drop of acetic acid. Close the flask with a cork stopper and place the flask in direct sunlight. (The flask may be clamped to an iron stand). Benzopinacol begins to separate within a day. Expose the flask to sunlight till no more solid appears to separate out. (That may take 3-4 days). Cool the flask in ice water, filter the mixture under suction, wash the solid with 3-4 ml of ice-cold 2-propanol, and dry. The product, almost pure benzopinacol, is obtained in greater than 90% yield, m.p. 185-186 °C.

Experiment 4. Reductive Chlorination of Diazonium Chloride with Cuprous Chloride (Sandmeyer reaction)

Metal Salt for Radical Generation by Electron Donation

Preparation of p-Chlorotoluene

Cuprous chloride should be prepared freshly as follows. Dissolve 3.5 g (0.014 mol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.95 g (0.016 mol) of good quality NaCl in 13 ml of distilled water in a 100 ml conical flask with warming on a water bath. Add a solution of 0.95 g (0.005 mol) of $\text{Na}_2\text{S}_2\text{O}_5$ (sodium metabisulphite) in 10 ml of distilled water to the hot solution with shaking. Colourless CuCl precipitates. Cool the flask in ice water, decant the supernatant solution, and wash the precipitate by decantation with a dilute solution (~0.5% solution) of $\text{Na}_2\text{S}_2\text{O}_5$. Dissolve the moist precipitate in 6-7 ml of conc HCl, stopper and keep it aside in an ice-bath, while p-toluene diazonium chloride is prepared.

Prepare a solution of 8.5 ml of conc HCl in 8.5 ml of distilled water in a 100 ml conical flask. Dissolve 3.5 g (0.032 mol) of freshly distilled p-toluidine and cool the mixture in an ice-salt bath with shaking; p-toluidine hydrochloride precipitates. Add a solution of 2.4 g (0.035 mol) of NaNO_2 in 5 ml of water slowly (3-5 minutes) with stirring. (The temperature of the reaction mixture should be maintained at 0-5 °C, by adding a little ice, if necessary). p-Toluidine hydrochloride disappears as the highly soluble diazonium chloride is formed. Pour the cold solution carefully with stirring into cold CuCl solution prepared earlier. A thick solid separates. Allow the mixture to warm to room temperature with occasional shaking. The solid starts breaking

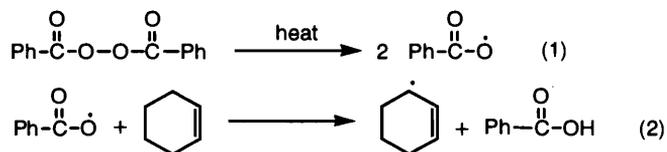


down at about 15 °C with the liberation of nitrogen and the formation of p-chlorotoluene as an oily product. Warm the mixture on a water bath at about 60 °C for 15-20 minutes and steam distil until the distillate is freed of oily drops. Collect p-chlorotoluene in the distillate by using a separating funnel. Wash it successively with 5 ml of 10% NaOH solution, 5 ml of water, 5 ml of a solution of 1:1 conc H₂SO₄: water and finally with 5 ml of water. Dry with a little MgSO₄ and distil the liquid at 158-162 °C to get 3.2 g (76%) of p-chlorotoluene.

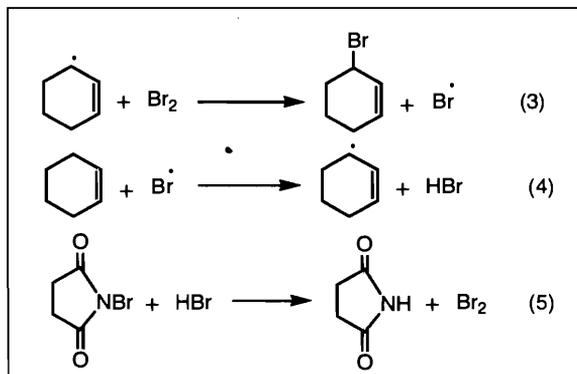
Discussion

Four experiments are described here. Each one of them is unique in the way the initial free radical reactant is formed from the starting compound.

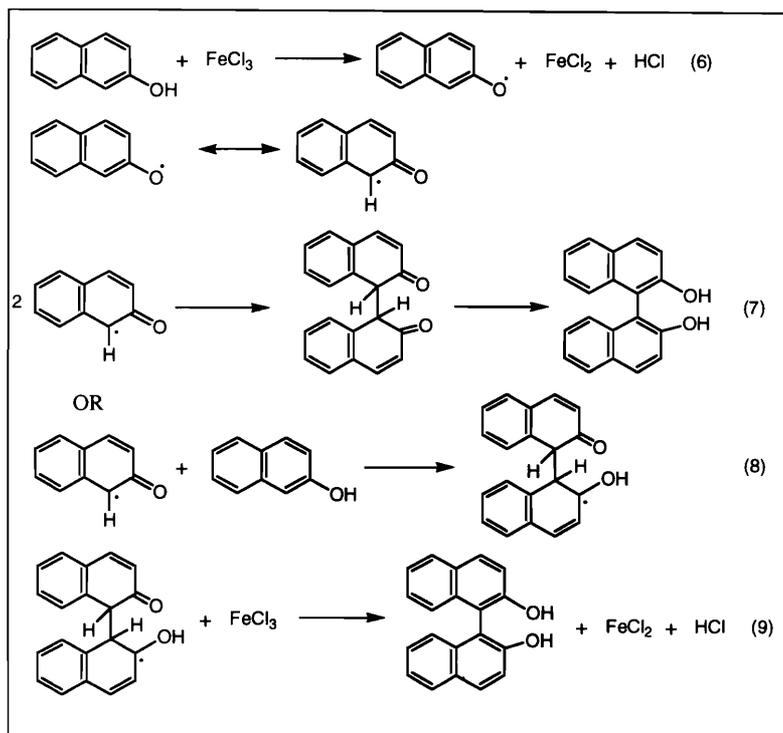
In the first experiment, a separate radical initiator, dibenzoyl peroxide is required. Broadly, the mechanism follows the following main steps 1-5.



The first two steps may be important only initially. Subsequently, cyclohexenyl radical is formed by the abstraction of hydrogen by bromine (eq. 4), *Scheme 1*.

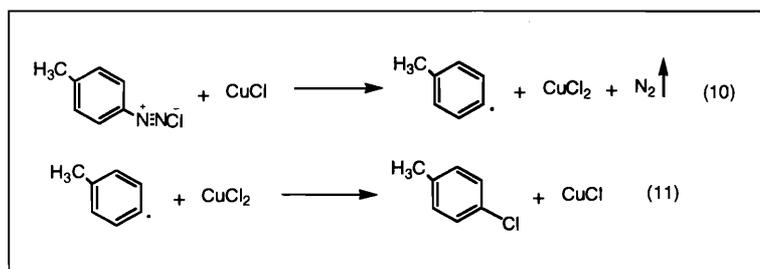


Scheme 1.

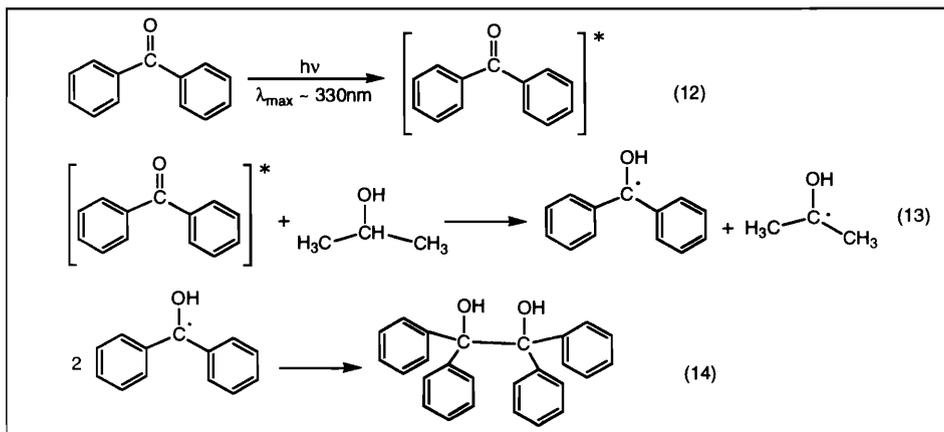


Scheme 2.

Experiments 2 and 4 make use of transition metal ions to initiate the reaction through the process of electron transfer. While Fe^{3+} in experiment 2 initiates the free radical process by removing an electron from the phenolic substrate (oxidation, eq 6-9, *Scheme 2*), Cu^+ in experiment 4 transfers an electron to the diazo group (reduction, eq 10-11, *Scheme 3*) to commence the course of the free radical reaction. The electron transfer in both cases takes place through the formation of intimate complexes of the metal ions with the substrates. Also note that *Method B* for binaphthol preparation is an example of Green Chemistry experiment.



Scheme 3.



Scheme 4.

Binaphthol exhibits atropisomerism as the rotation around the bond connecting the two naphthol rings is restricted. The product formed here is a racemic mixture. It can be resolved into pure enantiomers, which find application in enantioselective organic synthesis.

In experiment 3, benzophenone is excited by the UV radiation in sunlight (the λ_{\max} for $n\pi^*$ transition in benzophenone is ~ 330 nm). The excited benzophenone (a triplet) starts the radical process by abstracting a hydrogen atom from 2-propanol (eq 13, Scheme 4). Benzopinacol forms finally as depicted in Scheme 4.

Suggested Reading

- [1] B S Furmiss, A J Hannaford, P W G Smith and A R Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, Longman (ELBS), 1994.
- [2] C C Wamser and L T Scott, The NBS reaction, *J. Chem. Educ.*, Vol. 68, pp. 650-652, 1985.
- [3] J March, *Advanced Organic Chemistry*, Wiley, 4th Edition, 1992.
- [4] M B Smith and J March, *March's Advanced Organic Chemistry*, Wiley, 5th Edition, 2001.

Conclusion

The four experiments described are very simple to carry out, but they demonstrate various facets of free radical chemistry. They are also indicative of the profound and ubiquitous character of free radicals.

With this the six-part series, "An Appreciation of Free Radical Chemistry, ends. It is hoped that it has provided a glimpse of the importance of the all-pervading free radicals controlling virtually every facet of our lives. Unfortunately, our undergraduate syllabi give a very scanty picture of this topic. This needs to be changed, and due attention should be devoted to its teaching both UG and PG level.

