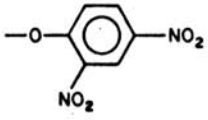
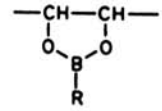
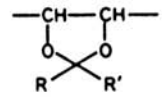
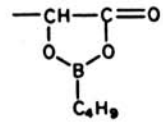
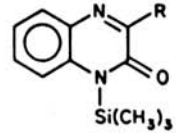
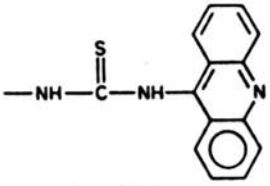
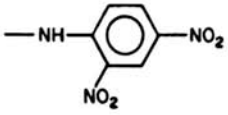
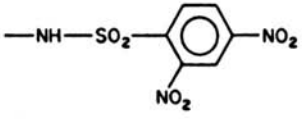
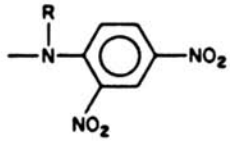
Derivatizace skupin obsahujících kyslík

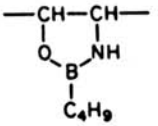
Funkční skupina	Postup	Příklady	Poznámky
–OH (Primary, secondary and tertiary alcohols; phenols; carbohydrates)	Silylation	$-O-Si(CH_3)_3$	
	Acylation	$-O-CO-CH_3$; $-O-CO-CF_3$	
	Benzoylation	$-O-CO-C_6H_5$; $-O-CO-C_6F_5$	
	Alkylation	$-O-CH_3$; $-O-CH_2-C_6F_5$	
	Dansylation	Ar–O–Dns	Fluorescent derivative (phenols)
	Reaction with Dis-Cl	–O–Dis	Fluorescent derivatives of phenols and alcohols
	Reaction with FDNB		For GLC of phenols with ECD
	Reaction with NBD-Cl	7-Nitrobenzofurazan	Fluorescent derivative (phenols)
	Ion-pair formation	$Ar-O^-M^+$	For phenols; 'M' can be a variety of counter-ions
>C=O (Aldehydes and ketones)	Oxime formation	>C=N–OH; >C=N–O–CH_3	May form *syn* and *anti* isomers
	Oxime formation and silylation	>C=N–O–$Si(CH_3)_3$	May form *syn* and *anti* isomers
	Ketal/acetal formation		
	Hydrazone formation	>C=N–NH–C_6H_5	Fluorescent and electron capturing derivatives available
	Schiff's base formation	>C=N–R	
	Silylation	=C(–O–$Si(CH_3)_3$)–CO–O–$Si(CH_3)_3$	Only when enol formation is favoured, e.g. pyruvate
	Oxidation	–COOH	For aldehydes and methyl ketones (iodoform reaction); derivatized as carboxylic acids

–COOH (Carboxylic acids)	Esterification (alkyl)	$-CO_2-CH_3$; $-CO_2-CH_2CF_3$	
	Esterification (aryl)	$-CO_2-CH_2C_6H_5$; $-CO_2-CH_2C_6F_5$	
	Silylation	$-CO_2-Si(CH_3)_3$	
	Ion-pair formation	$R-COO^-M^+$	'M' may be a variety of counter-ions
–C—C– (OH, OH) (Glycols)	As for –OH, but also: Cyclic boronate formation		R = alkyl (most often butyl), or phenyl
	Acetal or ketal formation		
–CH–COOH (OH) (α-Hydroxy acids)	As for the individual groupings, but also:		
	Boronation		
	Simultaneous acylation and esterification	–CH(O–CO–C_3F_7)–COO–C_2H_5	A number of variations of this approach are available
–CO–COOH (α-Keto acids)	As for the individual groupings, but also: Cyclization with 1,2-diaminobenzene followed by silylation		
R–CO–OR' (Esters)	Esters may be analysed chromatographically without derivatization, but where R' is involatile:		
	Ester interchange (transesterification)	$R-CO-OCH_3$	
R—CO, R'—CO, O (Acid anhydrides)	Esterification	R–CO–OR'' + R'–CO–OR''	Treat exactly the same as an acid, using e.g. EtOH/HCl

Derivatizace skupin obsahujících dusík

Funkční skupina	Postup	Příklady	Poznámka
$-NH_2$ (Primary amines; amino acids; amino sugars)	Acylation	$-NH-CO-CH_3$; $-NH-CO-CF_3$	
	Benzoylation	$-NH-CO-C_6H_5$; $-NH-CO-C_6F_5$	
	Silylation (mild)	$-NH-Si(CH_3)_3$	Mixtures may be obtained
	Silylation (vigorous)	$-N[Si(CH_3)_3]_2$	
	Treatment with CS_2	$-N=C=S$	Volatile, for use with GLC
	Thiourea formation		Fluorescent derivative
	Schiff's base formation	$-N=CH-C_6F_5$	
	2,4-Dinitrophenylation		
	Sulphonamide formation		
		$-NH-Dns$	Fluorescent derivative (several variants available)
	Carbamate formation	$-NH-CO_2-CH_3$	
	Treatment with fluorescamine	*N*-substituted 2-phenyl-pyrrolin-4-ones	Specific fluorogenic reagent for primary amino groups
	Treatment with pyridoxal	Pyridoxylidine derivative	Semi-specific fluorogenic reagent for primary amines
	Treatment with NBD-Cl	7-Nitrobenzo-furazan	Fluorescent product
	Alkylation	$-N\begin{matrix}CH_3\\CH_3\end{matrix}$	
	Ion-pair formation	$R-NH_3^+X^-$	'X' may be a variety of counter-ions
$-NH-R$ (Secondary amines, imino acids, substituted amino sugars)	Acylation	$-\overset{R}{\overset{\vert}{N}}-CO-CH_3$; $-\overset{R}{\overset{\vert}{N}}-CO-CF_3$	As with primary amines
	Benzoylation	$-\overset{R}{\overset{\vert}{N}}-CO-C_6H_5$; $-\overset{R}{\overset{\vert}{N}}-CO-C_6F_5$	As with primary amines
	Silylation	$-\underset{\underset{R}{\vert}}{N}-Si(CH_3)_3$	May need 'forcing' conditions

	2,4-Dinitrophenylation		As with primary amines
	Sulphonamide formation		As with primary amines (more probability of side reactions)
	Treatment with NBD–Cl		As with primary amines
	Ion-pair formation	$R_2NH_2^+X^-$	'X' may be a variety of counter-ions
$R-\underset{\underset{R''}{\vert}}{N}-R'$ (Tertiary amines)	Carbamate formation	$R_2N-CO_2-CH_2-C_6F_5$	
Quaternary ammonium salts	Thermal decomposition	Tertiary amines	HPLC directly Chapter 8 of first edition
	Ion-pair formation	$R_4N^+X^-$	'X' may be a variety of counter-ions
$-CO-NH_2$ (Amides)	Silylation (vigorous)	$-\underset{\underset{O-Si(CH_3)_3}{\vert}}{C}=N-Si(CH_3)_3$	Silylamides are themselves powerful silylating reagents
	Acylation (vigorous)	$-CO-NH-CO-C_6F_5$	
	Alkylation	$-CO-N(CH_3)_2$	e.g. CH_3I/NaH/DMSO
$R-NH-CO-NH-R'$ (substituted ureas; carbamides)	Acylation	$R-\underset{\underset{CO-CF_3}{\vert}}{N}-CO-\overset{\overset{R'}{\vert}}{N}-CO-CF_3$	
$-CO-NH-R$ (Alkylamides)	Acylation (vigorous)	$-CO-\underset{\underset{R}{\vert}}{N}-CO-C_6F_5$	
	Silylation	$-CO-\underset{\underset{Si(CH_3)_3}{\vert}}{N}-R$	Silylamides are themselves powerful silylation reagents
	Alkylation	$-CO-\underset{\underset{CH_3}{\vert}}{N}-R$	e.g. CH_3I/NaH/DMSO

Funkční skupina	Postup	Příklad produktu	Poznámka
R–NH–C(=NH)–NH–R′ (Substituted guanidines)	Acylation (vigorous)	R–N(CO–CF$_3$)–C(=N–CO–CF$_3$)–NR′–CO–CF$_3$	Acylation is difficult, and stability of the products is poor
	Cyclic derivatives		
R–CH(COOH)–NH$_2$ (Amino acids)	Silylation	R–CH(COOSi(CH$_3$)$_3$)–NH–Si(CH$_3$)$_3$	
	Esterification + Acylation	R–CH(COOC$_4$H$_9$)–NH–CO–CF$_3$	
–CH(OH)—CH(NH$_2$)– (Amino alcohols)	As for individual groups, but see also:		
	Cyclic boronate formation		
	Simultaneous acylation and silylation	–CH(O–Si(CH$_3$)$_3$)–CH(=)–NH–CO–CF$_3$	Using *N*-methyl-*N*-trimethylsilyl-trifluoroacetamide for example
–NO$_2$ (Nitro compounds)	Chromatograph without derivatization		Electron-capturing; coloured