

Isocyanates and Isothiocyanates **Alfa Aesar**[®]

A Johnson Matthey Company

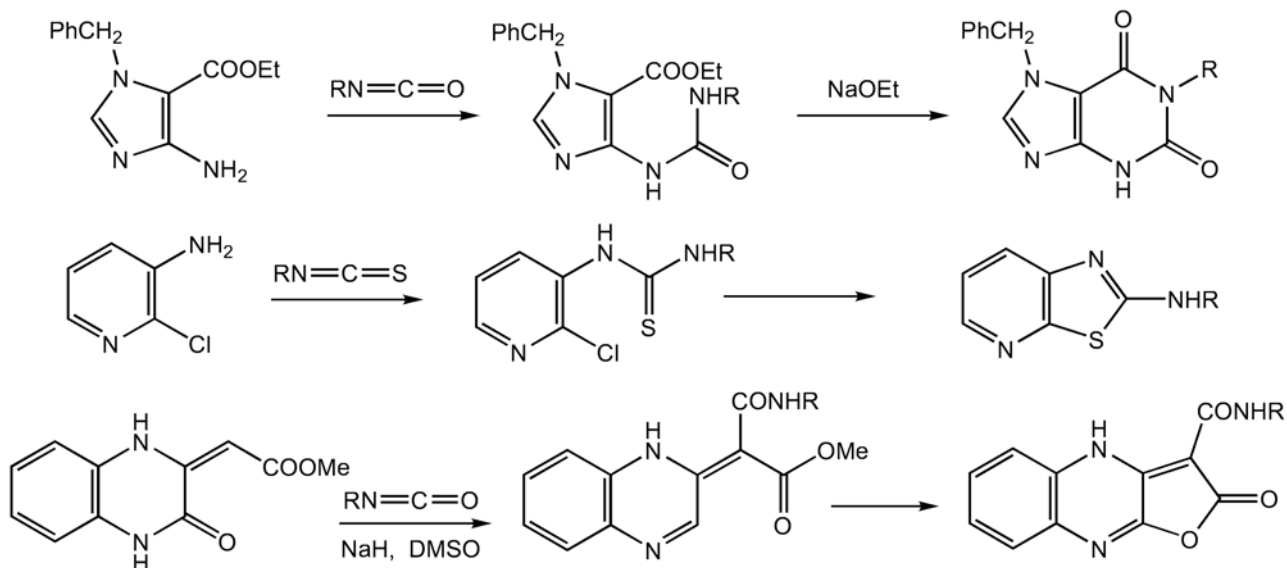
Isocyanates and isothiocyanates are important intermediates belonging to the family of compounds known as heterocumulenes. The chemistry of these molecules is dominated by two modes of reaction: nucleophilic addition and cycloaddition. Aspects of the chemistry of isocyanates and isothiocyanates are discussed in a number of books and review articles.¹⁻¹¹

Nucleophilic addition reactions

Alcohols and phenols readily attack isocyanates to give carbamates. Similarly, thiols give thiocarbamates, and amines ureas. In general, reactivity is in the order $\text{RSO}_2\text{NCO} > \text{RCONCO} > \text{Aryl-NCO} > \text{Alkyl-NCO}$, and for nucleophiles $\text{NH} > \text{OH} > \text{SH}$. The high yields and lack of byproducts with this type of reaction have led to their commercial exploitation in pharmaceuticals and agrochemicals, and particularly in the polymer field where the formation of polyurethanes from diisocyanates and diols accounts for the largest use of isocyanates. Reactions with carbon nucleophiles provide a useful synthetic access to substituted amides and other derivatives.

Isothiocyanates react with nucleophiles in a similar manner, although reaction rates are usually significantly lower. Isothiocyanates tend to be less sensitive to moisture and less unpleasant to handle, while still possessing a sufficient degree of reactivity for them to be very useful intermediates. A few illustrative examples of the reactions of isocyanates and isothiocyanates with nucleophiles are shown in Schemes 1-3.¹²⁻¹⁴

Schemes 1-3



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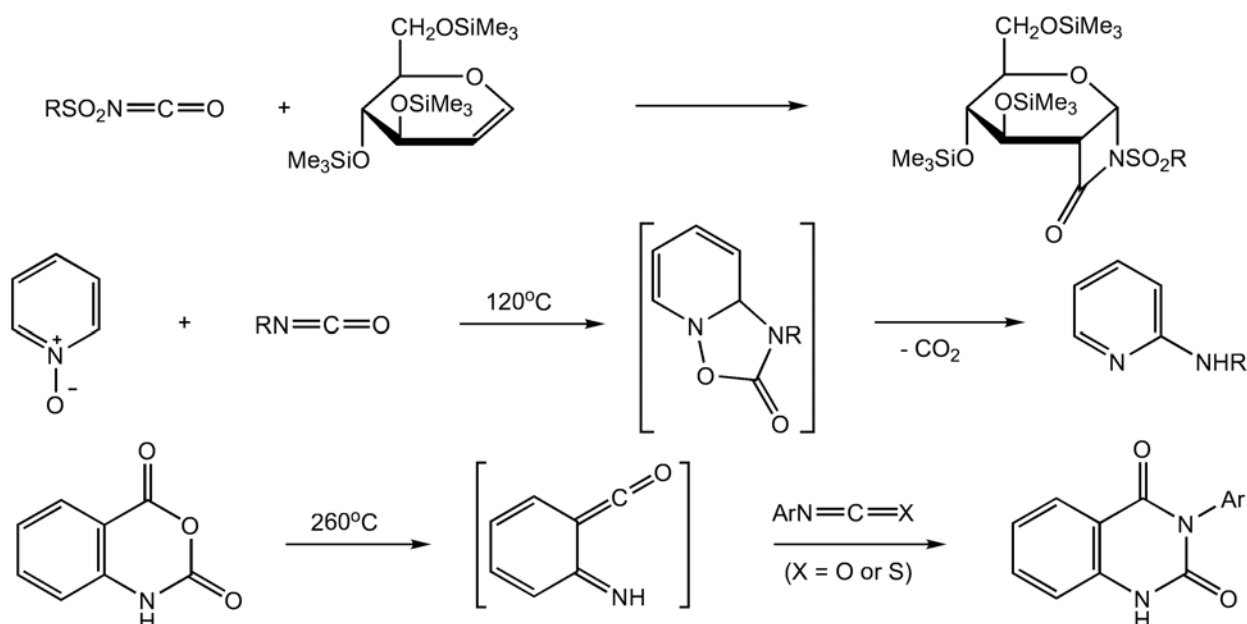
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Cycloaddition reactions

Isocyanates and isothiocyanates undergo cycloadditions, including [2+2], [3+2] dipolar and [4+2] reactions, with a variety of substrates. The products of these reactions (e.g. β -lactams) may be of interest in themselves, or they may undergo ring-opening to give other useful products. Some examples of various types of cycloaddition reactions involving isocyanates and isothiocyanates are shown in Schemes 4-6.¹⁵⁻¹⁷

Schemes 4-6



Product listings

Alkyl and aralkyl monoisocyanates

- | | |
|---|---|
| L18710 Allyl isocyanate | 41985 n-Butyl isocyanatoacetate |
| L02633 Benzyl isocyanate | A17289 2-Chloroethyl isocyanate |
| L20353 (1R,2R)-(-)-2-Benzyloxycyclohexyl isocyanate | L20226 (R)-(+)-(1-(4-Chlorophenyl)ethyl isocyanate |
| L20223 (1S,2S)-(+)-2-Benzyloxycyclohexyl isocyanate | L20227 (S)-(-)-1-(4-Chlorophenyl)ethyl isocyanate |
| L20224 (1R,2R)-(-)-Benzyloxycyclopentyl isocyanate | L15993 3-Chloropropyl isocyanate |
| L20225 (1S,2S)-(+)-2-Benzyloxycyclopentyl isocyanate | L20228 (R)-(-)-1-Cyclohexylethyl isocyanate |
| L20321 (R)-(+)-1-(4-Bromophenyl)ethyl isocyanate | L20229 (S)-(+)-1-Cyclohexylethyl isocyanate |
| L20322 (S)-(-)-1-(4-Bromophenyl)ethyl isocyanate | B23059 Cyclohexyl isocyanate |
| L11836 (+/-)-1-(4-Bromophenyl)ethyl isocyanate | L13380 1-Dodecyl isocyanate |
| L05664 1-Butyl isocyanate | B25180 Ethyl isocyanate |
| L13371 tert-Butyl isocyanate | L10609 Ethyl isocyanatoacetate |
| | L12751 Ethyl 6-isocyanatohexanoate |
| | L09988 Ethyl 2-isocyanato-3-methylbutyrate |
| | L13059 Ethyl 2-isocyanato-4-(methylthio)butyrate |

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Alkyl and aralkyl monoisocyanates con't

L11613 Ethyl 2-isocyanato-4-methylvalerate
L10993 Ethyl 2-isocyanato-3-phenylpropionate
L09367 Ethyl 2-isocyanatopropionate
L09616 Ethyl 3-isocyanatopropionate
L20230 (R)-(+)-1-(4-Fluorophenyl)ethyl isocyanate
L20231 (S)-(-)-1-(4-Fluorophenyl)ethyl isocyanate
B21793 1-Heptyl isocyanate
L20232 (R)-(-)-2-Heptyl isocyanate
L20233 (S)-(+)-2-Heptyl isocyanate
L20234 (R)-(-)-2-Hexyl isocyanate
L20235 (S)-(+)-2-Hexyl isocyanate
L20237 (R)-(-)-1-Indanyl isocyanate
L20238 (S)-(+)-1-Indanyl isocyanate
A12890 (3-Isocyanatopropyl)triethoxysilane
L16105 Isopropyl isocyanate
L20330 (R)-(+)-1-(3-Methoxyphenyl)ethyl isocyanate
L20331 (S)-(-)-1-(3-Methoxyphenyl)ethyl isocyanate
L20239 (R)-(+)-1-(4-Methoxyphenyl)ethyl isocyanate
L20240 (S)-(-)-1-(4-Methoxyphenyl)ethyl isocyanate

L20241 (R)-(-)-3-Methyl-2-butyl isocyanate
L20354 (S)-(+)-3-Methyl-2-butyl isocyanate
L12286 (R)-(+)-1-(1-Naphthyl)ethyl isocyanate
L20242 (S)-(-)-1-(1-Naphthyl)ethyl isocyanate
L20236 (R)-(-)-2-Nonyl isocyanate
L20243 (S)-(+)-2-Nonyl isocyanate
L18745 1-Octadecyl isocyanate
L18746 1-Octyl isocyanate
L20244 (R)-(-)-2-Octyl isocyanate
L20245 (S)-(+)-2-Octyl isocyanate
L18706 tert-Octyl isocyanate
L13399 1-Pentyl isocyanate
L10305 (R)-(+)-1-Phenylethyl isocyanate
L11141 (S)-(-)-1-Phenylethyl isocyanate
L20355 (R)-(+)-1-Phenylpropyl isocyanate
L20246 (S)-(-)-1-Phenylpropyl isocyanate
L18707 1-Tetradecyl isocyanate
L10370 Trichloromethyl isocyanate

Alkyl diisocyanates

43803 1,6-Diisocyanatohexane
L13759 Isophorone diisocyanate

43803 1,6-Diisocyanatohexane
L13759 Isophorone diisocyanate

Aryl monoisocyanates

L12030 3-Acetylphenyl isocyanate
L09665 4-Acetylphenyl isocyanate
L18714 3,5-Bis(methoxycarbonyl)phenyl isocyanate
L09582 3,5-Bis(trifluoromethyl)phenyl isocyanate
L11095 4-Bromo-2-methylphenyl isocyanate
L12521 2-Bromophenyl isocyanate
L12292 3-Bromophenyl isocyanate
L10834 4-Bromophenyl isocyanate
L09375 4-Bromo-2,6-dimethylphenyl isocyanate
L18716 2-(n-Butoxycarbonyl)phenyl isocyanate
L10606 4-(n-Butoxycarbonyl)phenyl isocyanate
L12877 4-n-Butoxyphenyl isocyanate
L12640 2-tert-Butyl-6-methylphenyl isocyanate
L09957 4-n-Butylphenyl isocyanate
L12955 5-Chloro-2,4-dimethoxyphenyl isocyanate
L10891 3-Chloro-4-fluorophenyl isocyanate
B22395 5-Chloro-2-methoxyphenyl isocyanate
L15995 2-(Chloromethyl)phenyl isocyanate
L11645 2-Chloro-6-methylphenyl isocyanate
L10802 3-Chloro-2-methylphenyl isocyanate

L12064 3-Chloro-4-methylphenyl isocyanate
L18711 4-(Chloromethyl)phenyl isocyanate
L10470 4-Chloro-2-methylphenyl isocyanate
L11567 5-Chloro-2-methylphenyl isocyanate
L12685 2-Chloro-4-nitrophenyl isocyanate
L15994 2-Chloro-5-nitrophenyl isocyanate
L11087 4-Chloro-3-nitrophenyl isocyanate
B21489 2-Chlorophenyl isocyanate
L11483 3-Chlorophenyl isocyanate
A14966 4-Chlorophenyl isocyanate
L09899 2-Chloro-5-(trifluoromethyl)phenyl isocyanate
L09850 4-Chloro-2-(trifluoromethyl)phenyl isocyanate
L12016 4-Chloro-3-(trifluoromethyl)phenyl isocyanate
L09432 3-Cyanophenyl isocyanate
L18744 2,6-Dibromo-4-fluorophenyl isocyanate
L18713 2,4-Dibromophenyl isocyanate
L14780 2,3-Dichlorophenyl isocyanate
L11089 2,4-Dichlorophenyl isocyanate
L09735 2,5-Dichlorophenyl isocyanate
L10421 2,6-Dichlorophenyl isocyanate

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A16298 3,4-Dichlorophenyl isocyanate
A19991 3,5-Dichlorophenyl isocyanate
L11339 2,6-Diethylphenyl isocyanate
A12415 2,4-Difluorophenyl isocyanate
L15996 2,5-Difluorophenyl isocyanate
L14779 2,6-Difluorophenyl isocyanate
L10613 2,6-Diisopropylphenyl isocyanate
L09762 2,4-Dimethoxyphenyl isocyanate
L11381 2,5-Dimethoxyphenyl isocyanate
L10443 4,5-Dimethyl-2-nitrophenyl isocyanate
L10225 2,3-Dimethylphenyl isocyanate
L11126 2,4-Dimethylphenyl isocyanate
L15999 2,5-Dimethylphenyl isocyanate
L12805 2,6-Dimethylphenyl isocyanate
L15998 3,4-Dimethylphenyl isocyanate
L11698 3,5-Dimethylphenyl isocyanate
L09560 2-(Ethoxycarbonyl)phenyl isocyanate
L09495 3-(Ethoxycarbonyl)phenyl isocyanate
L10681 4-(Ethoxycarbonyl)phenyl isocyanate
L11299 2-Ethoxyphenyl isocyanate
L11509 4-Ethoxyphenyl isocyanate
L15252 2-Ethylphenyl isocyanate
L12699 3-Ethylphenyl isocyanate
L12718 4-Ethylphenyl isocyanate
A17466 2-Fluorophenyl isocyanate
L01496 3-Fluorophenyl isocyanate
A12576 4-Fluorophenyl isocyanate
L16000 4-Iodophenyl isocyanate
L16002 3-Isocyanatobenzoyl chloride
L12703 2-Isopropyl-6-methylphenyl isocyanate
L10618 2-Isopropylphenyl isocyanate
L11217 4-Isopropylphenyl isocyanate
L12471 2-(Methoxycarbonyl)phenyl isocyanate

Aryl diisocyanates

L18712 4-Chloro-6-methyl-m-phenylene diisocyanate
L15740 4,4'-Methylenebis(phenyl isocyanate)

Acyl isocyanates

A11583 Benzoyl isocyanate
L00301 Chloroacetyl isocyanate

Sulfonyl isocyanates

L11182 Benzenesulfonyl isocyanate
L10019 4-Chlorobenzenesulfonyl isocyanate

L18709 3-(Methoxycarbonyl)phenyl isocyanate
L16001 2-Methoxy-5-methylphenyl isocyanate
L12086 4-Methoxy-2-methylphenyl isocyanate
A18075 2-Methoxyphenyl isocyanate
B24329 3-Methoxyphenyl isocyanate
A16805 4-Methoxyphenyl isocyanate
L19476 Methyl isocyanate, polymer-supported
L10636 2-Methyl-3-nitrophenyl isocyanate
L18715 2-Methyl-4-nitrophenyl isocyanate
L10850 2-Methyl-5-nitrophenyl isocyanate
L10757 4-Methyl-2-nitrophenyl isocyanate
L12669 4-Methyl-3-nitrophenyl isocyanate
L12008 3-(Methylthio)phenyl isocyanate
L12263 4-(Methylthio)phenyl isocyanate
A17200 1-Naphthyl isocyanate
A17210 2-Nitrophenyl isocyanate
A16920 3-Nitrophenyl isocyanate
A11194 4-Nitrophenyl isocyanate
L11686 4-Phenoxyphenyl isocyanate
A12808 Phenyl isocyanate
L12247 o-Tolyl isocyanate
L15255 m-Tolyl isocyanate
A13577 p-Tolyl isocyanate
L16003 2,4,6-Trichlorophenyl isocyanate
B20033 4-(Trifluoromethoxy)phenyl isocyanate
L11156 2-(Trifluoromethyl)phenyl isocyanate
L09448 3-(Trifluoromethyl)phenyl isocyanate
L12576 4-(Trifluoromethyl)phenyl isocyanate
L19206 4-(Trifluoromethylthio)phenyl isocyanate
L19349 2,4,6-Trifluorophenyl isocyanate
L09775 3,4,5-Trimethoxyphenyl isocyanate
L12611 2,4,6-Trimethylphenyl isocyanate

L04642 1,3-Phenylene diisocyanate
36733 Toluene-2,4-diisocyanate
L12745 Toluene-2,6-diisocyanate

L00226 Trichloroacetyl isocyanate

A17492 p-Toluenesulfonyl isocyanate

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