

UDC 541.644; 547.245

## SUPERBASES IN ORGANIC SYNTHESIS

**B.A. Trofimov, E.Yu. Schmidt**

*A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,  
1 Favorsky St., Irkutsk, 664033, Russia*

*Received 06.07.2022*

*Accepted 09.09.2022*

**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*

**DOI:** 10.32737/2221-8688-2022-3-325-340

### 1. Introduction

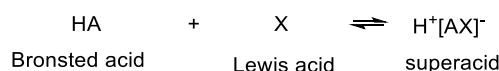
The proton transfer reaction (the acid-base interaction) stands second among the most important fundamental chemical reactions (after the electron transfer). Acids and bases are most versatile catalysts and reagents in transformations of organic and inorganic matter. That's why the controlling proton 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  $\text{Na}^+$  and  $\text{K}^+$ , and anions such as  $\text{OH}^-$ ,  $\text{OR}^-$  and  $\text{N}_2^-$ , deserve to be revisited.

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

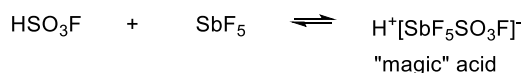
Although organic reactions in the presence of strong bases (carbanion chemistry) are as important and as widely distributed as acid-catalyzed processes (carbocation and onium cation chemistry), the term 'superbase' has appeared much later than the term 'superacid'. The latter, seemingly, was introduced 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.



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].



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

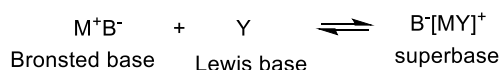
The superbasicity concept has been defined (1977) [8] and systematically developed on an example of acetylene chemistry [9-12] by the Irkutsk branch of Academician A. E. Favorsky's school. In the joint monograph

'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].



M = Li, Na, K, Rb, Cs; [MY]<sup>+</sup> = NR<sub>4</sub><sup>+</sup>

B = R (carbanion), H, OH, OR, NH<sub>2</sub>, NR<sub>2</sub>

Y = ethers (polyethers), amines (polyamines), NH<sub>3</sub>, cryptands, sulfoxides, sulfones, amides, phosphine oxides, etc.

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<sub>a</sub> = 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).

\*\* A common term 'aprotic dipolar' solvent cannot be considered correct as the majority of such solvents are typical CH-acids (i.e., they are not aprotic), while the 'dipolarity' (the existence of a dipole) is a common property of any polar molecule.

Such systems may provide basicity = 34-41) [10, 16]. comparable with that of typical superbases ( $pK_a$

#### 4. Representative classic reactions assisted by superbases

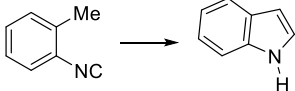
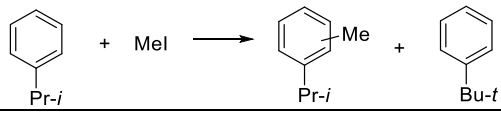

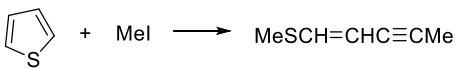
Superbase systems are widely applied in organic synthesis. Indeed, their use as catalysts and reagents had started long before the term appeared and the superbasicity concept was formulated.

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  $\text{KNH}_2/\text{NH}_3$  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 out elimination, substitution and addition reactions with participation of highly unsaturated heteroatomic compounds [20].

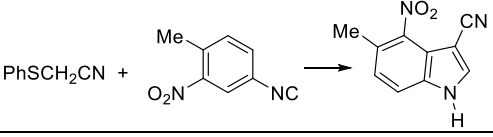
Typical superbase systems and examples of reactions they promote are presented in Tables 1-3.

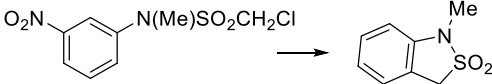
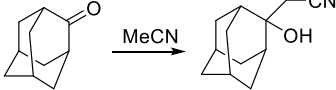
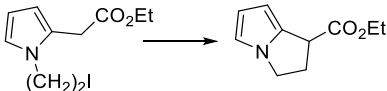
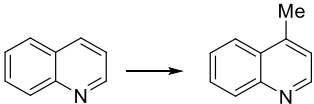
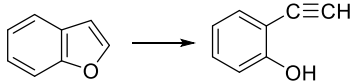
**Table 1.** Typical lithium-tailored superbase systems and reactions with their assistance

Base	Reaction	Reference
$\text{LiN}(\text{Pr-}i)_2$		[21]
$\text{LiOBu-}t/\text{DMSO}$	$\text{ClCH}_2\text{SO}_2\text{Ph} + \text{PhNO}_2 \longrightarrow \text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Ph}$	[22]
$\text{LiR}/\text{KOR}'$ R = Me, Bu- <i>n</i> , Bu- <i>t</i> , Bu- <i>s</i> ; R' = Bu- <i>t</i> , Pr- <i>n</i> , Et <sub>2</sub> CH, Et <sub>3</sub> C, Et <sub>2</sub> N		[23]
$\text{LiNH}(\text{CH}_2)_2\text{NH}_2/\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$	$\text{N}(\text{CH}_2)_n\text{C}\equiv\text{C}(\text{CH}_2)_n\text{Me} \longrightarrow \text{N}(\text{CH}_2)_{n+2}\text{C}\equiv\text{CH}$	[24]
$\text{LiBu-}n/\text{N}$ 	$\text{PhSMe} \longrightarrow \text{PhS}^-\text{CH}_2$	[25]
$\text{LiBu-}n/[2,2,2]\text{-cryptand}$	$(\text{Ph})_2\text{CH}_2 \longrightarrow (\text{Ph})_2\text{C}^-\text{H}$	[26]
$\text{LiN}(\text{SiMe}_3)_2/\text{HMPA}^a/18\text{-crown-}6/\text{THF}$		[27]

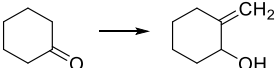
<sup>a</sup> Hexamethylphosphoramide.

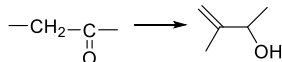
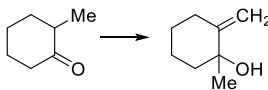
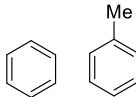
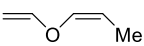

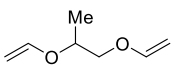
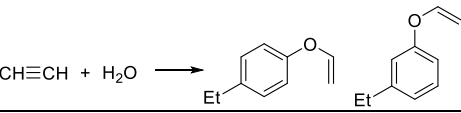
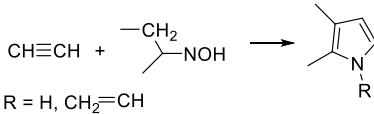
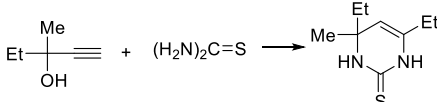
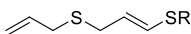
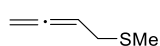
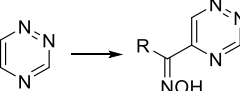

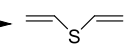
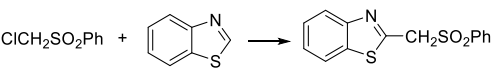
**Table 2.** Typical sodium-tailored superbase systems and reactions with their assistance

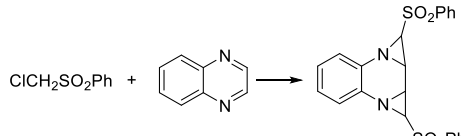
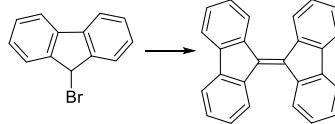
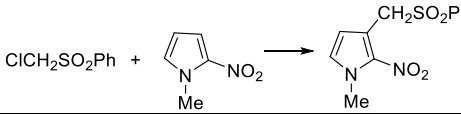
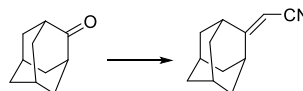
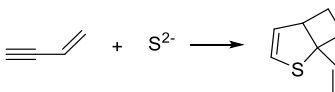
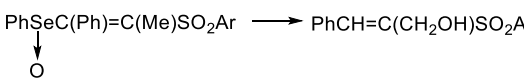
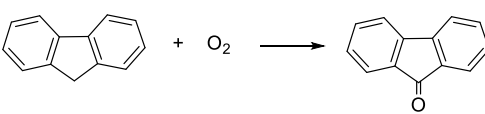
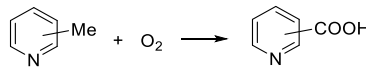

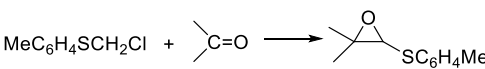
$\text{NaOH}/\text{NH}_3$		[28]
$\text{NaOH}/\text{DMSO}$	$\text{ClCH}_2\text{SO}_3\text{R} + \text{PhNO}_2 \longrightarrow \text{O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{SO}_3\text{R}$ R = Am- <i>neo</i> , Ph	[29]

	$(\text{PhS})_3\text{CH} + \text{PhNO}_2 \longrightarrow p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}(\text{SPh})_2$	[30]
		[31]
	$\text{ClCH}_2\text{SO}_2\text{Ph} + \text{NC-C}_6\text{H}_3(\text{NO}_2) \longrightarrow \text{O}_2\text{N-C}_6\text{H}_3(\text{SO}_2\text{Ph})$	[28]
	$\text{ClCH}_2\text{CN} + \text{PhNO}_2 \longrightarrow \text{O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CN}$	[32]
NaOH/DMSO/[ <sup>+</sup> NEt <sub>3</sub> Bz] <sup>-</sup> OH	$\text{Ph}(\text{R}')\text{CHCN} + \text{RC}\equiv\text{CH} \longrightarrow \text{Ph}(\text{R}')(\text{CN})\text{CCH}=\text{CHR}$ R = H, Ph; R' = Alk, Bz, Et <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub>	[33]
NaOMe/DMSO	$(\text{MeO})_2\text{CHC}\equiv\text{CMe} \longrightarrow \text{MeOCH}=\text{CHC}(\text{OMe})=\text{CH}_2$	[34]
NaOAm-t/[2,2,2]-cryptand	$(\text{Ph})_2\text{CH}_2 \longrightarrow (\text{Ph})_2\text{C}^-$	[26]
NaNH <sub>2</sub> /THF/[2,2,2]-cryptand	$(\text{Ph})_2\text{CH}_2 \longrightarrow (\text{Ph})_2\text{C}^-$	[26]
	$\text{PhSCH}_2\text{CO}_2\text{Me} + \text{PhNO}_2 \longrightarrow \text{O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{Me}$	[32]
NaH/DMSO		[35]
NaH/DMF		[36]
		[37]
NaCH <sub>2</sub> SOMe/DMSO		[37]
	$\text{PhC}\equiv\text{CPh} \longrightarrow \text{PhC}(\text{C}=\text{CPh})_2$	[38]
	$\text{PhC}\equiv\text{CH} + \text{CO}_2 \longrightarrow \text{PhC}\equiv\text{CCO}_2\text{H}$	[39]
NaNH(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> /H <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	$\text{N}(\text{CH}_2)\text{C}\equiv\text{CH}(\text{CH}_2)_n\text{Me} \longrightarrow \text{N}(\text{CH}_2)_{n+2}\text{C}\equiv\text{CH}$	[40]

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

	$(\text{Ph})_3\text{CH} \longrightarrow (\text{Ph})_3\text{C}^-$	[41]
KOH/DMSO	$(\text{Ph})_2\text{CH}_2 \longrightarrow (\text{Ph})_2\text{C}^-$	[41]
		[42]

		[43]
		[44]
	$(\text{ClCH}_2\text{CH}_2\text{O})_2\text{CH}_2 \longrightarrow (\text{CH}_2=\text{CHO})_2\text{CH}_2$	[45]
	$t\text{-BuCH}_2\text{CHBrCl} \longrightarrow t\text{-Bu}\text{---}\equiv$	[46]
	$\text{CH}\equiv\text{CH} \longrightarrow$ 	[47]
	$\text{CH}\equiv\text{CH} + \text{H}_2\text{O} \longrightarrow$ 	[48]
	$\text{CH}\equiv\text{CH} + \text{H}_2\text{O} \longrightarrow$ 	[47-50]
	$\text{CH}\equiv\text{CH} + \text{H}_2\text{O} \longrightarrow$ 	[51]
	$\text{CH}\equiv\text{CH} + \text{H}_2\text{O} \longrightarrow$ 	[52]
	$\text{CH}\equiv\text{CH} + (\text{HOCH}_2)_4\text{C} \longrightarrow (\text{CH}_2=\text{CHOCH}_2)_4\text{C}$	[53]
	$\text{CH}\equiv\text{CH} +$  R = H, CH <sub>2</sub> =CH	[10, 11]
		[54]
	$(\text{CH}_2=\text{CHCH}_2)_2\text{S}_2 + \text{RX} \longrightarrow$  R = Me, Et, Pr- <i>n</i> , Pr- <i>i</i> ; X = Br, I	[55]
		[56]
	$\text{RCH}_2\text{NO}_2 +$ 	[57]
	$\equiv\text{C} + \text{Se}_8 \longrightarrow$ 	[12, 58]
	$\text{RXCH}=\text{CHCX} \longrightarrow \text{RXC}\equiv\text{CXR}$ X = Se, R = Me; X = Te, R = Ph	[59]
	$\text{CH}\equiv\text{CH} + \text{S}^{2-} \longrightarrow$ 	[12, 60]
	$\text{ClCH}_2\text{SO}_2\text{Ph} +$ 	[61]

		[61]
KOH/DMSO/MeOH		[62]
KOH/DMSO/18-crown-6	$-\text{CH}_2\text{OH} + \text{O}_2 \longrightarrow -\text{CH}=\text{O}, -\text{COOH}$	[63]
KOH/DMSO/[2,2,2]-cryptand	$(\text{Ph})_2\text{CH}_2 \longrightarrow (\text{Ph})_2\text{C}^-$	[26]
KOH/NH <sub>3</sub>		[64]
KOH/MeCN		[35]
KOH/HMPA <sup>a</sup>	$\text{CH}\equiv\text{CH} + \text{H}_2\text{S} \longrightarrow \text{EtSH}$	[60]
KOH/Et <sub>3</sub> P=O		[58]
KOH <sup>a</sup> (NaOH) <sup>b</sup> /RY [(CHR <sup>1</sup> ) <sub>m</sub> Y] <sub>n</sub> R <sup>c</sup> /C <sub>6</sub> H <sub>6</sub> <sup>d</sup> R, R <sup>1</sup> = H, Alk C <sub>1</sub> -C <sub>4</sub> ; Y = O, S; m, n ≥ 1	$\text{ArCH}_2\text{CN} + \text{ClPr-}i \longrightarrow \text{ArCH(Pr-}i\text{)CN}$	[65]
KOH/MeO(CH <sub>2</sub> ) <sub>2</sub> OMe	$-\text{CH}=\text{O} + \text{O}_2 \longrightarrow -\text{COOH}$	[66]
KOH/THF/18-crown-6		[67]
KOH/THF/[2,2,2]-cryptand		[26]
KOH/Me <sub>2</sub> SO <sub>2</sub> /HOBu- <i>t</i>	$\text{CCl}_4 \longrightarrow \text{:CCl}_2$	[68]
KOBu- <i>t</i> /DMSO	$\text{H}_2\text{C}=\text{CHCH}_2\text{OR} \longrightarrow \text{CH}_3\text{CH}=\text{CHOR}$ R = Ph, C <sub>6</sub> H <sub>13-<i>n</i></sub> , Bu- <i>t</i> , HO(CH <sub>2</sub> ) <sub>3</sub> , HOCH <sub>2</sub> CH(Me)	[69]
	$\text{CH}\equiv\text{CH} + \text{AlkSSAlk} \longrightarrow \text{AlkSCH}=\text{CHSAIk}$	[12, 70]
KOBu- <i>t</i> /DMF		[71]
KOBu- <i>t</i> /HOBu- <i>t</i> /Et <sub>2</sub> O/ 		[72]
KHNPh/dioxane	$\text{CH}\equiv\text{CH} + \text{H}_2\text{NPh} \longrightarrow \text{PhNHCH(Me)C}\equiv\text{CH}$	[73]
KN(Ar)COMe/THF	$\text{CH}\equiv\text{CH} + \text{ArNHCOMe} \longrightarrow \text{ArNHCH(Me)C}\equiv\text{CH}$	[74, 75]

<sup>a</sup> 96% KOH. <sup>b</sup> Particle size 100-500 micrometers; prepared by stirring at a rate of 500-10000 rpm (better if ultrasound is simultaneously applied) at 140°C. <sup>c</sup> Also oligomers of polyoxyethylene type, quaternary ammonium salts, macromolecular amines, ZrO<sub>2</sub>, TiO<sub>2</sub>. <sup>d</sup> 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 Hammett 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 Buncl 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 Hammett 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>i</i> ) <sub>2</sub> /THF	40 [82]
LiN(Pr- <i>i</i> ) <sub>2</sub> /HN(Pr- <i>i</i> ) <sub>2</sub>	40 [17]
LiNEt <sub>2</sub> /HMPA/C <sub>6</sub> H <sub>6</sub>	38-40 [83, 84]
NaCH <sub>2</sub> SOMe/DMSO	> 30 [39]
NaNH <sub>2</sub> /NaOBu- <i>t</i> /THF	> 32 [85]
KOH/DMSO	31.4 [86] (30.5) <sup>a</sup> [41]
KOBu- <i>t</i> /DMSO	32.2 [86] (~30) [41]
KCH <sub>2</sub> SOMe/DMSO	35.1 [86] (32-34) <sup>b</sup>
K/NMP <sup>c</sup>	31 [87]
KHN(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> /H <sub>2</sub> N(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub> (KAPA)	40 [88, 89]
CsNHC <sub>6</sub> H <sub>11</sub> ( <i>cyclo</i> )/H <sub>2</sub> NC <sub>6</sub> H <sub>11</sub> ( <i>cyclo</i> )	40 [88, 89]

<sup>a</sup> Hereinafter in brackets are given values of acidity function ( $H_-$ ). <sup>b</sup> Depending on the base concentration (0.01-1.0 M).

<sup>c</sup> *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 ( $H_- \sim 40$ ) 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

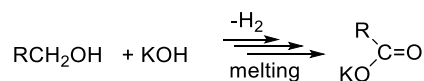
[103] has shown that the basicity of LIKOR reagents can be increased even more by adding a third base, tetramethylethylenediamine (TMEDA). For example, the triple system BuLi/*t*-BuOK/TMEDA is capable of metallating ethylene [103]. At the same time, basicities of pairs BuLi/TMEDA [104] and BuNa/TMEDA [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].

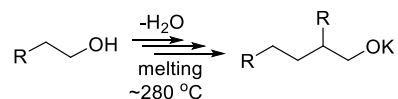
Meanwhile, a look into the past makes us recall Ecclesiastes: “*Is there any thing whereof*

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 Dumas-Stass reactions of alcohol dehydration (into acid salts) [112]:

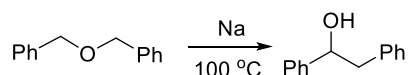


or Markownikoff-Zubov [113] or Herbe [114] dimerization of alcohols:



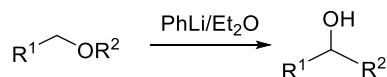
in the presence of melted alkali can quite be qualified as processes proceeding under the action of superbases: alcoholate plays the role of complex-forming agent toward the alkali metal cation.

Shorin 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.



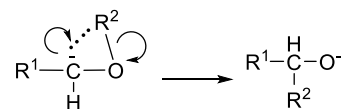
Carbanion formed upon the interaction of sodium with the methylene group (which acts as a CH-acid) here plays the role of a base, while the complex-forming agent toward the sodium cation is ether itself. Almost 20 years later

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.

### References

1. Fifty Ninth Mendeleev Reading, INFORMA Directorate Bulletin of Institute of Chemistry and the Chemical Department's Dean's Office. N 7/03 (202), 2003, p. 1 (in Russian).
2. Kostikov R.R., Domnin I.N. Fifty Ninth Mendeleev Reading. "Superbase Catalysts and Reagents: the Concept, Application and Perspectives" / Saint-Petersburg University. N 15-16 (3639-3640), 2003, p. 15 (in Russian).
3. Gillespie R.J., Peel T.E. Superacid Systems. *Adv. Phys. Org. Chem.* 1972, vol. 9, pp. 1-24. [https://doi.org/10.1016/S0065-3160\(08\)60232-4](https://doi.org/10.1016/S0065-3160(08)60232-4)
4. Koppel I.A., Burk P., Leito I., Sonoda T., Mishima M. Gas-Phase Acidities of Some Neutral Brønsted Superacids: A DFT and ab Initio Study. *J. Am. Chem. Soc.* 2000, vol. 122, pp. 5114-5124. <https://doi.org/10.1021/ja0000753>
5. IUPAC Glossary of Terms Used in Physical Organic Chemistry (Recommendations 1982) *Pure Appl. Chem.* 1983, 55, 1281-1371. <http://dx.doi.org/10.1351/pac198355081281>
6. Olah G.A., Prakash G.K.S., Sommer J. Superacids, New York: Wiley, 1985.
7. Olah G.A. Superelectrophiles. *Angew. Chem. Int. Ed.* 1993, vol. 32, pp. 767-788. <https://doi.org/10.1002/anie.199307673>
8. Trofimov B.A., Amosova S.V., Mikhaleva A.I., Gusarova N.K., Vyalykh E.P. Reactions of acetylene in superbasic media. *Fundamental Investigations. Chemical Sciences*, Ed. Boreskov G.K. Novosibirsk: Nauka Publ., Siberian Branch, 1977, pp. 174-178 (in Russian).
9. Trofimov B.A. Reactions of acetylene in superbasic media. *Rus. Chem. Rev.* 1981, vol. 50, no. 2, pp. 138-151. <https://doi.org/10.1070/RC1981v050n02ABEH002551>.
10. Trofimov B.A., Mikhaleva A.I. N-Vinylpyrroles. Novosibirsk: Nauka Publ., 1984. 10 p. (in Russian).
11. Trofimov B.A. Superbase media in acetylene chemistry. *Russ. J. Org. Chem.* 1986, vol. 22, no. 9, pp. 1991-2006 (in Russian).
12. Trofimov B.A. Chalcogenation in Multiphase Superbase Systems. *Sulfur Rep.* 1992, vol. 11, no. 2, pp. 207-227. <https://doi.org/10.1080/01961779208046184>
13. Sunner J., Kebarle P. Ion-solvent molecule interactions in the gas phase. The potassium ion and dimethyl sulfoxide, DMA, DMF, and acetone. *J. Am. Chem. Soc.* 1984, vol. 106, no. 21, pp. 6135-6139. <https://doi.org/10.1021/ja00333a002>
14. Magnera T.F., Caldwell G., Sunner J., Ikuta S., Kebarle P. Solvation of the halide anions in dimethyl sulfoxide. Factors involved in enhanced reactivity of negative ions in dipolar aprotic solvents. *J. Am. Chem. Soc.* 1984, vol. 106, no. 21, pp. 6140-6146. <https://doi.org/10.1021/ja00333a003>
15. Olmstead W.N., Margolin Z., Bordwell F.G. Acidities of water and simple alcohols in dimethyl sulfoxide solution. *J. Org. Chem.* 1980, vol. 45, no. 16, pp. 3295-3299. <https://doi.org/10.1021/jo01304a032>
16. Halpern M., Feldman D., Sasson Y., Rabinovitz M. Hydroxidion-initiierte Deuterierung sehr schwach CH-acider Verbindungen unter Phasentransferkatalyse-Bedingungen. *Angew. Chem.* 1984, vol. 96, no. 1, pp. 79-80. <https://doi.org/10.1002/ange.19840960133>
17. Arnett E.M., Venkatasubramanian K.G. Thermochemical acidities in three superbase systems. *J. Org. Chem.* 1983, vol. 48, no. 10, pp. 1569-1578. <https://doi.org/10.1021/jo00158a001>
18. Shatenstein A.I. Isotope Exchange and Hydrogen Substitution in Organic Compounds in the Light of Theory of Acids and Bases. Moscow: AN SSSR Publishers, 1960, 395 p. (in Russian).
19. Shatenshtein A.I. Advances in Physical Organic Chemistry. Ed. Gold V. London-

- New York: Academic Press, 1963, vol. 1, 153 p.
20. Brandsma L. Preparative Acetylenic Chemistry. Amsterdam-London-New York: Elsevier, 1971, 207 p.
  21. Ito Y., Kobayashi K., Seko N., Saegusa T. An One-Pot Synthesis of 3-Alkylindoles from o-Tolyl Isocyanides. *Chem. Lett.* 1979, vol. 8, no. 10, pp. 1273-1276. <https://doi.org/10.1246/cl.1979.1273>
  22. Makosza M., Glinka T. Reaction of organic anions. Part 108. On the mechanism of the vicarious nucleophilic substitution of hydrogen in nitroarenes. *J. Org. Chem.* 1983, vol. 48, no. 21, pp. 3860-3861. <https://doi.org/10.1021/jo00169a067>
  23. Schlosser M., Strunk S. The "super-basic" butyllithium/potassium tert-butoxide mixture and other liquor-reagents. *Tetrahedron Lett.* 1984, vol. 25, no. 7, pp. 741-744. [https://doi.org/10.1016/S0040-4039\(01\)80014-9](https://doi.org/10.1016/S0040-4039(01)80014-9)
  24. Mostamandi A., Remizova L.A., Yakimovich L.V., Favorskaya I.A. Isomerization of tertiary acetylenic amines under the influence of lithium 2-aminoethylamide in ethylenediamine. *Russ. J. Org. Chem.* 1981, vol. 17, no. 6, pp. 1166-1669 (in Russian).
  25. Corey E.J., Seebach D. Phenylthiomethyl lithium and Bis(phenylthio)methyl lithium. *J. Org. Chem.* 1966, vol. 31, no. 12, pp. 4097-4099. <https://doi.org/10.1021/jo01350a052>
  26. Dietrich B., Lehn J.M. Activation anionique a l'aide de cryptates I milieux fortement basiques. *Tetrahedron Lett.* 1973, vol. 14, no. 15, pp. 1225-1228. [https://doi.org/10.1016/S0040-4039\(01\)95803-4](https://doi.org/10.1016/S0040-4039(01)95803-4)
  27. Woo H.G., Han S.Y. Facile synthesis of mercaptovinylacetylene derivatives. *Indian J. Chem. Sect. B* 1982, vol. 21B, no. 9, pp. 803-804.
  28. Wojciechowski K., Makosza M. New synthesis of substituted indole derivatives via vicarious nucleophilic substitution of hydrogen. *Tetrahedron Lett.* 1984, vol. 25, no. 42, pp. 4793-4794. [https://doi.org/10.1016/S0040-4039\(01\)81521-5](https://doi.org/10.1016/S0040-4039(01)81521-5)
  29. Makosza M., Golinski J. Vicarious Nucleophilic Substitution of Hydrogen in Nitroarenes using 1-Chloroalkanesulfonic Esters; A Simple Synthesis of 1-(Nitrophenyl)-alkanesulfonic and (Nitrophenyl)-methanesulfonic Esters. *Synthesis.* 1983, no. 12, pp. 1023-1025. DOI: 10.1055/s-1983-30611
  30. Makosza M., Winiarski J. Nucleophilic Formulation of Nitroarenes via Vicarious Substitution of Hydrogen with Trisphenylthiomethane. *Chem. Lett.* 1984, pp. 1623-1624. <https://doi.org/10.1246/cl.1984.1623>
  31. Makosza M., Wojciechowski K. Intramolecular vicarious nucleophilic substitution of hydrogen. *Tetrahedron Lett.* 1984, vol. 25, no. 42, pp. 4791-4792. [https://doi.org/10.1016/S0040-4039\(01\)81520-3](https://doi.org/10.1016/S0040-4039(01)81520-3)
  32. Makosza M., Winiarski J. Reactions of organic anions. Part 109. Vicarious nucleophilic substitution of hydrogen in nitroarenes with carbanions of .alpha.-haloalkyl phenyl sulfones. *J. Org. Chem.* 1984, vol. 49, no. 9, pp. 1488-1494. <https://doi.org/10.1021/jo00183a003>
  33. Makosza M. Reactions of organic anions. XII. Vinylation of phenylacetonitrile derivatives. *Tetrahedron Lett.* 1966, vol. 7, no. 45, pp. 5489-5492. [https://doi.org/10.1016/S0040-4039\(00\)70128-6](https://doi.org/10.1016/S0040-4039(00)70128-6)
  34. Dowd P., Weber W. (1E)-1,3-dimethoxy-1,3-butadiene. *Tetrahedron Lett.* 1982, vol. 23, no. 21, pp. 2155-2156. [https://doi.org/10.1016/S0040-4039\(00\)87286-X](https://doi.org/10.1016/S0040-4039(00)87286-X)
  35. Skomorokhov M.Yu., Leonova M.V., Shiryaev A.K., Klimochkin Yu.N. Reaction of Adamantan-2-one with Acetonitrile in Basic Media. *Russ. J. Org. Chem.* 2003, vol. 39, pp. 1360-1361. <https://doi.org/10.1023/B:RUJO.0000010230.77371.3b>
  36. Carpio H., Galeazzi E., Greenhouse R., Guzmán A., Velarde E., Antonio Y., Franco F., Leon A., Pérez V., Salas R., Valdés D., Ackrell J., Cho D., Gallegra P., Halpern O., Koehler R., Maddox M.L., Muchowski J.M., Prince A., Tegg D., Thurber T.C., Van Horn A.R., Wren D. Synthesis of 1,2-

- dihydro-3H-pyrrolo[1,2-*a*]pyrrole-1-carboxylic acids and homologous pyridine and azepine analogues thereof. *Can. J. Chem.* 1982, vol. 60, no. 18, pp. 2295-2312. <https://doi.org/10.1139/v82-328>
37. Russell G.A., Weiner S.A. Methylation of Aromatic Hydrocarbons by Dimethyl Sulfoxide in the Presence of Base. *J. Org. Chem.* 1966, vol. 31, no. 1, pp. 248-251. <https://doi.org/10.1021/jo01339a056>
38. Iwai I., Ide J. 2,3-Diphenyl-1,3-butadiene. *Org. Syn.* 1970, vol. 50, p. 62. DOI: 10.15227/orgsyn.050.0062
39. Price G.G., Whiting M.C. The sodium derivative of dimethyl sulfoxide, Dimsylsodium. *Chemistry & Industry.* 1963, no. 19, pp. 775-776.
40. Mostamandi A., Remizova L.A., Favorskaya I.A. Prototropic isomerization of tertiary  $\beta$ -acetylenic amines. *Russ. J. Org. Chem.* 1982, vol. 18, no. 7, pp. 1559-1560 (in Russian).
41. Trofimov B.A., Vasil'tsov A.M., Amosova S.V. Basicity of saturated solutions of alkali metal hydroxides in dimethylsulfoxide. *Russ. Chem. Bull.* 1986, vol. 35, no. 4, pp. 682-686. <https://doi.org/10.1007/BF00954206>.
42. Trofimov B.A., Mikhaleva A.I., Petrova O.V., Sigalov M.V., Bzhezovsky V.M. An unusual methylenation reaction of cyclohexanone in the superbasic system KOH-DMSO. *Russ. J. Org. Chem.* 1985, vol. 21, no. 6, pp. 1356-1357 (in Russian).
43. Trofimov B.A., Mikhaleva A.I., Petrova O.V., Sigalov M.V. Reductive methylenation of ketones to give allyl alcohols. *Russ. Chem. Bull.* 1985, vol. 34, no. 5, p. 1111. <https://doi.org/10.1007/BF01142817>
44. Trofimov B.A., Mikhaleva A.I., Petrova O.V., Sigalov M.V. Rearrangement during reductive methylenation of 2-methylcyclohexanone by the KOH-DMSO system. *Russ. J. Org. Chem.* 1985, vol. 21, no. 12, pp. 2613-2614 (in Russian).
45. Voronkov M.G., Balesina G.G., Malysheva S.F., Shostakovskiy S.M. KOH-Dimethyl sulfoxide (DMSO) system as a dehydrohalogenating agent in the synthesis of  $\alpha,\beta$ -unsaturated esters. *Zh. Prikl. Khim.* 1975, vol. 48, no. 5, pp. 1172-1173 (in Russian).
46. Sowa J.R., Lamby E.J., Calamai E.C., Benko D.A., Gordinier A. Preparation of Alkynes. *Organic Preparations and Procedures International.* 1975, vol. 7, no. 3, pp. 137. <https://doi.org/10.1080/00304947509355133>
47. Amosova S.V., Tarasova O.A., Khil'ko M.Ya., Trofimov B.A. The interaction of esters of some thiophosphoric acids with acetylene. *Zh. Obshch. Khim.* 1976, vol. 46, no. 4, pp. 803-808 (in Russian).
48. Trofimov B.A., Amosova S.V., Tarasova O.A., Keyko V.V., Voronov V.K. Unusual addition of hydroxyl anion to acetylene. *Russ. J. Org. Chem.* 1974, vol. 10, no. 1, pp. 127-128 (in Russian).
49. Tarasova O.A., Amosova S.V., Trofimov B.A. Hydration trimerization of acetylene in superbasic media. I. Synthesis of 2-vinyloxy-1,3-butadiene and identification of reaction by-products. *Russ. J. Org. Chem.* 1982, vol. 18, no. 10, pp. 2042-2049 (in Russian).
50. Tarasova O.A., Amosova S.V., Istomina S.N., Trofimov B.A. Hydration trimerization of acetylene in superbasic media. II. Study of the conditions for the synthesis of 2-vinyloxy-1,3-butadiene in the alkali-dimethyl sulfoxide system. *Russ. J. Org. Chem.* 1984, vol. 20, no. 7, pp. 1353-1357 (in Russian).
51. Trofimov B.A., Tarasova O.A., Voronov V.K., Vitkovskiy V.Yu., Amosova S.V. Formation of 1,2-di(vinyloxy)propane during hydration trimerization of acetylene. *Russ. J. Org. Chem.* 1979, vol. 15, no. 6, p. 1318 (in Russian).
52. Trofimov B.A., Amosova S.V., Tarasova O.A., Kalabin G.A. Ethyl(vinyloxy)benzenes from acetylene and water in one step. *Russ. J. Org. Chem.* 1981, vol. 17, no. 5, p. 1099 (in Russian).
53. Trofimov B.A., Malysheva C.F., Vyalykh E.P., Sinegovskaya L.M., Gusarova N.K. Nucleophilic addition to acetylenes in overbasic catalytic systems. VIII. Exhaustive vinylation of pentaerythritol. *Russ. J. Org. Chem.* 1998, vol. 34, no. 4, pp. 507-510 (in Russian).

54. Tarasova O.A., Amosova S.V., Ryskiewa G.K., Zoi L.A., Sigalov M.V., Trofimov B.A. Tetrahydropyrimidine-2-thiones from tertiary acetylenic alcohols and thiourea. *Russ. J. Org. Chem.* 1983, vol. 19, no. 11, pp. 2452-2453 (in Russian).
55. Trofimov B.A., Amosova S.V., Nosyreva V.V., Musorin G.K., Sigalov M.V., Sinegovskaya L.M. A Rearrangement During the Alkylation of Diallyl Disulfide in the Superbasic KOH-DMSO System. *Sulfur Lett.* 1984, vol. 2, no. 3, pp. 105-108.
56. Musorin G.K., Amosova S.V., Tsherbakov V.V., Kalabin G.A., Trofimov B.A. Rearrangement of methyl 2,3-butadien-1-yl sulfide to methyl 1,3-butadien-2-yl sulfide in the dimethyl sulfoxide-base system. *Russ. J. Org. Chem.* 1982, vol. 18, no. 12, pp. 2613-2614 (in Russian).
57. Rykowski A., Makosza M. Reaction of 1,2,4-triazines with nitronate anions, direct nucleophilic acylation of 1,2,4-triazines. *Tetrahedron Lett.* 1984, vol. 25, no. 42, pp. 4795-4796. [https://doi.org/10.1016/S0040-4039\(01\)81522-7](https://doi.org/10.1016/S0040-4039(01)81522-7)
58. Trofimov B.A., Amosova S.V., Al'pert M.L., Musorin G.K. Nucleophilic addition of sulfide and thioacetate ions to acetylenes in the  $(C_2H_5)_3PO$ -KOH system. *Russ. J. Org. Chem.* 1982, vol. 18, no. 6, pp. 1156-1159 (in Russian).
59. Martynov A.V., Le Guillanton G. A new approach to the synthesis of symmetrical bis(organylchalcogeno)acetylenes: scope and limitations. *Bull. Soc. Chim. Fr.* 1997, vol. 134, pp. 823-831.
60. Trofimov B.A., Amosova S.V., Kriutchkov V.V., Vasil'tsov A.M. Divinyl sulfide. VIII. Reactions of acetylene with hydrogen sulfide in alkali-dimethyl sulfoxide and alkali-hexamethylphosphotriamide systems. *Russ. J. Org. Chem.* 1981, vol. 17, no. 10, pp. 2061-2064 (in Russian).
61. Makosza M. Vicarious nucleophilic substitution of hydrogen. A new method of nucleophilic alkylation of nitroarenes. *Current Trends in Organic Synthesis / Ed. Nozaki H.* Oxford: Pergamon Press, 1983. P. 401-412.
62. Handoo K.L., Gadru K. Potassium hydroxide-dimethyl sulfoxide reagent in organic synthesis: preparation of bifluorenylidene from 9-bromofluorene. *Indian J. Chem. Sect. B* 1983, vol. 22B, no. 9, pp. 909.
63. Artamkina G.A., Grinfel'd A.A., Beletskaya, I.P. Oxidation of hydrocarbons of the monoarylmethane series by oxygen in a basic medium. *Russ. Chem. Bull.* 1984, vol. 33, no. 7, pp. 2085-2091. <https://doi.org/10.1007/BF00954087>
64. Makosza M., Slomka E. Reactions of organic anions. 118. Vicarious nucleophilic substitution of hydrogen in nitro derivatives of 5-membered aromatic heterocycles. *Bull. Polish Acad. Sci. Chem.* 1984, vol. 32, no. 1-2, pp. 69-74.
65. Pat. US 4307034 (publ. 1981). Inert organic solvent dispersion of alkali hydroxide and reaction using the same.
66. Grinfel'd A.A., Artamkina G.A., Beletskaya, I.P. Oxidation of alcohols and aldehydes in KOH-dimethoxyethane-O<sub>2</sub> systems. *Russ. Chem. Bull.* 1984, vol. 33, no. 7, pp. 1438-1442. <https://doi.org/10.1007/BF00956521>
67. Back T.G., Collins S., Gokhale U., Law K.-W. Selenosulfonation of disubstituted acetylenes: reactions of corresponding vinyl selenoxides and anomalous formation of a ketene diselenoacetal. *J. Org. Chem.* 1983, vol. 48, no. 24, pp. 4776. <https://doi.org/10.1021/jo00172a066>
68. Poon C.-D., Yuen P.-W., Man T.-O., Li C.-S., Chan T.-L. Carbon tetrachloride-dimethyl sulphone-potassium hydroxide-t-butyl alcohol: a convenient new reagent for gem-dichloromethylenation of alkenes. *J. Chem. Soc. Perkin Trans. I.* 1984, no. 7, pp. 1561-1563. <https://doi.org/10.1039/P19840001561>
69. Price C.C., Snyder W.H. Solvent Effects in the Base-Catalyzed Isomerization of Allyl to Propenyl Ethers. *J. Am. Chem. Soc.* 1961, vol. 83, no. 7, p. 1773. <https://doi.org/10.1021/ja01468a062>
70. Trofimov B.A., Gusarova N.K., Atavin A.S., Amosova S.V., Gusarov A.V., Kazantseva N.I., Kalabin G.A. Reaction of organic disulfides with acetylene. IX. Influence of the structure of disulfides and acetylenes. *Zh. Org. Khim.* 1973, vol. 9, no. 1, pp. 8-14 (in Russian).

71. Bartok W., Rosenfeld D.D., Schriesheim A. Anionic Oxidation of Heterocyclic Nitrogen Bases and the Effect of Solvent on Such Reactions. *J. Org. Chem.* 1963, vol. 28, no. 2, pp. 410-412. <https://doi.org/10.1021/jo01037a032>
72. Tavares D.F., Estep R.E.  $\alpha,\beta$ -Epoxy sulphides a new sulfur-substituted oxirane. *Tetrahedron Lett.* 1973, vol. 15, no. 15, pp. 1229-1232. [https://doi.org/10.1016/S0040-4039\(01\)95804-6](https://doi.org/10.1016/S0040-4039(01)95804-6)
73. Trofimov B.A., Malysheva S.F., Vyalykh E.P. Basic catalytic synthesis of 3-phenylamino-1-butyne from aniline and acetylene. *Russ. J. Org. Chem.* 1979, vol. 15, no. 4, p. 880.
74. Trofimov B.A., Istomina S.N., Malysheva S.F., Vyalykh E.P. Study of reaction of acetylene with anilides by the mathematical planning method. *Russ. Chem. Bull.* 1978, vol. 27, no. 10, pp. 2135-2138. <https://doi.org/10.1007/BF00946546>.
75. Trofimov B.A., Malysheva S.F., Vyalykh E.P. One-step synthesis of 3-arylamino-1-butyne from anilides and acetylene. *Russ. J. Org. Chem.* 1981, vol. 17, no. 8, pp. 1583-1587 (in Russian).
76. Vasil'tsov A.M., Trofimov B.A., Amosova, S.V. Mathematical model of the alkali-DMSO superbase system at low concentrations of water. *Russ. Chem. Bull.* 1987, vol. 36, no. 8, pp. 1653-1658. <https://doi.org/10.1007/BF00960125>
77. Mikhaleva A.I., Gusarova N.K. // Acetylene: Reactions and Derivatives. Bibliography of B.A. Trofimov's Publications / Novosibirsk: SB RAS Publishers, 1999, p. 18 (in Russian).
78. Bowden K. Acidity Functions for Strongly Basic Solutions. *Chem. Rev.* 1966, vol. 66, no. 2, pp. 119-131. <https://doi.org/10.1021/cr60240a001>
79. Reutov O.A., Beletskaya I.P., Butin K.P. // CH-Acids. Moscow: Nauka Publ., 1980, p. 247 (in Russian).
80. Buncl E., Wilson H. Advances in Physical Organic Chemistry. Eds. Gold V., Bethell D. London-New York-San-Francisco: Academic Press, 1977, vol. 14, p. 133.
81. Cox R.A., Yates K. Acidity functions: an update. *Can. J. Chem.* 1983, vol. 61, no. 10, pp. 2225. <https://doi.org/10.1139/v83-388>
82. Fraser R.R., Bresse M., Mansour T.S. pKa Measurements in tetrahydrofuran. *J. Chem. Soc., Chem. Commun.* 1983, no 11, pp. 620-621. <https://doi.org/10.1039/C39830000620>
83. Cuvigny T., Le Borgne J.F., Larcheveque M., Normant H. Hyperbasic Media I. Metallation of Hydrazones. A Direct Synthesis of Nitriles. *Synthesis.* 1976, pp. 237-238. DOI: 10.1055/s-1976-23995
84. Le Borgne J.F., Cuvigny T., Larcheveque M., Normant H. Hyperbasic Media. II. Metallation of Hydrazones. Synthesis of Substituted or Functional Nitriles, 2-Iminotetrahydrofurans and  $\gamma$ -Butyrolactones. *Synthesis.* 1976, pp. 238-240. DOI: 10.1055/s-1976-23996
85. Caubere P. Topics in Current Chemistry, Organic Chemistry / Berlin-Heidelberg-New York: Springer-Verlag, 1978, vol. 73, p. 49.
86. Olmstead W.N., Margolin Z., Bordwell F.G. Acidities of water and simple alcohols in dimethyl sulfoxide solution. *J. Org. Chem.* 1980, vol. 45, no. 16, pp. 3295-3299. <https://doi.org/10.1021/jo01304a032>
87. Bordwell F.G., Branca J.C., Hughes D.L., Olmstead W.N. Equilibriums involving organic anions in dimethyl sulfoxide and N-methylpyrrolidin-2-one: acidities, ion pairing, and hydrogen bonding. *J. Org. Chem.* 1980, vol. 45, no 16, pp. 3305-3313. <https://doi.org/10.1021/jo01304a034>
88. Arnett E.M., Venkatasubramaniam K.G. Thermochemical comparison of deprotonation in KAPA (potassium 3-aminopropanamide) and potassium DMSYL. *Tetrahedron Lett.* 1981, vol. 22, no. 11, pp. 987-990. [https://doi.org/10.1016/S0040-4039\(01\)82846-X](https://doi.org/10.1016/S0040-4039(01)82846-X)
89. Streitwieser A., Scannon P.J. Acidity of hydrocarbons. I. Equilibrium ion pair acidities of thiophene, benzothiophene, thiazole, benzothiazole, and benzofuran toward cesium cyclohexylamide in cyclohexylamine. *J. Am. Chem. Soc.* 1973, vol. 95, no. 19, pp. 6273-6276. <https://doi.org/10.1021/ja00800a020>
90. Bell R.P. Acids and Bases: Their Quantitative Behavior. Second Edition. Methuen & Co. Ltd, 1969, p. 36.

91. Bell R.P. The Proton in Chemistry. Second Edition. London: Chapman & Hall, 1973.
92. Cram D.J. Fundamentals of Carbanion Chemistry. New York: Academic Press, 1965.
93. Gordon J.E. The Organic Chemistry of Electrolyte Solutions. New York: Wiley, 1975.
94. Lochman L., Pospisil J., Lim D. On the interaction of organolithium compounds with sodium and potassium alkoxides. A new method for the synthesis of organosodium and organopotassium compounds. *Tetrahedron Lett.* 1966, no 2, pp. 257-262. [https://doi.org/10.1016/S0040-4039\(00\)70224-3](https://doi.org/10.1016/S0040-4039(00)70224-3)
95. Schlosser M. Zur aktivierung lithiumorganischer reagenzien. *J. Organomet. Chem.* 1967, vol. 8, pp. 9-16. [https://doi.org/10.1016/S0022-328X\(00\)84698-7](https://doi.org/10.1016/S0022-328X(00)84698-7)
96. Wilhelm D., Clark T., Schleyer P.V.R., Courtneidge J.L., Davies A.G. The nature of the counterion in butyllithium/potassium t-alkoxide reaction mixtures: An ESR study. *J. Organomet. Chem.* 1984, vol. 273, pp. C1-C3. [https://doi.org/10.1016/0022-328X\(84\)80513-6](https://doi.org/10.1016/0022-328X(84)80513-6)
97. Caubere P. Applications of sodamide-containing complex bases in organic synthesis. *Acc. Chem. Res.* 1974, vol. 7, no. 9, pp. 301-308. <https://doi.org/10.1021/ar50081a004>
98. Caubere P. Unimetal super bases. *Chem. Rev.* 1993, vol. 93, no. 6, pp. 2317-2334. <https://doi.org/10.1021/cr00022a012>
99. Kennedy A. R., MacLellen J. G., Mulvey R. E. Landmark Crystal Structure of an Experimentally Utilized Tetralithium–Tetrapotassium Amide–Alkoxide Superbase. *Angew. Chem. Int. Ed.* 2001, vol. 40, no. 17, pp. 3245-3247. [https://doi.org/10.1002/1521-3773\(20010903\)40:17%3C3245::AID-ANIE3245%3E3.0.CO;2-3](https://doi.org/10.1002/1521-3773(20010903)40:17%3C3245::AID-ANIE3245%3E3.0.CO;2-3)
100. Mordini A. Advances in Carbanion Chemistry. Vol. 1. Ed. Sniechus V. London: YAI, 1992. p. 1.
101. Schlosser M. Organometallics in Synthesis. Chichester: Wiley, 1994. p. 1.
102. Lochmann L. Reaction of Organolithium Compounds with Alkali Metal Alkoxides – A Route to Superbases. *Eur. J. Inorg. Chem.* 2000, no. 6, pp. 1115-1126. [https://doi.org/10.1002/\(SICI\)1099-0682\(200006\)2000:6%3C1115::AID-EJIC1115%3E3.0.CO;2-K](https://doi.org/10.1002/(SICI)1099-0682(200006)2000:6%3C1115::AID-EJIC1115%3E3.0.CO;2-K)
103. Brandsma L., Verkrujssse H.D., Schade C., Schleyer P.V.R. The first successful direct metallation of ethane. *J. Chem. Soc. Chem. Commun.* 1986, no. 3, pp. 260-261. <https://doi.org/10.1039/C39860000260>
104. Rausch M.D., Ciapenelli D.J. Organometallic  $\pi$ -complexes XII. The metalation of benzene and ferrocene by n-butyllithium-N,N,N',N'-tetramethylethylenediamine. *J. Organomet. Chem.* 1967, vol. 10, no. 1, pp. 127-136. [https://doi.org/10.1016/S0022-328X\(00\)81725-8](https://doi.org/10.1016/S0022-328X(00)81725-8)
105. Schade C., Bauer W., Schleyer P.V.R. n-Butylsodium: The preparation, properties and NMR spectra of a hydrocarbon- and tetrahydrofuran-soluble reagent. *J. Organomet. Chem.* 1985, vol. 295, pp. C25-C28. [https://doi.org/10.1016/0022-328X\(85\)80326-0](https://doi.org/10.1016/0022-328X(85)80326-0)
106. Brandsma L., Verkrujssse H.D. Synthesis of Acetylenes, Allenes and Cumulenes. A Laboratory Manual. Amsterdam-Oxford-New York: Elsevier, 1981.
107. Brandsma L., Verkrujssse H.D. Preparative Polar Organometallic Chemistry. Vol. 1. Berlin-Heidelberg: Springer-Verlag, 1987.
108. Brandsma L. Preparative Polar Organometallic Chemistry. Vol. 2. Berlin-Heidelberg: Springer-Verlag, 1990.
109. Klusener P.A.A. Synthetic Applications of Strongly Basic Reagents. Ph.D. Thesis. Utrecht University, 1989.
110. Fossatelli M. New Applications of Super Bases in Organic Synthesis. Ph.D. Thesis. Utrecht University, 1994.
111. den Besten R. Structure and Reactivities of Polar Organometallic Compounds. Ph.D. Thesis. Utrecht University, 1997.
112. Dumas J., Stass I.S. Ueber die chemischen Typen. *Liebigs Ann. Chem.* 1840, vol. 35, no. 2, pp. 129-173. <https://doi.org/10.1002/jlac.18400350202>

113. Markownikoff W.W., Zubov P. Ueber die Condensation höherer Alkohole: Tricaprylalkohol. *Berichte der deutschen chemischen Gesellschaft*. 1901, vol. 34, no. 3, pp. 3246-3249. <https://doi.org/10.1002/cber.19010340304>
114. Veibel S., Nielsen J.I. On the mechanism of the Guerbet reaction. *Tetrahedron*. 1967, vol. 23, no. 4, pp. 1723-1733. doi:10.1016/S0040-4020(01)82571-0
115. Shorigin P. Über die Umlagerungen von Benzyläthern (II.). *Berichte der deutschen chemischen Gesellschaft*. 1925, vol. 58, no. 9, pp. 2028-2036. <https://doi.org/10.1002/cber.19250580915>
116. Wittig G., Loehmann L. Über die kationtrophe Isomerisation gewisser Benzyläther bei Einwirkung von Phenyllithium. *Liebigs Ann. Chem.* 1942, vol. 550, no. 1, pp. 260-268. <https://doi.org/10.1002/jlac.19425500117>
117. Trofimov B.A. Acetylene and its Derivatives in Reactions with Nucleophiles: Recent Advances and Current Trends. *Curr. Org. Chem.* 2002, vol. 6, pp. 1121-1162. <https://doi.org/10.2174/1385272023373581>
118. Trofimov B.A., Gusarova N.K. Acetylene: new prospects of classical reactions. *Russ. Chem. Rev.* 2007, vol. 76, no. 6, pp. 507-527. <https://doi.org/10.1070/RC2007v076n06ABEH003712>
119. Trofimov B.A., Schmidt E.Yu. New reactions of alkynes with ketones in superbasic media. *Russ. Chem. Bull. International Edition*. 2013, vol. 62, no. 11, pp. 2292-2300. <https://doi.org/10.1007/s11172-013-0332-6>
120. Gusarova N.K., Mikhaleva A.I., Schmidt E.Yu., Mal'kina A.G. Chemistry of Acetylene: New Chapters. Ed. Egorov M.P. Novosibirsk: Nauka. 2013, 368 p (in Russian).
121. Trofimov B.A., Schmidt E.Yu. Reactions of acetylenes in superbasic media. Recent advances. *Russ. Chem. Rev.* 2014, vol. 83, no. 7, pp. 600-619. <https://doi.org/10.1070/RC2014v083n07ABEH004425>
122. Trofimov B.A., Mikhaleva A.I., Schmidt E.Yu., Sobenina L.N. Chemistry of Pyrroles. CRC Press. 2014. 398 p.
123. Trofimov B.A., Schmidt E.Yu. Acetylenes in the superbase-promoted assembly of carbocycles and heterocycles. *Accounts of Chemical Research*. 2018, vol. 51, no. 5, pp. 1117-1130. DOI: 10.1021/acs.accounts.7b00618

## СУПЕРОСНОВАНИЯ В ОРГАНИЧЕСКОМ СИНТЕЗЕ

Б.А. Трофимов, Е.Ю. Шмидт

Иркутский Институт химии им. А.Е.Фаворского СО РАН  
Россия, 664033, г. Иркутск, ул. Фаворского, 1

**Аннотация:** В этом кратком обзоре обращено внимание на важную роль супероснований 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****B.A. Trofimov, E.Yu. Şmidt**

*Rusiya EA-nın A.E. Favorski adına İrkutsk Kimya İnstitutu  
Rusiya, 664033, İrkutsk, Favorski küç., 1*

**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 tərifı 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