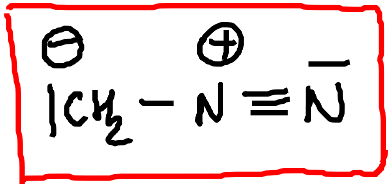
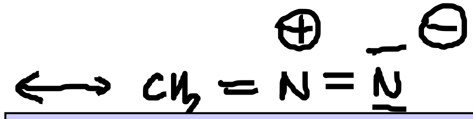
Diazoalkanes

Diazomethane

CH_2N_2



$\overset{\ominus}{|CH_2} - \overset{\oplus}{N} \equiv \overline{N}$



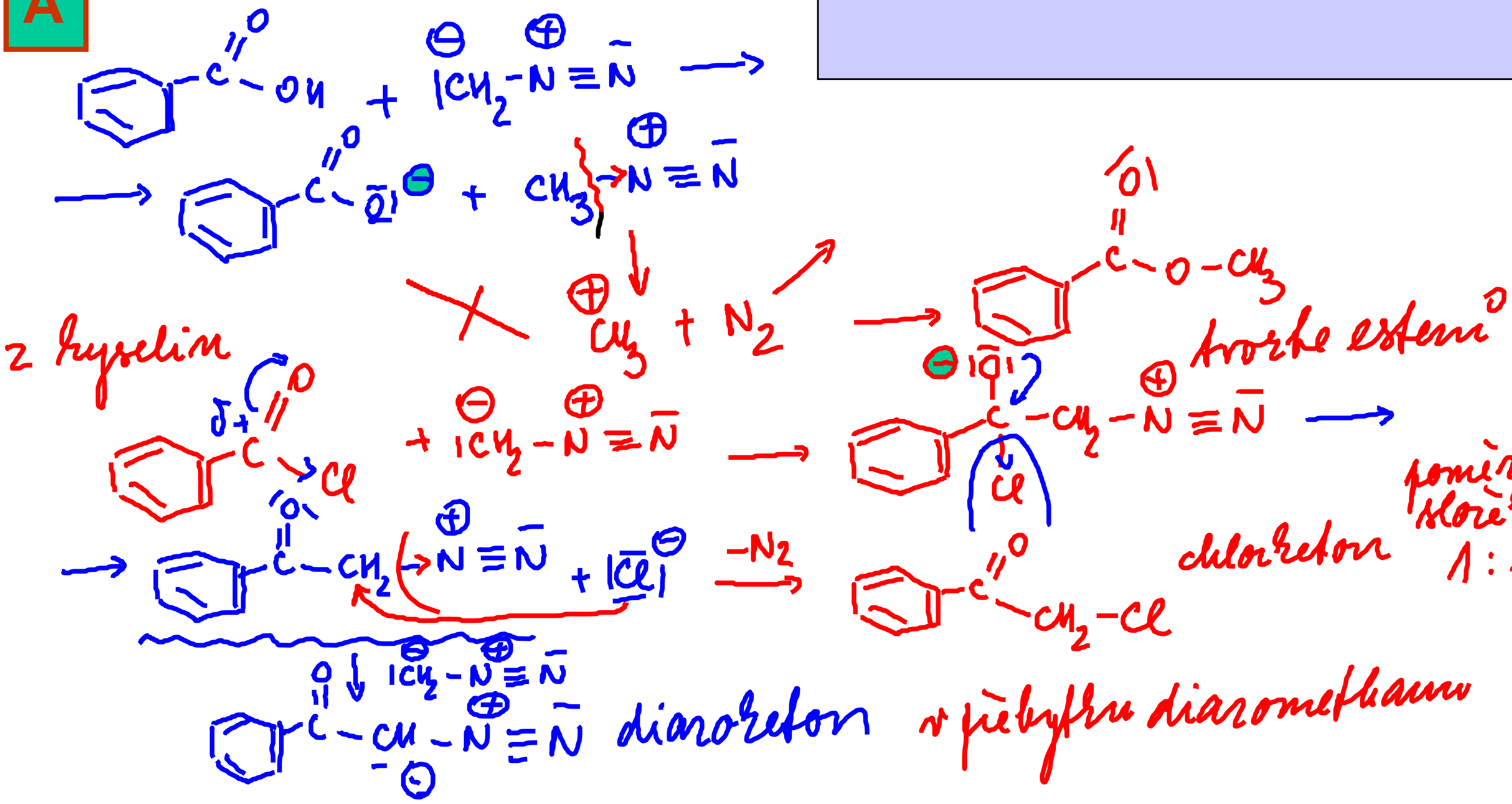
$\longleftrightarrow CH_2 = \overset{\oplus}{N} = \overset{\ominus}{\underline{\overline{N}}}$

$R^1R^2C = N_2$

a) basicity and nucleophility at carbon atom

b) decomposition by UV light

A



Diazoalkanes

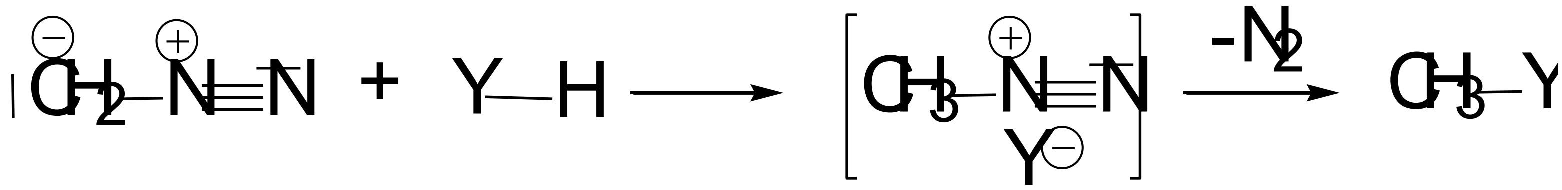
A

diazoalkany
diazoketony
diazoestery

$|N\equiv\overset{\oplus}{N}-\overset{\ominus}{\overline{C}H}-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

elektroneutrální molekule

1. reaction with acids



$$|\overset{\ominus}{C}H_2-\overset{\oplus}{N}\equiv N + Y-H \longrightarrow \left[CH_3-\overset{\oplus}{N}\equiv N \quad Y^{\ominus}\right] \xrightarrow{-N_2} CH_3-Y$$

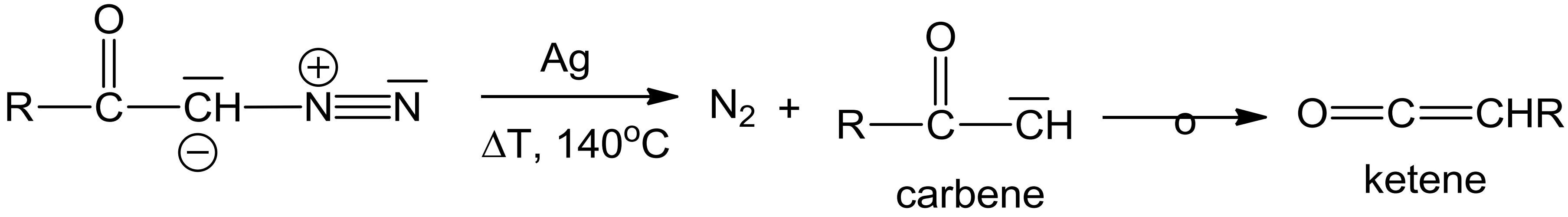
$R-COOH$
$ArOH$
$R-SH$
$R-NH_2$
$R-CO-NH_2$

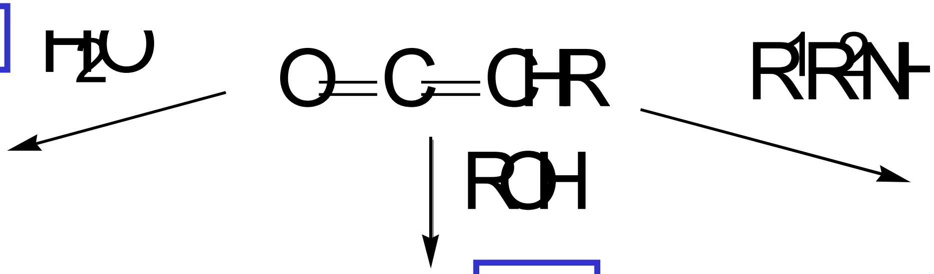
$$N\equiv\overset{\oplus}{N}-\overset{\ominus}{C}H-COOC_2H_5 + RCOOH \xrightarrow{-N_2} RCOO-CH_2-COOC_2H_5$$

Diazoalkanes

Diazoketones

Arndt, Eistert, Wolf rearrangement





acid + 1 carbon atom

ester

amide

Diazoalkanes

Preparation

N-nitroso-N-methylurea + NaOH = diazomethane

N-nitroso-N-methylacylamide

N-nitroso-N-methylurethane

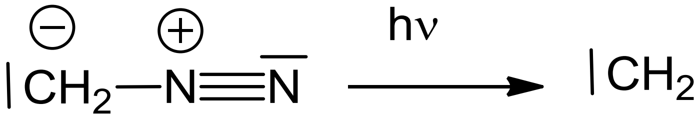
Preparation of diazoesters

diazotation of aminoacid esters

Diazoalkanes

B

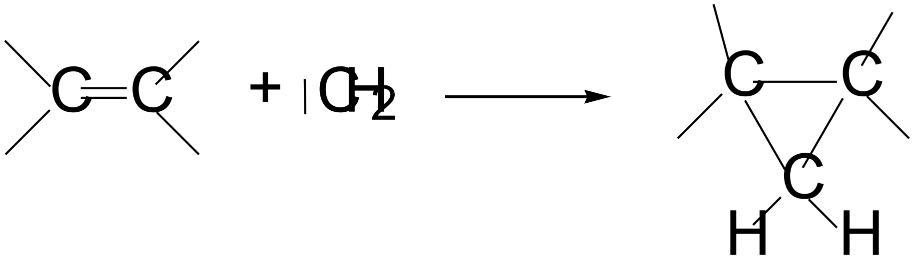
Diazocompounds under UV irradiation:

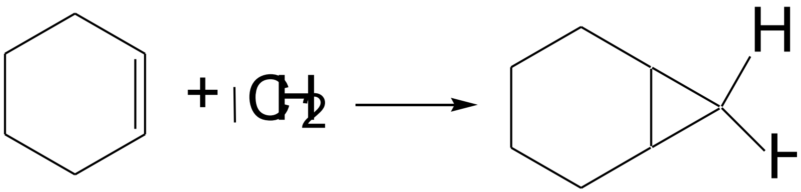


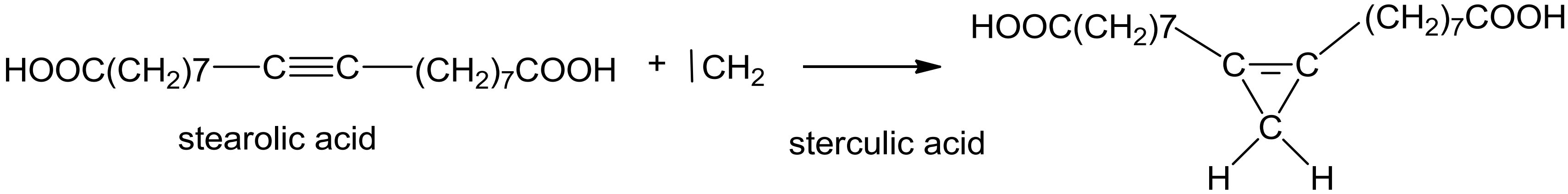
$$|\overset{\ominus}{C}H_2-\overset{\oplus}{N}\equiv\overline{N} \xrightarrow{h\nu} |CH_2$$

formation of carbene

electrophile reacts with π electrones





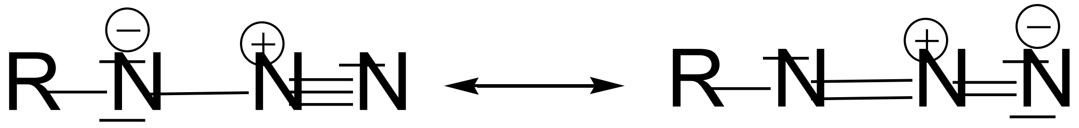


stearolic acid

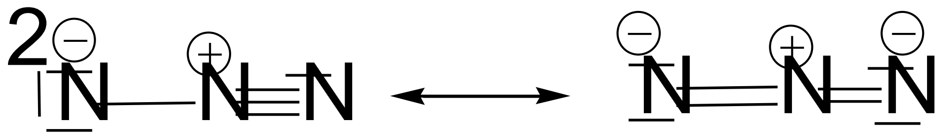
sterculic acid

isolated from tropical plants oil

Organic azides



Their preaparation by reaction of azide ion in S_N with alkyl halogenide or acyl halogenide



very strong nucleophiles and weak bases

Azides are sensitive to thermal decomposition (sometimes with explosion)

decomposition of alkyl ayide is non-selective to mixture of products and therefore has no aplication

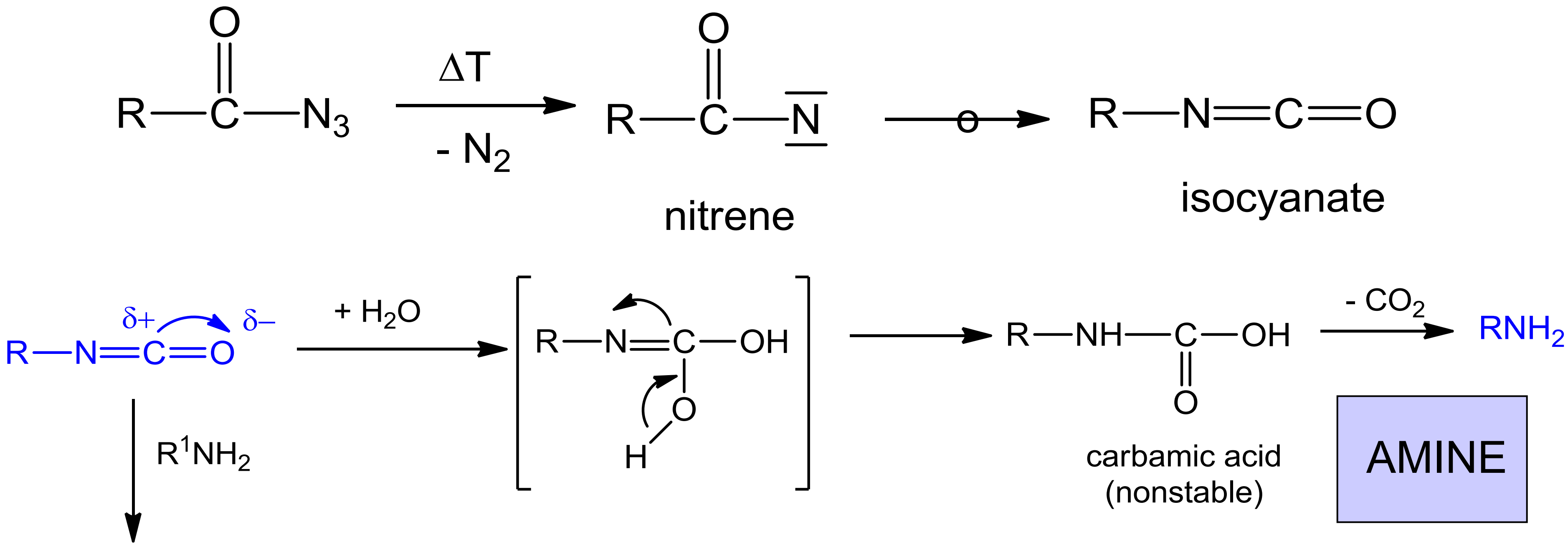
acylazides are sources of nitrenes

Azides may be reduced either under catalytic conditions (H_2 / Pt) or by $LiAlH_4$

products are amines

Organic azides

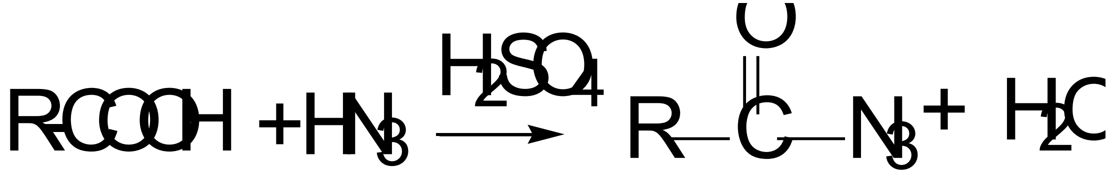
Tepelný rozklad acyl azidů - Curtiův přesmyk (odbourání) azidů



Organic azides

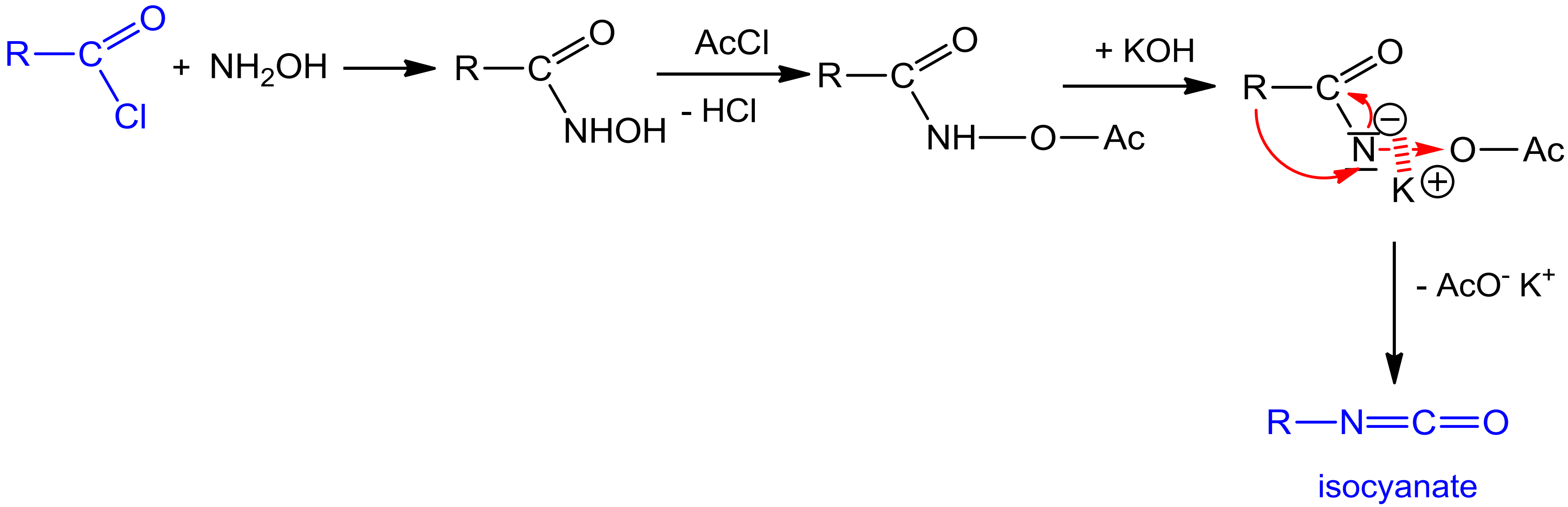
Similar is also **Schmidt rearrangement**, diference only in the preparation.

Azide is preparted by sulfuric acid with N_3H



$$RCOOH + HN_3 \xrightarrow{H_2SO_4} R-\overset{\overset{O}{\|}}{C}-N_3 + H_2C$$

Lossen decomposition is starting from hydroxamic acids

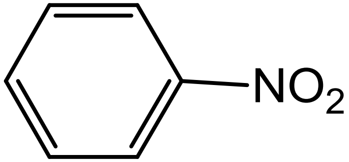


Nitro compounds

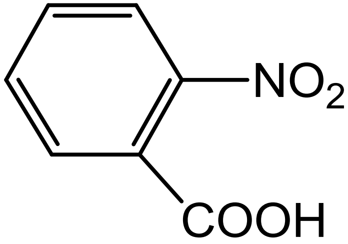
Nomenclature

only prefix **nitro-**

dinitro- …atc.

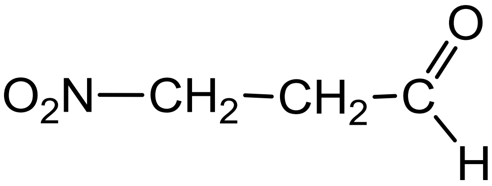


nitrobenzene



2-nitrobenzoic acid

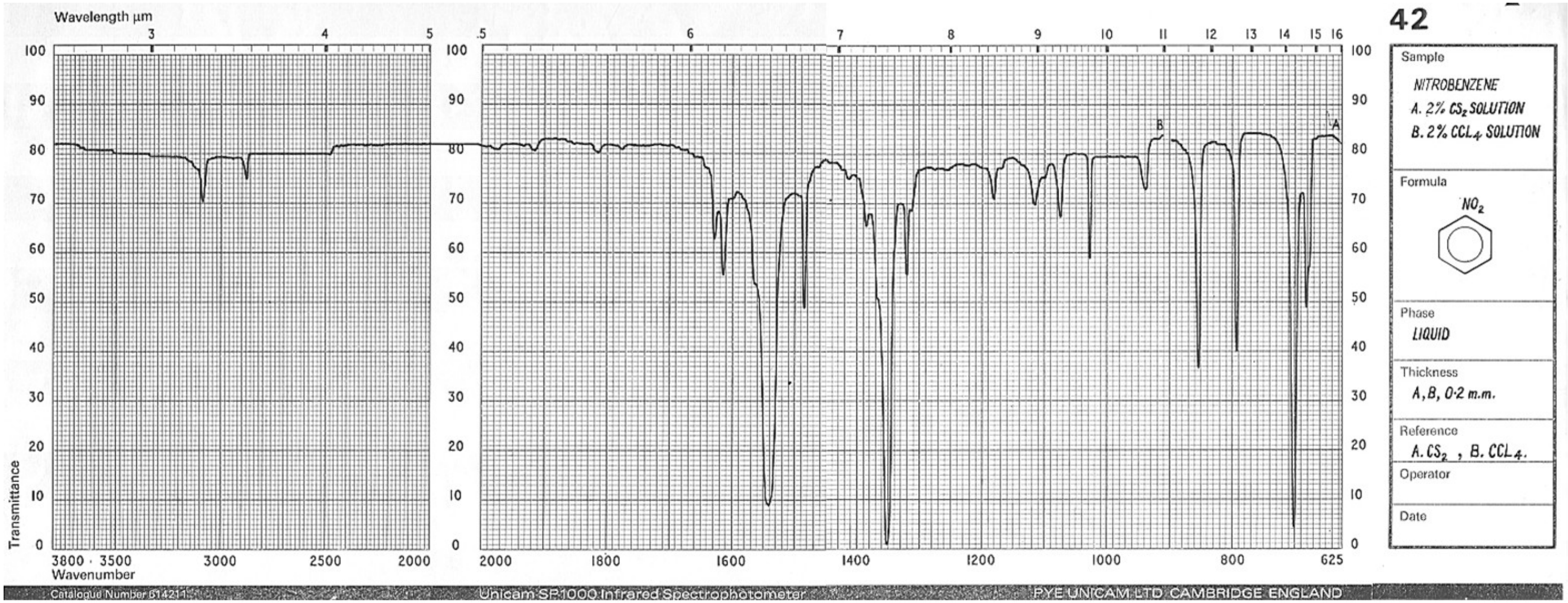
CH_3-NO_2 **nitromethane**



$O_2N-CH_2-CH_2-CHO$

3-nitropropanal

Nitro compounds



Sample
NITROBENZENE
A. 2% CS_2 SOLUTION
B. 2% CCL_4 SOLUTION

Formula
NO_2

Phase
LIQUID

Thickness
A, B, 0·2 m.m.

Reference
A. CS_2 , B. CCL_4.

Operator

Date

$\nu_{\text{as N-O}}$ **1650 – 1500 cm^{-1}**

$\nu_{\sigma\ \text{N–O}}$ 1370 – 1300 cm^{-1}

$\nu_{\text{as N-O}}$ **arom. 1550 cm^{-1}**

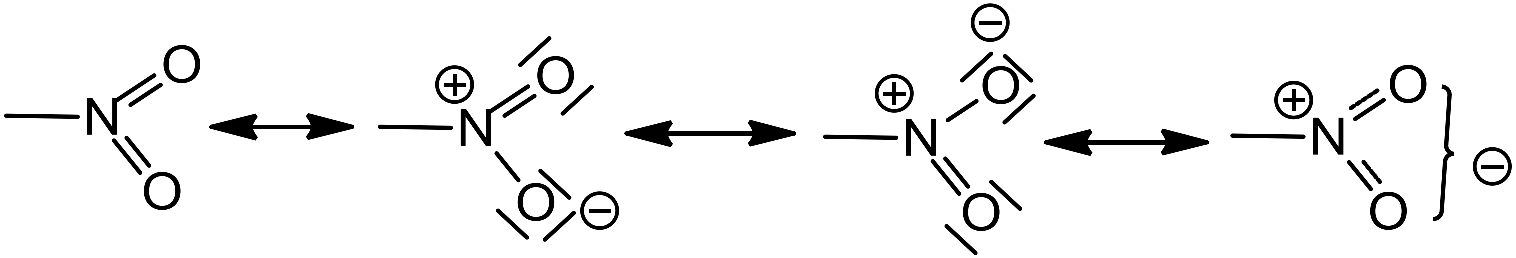
$\nu_{\text{sym N-O}}$ **arom. 1360 cm^{-1}**

Nitro compounds

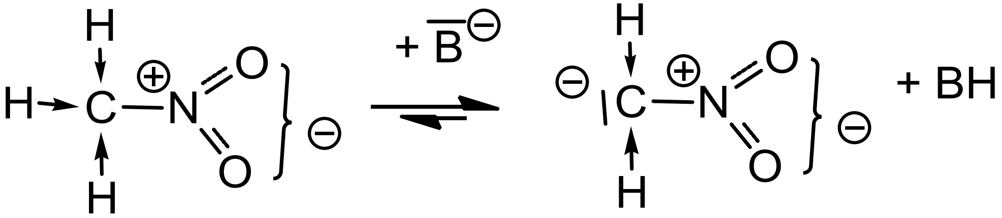
REACTIVITY:

1) rather nonreactive group – strong electronwithdrawing

2) senstitive to reductions under formation of other nitrogen compounds



α-hydrogen atoms are acidic



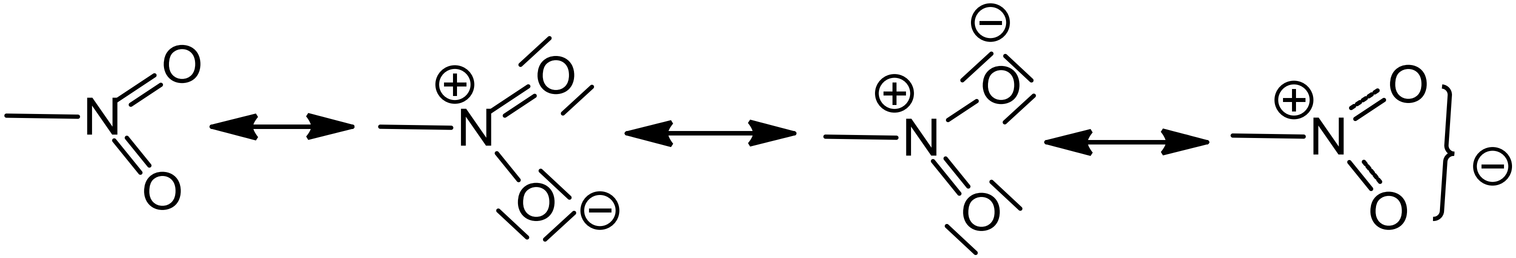
pK_a	**CH_3NO_2**	**10,2**
	$CH_3CH_2NO_2$	**8,5**
	$CH_3CH_2CH_2NO_2$	**7,8**
	$O_2N\text{-}CH_2\text{-}NO_2$	**3,57**

Nitro compounds

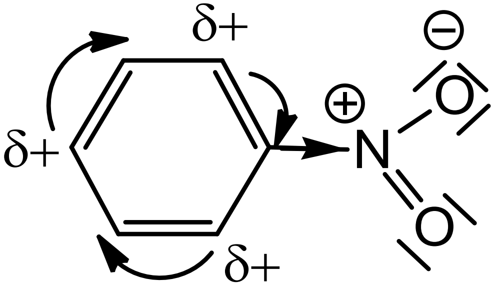
REACTIVITY:

1) **rather nonreactive group – strong electronwithdrawing**

2) senstitive to reductions under formation of other nitrogen compounds



Nitro group is electronwithdrawing group and at aromatic ring is causing deminishing electrondensity and this way unables S_EAr



HAMMETT CONSTANT

$\sigma_m = 0,71$ **-I a – M efekt**

$\sigma_p = 0,81$

reaction proceed only with strong electrophiles and at harsh conditions

(they do not react in F.C. alkylation, acylation, azocopulation etc.

Nitro compounds

REACTIVITY:

1) rather nonreactive group – strong electronwithdrawing

2) senstitive to reductions under formation of other nitrogen compounds

reactions are pH dependent and are important at aromatic systems