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SUPERBASES IN ORGANIC SYNTHESIS

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Abstract: *In this concise review, an emphasis is laid on the important role of superbases as catalysts and reagents in organic synthesis that so far remain underestimated. Diverse approaches to understand the superbasicity phenomenon are considered and the definition of superbase is given. Typical compositions of most widespread superbase systems are systematized and tabulated. The representative classic organic reactions assisted by superbases are surveyed.*
Keywords: *superbases, organic synthesis, the acid-base interaction, catalysts*

1. Introduction

The proton transfer reaction (the acid-base interaction) stands second among the most important fundamental chemical reactions (after the electron transfer). Acids and bases are most versatile catalysts and reagents in transformations of organic and inorganic matter. That's why the controlling proton transfer processes is a key to the targeted synthesis of compounds and materials with tailor-made properties. The superbase catalysts and reagents are now all more widely used in organic synthesis due to their fundamental simplicity, accessibility, efficacy and ecological neutrality as compared to more sophisticated and less "greener" transition and heavy metal-tailored synthetic auxiliaries. In the light of growing importance of ecological agenda, superbases mostly designed on alkaline metal cations, particularly on biologically friendly Na^+ and K^+, and anions such as OH^-, OR^- and N_2^-, deserve to be revisited.

2. Superbase media: what does it mean? A short historical survey

Although organic reactions in the presence of strong bases (carbanion chemistry) are as important and as widely distributed as acid-catalyzed processes (carbocation and onium cation chemistry), the term 'superbase' has appeared much later than the term 'superacid'. The latter, seemingly, was introduced by Gillespie in 1972 [3, 4], who defined superacids as systems more acidic than sulfuric acid, i.e., systems with acidity function H_0 of less than –12. In the glossary of physical organic chemistry (1982) [5] this definition was given with a remark that the superacid is the system composed of a Bronsted acid and a Lewis acid.

$$\underset{\text{Bronsted acid}}{HA} + \underset{\text{Lewis acid}}{X} \rightleftharpoons \underset{\text{superacid}}{H^+[AX]^-}$$

An example of such system is a mixture of fluorosulfonic acid and antimony pentafluoride (the 'magic' acid), having the acidity function $H_0 < –30$, which is 18 orders more acidic than sulfuric acid [4, 6, 7].

$$HSO_3F + SbF_5 \rightleftharpoons \underset{\text{"magic" acid}}{H^+[SbF_5SO_3F]^-}$$

Of interest is the fact that the above mentioned glossary still lacked a definition of the term 'superbase'.

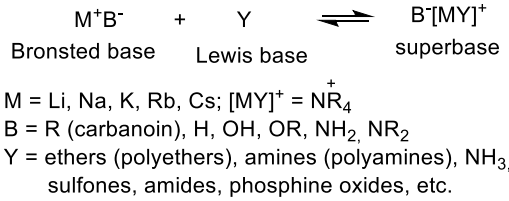
The superbasicity concept has been defined (1977) [8] and systematically developed on an example of acetylene chemistry [9-12] by the Irkutsk branch of Academician A. E. Favorsky's school. In the joint monograph 'Fundamental investigations. Chemical sciences' (1977) [8] we for

the first time defined superbases as follows: “A superbase medium is the medium composed of a strong base and a solvent or reagent (ligand) capable of specific binding (coordinating) cation to form the ‘naked’ conjugated counter-anion...”.

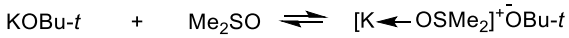
3. How to compose superbases?

Obviously, in the light of this concept, the superbasicity definition is in accord with the ‘mirror reflection’ of the superacidity term: a superbase is the complex of a strong ionized base

(Bronsted base) with a ligand which interacts specifically with this base’s cation (Lewis base) in a poorly anion-solvating medium (as a rule, in the medium of a polar non-hydroxylic solvent[**]) [8-12].



A typical superbase is, for example, the system KOBu-*t*-dimethyl sulfoxide (DMSO), in which the potassium cation is complexed by DMSO molecules (see experimental and quantum chemical 4-3G evidences, for example, in [13]), while the poorly solvated *t*-butoxy anion (see experimental and quantum chemical 4-3G evidences of increasing anion activity in DMSO, for example, in [14]) provides a basicity (pK_a = 32.2) [15], which is 14 orders higher than that of aqueous or alcohol alkali solutions.



The most common cations in such systems are alkali metal- or tetralkylammonium cations. Examples of anions (Bronsted bases) are carbanions, hydride ion, hydroxide-, alkoxide- and amide anions, and ligands (Y) are such typical Lewis bases as ethers (polyethers), crown ethers, amines (polyamines), liquid ammonia, phosphines, cryptands, sulfoxides, sulfones, amides, phosphine oxides, and so on.

In other words, superbases are solvent-separated ion pairs of strong bases or their synergetic complexes both with themselves and with weaker Lewis bases, possessing enhanced anion activities (owing to the weakening of their interaction with cations).

Quaternary ammonium bases in two-phase aqueous-organic alkaline media (phase-transfer catalysis) represent a special kind of superbase systems: the hydroxide ion weakly interacts with a bulky organic cation and remains virtually unsolvated by a hydrocarbon (most often used organic phase). Such systems may provide basicity comparable with that of typical superbases (pK_a = 34-41) [10, 16].

4. Representative classic reactions assisted by superbases

Superbase systems are widely applied in organic synthesis. Indeed, their use as catalysts and reagents had started long before the term appeared and the superbasicity concept was formulated.

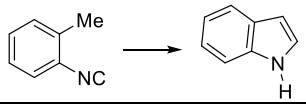
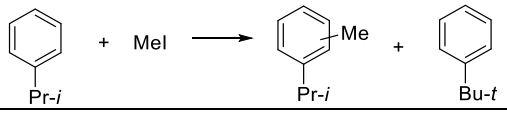
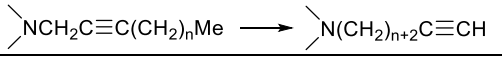
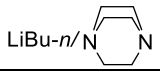
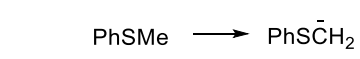
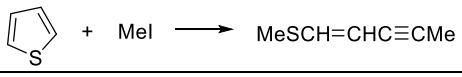
Among superbase media, the systems “alkali metal amide – liquid ammonia” are ‘veterans’ with a nearly 200 year experience. They were introduced in chemistry yet by Davi and Gey Lussac (see references to original works in [17]). A fundamental investigation of the system $KNH_2/NH_{3\ liq.}$ was carried out by Shatenshtein [18, 19] who extensively used it for determination of kinetic acidity of CH-acids, including such weak ones as parafinic hydrocarbons. Advantages and drawbacks of these superbases are now well known. They are most widely and systematically utilized for carrying

[**] A common term ‘aprotonic dipolar’ solvent cannot be considered correct as the majority of such solvents are typical CH-acids (i.e., they are not aprotonic), while the ‘dipolarity’ (the existence of a dipol) is a common property of any polar molecule.

out elimination, substitution and addition reactions with participation of highly unsaturated heteroatomic compounds [20].

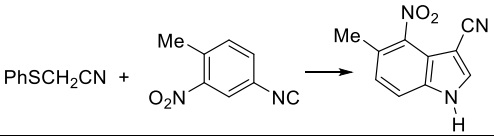
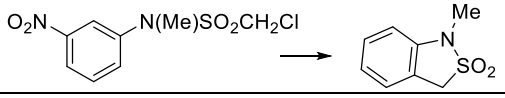
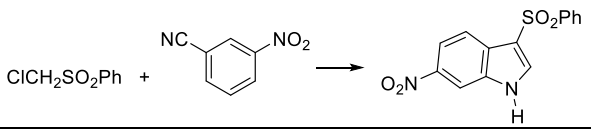
Typical superbase systems and examples of reactions they promote are presented in Tables 1-3.

Table 1. Typical lithium-tailored superbase systems and reactions with their assistance

Base	Reaction	Reference
$LiN(Pr\text{-}i)_2$		[21]
LiOBu-*t*/DMSO	$ClCH_2SO_2Ph + PhNO_2 \longrightarrow NO_2C_6H_4CH_2SO_2Ph$	[22]
LiR/KOR′ R = Me, Bu-*n*, Bu-*t*, Bu-*s*; R′ = Bu-*t*, Pr-*n*, Et_2CH, Et_3C, Et_2N		[23]
$LiNH(CH_2)_2NH_2/H_2N(CH_2)_2NH_2$		[24]
		[25]
LiBu-*n*/[2,2,2]-cryptand		[26]
$LiN(SiMe_3)_2$/HMPA[a]/18-crown-6/THF		[27]

[a] Hexamethylphosphoramide.

Table 2. Typical sodium-tailored superbase systems and reactions with their assistance

$NaOH/NH_3$		[28]
NaOH/DMSO	$ClCH_2SO_3R + PhNO_2 \longrightarrow O_2NC_6H_4CH_2SO_3R$ R = Am-*neo*, Ph	[29]
	$(PhS)_3CH + PhNO_2 \longrightarrow p\text{-}O_2NC_6H_4CH(SPh)_2$	[30]
		[31]
		[28]
	$ClCH_2CN + PhNO_2 \longrightarrow O_2NC_6H_4CH_2CN$	[32]
$NaOH/DMSO/[^+NEt_3Bz]^-OH$	$Ph(R')CHCN + RC{\equiv}CH \longrightarrow Ph(R')(CN)CCH{=}CHR$ R = H, Ph; R' = Alk, Bz, $Et_2N(CH_2)_2$	[33]
NaOMe/DMSO	$(MeO)_2CHC{\equiv}CMe \longrightarrow MeOCH{=}CHC(OMe){=}CH_2$	[34]

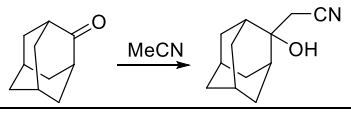
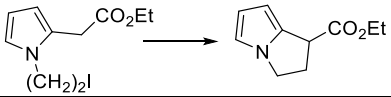
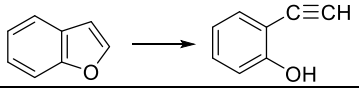
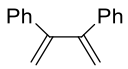
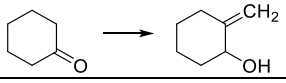
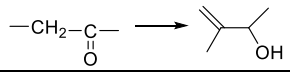
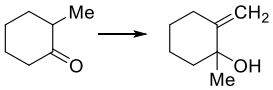
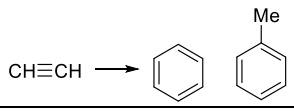
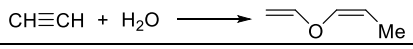
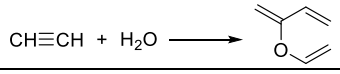
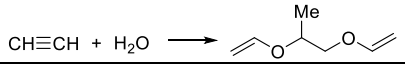
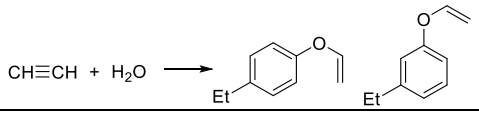
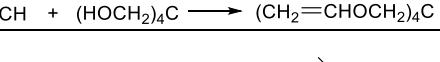
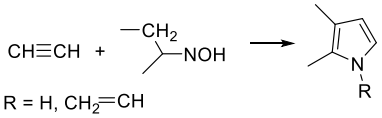
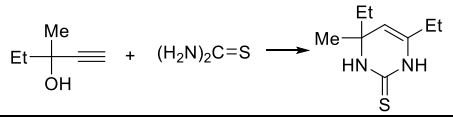
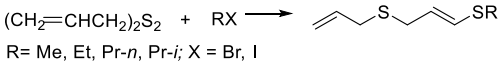
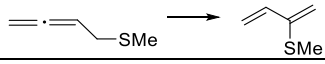
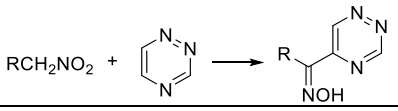
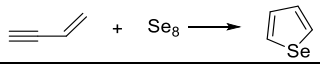
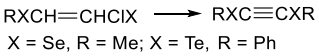
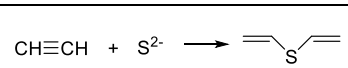
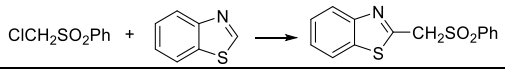
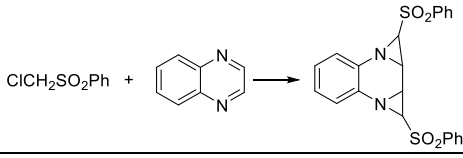
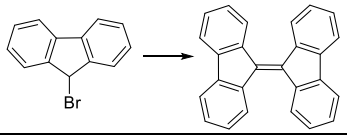
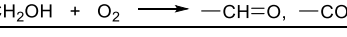
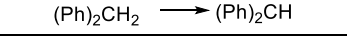
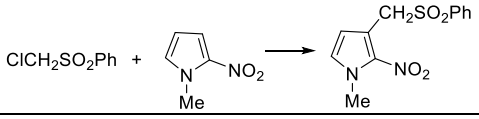
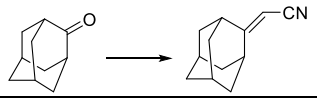
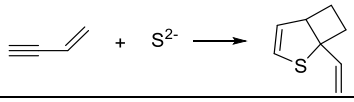
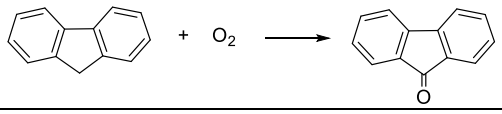
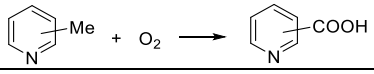
NaOAm-*t*/[2,2,2]-cryptand	$(Ph)_2CH_2 \longrightarrow (Ph)_2\bar{C}H$	[26]
$NaNH_2$/THF/[2,2,2]-cryptand	$(Ph)_2CH_2 \longrightarrow (Ph)_2\bar{C}H$	[26]
NaH/DMSO	$PhSCH_2CO_2Me + PhNO_2 \longrightarrow O_2NC_6H_4CH_2CO_2Me$	[32]
		[35]
NaH/DMF		[36]
$NaCH_2SOMe$/DMSO		[37]
		[37]
	$PhC{\equiv}CPh \longrightarrow$ 	[38]
	$PhC{\equiv}CH + CO_2 \longrightarrow PhC{\equiv}CCO_2H$	[39]
$NaNH(CH_2)_3NH_2/H_2N(CH_2)_3NH_2$	$N(CH_2){\equiv}CH(CH_2)_nMe \longrightarrow N(CH_2)_{n+2}C{\equiv}CH$	[40]

Table 3. Typical potassium-tailored superbase systems and reactions with their assistance

KOH/DMSO	$(Ph)_3CH \longrightarrow (Ph)_3\bar{C}$	[41]
	$(Ph)_2CH_2 \longrightarrow (Ph)_2\bar{C}H$	[41]
		[42]
		[43]
		[44]
	$(ClCH_2CH_2O)_2CH_2 \longrightarrow (CH_2{=}CHO)_2CH_2$	[45]
	$t\text{-}BuCH_2CHBrCl \longrightarrow t\text{-}Bu{-}{\equiv}$	[46]
		[47]
		[48]

		[47-50]
		[51]
		[52]
		[53]
		[10, 11]
		[54]
		[55]
		[56]
		[57]
		[12, 58]
		[59]
		[12, 60]
		[61]
		[61]
KOH/DMSO/MeOH		[62]
KOH/DMSO/18-crown-6		[63]
KOH/DMSO/[2,2,2]-criptand		[26]
KOH/NH_3		[64]

KOH/MeCN		[35]
KOH/HMPA[a]	$CH{\equiv}CH + H_2S \longrightarrow EtSH$	[60]
KOH/$Et_3P{=}O$		[58]
KOH[a](NaOH)[b]/RY [$(CHR^1)_mY]_nR^c$/C_6H_6[d] R, R^1 = H, Alk C_1-C_4; Y = O, S; m, n ≥ 1	$ArCH_2CN + ClPr\text{-}i \longrightarrow ArCH(Pr\text{-}i)CN$	[65]
KOH/$MeO(CH_2)_2OMe$	$-CH{=}O + O_2 \longrightarrow -COOH$	[66]
KOH/THF/18-crown-6	$PhSeC(Ph){=}C(Me)SO_2Ar \longrightarrow PhCH{=}C(CH_2OH)SO_2Ar$ (O)	[67]
KOH/THF/ [2,2,2]-criptand		[26]
KOH/Me_2SO_2/HOBu-*t*	$CCl_4 \longrightarrow :CCl_2$	[68]
KOBu-*t*/DMSO	$H_2C{=}CHCH_2OR \longrightarrow CH_3CH{=}CHOR$ R = Ph, C_6H_{13}-*n*, Bu-*t*, $HO(CH_2)_3$, $HOCH_2CH(Me)$	[69]
	$CH{\equiv}CH + AlkSSAlk \longrightarrow AlkSCH{=}CHSAlk$	[12, 70]
KOBu-*t*/DMF		[71]
KOBu-*t*/HOBu-*t*/Et_2O/ 	$MeC_6H_4SCH_2Cl + C{=}O \longrightarrow SC_6H_4Me$ (O)	[72]
KHNPh/dioxane	$CH{\equiv}CH + H_2NPh \longrightarrow PhNHCH(Me)C{\equiv}CH$	[73]
KN(Ar)COMe/THF	$CH{\equiv}CH + ArNHCOMe \longrightarrow ArNHCH(Me)C{\equiv}CH$	[74, 75]

[a] 96% KOH. [b] Particle size 100-500 micrometers; prepared by stirring at a rate of 500-10000 rpm (better if ultrasound is simultaneously applied) at 140°C. [c] Also oligomers of polyoxyethylene type, quaternary ammonium salts, macromolecular amines, ZrO_2, TiO_2. [d] Also, there are toluene, xylene and other organic solvents with b. p. > 100°C.

Thus, to superbases we assigned [76, 77] the systems having the Hammet acidity function ($H\_$) over 18.5, i.e., systems with basicities which cannot be achieved in hydroxyl-containing solvents (water and alcohols) due to limitations imposed by the acidity of the medium itself. Earlier, Bouden [78] added to highly basic systems diluted solutions of alkali metal hydroxides or alkoxides in DMSO and its mixtures with water and alcohols, which could ionize acids in a higher degree than 0.1 M aqueous alkalis. Superbases of the type "alkali metal alkoxide – DMSO (H_2O, alkanol)" have been used for building acidity scales since 60-s (see, for example, [79] and references therein).

Quantitative and physical chemical characteristics of some superbase media (mainly, solutions of bases in DMSO) are given in reviews of Buncel and Wilson [80], Cox and Yates [81], and in the work of Arnett [17]. There is no opportunity to describe in detail the quantitative superbasicity aspect in this article. It should only be noted that this problem still has no acceptable common solution [79]: in fact, due to the approximate character of the Hammet postulate, one has to build its own acidity scale for each system. As a result, for example, in the review [81], over 400 scales of different acidity functions are compared.

pK_a values of conjugated acids of most superbases lie within an interval of 30-40 (Table 4), that corresponds approximately to the same acidity function $H\_$ interval.

Table 4. pK_a Values of conjugated acids of some superbases

Superbase	pK_a
LiN(Pr-*i*)$_2$/THF	40 [82]
LiN(Pr-*i*)$_2$/HN(Pr-*i*)$_2$	40 [17]
LiNEt$_2$/HMPA/C_6H_6	38-40 [83, 84]
NaCH$_2$SOMe/DMSO	> 30 [39]
NaNH$_2$/NaOBu-*t*/THF	> 32 [85]
KOH/DMSO	31.4 [86] (30.5)[a] [41]
KOBu-*t*/DMSO	32.2 [86] (~30) [41]
KCH$_2$SOMe/DMSO	35.1 [86] (32-34)[b]
K/NMP[c]	31 [87]
KHN(CH$_2$)$_3$NH$_2$/H$_2$N(CH$_2$)$_3$NH$_2$ (KAPA)	40 [88, 89]
CsNHC$_6$H$_{11}$ (*cyclo*)/H$_2$NC$_6$H$_{11}$ (*cyclo*)	40 [88, 89]

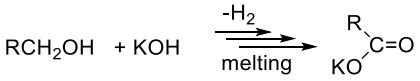
[a] Hereinafter in brackets are given values of acidity function (H_-). [b] Depending on the base concentration (0.01-1.0 M). [c] *N*-Methylpyrrolidone.

Some aspects of strong basicity increase in polar non-hydroxylic solvents (mainly in DMSO) and the use of such systems in organic synthesis are covered in monographs [79, 90-93].

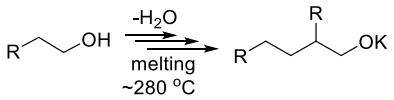
The highest basicity (H_- ~40) is exhibited by systems of the "alkyllithium – potassium *t*-alkoxide" (LIKOR) type which had first been introduced into the chemical practice by Lochmann [94] and Schlosser [95]. The synergism of two strong bases in this case is due to the same effect of additional binding of cations due to the formation of associates (weakly bound complexes) [96-99]. The literature concerning these systems is numerous today and continues to expand rapidly (for example, see reviews [100-102]). Brandsma [103] has shown that the basicity of LIKOR reagents can be increased even more by adding a third base, tetramethylethylenediamine (TMEDA). For example, the triple system BuLi/*t*-BuOK/TMEDA is capable of metallating ethylene [103]. At the same time, basicities of pairs BuLi/TMEDA [104] and BuNa/TMEDA [105] are insufficient for this purpose, although they are capable of deprotonating benzene and toluene, respectively.

Preparative aspects of LIKOR reagents and their various modifications have been comprehensively studied by the Brandsma school [106-111].

Meanwhile, a look into the past makes us recall Ecclesiastes: *"Is there any thing whereof it may be said, See, this is new? it hath been already of old time, which was before us"* (Eccl. 1, 10). In fact, for example, almost forgotten Dumah-Stass reactions of alcohol dehydration (into acid salts) [112]:

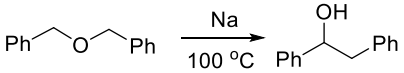


or Markownikoff-Zubov [113] or Herbe [114] dimerization of alcohols:

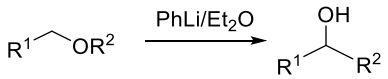


in the presence of melted alkali can quite be qualified as processes proceeding under the action of superbases: alcoholate plays the role of complex-forming agent toward the alkali metal cation.

Shorigin rearrangement (transformation of ethers into alcohols in the presence of sodium metal) [115] can also be considered as process proceeding under the effect of superbases.

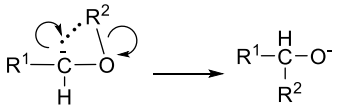


Carbanion formed upon the interaction of sodium with the methylene group (which acts as a CH-acid) here plays the role of a base, while the complex-forming agent toward the sodium cation is ether itself. Almost 20 years later Wittig repeated this reaction using another superbase system, phenyllithium-ether [116]. Since then this rearrangement has been bearing his name.



Today this rearrangement can be successfully effected with such typical superbases as sodium or potassium amide in liquid ammonia.

The driving force of the rearrangement is high thermodynamical stability of the alkoxide ion as compared to the carbanion:



In recent years, superbase media occupied significant place in the chemistry of acetylene enriching it with principally new reactions, approaches, and concepts (*See*, for instance, monographs and reviews [117-123]). The major achievements in this area will be considered in our follow-up reviews.

Summary

In conclusion, this compact survey, covering different aspects of superbasicity and its place in organic chemistry, represents a concise introduction to the superbase-assisted synthesis. The survey sets an aim to attract attention to a wider application of this powerful synthetic tool, which, due to its simplicity, availability and ecological neutrality, has robust prospects to replace more sophisticated and environmentally dangerous transition- and heavy metal-based technologies.

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СУПЕРОСНОВАНИЯ В ОРГАНИЧЕСКОМ СИНТЕЗЕ

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Аннотация: В этом кратком обзоре обращено внимание на важную роль суперосновaний как катализаторов и реагентов в органическом синтезе, которая до настоящего времени остается недооцененной. Рассмотрены различные подходы к пониманию феномена сверхосновности. Типовые составы наиболее распространенных сверхосновных систем систематизированы и сведены в таблицы. Рассмотрены типичные классические органические реакции, в которых участвуют супероснования**.**
Ключевые слова: *супероснования, органический синтез, кислотно-основное взаимодействие, катализаторы*

ÜZVİ SİNTEZDƏ SUPERƏSASLAR

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Xülasə**:** Bu qısa icmal, indiyədək lazımi səviyyədə qiymətləndirilməmiş üzvi sintezdə katalizator və reagent kimi super əsasların mühüm roluna diqqət çəkir. Superəsas fenomenini başa düşmək üçün müxtəlif yanaşmalar nəzərdən keçirilir və onun tərifi verilir. Ən çox yayılmış superəsas sistemlərin tipik kompozisiyaları sistemləşdirilmiş və cədvəllərdə ümumiləşdirilmişdir. Superəsasların iştirak etdiyi tipik klassik üzvi reaksiyalar nəzərdən keçirilir.
Açar sözlər: superəsaslar, üzvi sintez, turşu-qələvi qarşılıqlı təsiri, katalizator