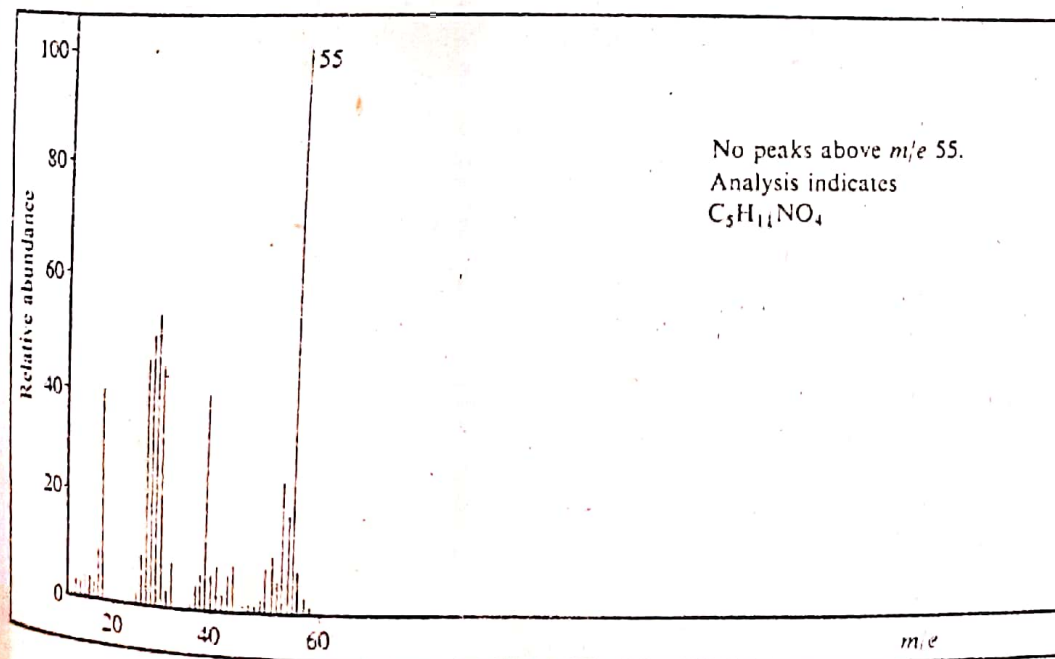
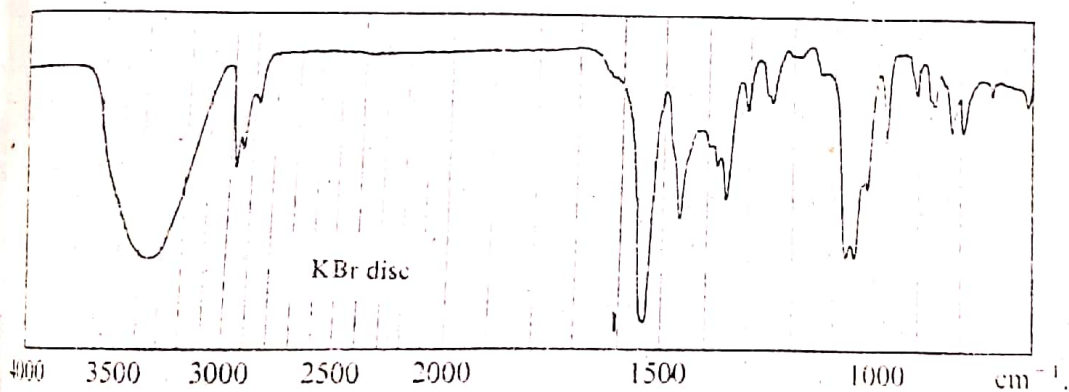
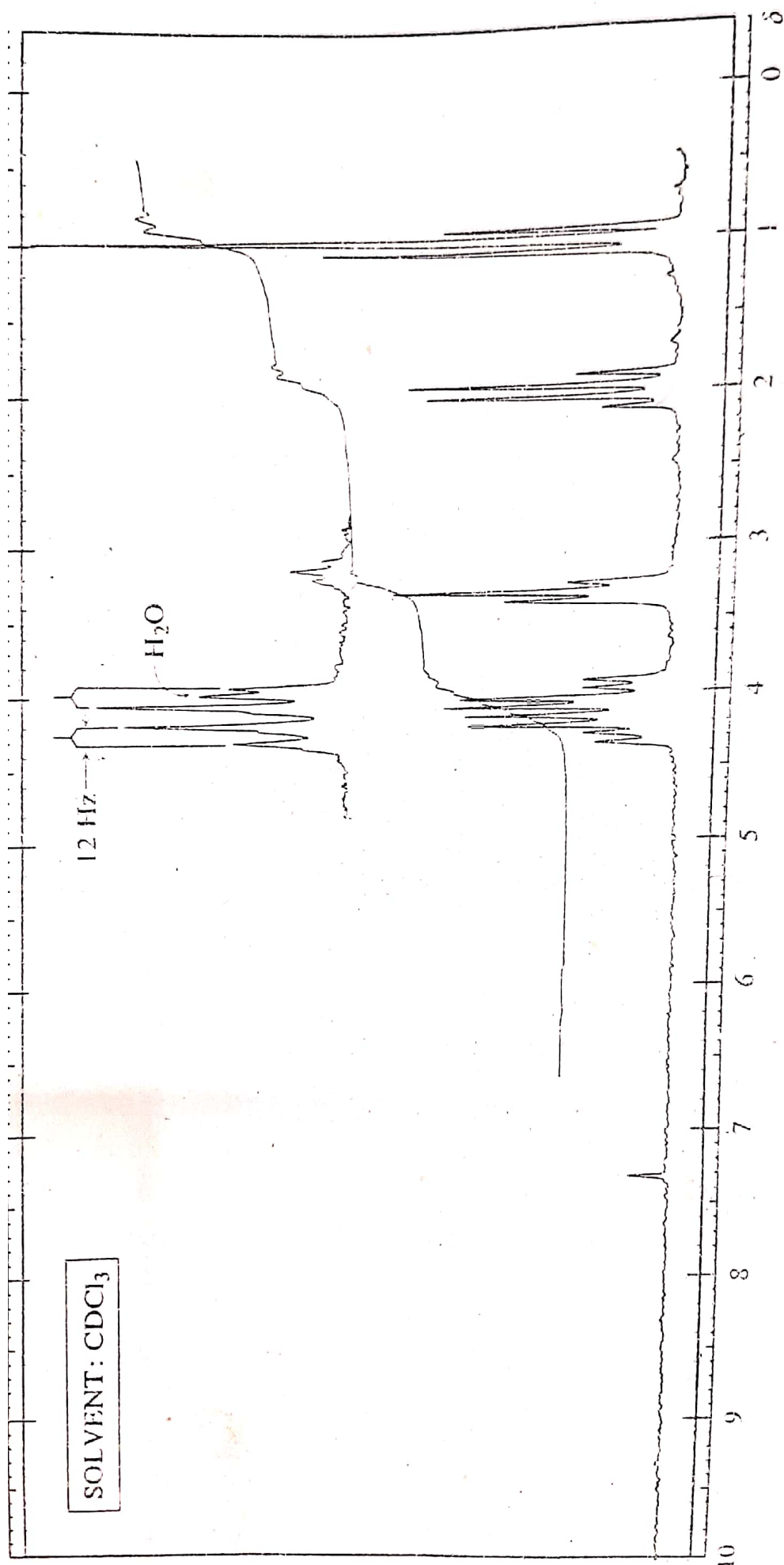


Example 2



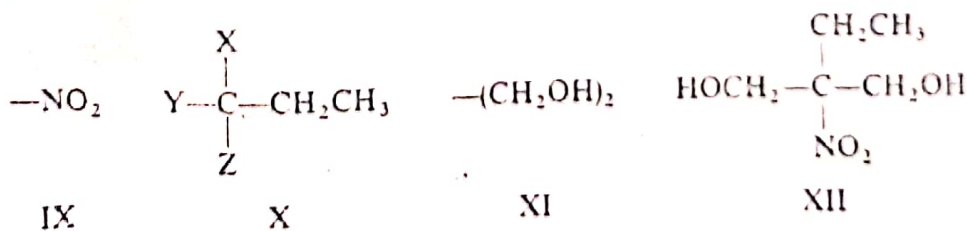


at lower temperatures. The metastable peak at m/e 45.5 in the mass spectrum corresponds to the transition m/e 93 \rightarrow m/e 65, which suggests the elimination of carbon monoxide from b to give $C_5H_5^+$.

Example 2

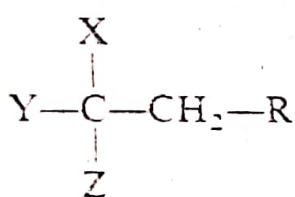
The molecular formula of this compound, $C_5H_{11}NO_4$, corresponds to one double bond equivalent. In this case the IR spectrum shows a very strong band at 1545 cm.^{-1} due, very likely, to a nitro group. Such a formulation is supported, in the first place, by the UV spectrum where a very weak band (ϵ is calculated to be 24) is due to an $n \rightarrow \pi^*$ transition (a ketone cannot be present since no band is evident in the $1800\text{--}1600\text{ cm.}^{-1}$ region) and, secondly, by the mass spectrum, since a parent ion is usually absent with aliphatic nitro compounds. The nitro group therefore accounts for all the unsaturation of the molecule. The IR spectrum also shows the unmistakable presence of a hydroxyl group.

The NMR spectrum strongly suggests the presence of an ethyl group, which must be attached to a fully substituted carbon atom (1:2:1 triplet at $\delta = 1.00$ ppm and 1:3:3:1 quartet at $\delta = 2.00$ ppm). The remaining six protons in the molecule resonate as a two-proton triplet at 3.32 ppm and as a four-proton eight-line pattern centred at 4.12 ppm (see integral trace). When the deuteriochloroform solution of the compound is shaken with a few drops of deuterium oxide, the two-proton signal disappears almost completely (see superimposed trace). The compound must therefore contain two OH groups. The small portion of the signal remaining after shaking with deuterium oxide, due to unexchanged OH groups, occurs with a slightly different chemical shift, as might be expected for an OH resonance. Since the hydroxyl groups' protons resonate as a triplet, both alcohol groups must be primary. The units (IX–XI) which have been deduced can be fitted together in only one way to give the structure XII.

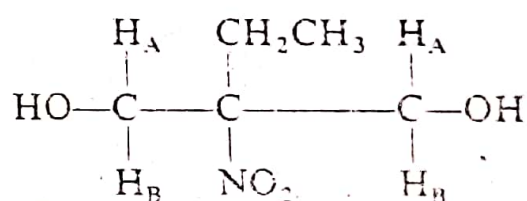


A remarkable feature of the NMR spectrum is that after the addition of deuterium oxide, the methylene protons which are adjacent to oxygen resonate as an AB quartet ($\delta_A = 4.00$,

$\delta_B = 4.24$ ppm, $J_{AB} = 12$ Hz). The two protons of a methylene group adjacent to an asymmetrically substituted carbon atom (XIII) may thereby be magnetically non-equivalent, and spin-spin coupling may therefore be observed between them. This phenomenon is, moreover, not restricted to an asymmetric carbon atom, but may be shown by methylene protons adjacent to any dissymmetric moiety. Hence, the H_A and H_B protons of XIV are magnetically non-equivalent, because either of the $-\text{CH}_2\text{OH}$ groups 'sees' three *different* groups attached to the central carbon atom. In XIV, the methylene protons of the ethyl group are equivalent.



XIII



XIV

Additional multiplicity of the H_A and H_B resonances is observed before the deuteration experiment, because both H_A and H_B are coupled to the hydroxyl proton ($J = 6$ Hz). It should be remembered that the observation of coupling, in deuteriochloroform or carbon tetrachloride solution, between the protons of a $\text{CH}-\text{OH}$ group is the exception rather than the rule (see, for example, Fig. 2-4). The resonance at $\delta = 3.99$ ppm, which appears in the superimposed trace, is due to traces of water present in the deuterium oxide. The peak at m/e 55 in the mass spectrum is due to C_4H_7^+ .

Example 3