

T.D.C. Part II ; Chem (Hons) Paper IV
Unit I Specification of configuration

Configuration of geometrical isomers and enantiomers can easily be specified by Cahn-Ingold-Prelog system. In this system the groups and atoms attached to the double bonded atoms and to a chiral atom are assigned priority following certain rules as given below.

The Cahn-Ingold-Prelog system: \rightarrow

1. Substituents are listed in order of decreasing atomic number of the atom directly attached to the carbon.

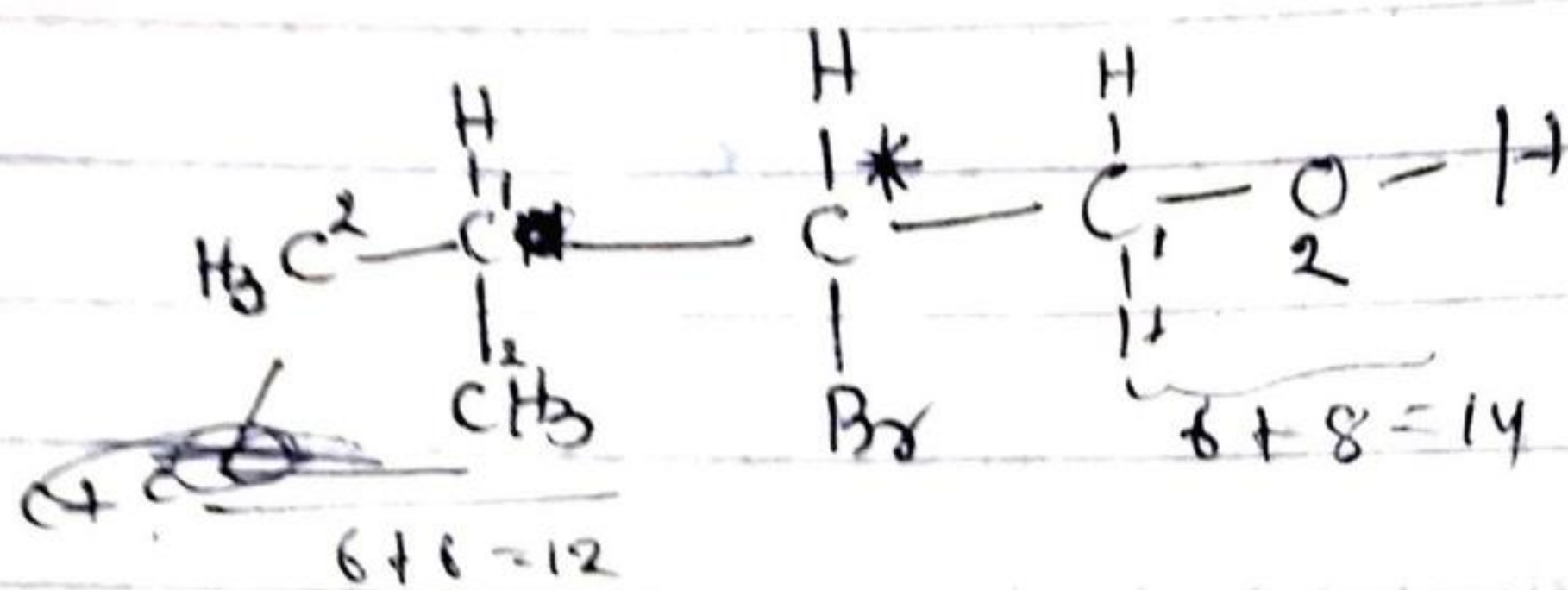
or

Higher the atomic no. of the atom attached to the involved atom higher is its priority, eg. N has priority over C, O over N, X over C, I over Br. etc.
($X = F, Cl, Br, I$)

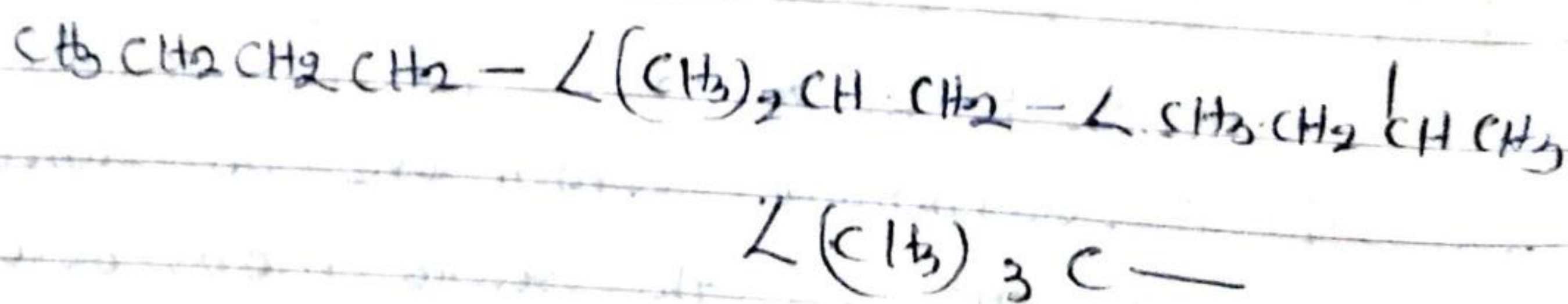
2. For isotopes, the atom with higher mass has the priority, eg. C^{14} over C^{12} , H^3 over H^2 , H^2 over H^1 . etc.

3. Where two or more of the atoms connected to the asymmetric carbon are the same, the atomic no. of the second atom determine the order. For example, in the molecule $Me_2CH-CHBr-CH_2OH$, the CH_2OH group takes the precedence over the Me_2CH group.

because oxygen has a higher atomic number than carbon. Note that this is so even though there are two carbons in CH_2CH and only one oxygen in CHO . If the two or more atoms are connected to the second atom are the same, the third atom determines the precedence, etc.



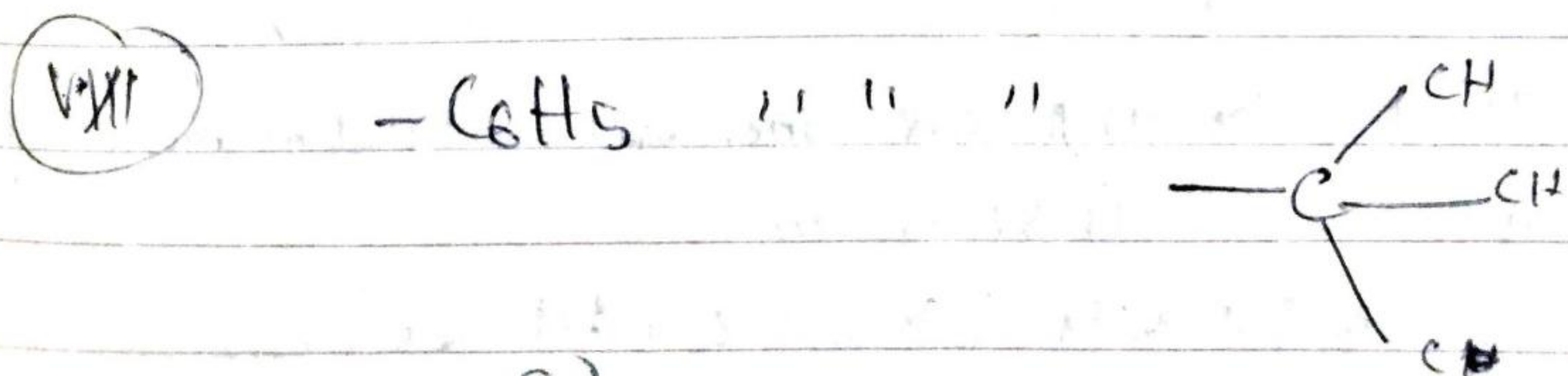
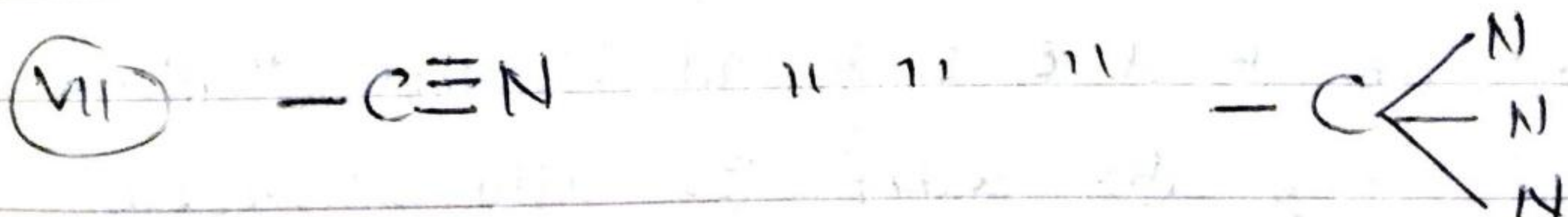
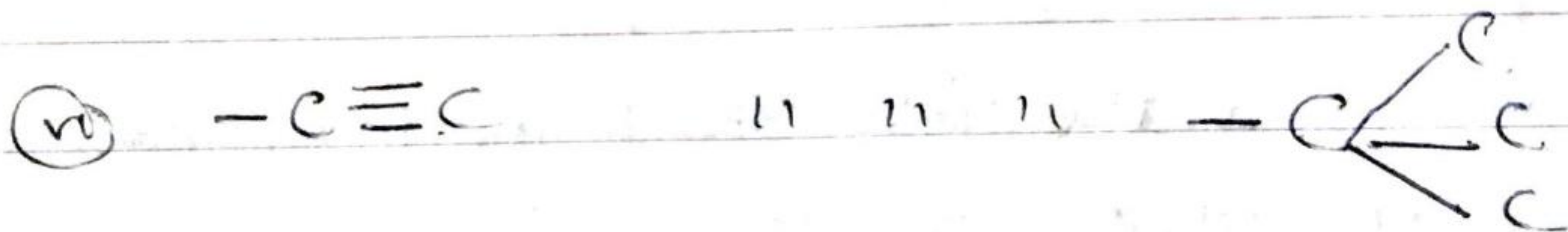
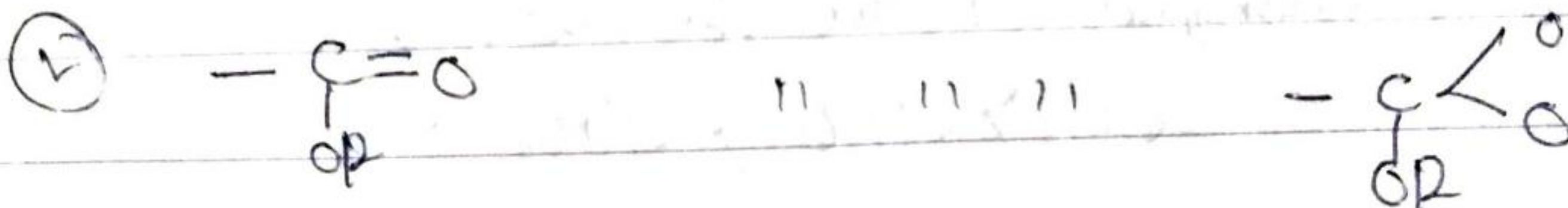
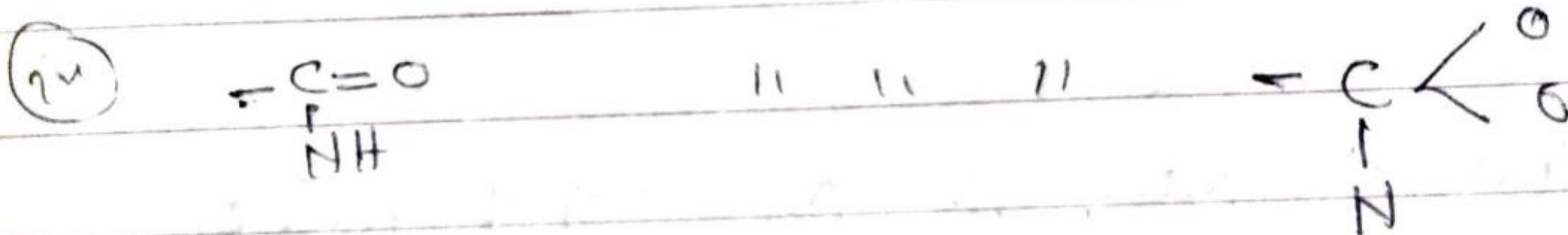
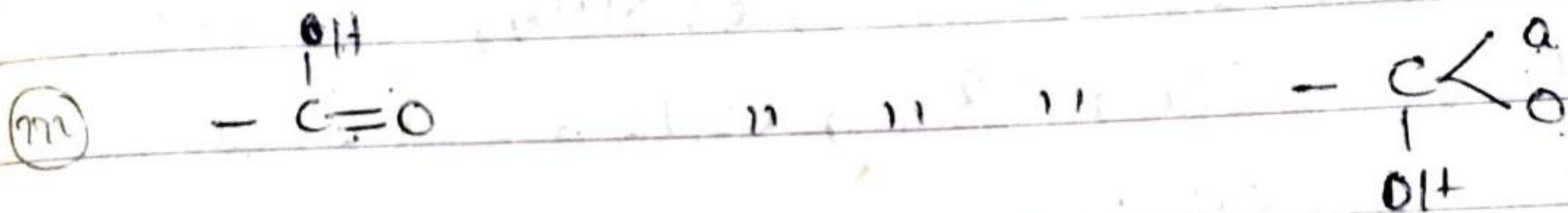
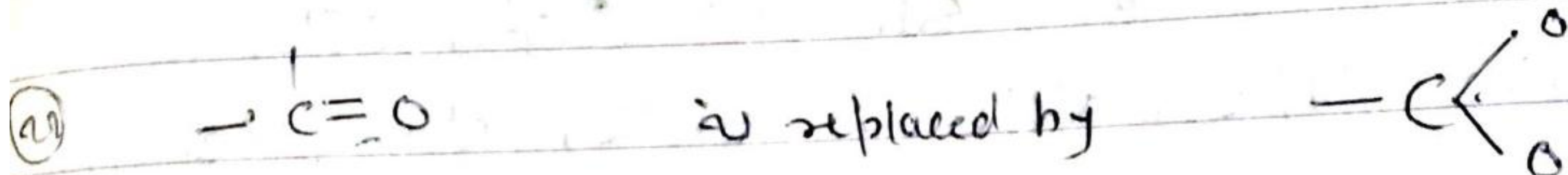
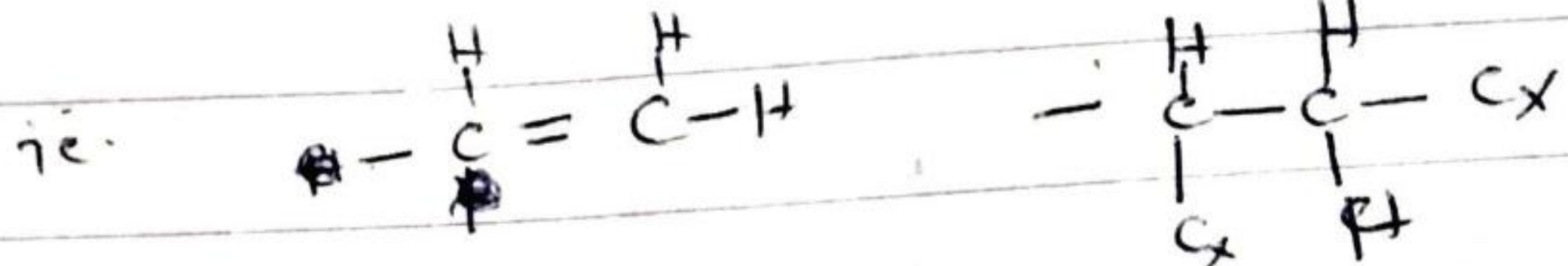
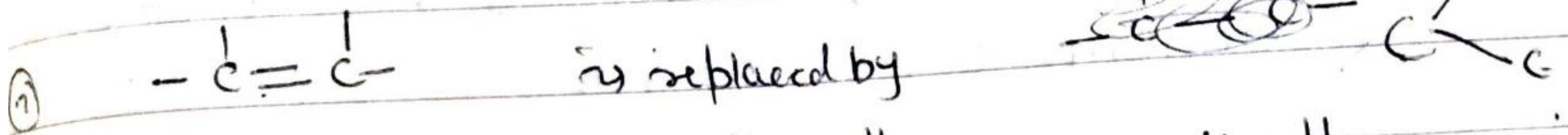
If the first bonded atom is identical in at least two groups, the priority is determined by the next atom or atoms present in those groups. e.g., ethyl group has priority over methyl group. as the next atom in methyl is an H, but that in ethyl is a C-atom. The increasing priority order amongst different alkyl group is



④ Double and triple bonds are counted as if they were split into two or three single bonds respectively, as in these examples.

Group

Treated as if it were



By application of the above criteria, groups in descending order of precedence are: COOH , COF_3 , COBr_2 , COCl_2 , CHO , CH(OH)_2 , C-alkyl , m-alkyl , p-alkyl , phenyl , $\text{C}\equiv\text{CH}$, t-butyl , cyclopropyl , vinyl , isopropyl , benzyl , neopentyl , allyl , n-butyl , ethyl , methyl , deuterium , and hydrogen .

or,

I , Br , Cl , SO_3H , SH , F , COR , OR , OH , NO_2 , NR_2 , NHCOR , NHR , NH_2 , Cl_3 , COCl , CO_2R , COOH , CONH_2 , CR , CHO , CH_2OH , CN , CR_3 , C_6H_5 , CHR_2 , Cl_2R , CH_3 , D , H .

Thus the four groups of glyceraldehyde are arranged in the sequence —

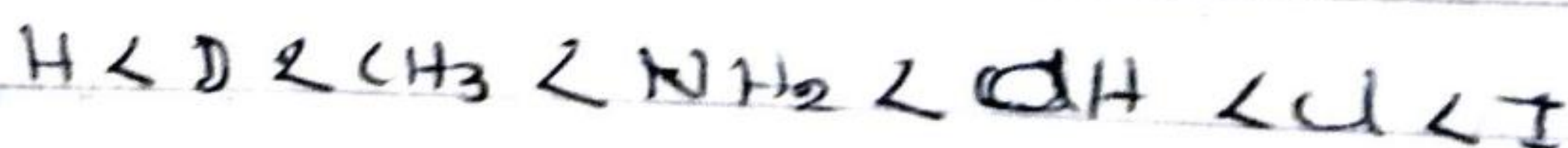


Q2 Write down the following groups in an increasing priority order.

- (1) (a) CH_3 (b) Cl (c) I (d) OH (e) NH_3 (f) D (g) H
 (2) (a) $-\text{CH}=\text{CH}_2$ (b) $-\text{CHF}_2$ (c) $-\text{CHO}$ (d) $-\text{COCH}_3$

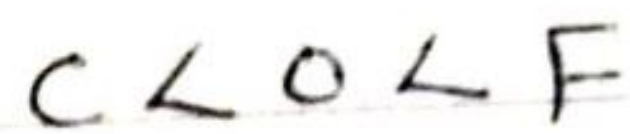
Ans

(a) As the priority grs. increase with the increasing mass of the first atom

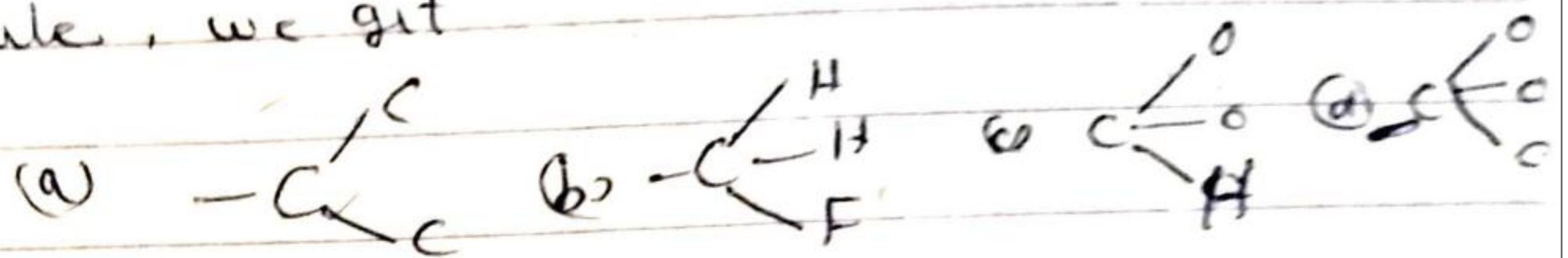


(b) In each of the cases, the first bonded atom is a C. Hence in determining priority order

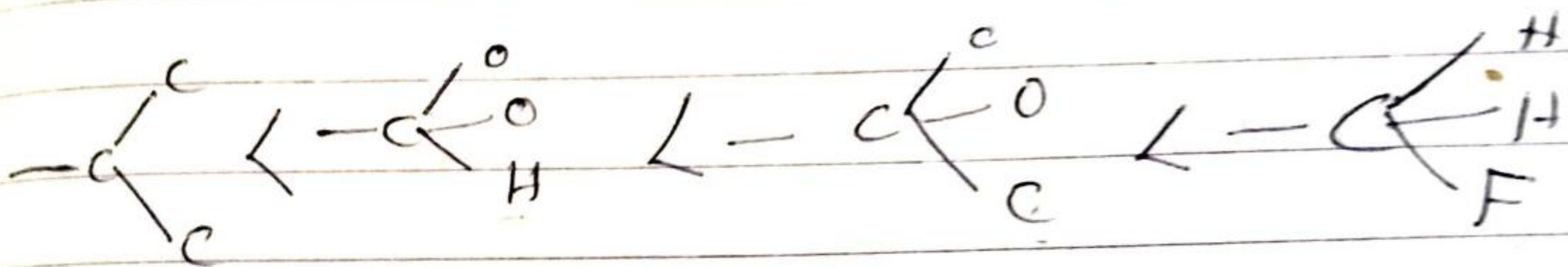
we need consider the second atom and even the third atom. The increasing priority order of the second atoms in these groups is



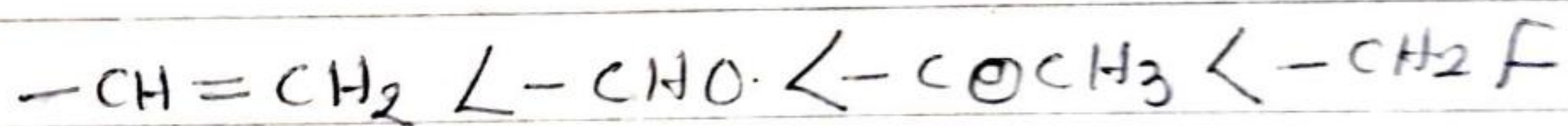
if we now rewrite the grps according to the rule, we get



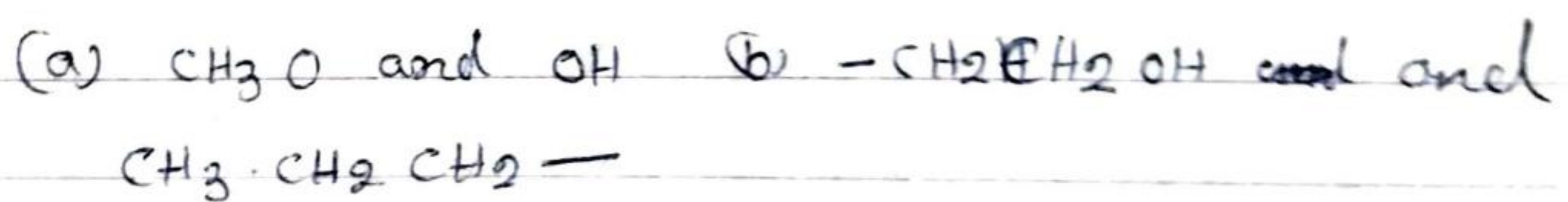
We see that the increasing priority order is



Hence the increasing priority order of the given groups is



Que Find out the higher priority group from each of the given pairs:



Ans

(a) $\text{CH}_3\text{O}-$ has higher priority over $-\text{OH}$ as C has higher priority over H .

(b) $-\text{CH}_2\text{CH}_2\text{OH}$ has priority over $-\text{CH}_2\text{CH}_2\text{CH}_3$ as O has higher priority over C .