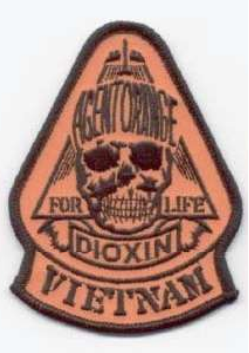
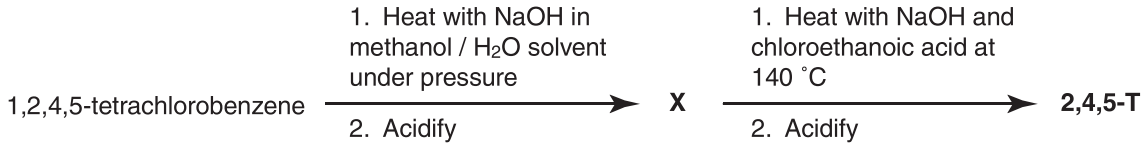
4. This question is about Agent Orange

Agent Orange was the name given to the powerful defoliant used during the Vietnam War. It consisted of a 1:1 mixture of two herbicides, '2,4-D' and '2,4,5-T'.



Shown below is a route for synthesising 2,4,5-T.



The proton NMR spectra for the starting material, 1,2,4,5-tetrachlorobenzene, the intermediate **X**, and 2,4,5-T are shown over the page.

After the first step in the synthesis, if the reaction mixture is acidified not with normal acid, H_3O^+, but with deuterated acid, D_3O^+, then the signal at 5.8 ppm in the ^1H NMR spectrum of **X** disappears. [Deuterium, D, is the ^2H isotope of hydrogen.]

(a) Draw the structure of 1,2,4,5-tetrachlorobenzene**.**

(b) Suggest a structure for the intermediate **X**.

(c) Give the systematic name for intermediate **X**.

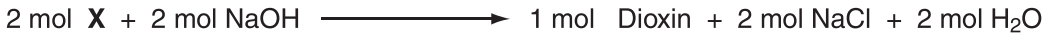
(d) Draw the structure for **X** if the reaction mixture had been acidified with D_3O^+ instead of H_3O^+.

(e) Draw the structure of chloroethanoic acid.

(f) Suggest a structure for 2,4,5-T.

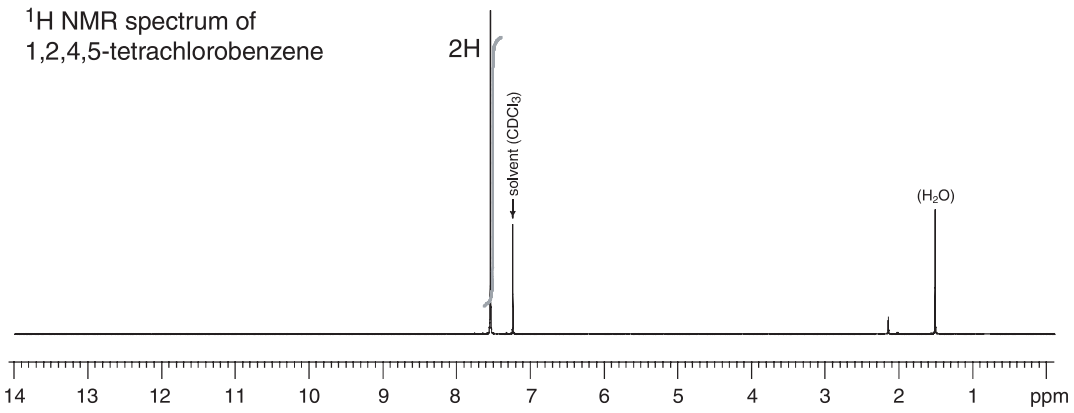
(g) On your structure, indicate as far as you are able which hydrogens correspond to which signals (**A**, **B**, **C** or **D**) in the ^1H NMR spectrum of 2,4,5-T.

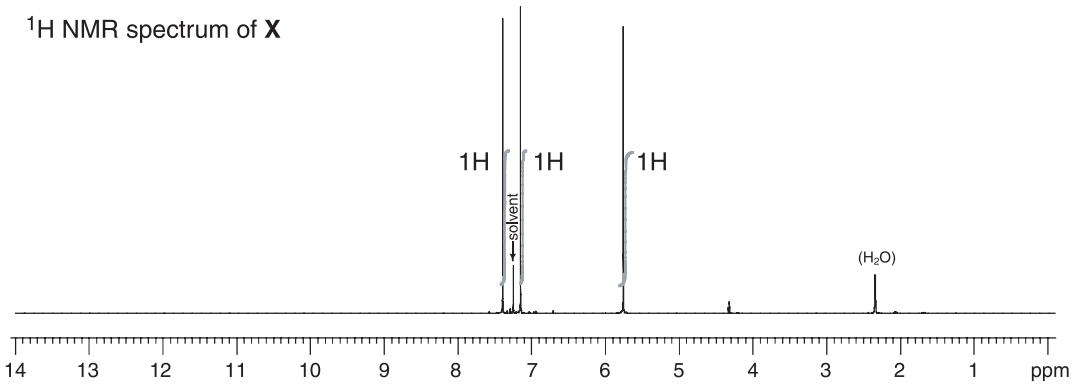
Whilst 2,4,5-T is a highly effective herbicide, its commercial use has been discontinued due to the presence of an incredibly toxic impurity called Dioxin which may be formed from intermediate **X** during the synthesis of 2,4,5-T.

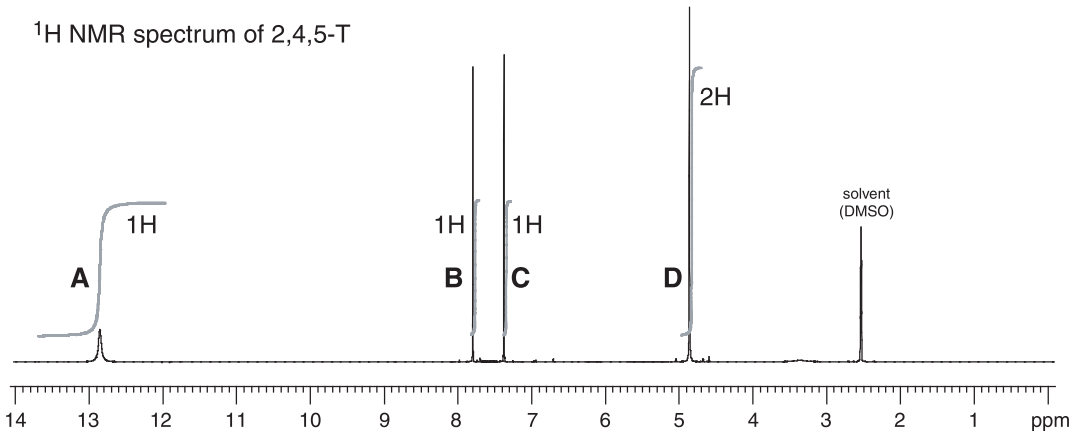


The ^1H NMR spectrum of Dioxin shows just a single peak at 7.2 ppm.

(h) Suggest a structure for Dioxin.







[The faint lines are the integrals used in working out the relative numbers of hydrogens.]