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# RADICALS AND THEIR REACTION PATHWAYS

Peter Sykes



CHEMISTRY CASSETTE

## CHEMISTRY CASSETTES

General Editor:  
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The University of Aston in Birmingham

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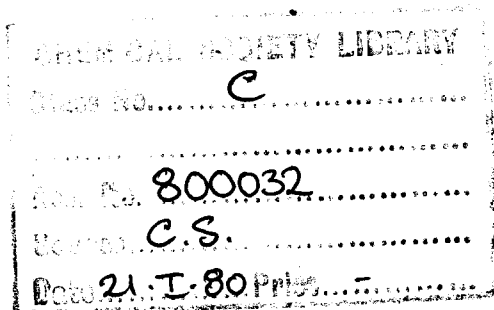
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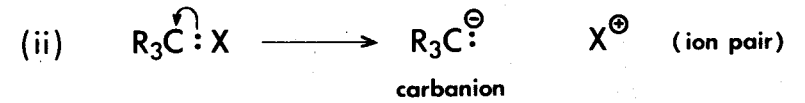
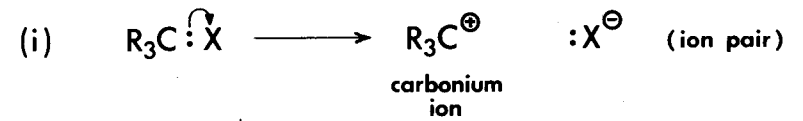
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# RADICALS AND THEIR REACTION PATHWAYS



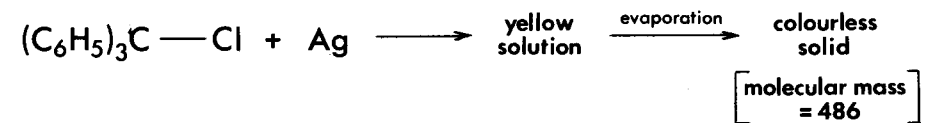
①

POLAR FISSION OF C:X BOND



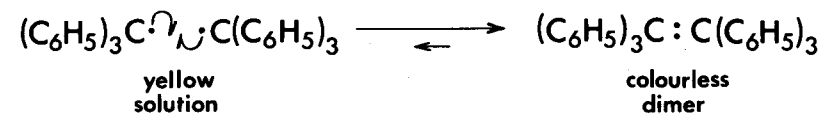
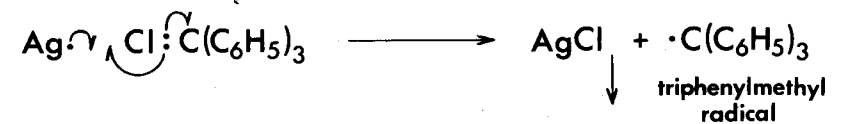
②

NON-POLAR(HOMOPOLAR) FISSION OF C:X BOND



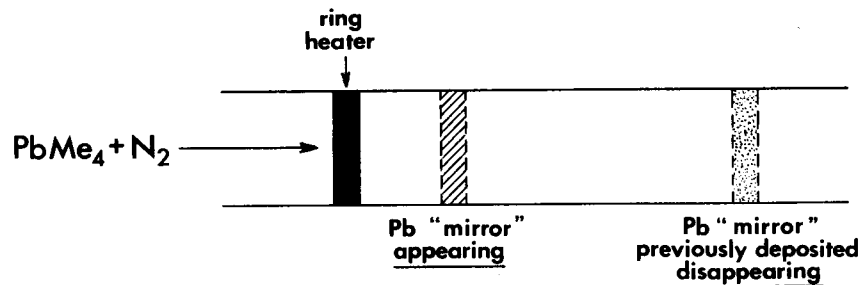
③

REACTION OF  $(\text{C}_6\text{H}_5)_3\text{C}-\text{Cl}$  WITH Ag

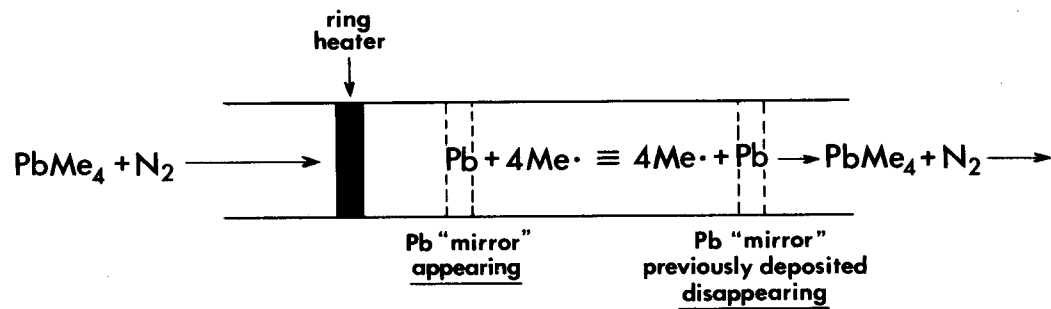


④

GOMBERG'S INTERPRETATION OF  $(\text{C}_6\text{H}_5)_3\text{C}-\text{Cl}/\text{Ag}$  REACTION



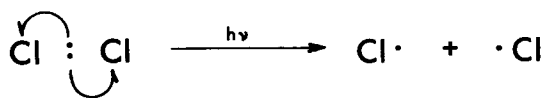
5 FORMATION AND DISAPPEARANCE OF Pb MIRRORS WITH HEATED PbMe<sub>4</sub>



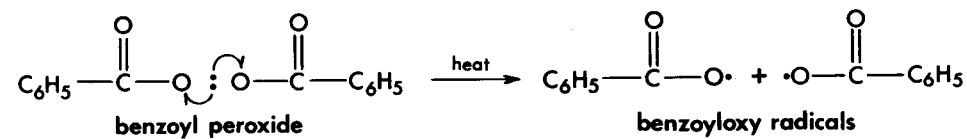
6 FORMATION OF Me· RADICALS AND THEIR REACTION WITH Pb



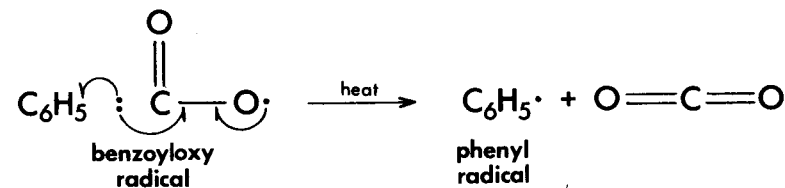
7 DIMERISATION OF 2CH<sub>3</sub>· → CH<sub>3</sub>:CH<sub>3</sub>



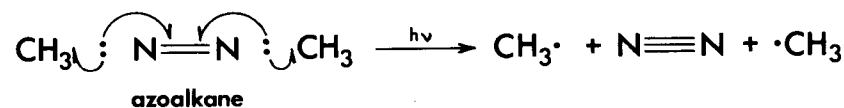
8 PHOTOLYSIS OF Cl : Cl



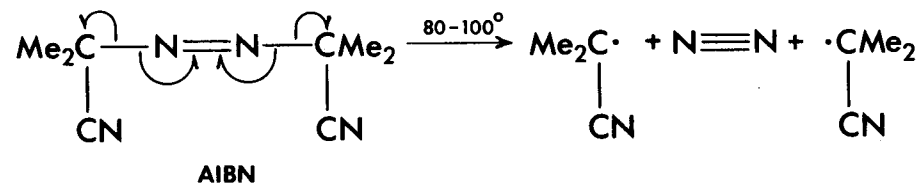
9 THERMAL FISSION (THERMOLYSIS) OF BENZOYL PEROXIDE



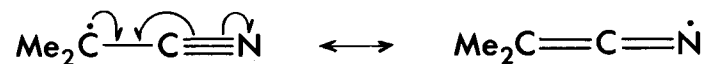
10 DECARBOXYLATION OF BENZOYLOXY RADICALS



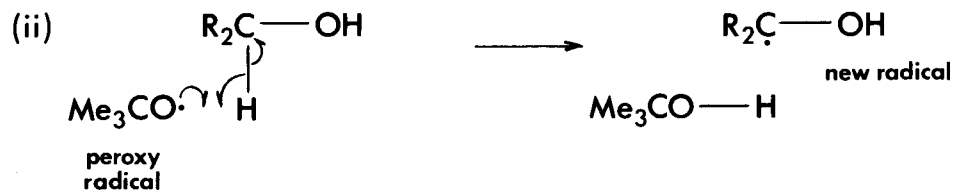
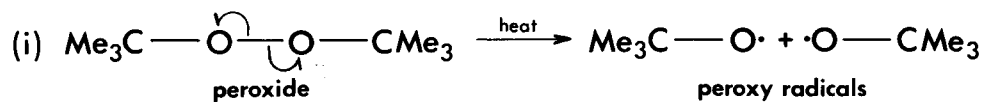
11 PHOTOLYSIS OF AN AZOALKANE



12 THERMOLYSIS OF AZISOBUTYRONITRILE (AIBN)



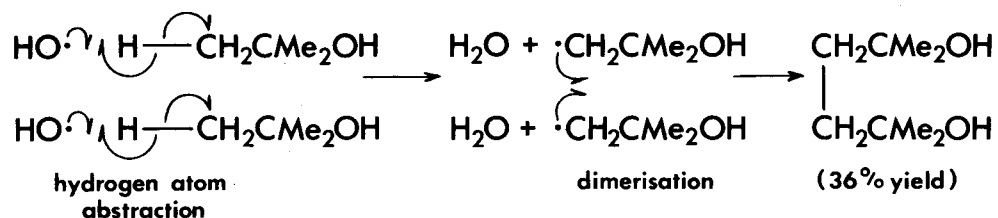
13 RADICAL STABILISATION THROUGH DELOCALISATION



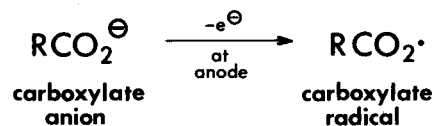
INDUCED RADICAL FORMATION



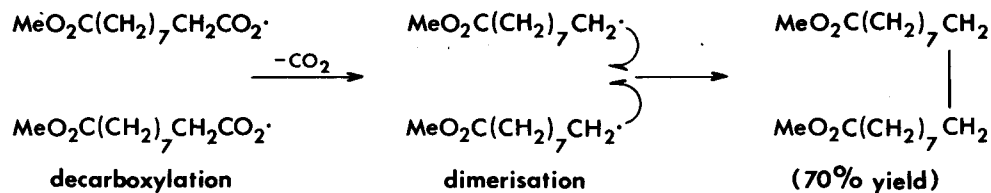
FENTON'S REAGENT : GENERATION OF HYDROXYL RADICALS



PREPARATIVE USE OF FENTON'S REAGENT

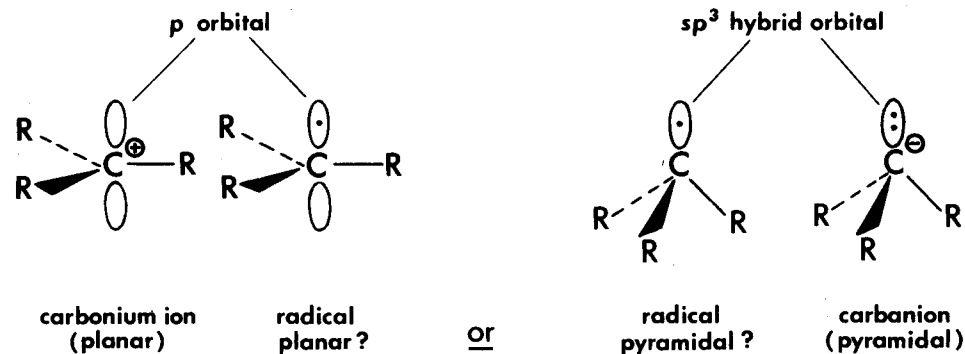


ANODIC OXIDATION OF CARBOXYLATE ANIONS

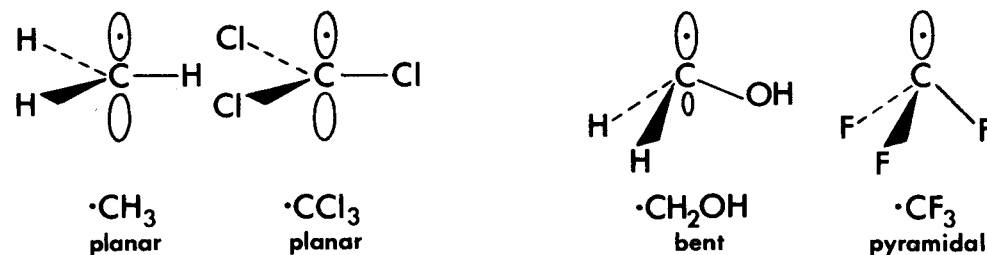


18

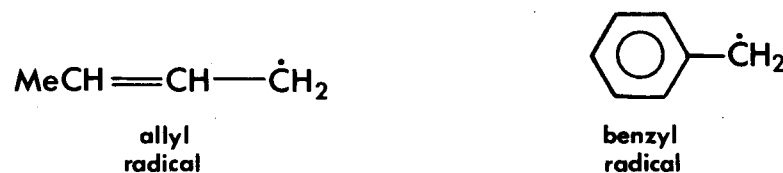
KOLBE ELECTROLYTIC SYNTHESIS



SHAPES OF RADICALS, CARBONIUM IONS AND CARBANIONS



ACTUAL SHAPES OF SOME SIMPLE RADICALS



CONJUGATED RADICALS

14

15

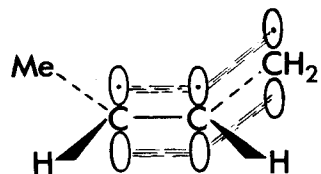
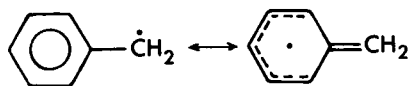
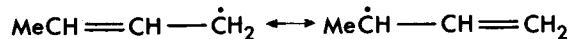
16

17

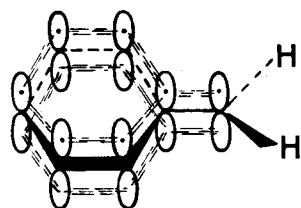
19

20

21



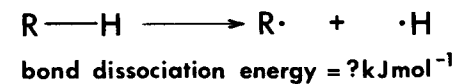
allyl radical



benzyl radical

22

STABILISATION BY DELOCALISATION IN CONJUGATED RADICALS



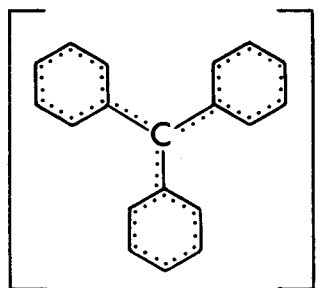
CH <sub>3</sub> —H	MeCH <sub>2</sub> —H	Me <sub>2</sub> CH—H	Me <sub>3</sub> CH—H	
methyl	primary	secondary	tertiary	
435	406	395	380	kJmol <sup>-1</sup>

- (i) increasing ease of formation of radical  
 (ii) increasing stability of radical so formed

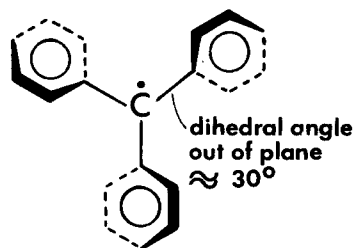
CH <sub>2</sub> =CHCH <sub>2</sub> —H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —H	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH—H	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C—H	
allyl	benzyl	diphenylmethyl	triphenylmethyl	
355	355	331	314	kJmol <sup>-1</sup>

25

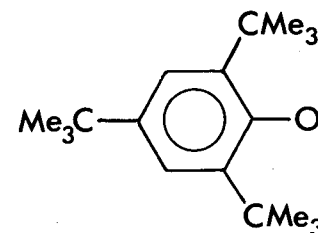
RELATIVE (i) EASE OF FORMATION AND (ii) STABILITY OF RADICALS



shape for maximum stabilisation



actual shape

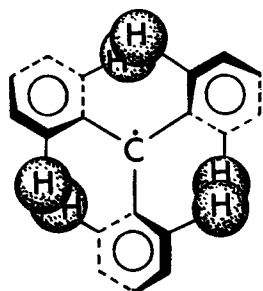


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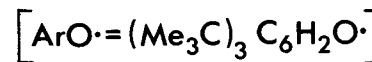
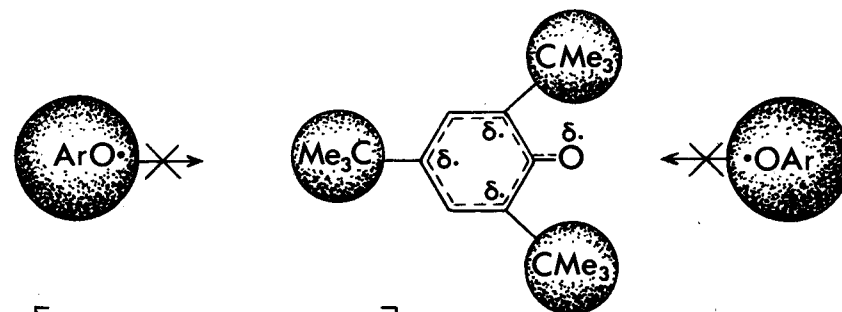
STABLE 2,4,6-TRI(ME<sub>3</sub>C) PHENOXY RADICAL

23

SHAPE AND STABILISATION OF (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C·

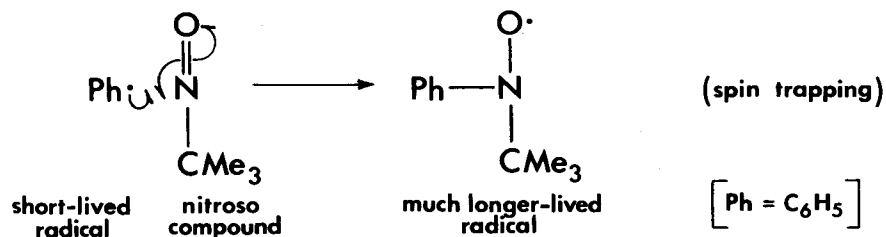


H/H INTERACTION IN (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C·

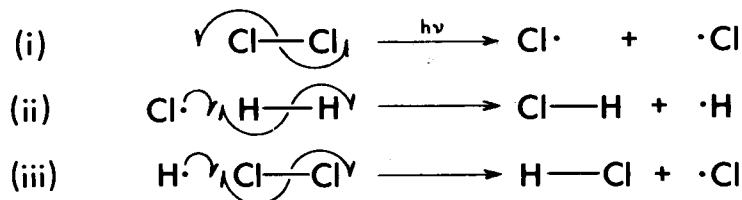


27

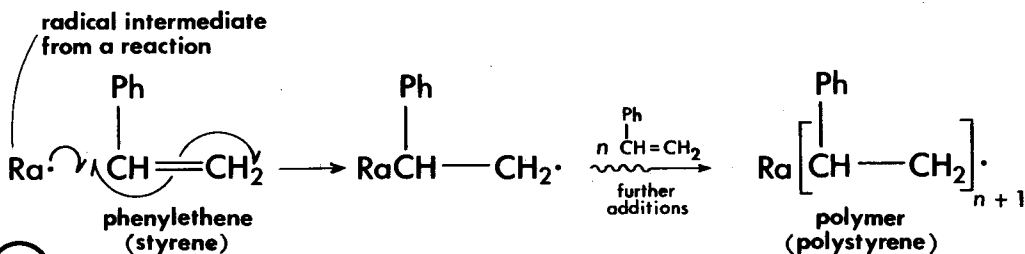
STABILITY TO DIMERISATION OF 2,4,6-TRI(ME<sub>3</sub>C) PHENOXY RADICAL



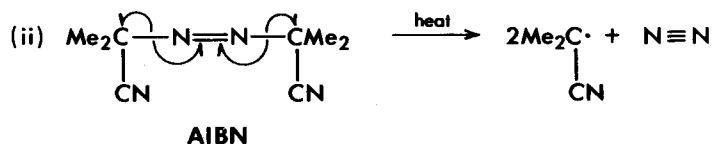
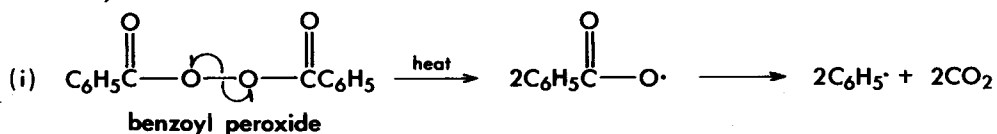
**28** RADICAL LIFE-PROLONGATION BY SPIN-TRAPPING



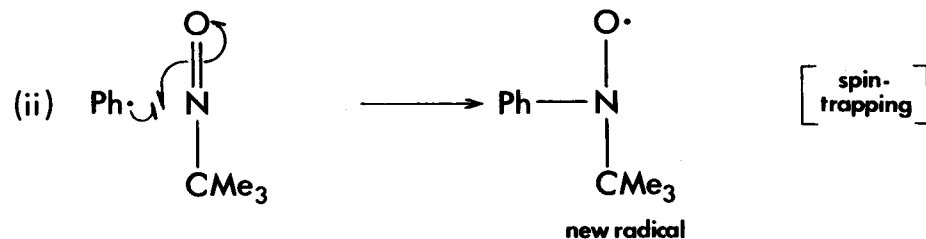
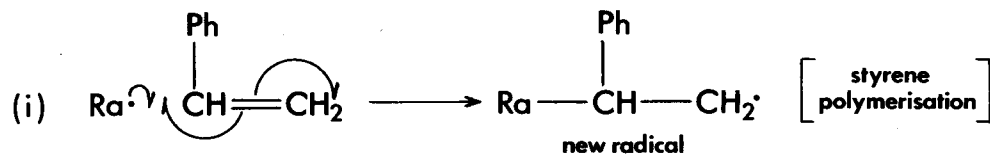
**29** PHOTOCHEMICAL FORMATION OF HCl



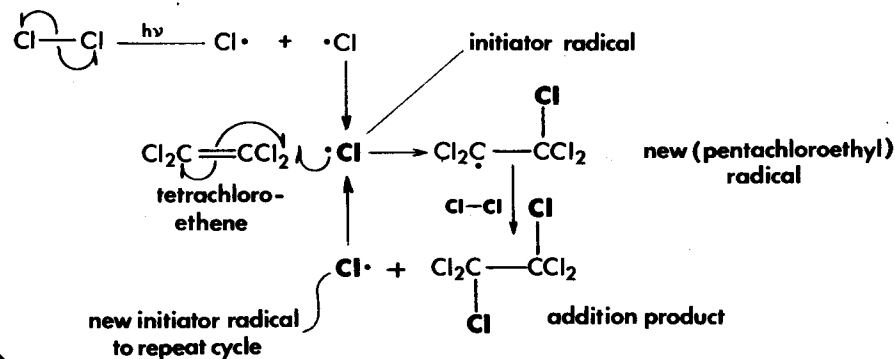
**30** RADICAL DETECTION BY POLYMERISATION OF PhCH=CH<sub>2</sub>



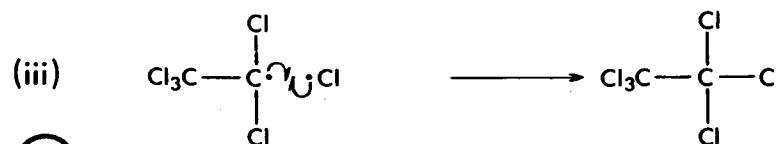
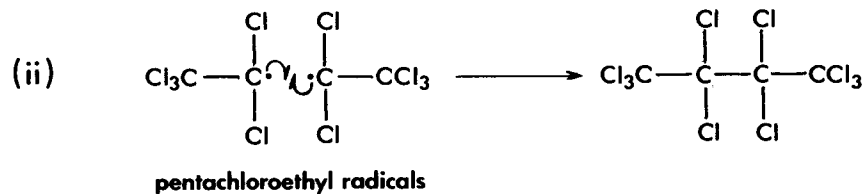
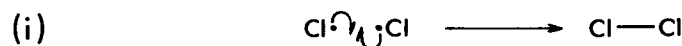
**31** READY SOURCES OF RADICALS (INITIATORS)



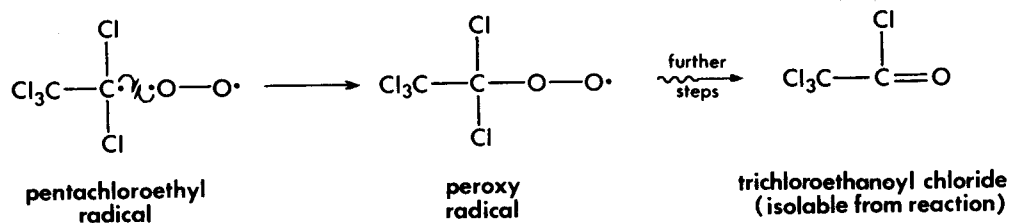
**32** RADICAL + REACTANT → NEW RADICAL



**33** ADDITION OF Cl<sub>2</sub> TO Cl<sub>2</sub>C=CCl<sub>2</sub>: CHAIN REACTION

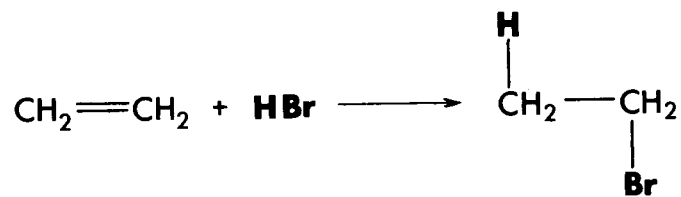


**34** TERMINATION OF CHAIN REACTION BY RADICAL DIMERISATION



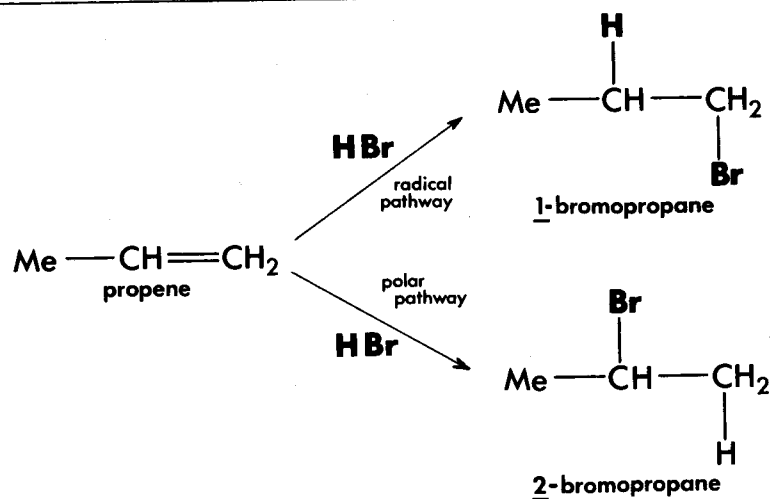
INHIBITION OF CHAIN REACTION BY OXYGEN

35



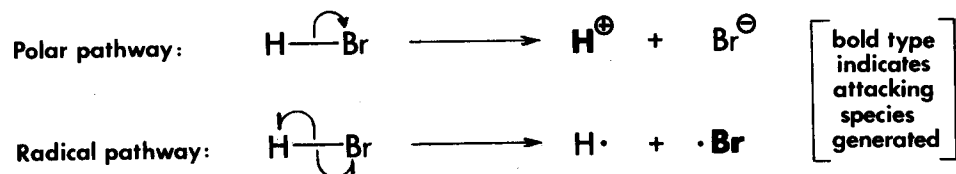
ADDITION OF HBr TO CH<sub>2</sub>=CH<sub>2</sub>

36



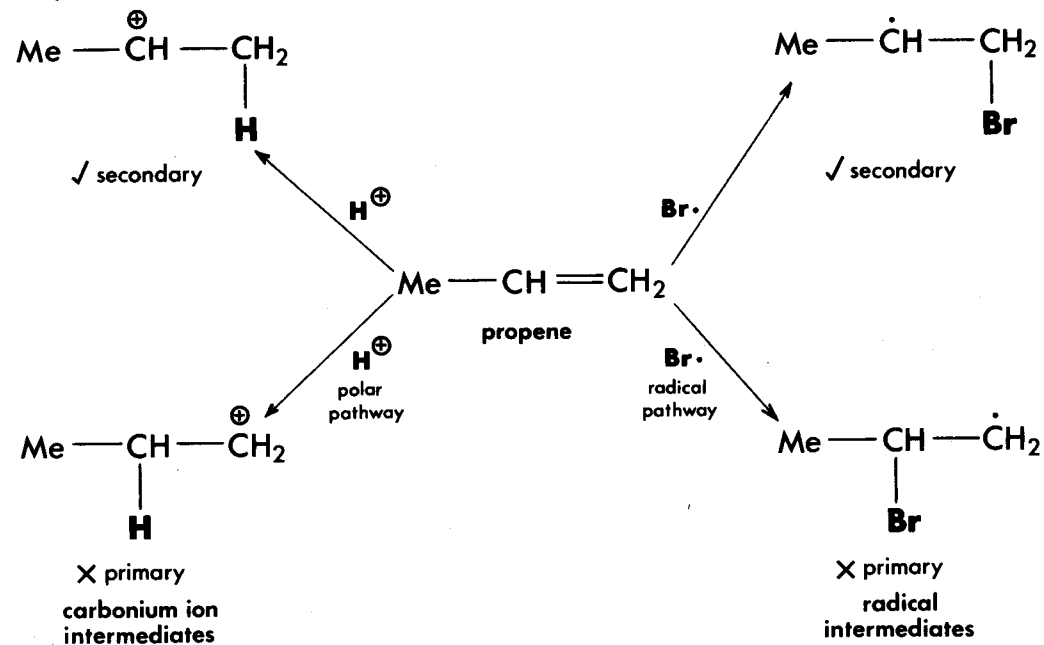
RADICAL AND POLAR ADDITION OF HBr TO PROPENE

37



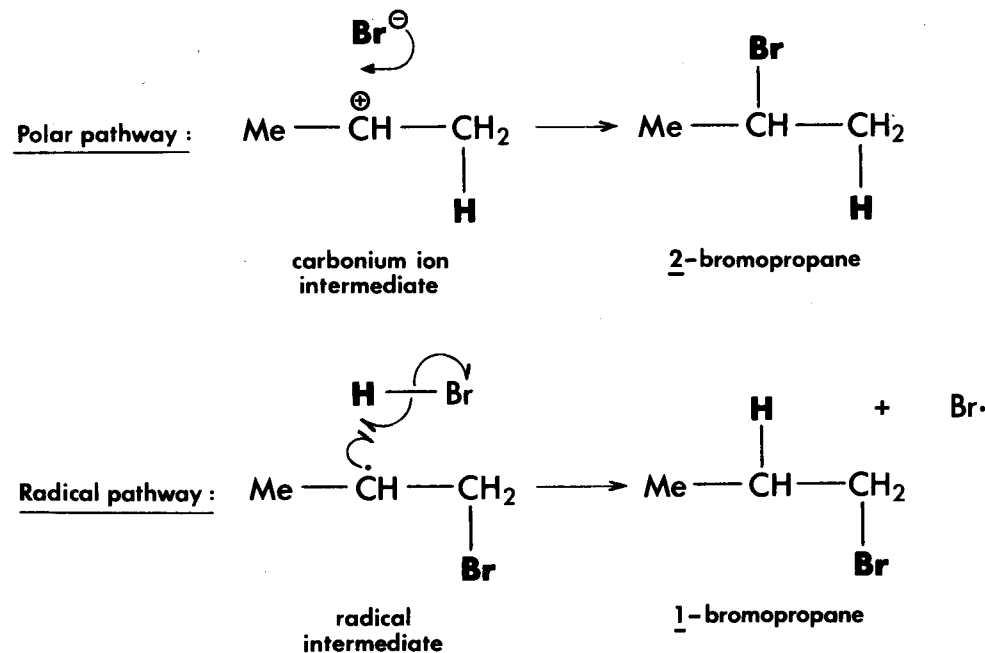
ALTERNATIVE ATTACKING SPECIES IN HBr ADDITION

38



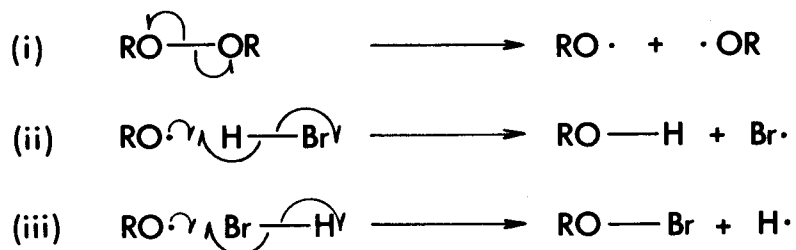
INTERMEDIATES FROM POLAR AND RADICAL PATHWAYS

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COMPLETION OF POLAR AND RADICAL ADDITIONS

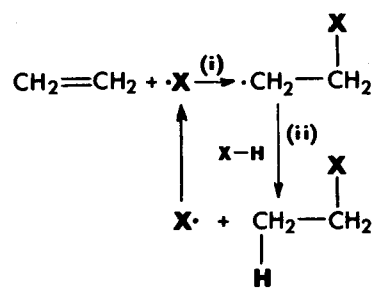
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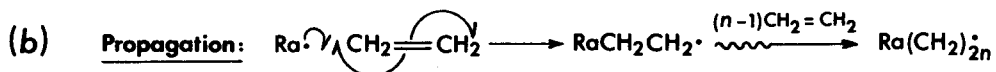
41

## INITIATION OF RADICAL ADDITION OF HBr

Addition of:	Heats of reaction ( $\text{kJmol}^{-1}$ )	
	step (i):	step (ii):
H-F	-188	+155
H-Cl	-109	+21
H-Br	-21	-46
H-I	+29	-113

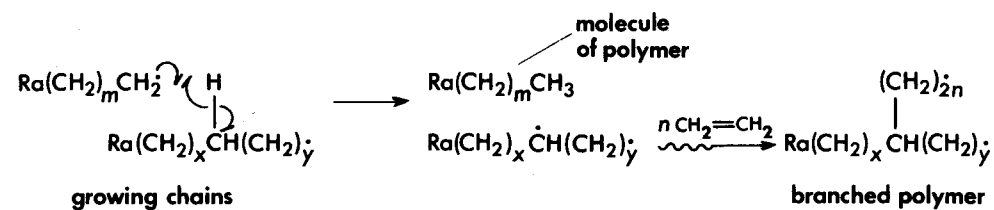


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HEATS OF REACTION FOR STEPS IN RADICAL PATHWAY:  $\text{H}-\text{X} + \text{CH}_2=\text{CH}_2$ 

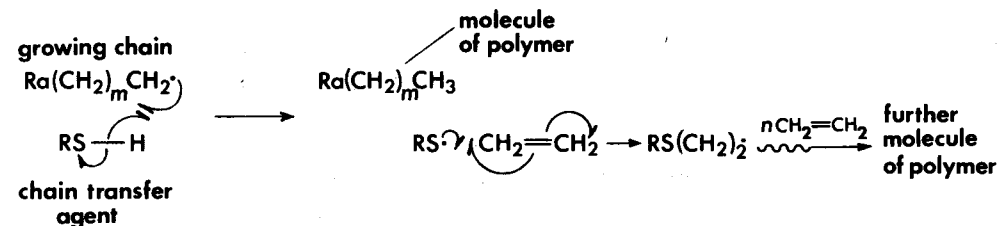
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## STEPS IN ALKENE POLYMERISATION



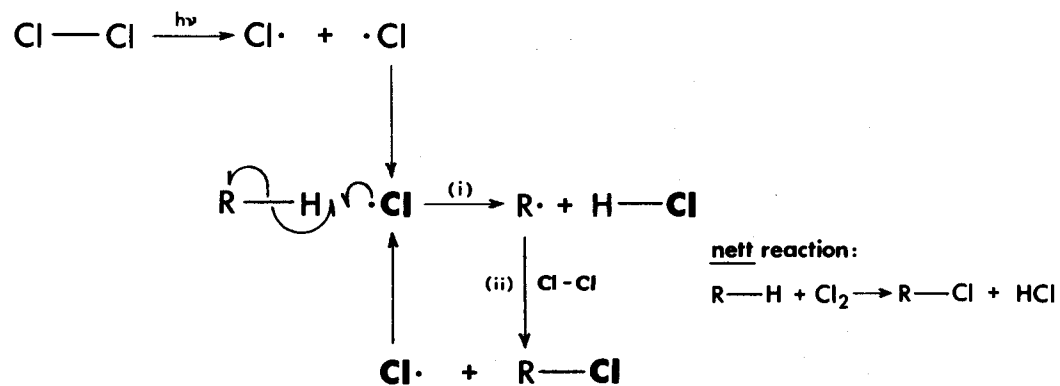
44

## CHAIN BRANCHING THROUGH H-ABSTRACTION



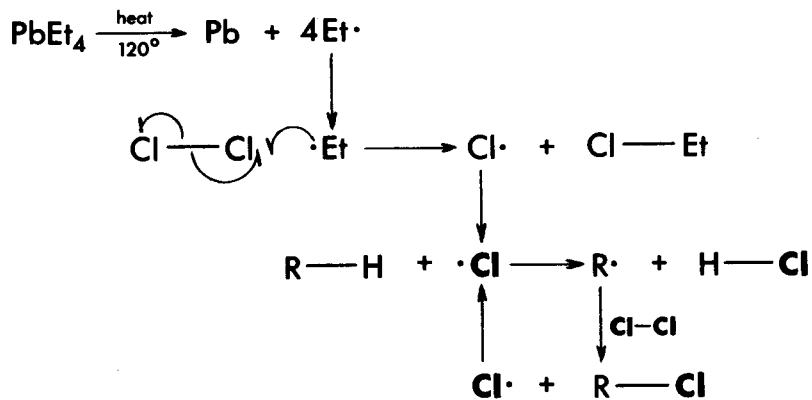
45

## CONTROL OF POLYMERISATION BY CHAIN TRANSFER AGENTS

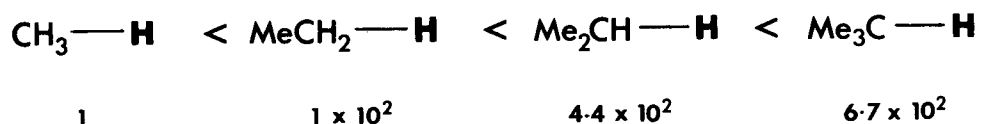


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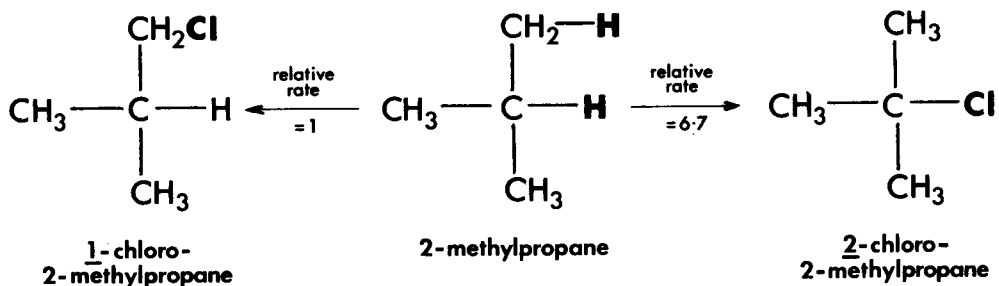
## PHOTOCHEMICAL CHLORINATION OF AN ALKANE



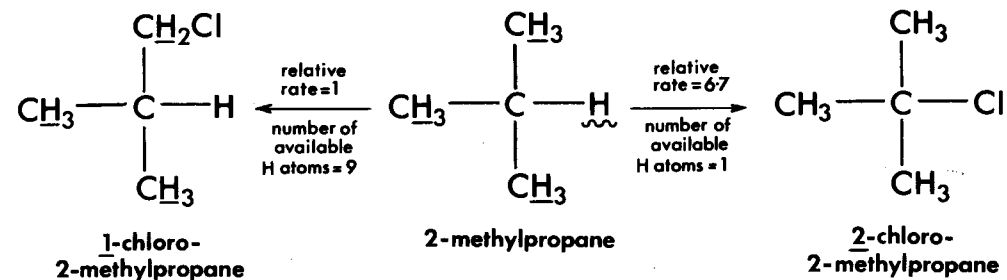
47 INITIATION OF CHLORINATION BY  $\text{PbEt}_4$



48 RELATIVE RATES OF CHLORINATION AT  $25^\circ$



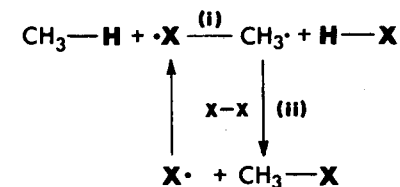
49 MONOCHLORINATION OF 2-METHYLPROPANE



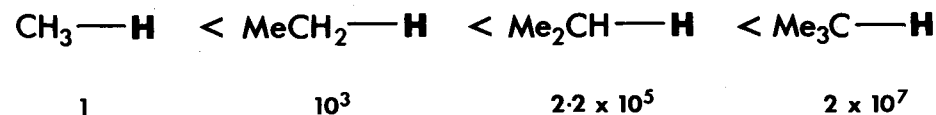
$$\begin{aligned} \underline{\text{1-chloro}} &: 1 \times \underline{9} = 9.0 & \frac{9}{15.7} \times 100 = 57\% \\ \underline{\text{2-chloro}} &: 6.7 \times \underline{1} = \frac{6.7}{15.7} & \frac{6.7}{15.7} \times 100 = \underline{43\%} \end{aligned}$$

50 MONOCHLORINATION OF 2-METHYLPROPANE (CONCLUDED)

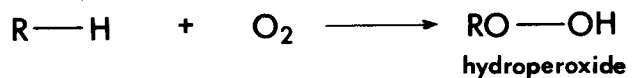
Halogen :	Heats of reaction ( $\text{kJ mol}^{-1}$ )	
	step (i) :	step (ii) :
$\text{F}_2$	-134	-292
$\text{Cl}_2$	-4	-96
$\text{Br}_2$	+63	-88
$\text{I}_2$	+138	-75



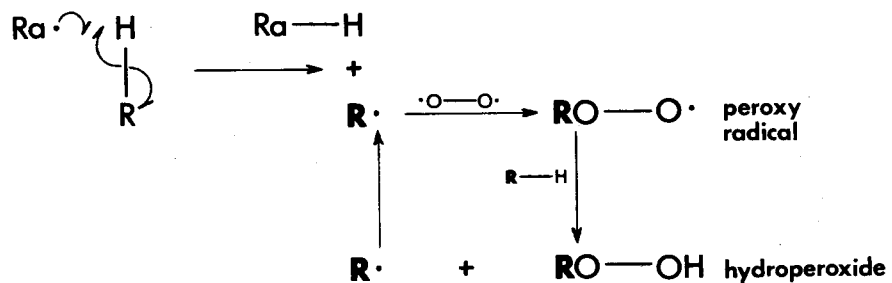
51 HEATS OF REACTION FOR STEPS IN CHAIN REACTION:  $\text{X}_2 + \text{CH}_4$



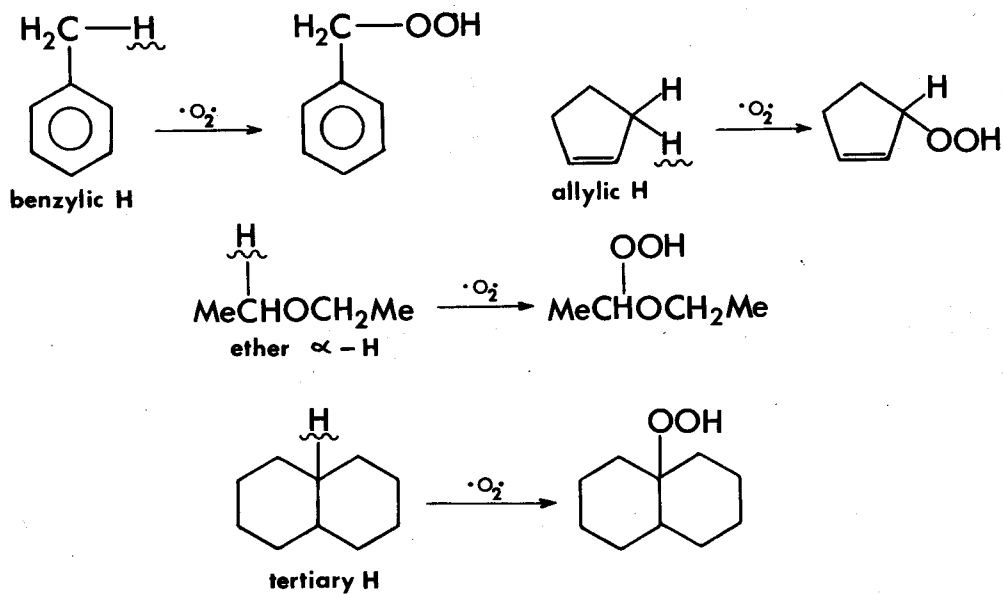
52 RELATIVE RATES OF BROMINATION AT  $25^\circ$



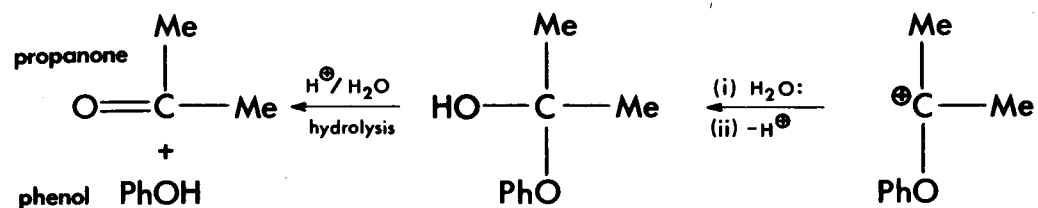
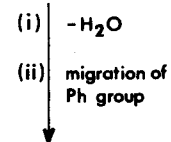
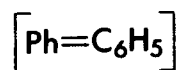
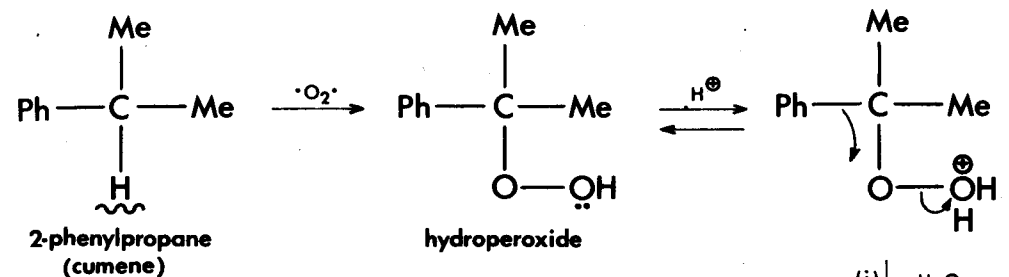
HYDROPEROXIDE FORMATION IN AUTOXIDATION



HYDROPEROXIDE-FORMING CHAIN REACTION



SELECTIVITY IN HYDROPEROXIDE FORMATION



INDUSTRIAL PREPARATION OF PhOH + Me<sub>2</sub>C=O FROM PhCHMe<sub>2</sub> (CUMENE)

