Chem Factsheet

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Electrophilic Addition To Alkenes

Alkenes are **unsaturated hydrocarbons** which characteristically contain a carbon-carbon double bond (C=C) which consists of a stronger (sigma) bond and a weaker (pi) bond. The typical reactions of alkenes are **addition reactions** which involve the "opening" of the weaker bond and the bonding of the reactant (represented by X-Y in fig. 1) partially (X) to the first C atom of the C=C group and partially (Y) to the second C atom to form a single saturated carbon chain.

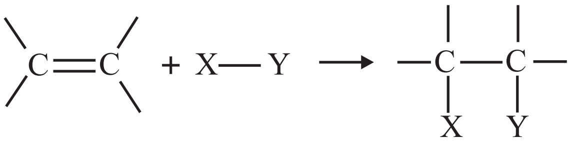


Figure 1

The C=C double bond is a region of high electron density. Consequently it tends to react with **electrophiles** [reactants which can accept a pair of electrons (here, from the weaker pi bond in the C=C bond) to form a new covalent bond]. Hence, the typical reactions of alkenes are classified as **electrophilic addition** reactions.

In general, the electrophile is provided by the **more electron deficient (δ+)** part of X-Y. The examples most commonly experienced at A-level (check your specification for details) are summarised in table 1 with the consequent reactions shown in figure 2.

	Rectant (X-Y)	Electrophile ($X^{\delta+}$)	Polarity ($^{\delta+}X—Y^{\delta-}$)	Dipole Type
1	Br_2	Br^+	$^{\delta+}Br—Br^{\delta-}$	Induced
2	H_2	H^+	$^{\delta+}H—H^{\delta-}$	Induced
3	Hbr	H^+	$^{\delta+}H—Br^{\delta-}$	Permanent
4	HOBr	Br^+	$^{\delta+}Br—^{\delta-}OH$	Permanent
5	H_2SO_4	H^+	$^{\delta+}H—^{\delta-}OSO_2OH$	Permanent
	H_2O	H^+	$^{\delta+}H—^{\delta-}OH$	Permanent

Table 1

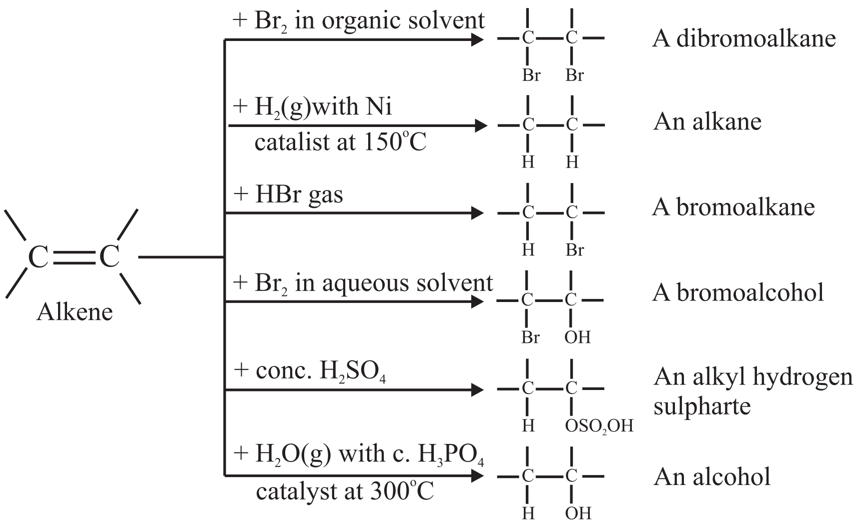


Figure 2

NOTE: The induced dipoles involved in cases 1 and 2 are produced during the reaction process (***see later***), especially on the surface of the catalyst in case 2.

Q1 Apply the reactions described above to deduce the equation for each of the following reactions. In each case, name the product.

(a) But-1-ene with bromine in hexane solution

(b) Propene with hydrogen using a nickel catalyst at 150°C

(c) But-2-ene with hydrogen bromide

(d) Ethene with hydrogen bromate(I) [HOBr]

(e) But-2-ene with concentrated sulphuric acid

(f) 2,3-dimethylbutane with steam using a concentrated phosphoric acid catalyst.

NOTE: The reactions considered in Q1 **ALL** involve **symmetrical** reactants (H_2, Br_2) and / or alkenes (ethene, but-2-ene, 2,3-dimethylbutane). This means the orientation of the addition of "X-Y" to the C=C bond does not need to be considered and a single product results. When **both** reactant and alkene are **non-symmetrical** (e.g. propene + HBr) different orientations of addition of "X-Y" occur, resulting in a mixture of two or more products. This, and the preference for one of products, will be considered later.

The mechanism of an electrophilic addition can be generalised using X-Y as the reactant. In order to describe any particular reaction mechanism, all you need to do is replace X-Y by an appropriate reactant in the generalised mechanism of figure 3.

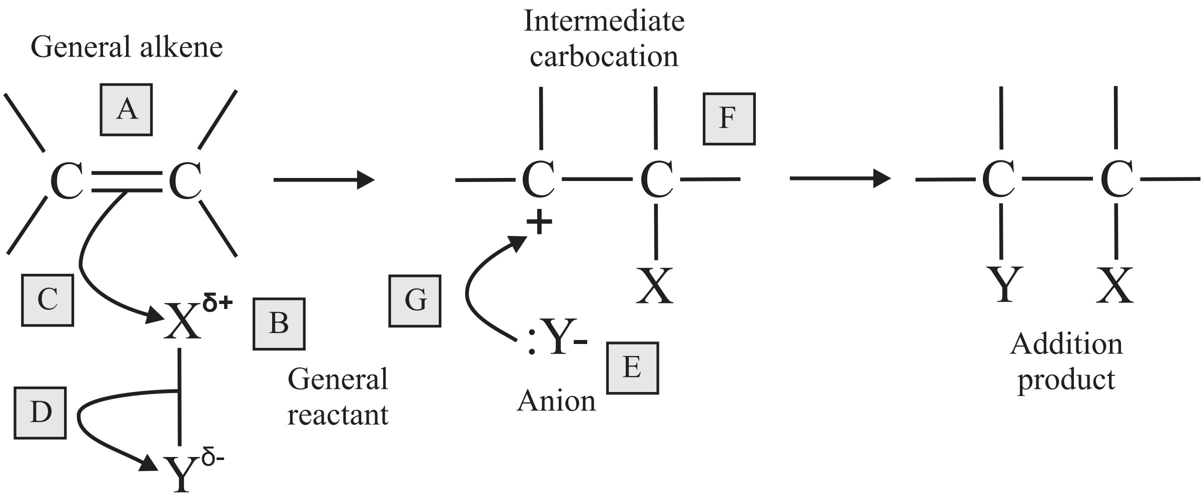


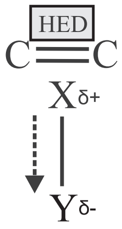
Figure 3

[A] Clearly **draw the structure of the alkene** involved in the question by adding appropriate groups to the four "free bonds" in the general alkene. e.g. 4H's for ethene, 3H's and a CH_3 for propene, 4 CH_3's for 2,3-dimethylbutane.

[B] **Draw the structure of the reactant (X-Y)** involved in the question with the dipole clearly shown. It is advised to draw X-Y at right-angles to the C=C bond to improve clarity, making sure that the more electropositive group ($X^{\delta+}$ – the source of the electrophile) is positioned nearer the C=C bond of the alkene.

Reactant	H_2	B_2	HBr	HOBr	H_2SO_4	H_2O
$X^{\delta+}$ $Y^{\delta-}$	$H^{\delta+}$ $H^{\delta-}$	$Br^{\delta+}$ $Br^{\delta-}$	$H^{\delta+}$ $Br^{\delta-}$	$H^{\delta+}$ $^{\delta-}$ OBr	$H^{\delta+}$ $^{\delta-}$ OSO_2OH	$X^{\delta+}$ $^{\delta-}$ OH

NOTE:



Make it clear that the dipole is **induced** in the cases of H_2 and Br_2. As these molecules approach (during collision with Br_2 or on the surface of the nickel catalyst for H_2) the high electron density of the C=C bond [HED] causes the electron density in the X-Y bond to be repelled ($\dashrightarrow$) away from X and towards Y, creating the induced dipole.

[C] The **electron pair from the weaker (pi) bond** of the C=C bond moves and is shown by a clear **curly arrow** starting on the C=C bond and ending near $X^{\delta+}$. Since the electrons are moving away from the C=C bond, one of the C atoms becomes positively charged in the **intermediate carbocation** (an ion with a positive charge on a carbon atom) [F]. Make sure this + charge is shown clearly. This electron movement also creates the C-X bond in the intermediate carbocation.

[D] Simultaneous with the electron movement described in [C], **the electron pair of the X-Y bond moves towards Y.** Again, show this by a clear curly arrow starting on the X-Y bond and ending near Y. This breaks the X-Y bond and releases Y in the form of an anion [E]. The negative charge and the lone pair of electrons (from the X-Y bond fission) must be shown clearly on $:Y^-$.

[E] As already discussed, **Y is temporarily released as an anion**, $:Y^-$.

[F] As already discussed, the **alkene is temporarily converted to a carbocation** with X covalently bonded to one of the C atoms of the original C=C bond and a + charge of the other.

[G] The mechanism is completed to form the final addition product by another curly arrow showing the **lone pair on $:Y^-$ [E] moving towards the C+** of the intermediate carbocation [F]. This **creates the new C-Y bond**.

NOTE: In order to gain maximum credit, take care with the layout of your mechanism and remember to show all the details mentioned above. Above all, avoid layouts that necessitate curly arrows that "twist and bend" all over the page!

Q2 Apply the general mechanism to give a mechanism for the addition of bromine to propene.

Q3 Apply the general mechanism to give a mechanism for the addition of concentrated sulphuric acid to but-2-ene.

As mentioned earlier, when **both reactant and alkene are non-symmetrical** different orientations of addition of "X-Y" occur, resulting in a mixture of two or more products. This is shown for propene reacting with HBr in figure 4.

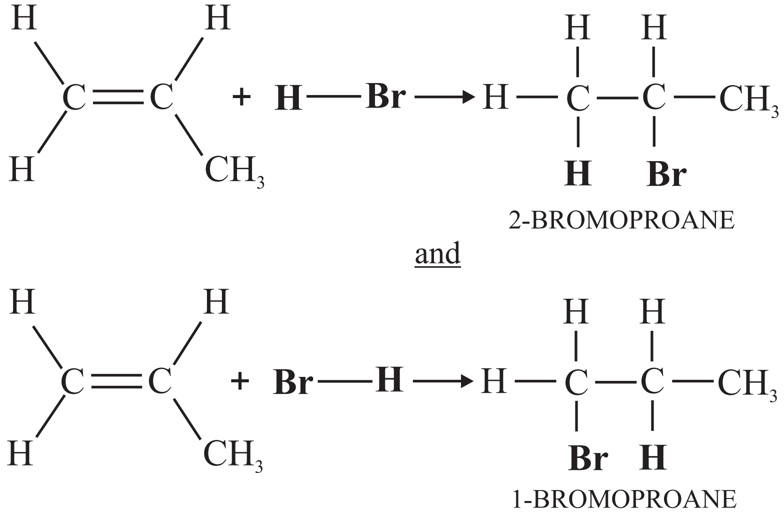


Figure 4

Experiment shows that **both** isomers of bromopropane are formed **but 2-bromopropane is predominant**. Why?

The preferred product is controlled by the **relative stabilities of the different possible carbocation intermediates**.

2-Bromopropane is formed via a **more stable secondary carbocation** whereas 1-bromopropane is formed via a **less stable primary carbocation**. The **more stable carbocation is more likely to form** during the initial bonding of the electrophile to the C=C bond, leading to a majority of 2-bromopropane.

> **NOTE:** Be careful NOT to say "the 2-bromopropane product is more stable than 1-bromopropane". It is the relative stabilities of the intermediate carbocations that control the orientation of addition!.

But what are the different types of carbocation and why do they have different stabilities?

There are 3 types of carbocation ; **primary, secondary and tertiary** as shown in figure 5.

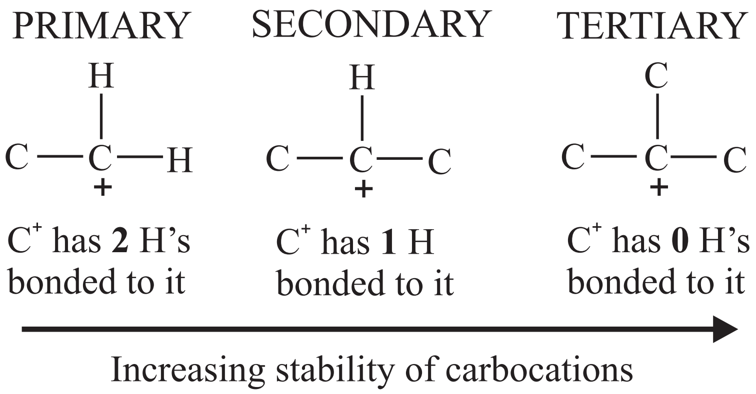
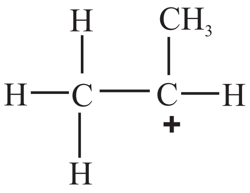
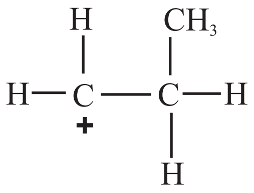
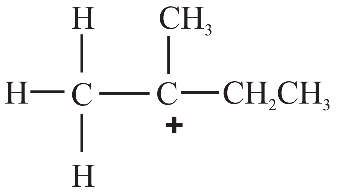


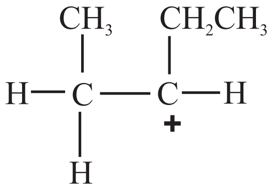
Figure 5

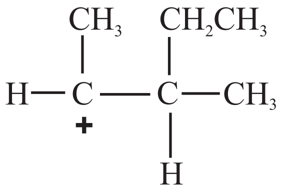
Q4 Classify each of the following carbocations as primary, secondary or tertiary.

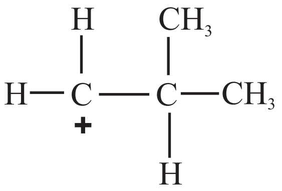
1.

$H-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{+}{C}}-H$

2.

$H-\overset{H}{\underset{+}{C}}-\overset{CH_3}{\underset{H}{C}}-H$

3.

$H-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{+}{C}}-CH_2CH_3$

4.

$H-\overset{CH_3}{\underset{H}{C}}-\overset{CH_2CH_3}{\underset{+}{C}}-H$

5.

$H-\overset{CH_3}{\underset{+}{C}}-\overset{CH_2CH_3}{\underset{H}{C}}-CH_3$

6.

$H-\overset{H}{\underset{+}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_3$

The different stabilities are accounted for in term of the **"inductive effects" of the C groups bonded to the C atom** with the + charge. This depends on the experimentally measurable tendency of **alkyl groups ("C group") to repel electron density**. This is illustrated in figure 6 where ⇢ represents this repulsion.

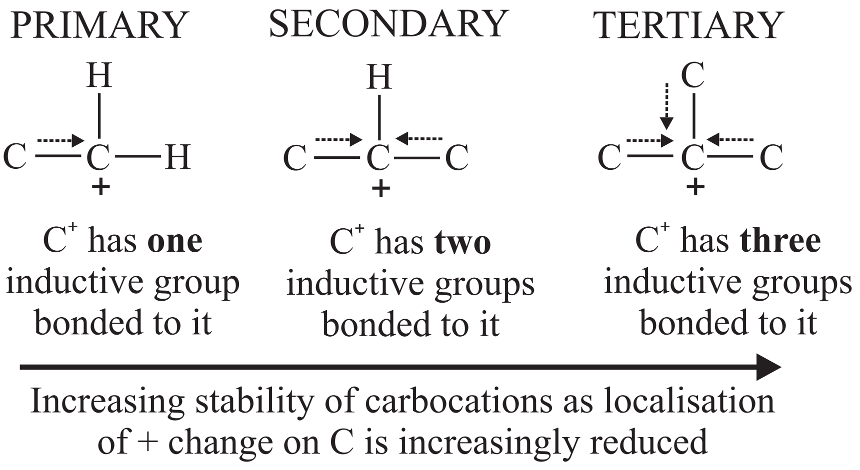


Figure 6

The more alkyl groups that are bonded to the C+ atom, the more the **+ charge is delocalised** by the electron density being pushed towards it. **More delocalisation is associated with increased stability**. Hence the order of increasing stability of carbocations is **primary < secondary < tertiary**.

Hence, returning to the example of propene reacting with HBr, the two possible routes are shown in figure 7.

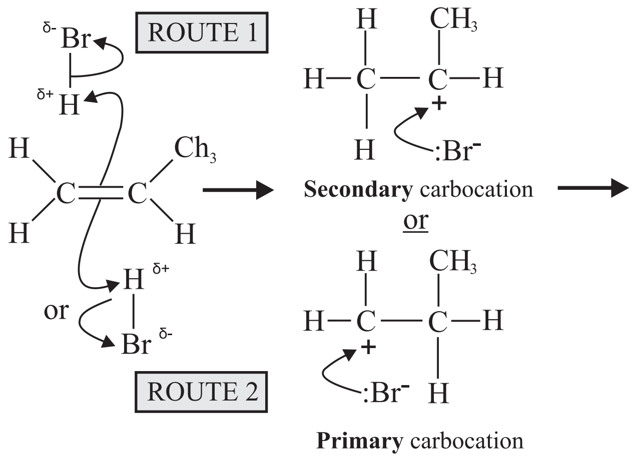


Figure 7

Route 1 involves a more stable secondary carbocation rather than the less stable primary carbocation of route 2. Hence, route 1 is preferred making 2-brompropane the preferred product.

Q5 Predict, where appropriate, the predominant addition product for each of the following reactions.

(a) 2-methylpropene + HBr

(b) Pent-2-ene + HBr

(c) 2-methyl-but-2-ene + HCl

ADDITIONAL NOTE FOR YEAR 2 A-LEVEL ONLY

It **is possible** to form mixtures of products when the reactant is symmetrical! This is because mixtures of **optical isomers** are possible.

For example, when symmetrical bromine adds to propene, the product (1,2-dibromopropane) can exist as **two non-superimposable mirror images.** This is because the molecule contains a chiral C atom (circled in figure 8) since it is bonded to 4 different groups.

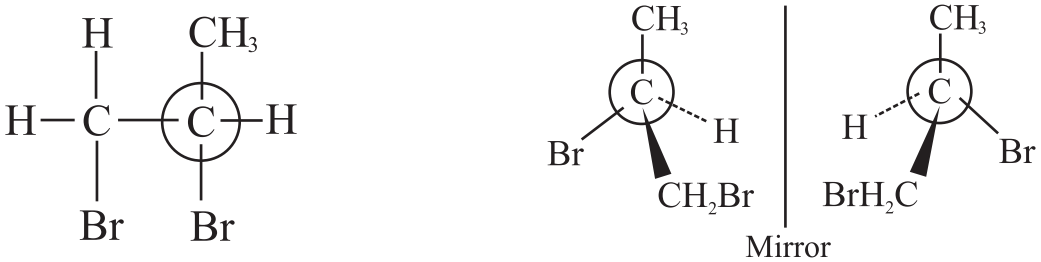


Figure 8

This occurs because the intermediate **carbocation is planar** (see figure 9), allowing the bromide ion to bond to it from above or below that plane.

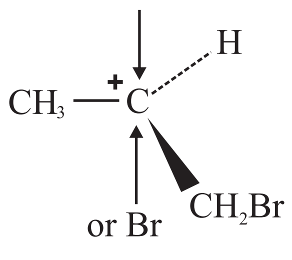


Figure 9

Furthermore, the product will be a 50:50 mixture of the 2 optical isomers since there is a 50:50 chance of the bromide ion bonding from above or below the plane. Hence, the reaction product is an **optically inactive racemic mixture**.

ANSWERS TO QUESTIONS

Q1 (a) $CH_3CH_2CH{=}CH_2 + Br_2 \rightarrow CH_3CH_2CHBrCH_2Br$; 1,2-dibromobutane

(b) $CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$; propane

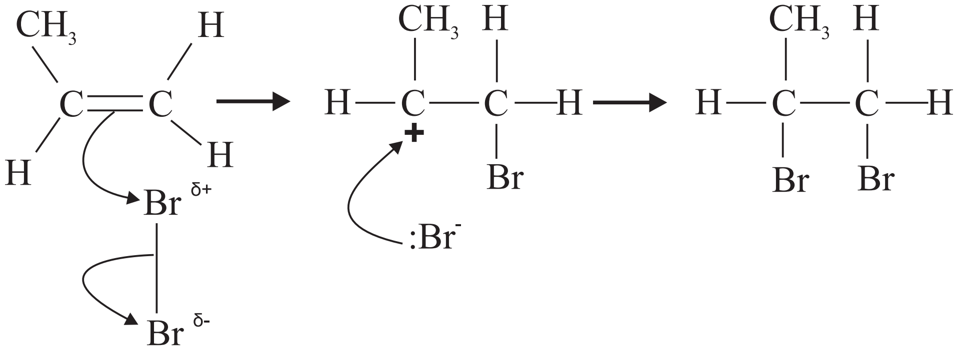
(c) $CH_3CH{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_2CH_3$; 2-bromobutane

(d) $CH_2{=}CH_2 + HOBr \rightarrow CH_2BrCH_2OH$; 2-bromoethanol

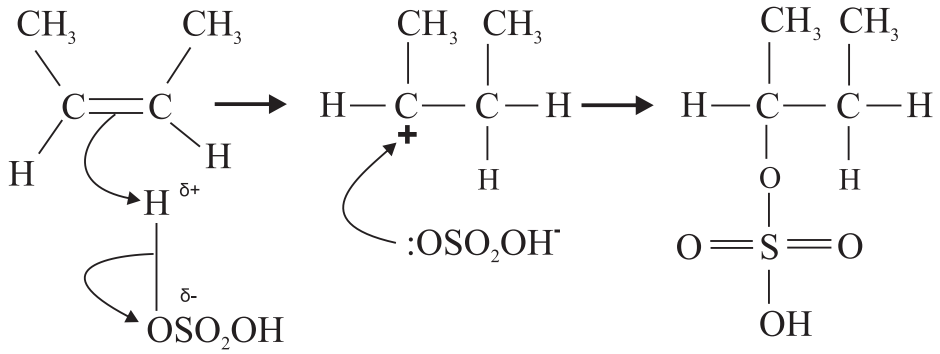
(e) $CH_3CH{=}CHCH_3 + H_2SO_4 \rightarrow CH_3CH(OSO_2OH)CH_2CH_3$; 2-butylhydrogensulphate

(f) $(CH_3)_2C{=}C(CH_3)_2 + H_2O \rightarrow (CH_3)_2CHC(OH)(CH_3)_2$; 2,3-dimethylbutan-2-ol.

Q2 For propene, insert CH_3, H, H and H on the free bonds of the general alkene.
For bromine, insert Br for X and Br for Y.
This gives



Q3 For but-2-ene, insert CH_3, CH_3, H and H on the free bonds of the general alkene.
For sulphuric acid, insert H for X and OSO_2OH for Y.
This gives



Q4 1. Secondary 2. Primary 3. Tertiary 4. Secondary 5. Secondary 6. Primary

Q5 (a) **2-Bromo-2-methylpropane** rather than 1-bromo-2-methylpropane because the $(CH_3)_3C^+$ carbocation is tertiary and more stable than the primary $^+CH_2CH(CH_3)CH_3$ carbocation. The preferred formation of the more stable $(CH_3)_3C^+$ carbocation leads to 2-bromo-2-methylpropane as the major product.

(b) **2-Bromopentane and 3-bromopentane will occur in about 50:50 proportions** because the possible intermediate carbocations are both secondary. i.e. $CH_3C^+HCH_2CH_2CH_3$ and $CH_3CH_2C^+HCH_2CH_3$. Thus, being equally stable, they are equally likely to form leading to a 50:50 mixture of the two products.

(c) **2-chloro-2-methylbutane** rather than 2-chloro-3-methylbutane because the $CH_3CH_2C^+(CH_3)_2$ carbocation is tertiary and more stable than the secondary $CH_3C^+HCH(CH_3)_2$ carbocation. The preferred formation of the more stable $CH_3CH_2C^+(CH_3)_2$ carbocation leads to 2-chloro-2-methylbutane as the major product.

Acknowledgements: *This Factsheet was researched and written by Mike Hughes.*
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