Chemistry of Heterocyclic Compounds, Vol. 30, No. 6, 1994

USE OF ULTRASOUND IN HETEROCYCLIC CHEMISTRY (REVIEW)

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We review literature data on synthesis and conversions of heterocyclic compounds using ultrasonic treatment. We analyze the effect of ultrasound on organic reactions involving participation of heterocyclic compounds.

Presently the terms "sonochemical reactions" and "sonolysis" are used to define chemical processes occurring upon exposure to ultrasound. "Sonochemistry" has a number of advantages over "photochemistry" or "thermochemistry". In photochemical processes, interaction of matter with high-energy light waves occurs but this interaction is brief. In thermal processes, matter may interact for a prolonged period with the energy source, but as a rule these are lower-level energy sources. When using ultrasound, the matter is exposed to high energy generated as a result of the cavitation effect (local zones are formed with temperatures of several thousand of degrees and pressures of hundreds of atmospheres). As a result, when using ultrasound, generally we have acceleration of the reaction, the use of less vigorous conditions, a decrease in the induction period, a decrease in the number of stages, often occurrence of the reactions via an alternate route, and elimination of the use of initiators or promoters [1].

Systematic study of the effect of ultrasound on reactions of organic compounds began at the end of the 1970's and beginning of the 1980's. Sonochemistry of organic compounds has been most developed over the past 10-15 years: more than 80% of the publications on the use of ultrasound in organic chemistry have appeared in this period. International symposia have already been held [2-4] on the physical nature of ultrasound and its use in different areas of science and technological and the journal Ultrasonics is now published.

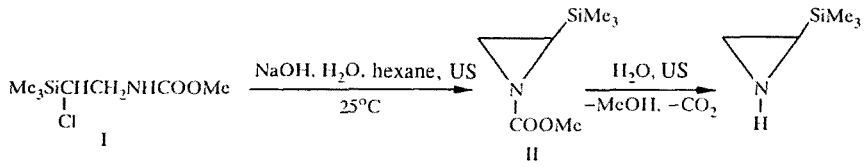
A number of reviews have been devoted to the use of ultrasound in chemistry. However, in practically all these reviews, only fragmentary information is available on heterocyclic compounds. Only one review [5] is completely devoted to consideration of the major papers on synthesis and conversions of heterocyclic compounds published up to 1987 inclusively.

This review includes material illustrating the universality and prospects for the use of sonochemistry in synthesis and conversions of heterocyclic compounds. In fact, the use of ultrasound makes it possible to carry out homogeneous and heterogeneous reactions of various types in liquid media and also in solid-liquid systems, as a rule under milder conditions and in higher yields than by classical methods.

1. THREE-MEMBERED HETEROCYCLIC COMPOUNDS

1.1. Nitrogen-Containing Heterocycles

The methyl ester (I) with ultrasonic treatment (frequency 55 kHz, power 100 W) undergoes ring closure to form 1-methoxycarbonyl-2-trimethylsilylaziridine (II), which under the reaction conditions is converted to 2-trimethylsilylaziridine; 45% yield [6]:



A. N. Kosygin State Technical Academy, Moscow 117918. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 723-755, June 1994. Original article submitted December 22, 1993.

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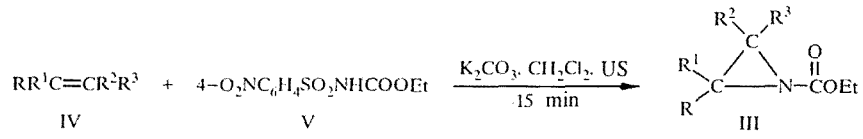
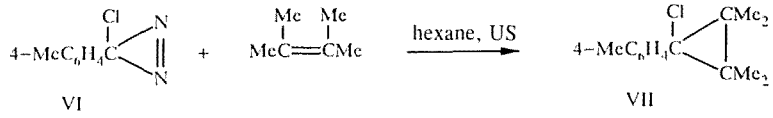
Derivatives of aziridine (III) are obtained under heterogeneous conditions with ultrasonic treatment (44 kHz, 2000 W) in the presence of potassium carbonate from alkenes (IV) and the ester (V), in 23-43% yields. The authors of [7] assume that the nitrene NCOOEt is formed in the reaction as an intermediate.



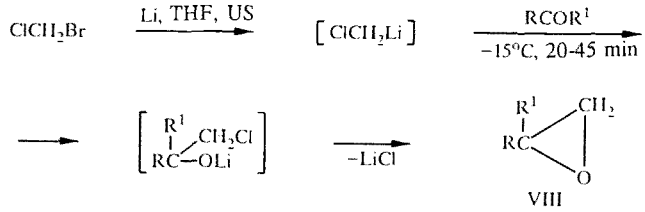
When the indicated reaction is carried out under phase transfer catalysis conditions without ultrasonic treatment, the reaction time increases by a factor of 10.

From the diaziridine derivative (VI) and 2,3-dimethylbutene under sonolysis conditions, the substituted cyclopropane (VII) is formed in 75% yield [8]:



1.2. Oxygen-Containing Heterocycles

Sonolysis (60 W) of $ClCH_2Br$ and lithium in THF leads to $ClCH_2Li$, which reacts *in situ* with aldehydes or ketones, forming the corresponding epoxides (VIII) in 70-91% yields [8]:



If the reaction with acetophenone is carried out with stirring but without ultrasonic treatment (4 h, 20°C), then the yield of epoxide VIII (R = Me, R^1 = Ph) is reduced from 82% to 55%.

The oxide of *trans*-stilbene upon reaction with lithium under sonolysis conditions in the presence of $(4\text{-}Me_3CC_6H_4)_2$ is converted to dibenzyl in 95% yield [10].

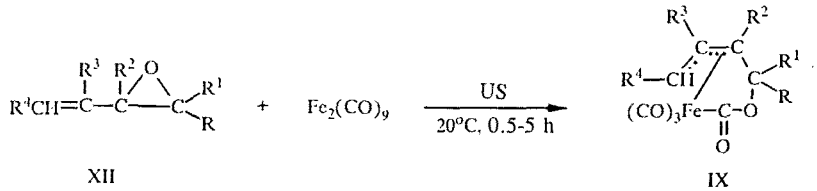
The unsaturated compounds $4\text{-}RC_6H_4SO_2CH{=}CHCH_2OH$ are formed from epichlorhydrin and $4\text{-}RC_6H_4SO_2{}^-Na^+$ with ultrasonic treatment (for R = H, ultrasonic treatment, 40 kHz, 480 W, 25°C, over Al_2O_3, 42% yield; for R = Me, ultrasonic treatment, 20 kHz, 90-100 W, 20°C, DMF-H_2O, 72% yield) [12].

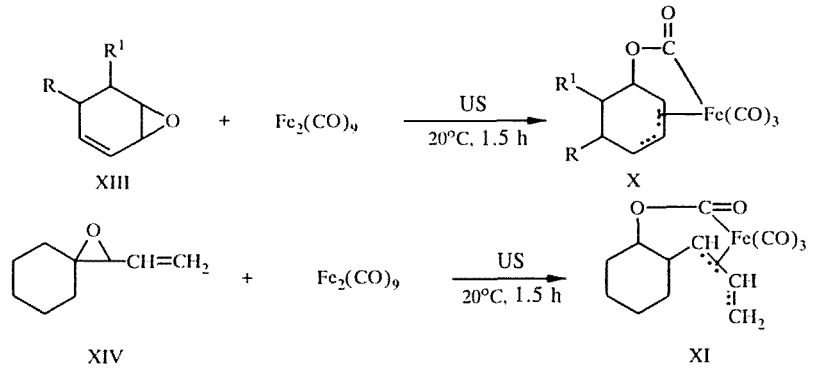
The reaction of $PhSe^-Na^+$ (formed from PhSeSePh and Na with ultrasonic treatment, 50 kHz, 80 W) with

$$PhCHCH_2O \quad \text{or} \quad CH_2{=}CHCH_2OCH_2CHCH_2O$$

for 15 min leads to the compounds $PhCH(OH)CH_2SePh$ or $PhSeCH_2CH(OH)CH_2OCH_2CH{=}CH_2$ in 78% and 86% yields respectively [13].

A series of complexes of π-allyltricarbonyliron (ferryllactones) (IX-XI) are obtained in 34-100% yields from epoxides (XII-XIV), containing a double bond, and $Fe_2(CO)_9$ with ultrasonic treatment (50 KHz, 80 W) in PhH or Et_2O [14, 15]:

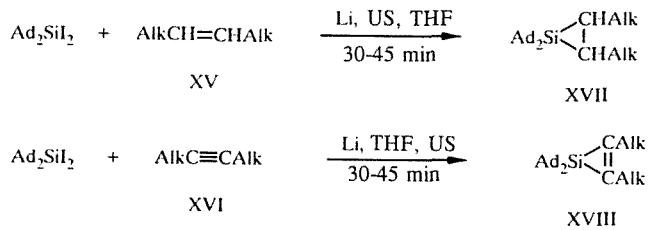




XIII X XIV XI

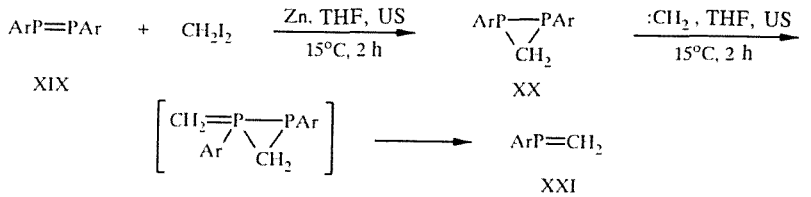
1.3. Other Heterocycles

When a mixture of Ad_2SiI_2 and Li is exposed to ultrasound, obviously the silicon analog of carbine Ad_2Si is formed, since upon sonolysis of mixtures of Ad_2SiI_2 and alkenes (XV) or alkynes (XVI), the compounds (XVII) or (XVIII) are formed in 45-87% yields, containing a three-membered ring including two carbon atoms and one silicon atom [16].



XV XVII XVI XVIII

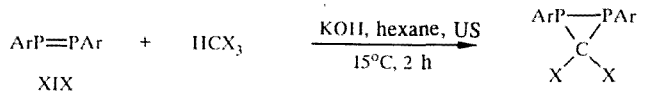
The reaction proceeds stereoselectively with alkenes with retention of their configuration [16]. From diphosphene (XIX) and CH_2I_2 under sonolysis conditions (20 kHz, 600 W) in the presence of zinc in THF, the diphosphirane (XX) is formed, which upon more prolonged ultrasonic treatment is converted to the phosphaalkene (XXI) [17]:



XIX XX XXI

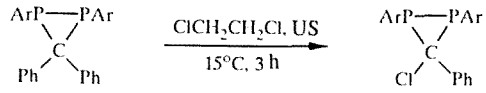
We should noted that cyclopropanation of the diphosphene XIX cannot be carried out by the Simmons–Smith method even with preliminary activation by zinc [17].

In the cyclopropanation reaction, instead of CH_2I_2 the haloforms XCX_3 (X = Cl, Br) were also used in the presence of potassium hydroxide, and in this case the corresponding diphosphiranes were obtained in quantitative yields:



XIX

With ultrasonic treatment (20 kHz, 600 W) of the phosphirane (XXII, Ar = 2,4,6-$Me_3C_6H_2$) in 1,2-dichloroethane, substitution of the Ph by Cl occurs without ring opening; the yield of the substitution product (XXIII) is 30% [17]:

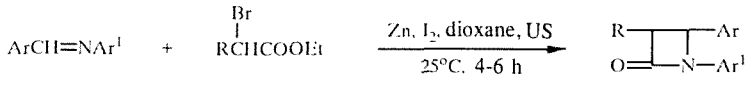


XXII XXIII

2. FOUR-MEMBERED HETEROCYCLIC COMPOUNDS

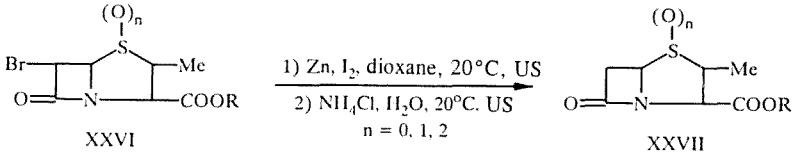
2.1. Nitrogen-Containing Heterocycles

When using the standard technique for obtaining derivatives of β-lactam for $BrCH_2COOEt$ and azomethines (Schiff base XXIV), it is necessary to carry out the reaction for a prolonged period in boiling toluene in the presence of Zn and I_2 [18]. The use of ultrasound makes it possible to carry out the process at 25°C over the course of 4-6 h and to obtain β-lactam derivatives (XXV) in 70-95% yields [19, 20]:



XXIV XXV

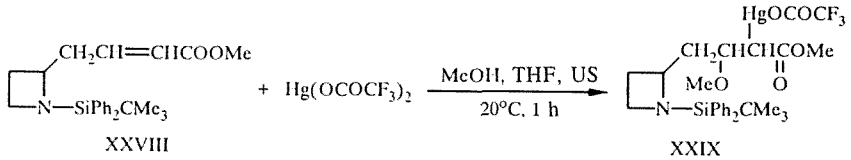
Esters of 6-bromopennicillanic acid (XXVI) in the presence of zinc and iodine under sonolysis conditions are selectively reduced in 57-72% yields to esters of penicillinic acid (XXVII) [21]:



XXVI XXVII

Without ultrasound, it is necessary to use large amounts of platinum catalyst or Bu_3SnH to reduce the bromo derivative XXVI.

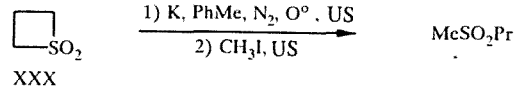
Under sonochemical reaction conditions, the unsaturated ester (XXVIII) reacts with $Hg(OCOCF_3)_2$ with formation of compound (XXIX) [22]:



XXVIII XXIX

2.2. Other Heterocycles

When metallic potassium is subjected to ultrasonic treatment (45 kHz, 100 W) in toluene, dispersed potassium is formed, which easily cleaves the cyclic sulfone (XXX) at the C–S bond; and when CH_3I is introduced into the reaction mixture, methylpropylsufone is obtained in 84% yield [23]:



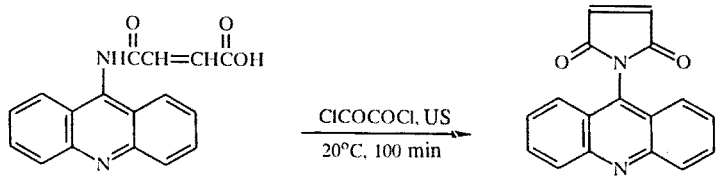
XXX

Under sonolysis conditions (50-60 kHz, 150 W), diphenyldichlorosilane in the presence of alkali metals is converted in 95% yield to octaphenylcyclotetrasilane [24].

3. FIVE-MEMBERED HETEROCYCLIC COMPOUNDS

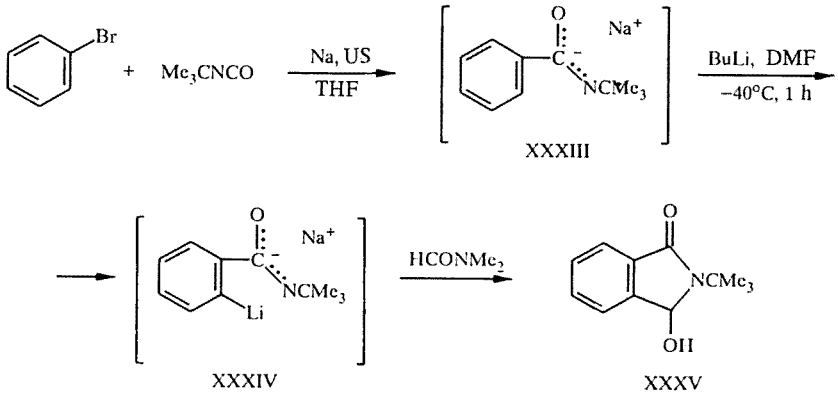
3.1. Nitrogen-containing Heterocycles

The N-substituted amide of maleic acid (XXXI) in the presence of oxalyl chloride with ultrasonic treatment undergoes ring closure to form the N-substituted pyrrolidine-2,5-dione (XXXII), 34.6% yield [25]:



XXXI XXXII

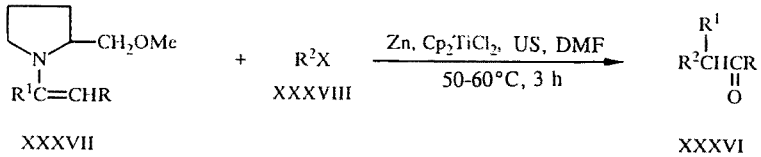
Ultrasonic treatment of bromobenzene and Me_3CNCO in the presence of Na leads to the salt (XXXIII), which upon treatment with butyllithium is converted to the lithium derivative (XXXIV); the reaction of the latter with DMF leads to the compound (XXXV) [26]:



XXXIII

XXXIV XXXV

The optically active ketones (XXXVI), containing perfluoroalkyl substituents, are formed upon ultrasonic treatment (45 kHz, 100 W) from derivatives of pyrrolidine (XXXVII) and polyhaloalkanes (XXXVIII) in the presence of dichlorobis(π-cyclopentadienyl)titanium [27]:

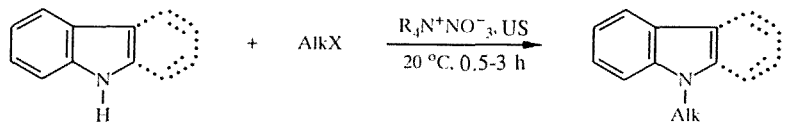


XXXVII XXXVIII XXXVI

R, R^1, R^2X, yield XXXVI in%: Et, Me, CF_3I, 38; Et, Me, CF_3Br, 46; Et, Me, C_2F_5I, 51; Et, Me, C_3F_7I, 48; Et, Me, C_4F_9I, 58; $(CH_2)_4$, $C_6F_{13}I$, 57; Et, Me, $C_8F_{17}I$, 56

Under sonolysis conditions (45 kHz, 100 W), the alkenes $RR^1C{=}CR^2R^3$ react with 1-bromo- or 1-iodosuccinimide in the presence of NH_4HF_2 and AlF_3, being converted to $RR^1CFBr(I)R^2R^3$ and/or $RR^1CBr(I)CFR(I)CFR^2R^3$ [28].

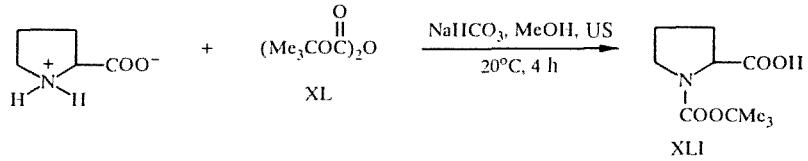
N-Alkylation of indole or carbazole with ultrasonic treatment (Dawe Instruments ultrasonic bath) in the presence of phase-transfer catalysts $R_4N^+NO_3^-$ (R = Bu, C_6H_{13}) leads to the products (XXXIX) in 60-96% yields [29]:



XXXIX

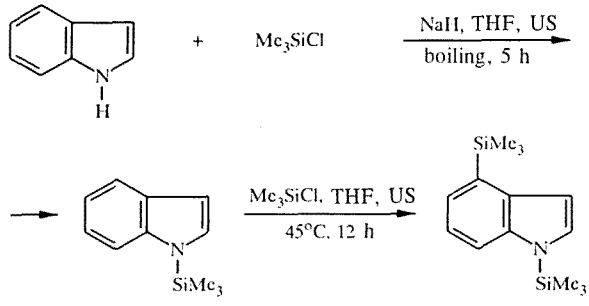
Without ultrasonic treatment, this reaction takes 5-72 h, and the yields of products XXXIX are 50-80%. We should note that in the absence of phase-transfer catalysts, alkylation of indole or carbazole does not proceed either with stirring or with ultrasonic treatment [29].

Ultrasonic treatment promotes reaction of proline with anhydride (XL), and the reaction product (XLI) is formed in 86% yield [30]:



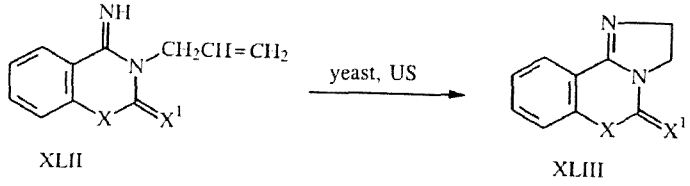
XLI

We can introduce one (93% yield) or two (55% yield) Me_3Si groups into the indole molecule by treatment with Me_3SiCl in the presence of NaH or Li in an ultrasonic bath [31]:



1,3,3-Trimethyl-2-(formylmethylene)indoline under sonolysis conditions (20-100 kHz, 350 W) is condensed with aromatic amines in the presence of acids with formation of dyes [32].

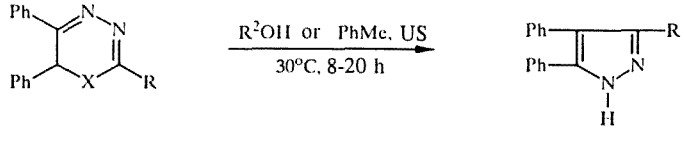
Cyclization of compounds (XLII) in the presence of baker's yeast with ultrasonic treatment (Branson Sonifier B-30) occurs in two days with product (XLIII) yields 80-86% (without ultrasonic treatment, the reaction takes five days, yields 27-53%) [33]:



XLII XLIII

X,X^1 = O,O; O,S; NH,NMe; NPh,S

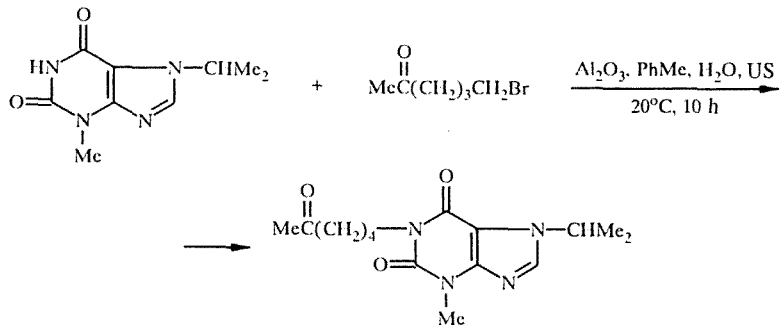
6-H-1,3,4-Thiadiazines (XLIV, X = S) and 6-H-1,3,4-selenodiazines (XLIV, X = SE) upon ultrasonic treatment (25 kHz) under mild conditions are converted to pyrazole derivatives (XLV) in 80-90% yields [34]:



XLIV XLV

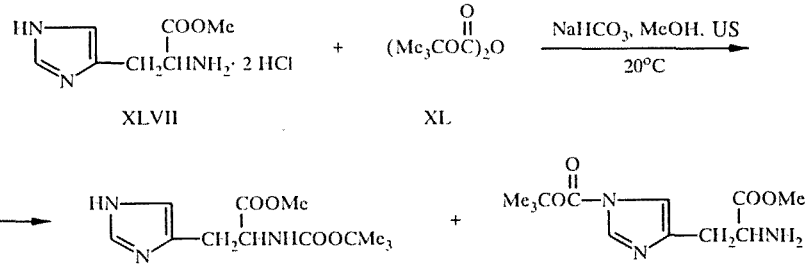
Under ordinary reaction conditions (without ultrasonic treatment), the analogous conversion takes more than 100 h [34].

N-Alkylation of 3-methyl-7-isopropylxanthine by 6-bromohexan-2-one under sonolysis conditions in the presence of aluminum oxide occurs at 20°C, product yield (XLVI) 87% [35]:



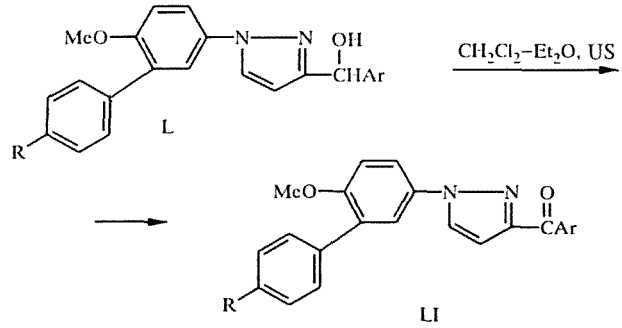
XLVI

Bishydrochloride (XLVII) under sonochemical reaction conditions reacts with the anhydride XL, forming two compounds (XLVIII) and (XLIX) with overall yield 84% [30]:



XLVII XL XLVIII XLIX

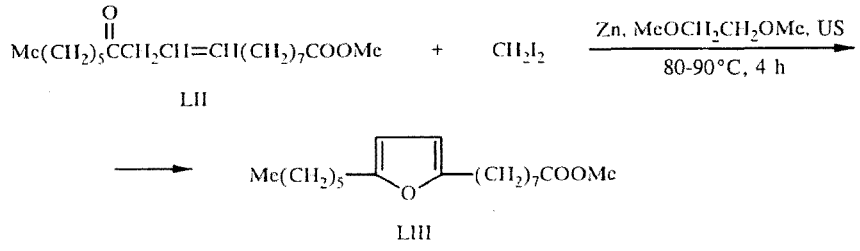
The alcohols (L) are oxidized to ketones (LI) in 24-99% yields by pyridinium chlorochromate over the course of one hour in a Branson ultrasonic bath (200-400 W) [36]:



L LI

3.2. Oxygen-Containing Heterocycles

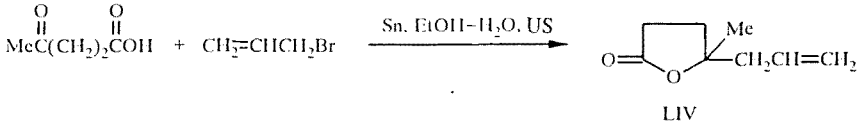
The methyl ester (LII) reacts with CH_2I_2 in the presence of zinc and undergoes ring closure to form the 2,5-disubstituted furan (LIII) in 46% yield upon ultrasonic treatment (55 kHz, 150 W) [37]:



LII LIII

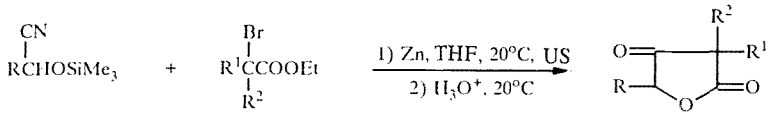
When using cobalt instead of zinc, the yield decreases to 10%. The reaction does not occur in the presence of copper [37].

From 4-ketovalerianic acid and allyl bromide in the presence of tin with ultrasonic treatment (50 kHz), the substituted butyrolactone (LIV) is obtained in 77% yield [38].



LIV

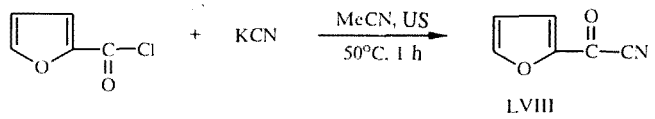
Sonolysis (32 kHz, 35 W) of the cyanohydrin ethers (LV) and the esters (LVI) in presence of zinc leads to the cyclic compounds (LVII) in 48-68% yields [39]:



LV LVI LVII

Substitution of the OMe group by hydrogen or deuterium occurs in quantitative yields upon treatment of 2-methoxydimethylsilyl-4,5-dihydrofuran or 2-methoxydimethylsilyltetrahydrofuran with $LiAlH_4$ or $LiAlD_4$ respectively in nonpolar solvents with ultrasonic treatment (55 kHz, 100 W) at 25°C for 2-3 h. The reduction does not occur without ultrasonic treatment in nonpolar solvents [40].

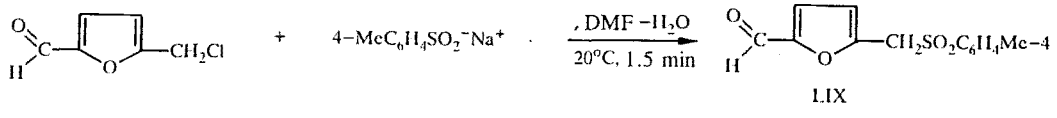
Upon ultrasonic treatment (55 kHz, 100 W), synthesis of acylcyanide (LVIII) has been successfully accomplished (76% yield) from the acid chloride of pyromusic acid and potassium cyanide in acetonitrile [41]:



LVIII

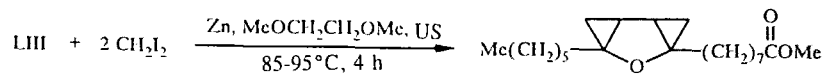
Using the standard technique (without ultrasonic treatment) to obtain acylcyanides from acid chlorides and KCN, it is necessary to use cyanides of heavy metals (Cu, Ag, Ti) with heating and the use of strictly limited amounts of water. Also the synthesis of acylcyanides is much less efficient in the presence of phase-transfer catalysts [42].

Upon reaction of 5-chloromethylfurfurol with the salt $4\text{-}MeC_6H_4SO_2^-Na^+$ in an ultrasonic bath (20 kHz, 90-100 W), the chlorine atom is substituted by a $4\text{-}MeC_6H_4SO_2$ group and the yield of the substitution product (LIX) is 82% [12]:



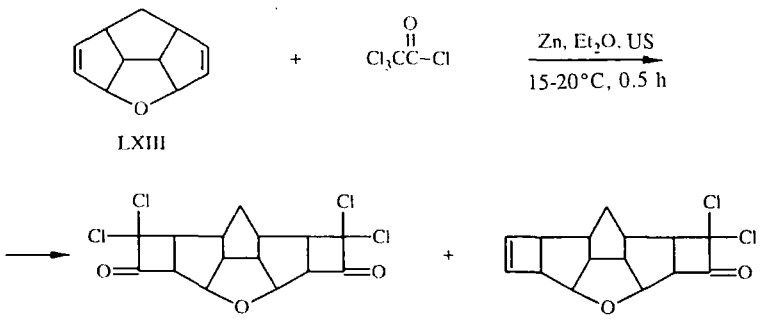
LIX

The furan derivative LIII reacts with CH_2I_2 in the presence of zinc under sonolysis conditions (55 kHz, 150 W) and is converted to the tricyclic compound (LX) in 57% yield [37]:



LX

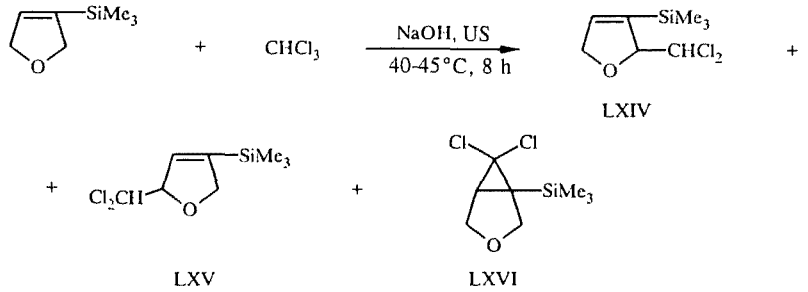
The polycyclic compounds (LXI) and (LXII) were synthesized in 45% and 20% yields respectively upon reaction of compound (LXIII) with Cl_3CCOCl in the presence of zinc with ultrasonic treatment (35 kHz, 100 W) [43]:



LXIII LXI LXII

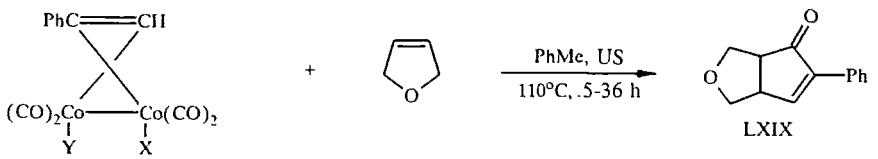
Inactivated zinc can be used in this reaction. Without ultrasonic treatment, the reaction takes 16 h and requires the use of activated zinc (Zn/Cu alloy) [44].

Sonochemical reaction of 3-trimethylsilyl-2,5-dihydrofuran with chloroform in the presence of solid KOH with ultrasonic treatment (55 kHz, 100 W) leads to the compounds (LXIV-LXVI) in 20, 23, and 32% yields [45]:



LXIV LXV LXVI

Cobalt-containing complexes of phenylacetylene (LXVII) and (LXVIII) under sonolysis conditions react with 2,5-dihydrofuran, forming compound (LXIX) in 8-45% and 5% yields respectively [46]:



LXIX

LXVII Y = CO, X = CO, PPh_3, PBu_3, $P(OPh)_3$, $P(OMe)_3$

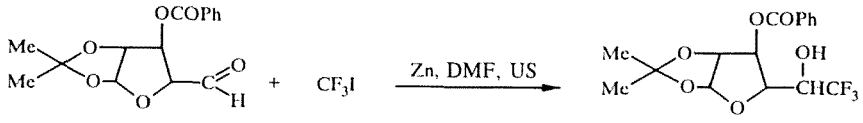
LXVIII X = Y = PPh_3

An especially great advantage of sonochemical reactions over standard methods is apparent when using organomagnesium or organolithium compounds. In standard methods, we need to use anhydrous solvents to carry out the reactions under an inert atmosphere (especially with RLi), and to use activating additives (I_2, MeI). When using sonolysis, these special conditions are not necessary.

Upon reaction of furan with butyllithium and then with benzaldehyde in an HE 2500 ultrasonic bath, α-(furyl-2)benzyl alcohol is formed in 72% yield (20°C, 30 min, THF) [47].

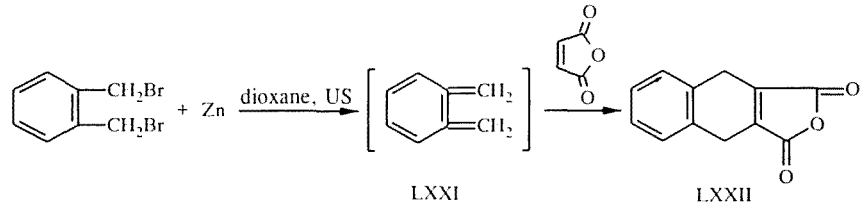
Condensation of furfurol with CH_3I in the presence of Li when using ultrasound (50 kHz, 60 W) can be carried out in ordinary THF; the yield of the α-(furyl-2)-ethanol formed after 10 min is quantitative [48].

Sonolysis of the aldehyde (LXX) and CF_3I in the presence of zinc in DMF leads to a 1:2.5 mixture of diastereomers of compound (LXXI) with 47% overall yield [49]:



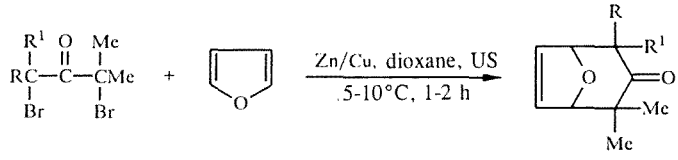
LXX LXXI

Upon reaction of 1,2-di(bromomethyl)benzene with zinc and ultrasonic treatment (50-60 kHz, 150 W), the dimethylidene derivative (LXXII) is formed, which reacts *in situ* with maleic anhydride, and the diene synthesis product (LXXII) is obtained in 89% yield [50]:



LXXI LXXII

Treatment of α,α^1-dibromoketones (LXXIII) with furan in the presence of zinc in a Branson 220 ultrasonic bath leads to the bicyclic compounds (LXXIV) in 88-91% yields [51]:

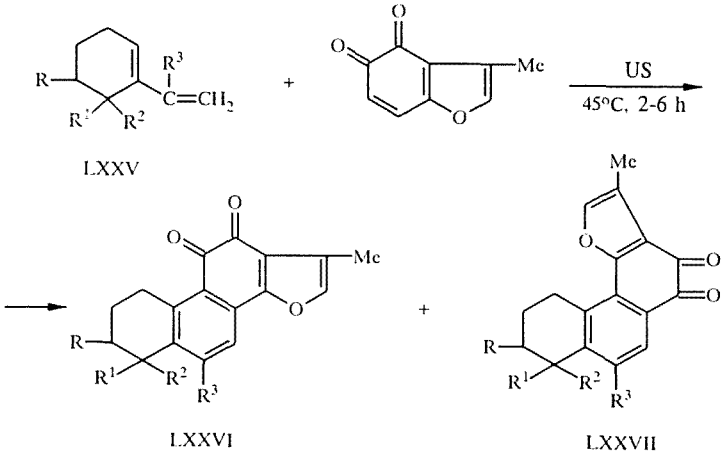


LXXIII LXXIV

R, R^1: Me, Me; $(CH_2)_3$

When carrying out this reaction without ultrasonic treatment (stirring for 24 h in the presence of Me_3SiCl), the yield of compound LXXIV (R = R^1 = Me) is 60% [51].

As a result of the reaction of dienes (LXXV) with 7-substituted derivatives of 3-methylbenzofuran-4,5-dione with ultrasonic treatment (50-60 kHz, 125 W) followed by aromatization, mixtures of regioisomers (LXXVI) and (LXXVII) were obtained with overall yields 56-76% [52-55]:



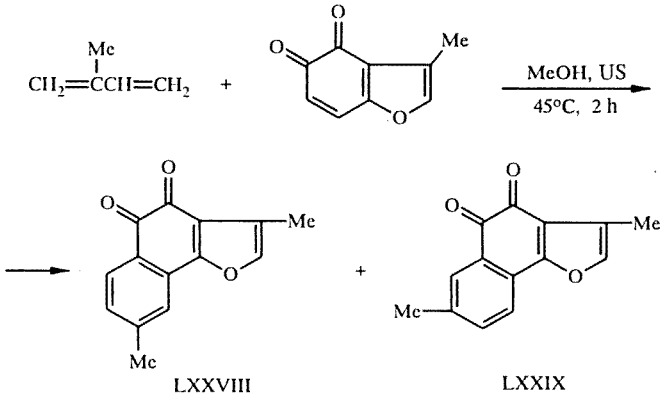
LXXV

LXXVI LXXVII

R, R^1, R^2, R^3 = H, H, H, $SiMe_3$; H, Me, Me, H; H, $—OCH_2CH_2O—$, H; $—OCH_2CH_2O—$, Me, H [52]; H, COOMe, Me, H; H, $Me_3CSiMe_2OCH_2—$, H; H, H, Me, H [53]; H, COOMe, Me, H (one isomer of XXVII) [54]; H, H, COOMe, H; H, $—OCMe_2CH_2O—$, H [55]

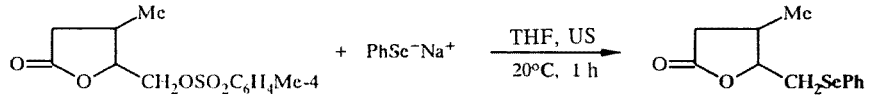
In these reactions, ultrasound not only accelerates the process but also improves the regioselectivity. In almost all cases, the yield of adducts is higher when carrying out the reaction without a solvent than in methanol, toluene, or dioxane.

3-Methylbenzofuran-4,5-dione reacts analogously with isoprene: the two isomers (LXXVIII) and (LXXIX) are formed in 5:4 ratio with 38% overall yield [52-55]:



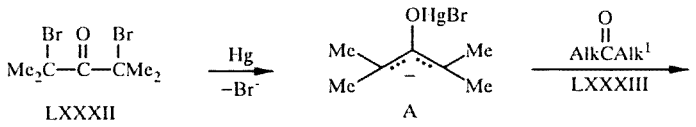
LXXVIII LXXIX

Sodium phenylselenide formed from PhSeSePh and sodium under sonolysis conditions (50 kHz, 80 W) reacts with compound (LXXX), exchanging the OTs for the SePh group. As a result, the substitution product (LXXXI) is obtained in 83% yield [13]:

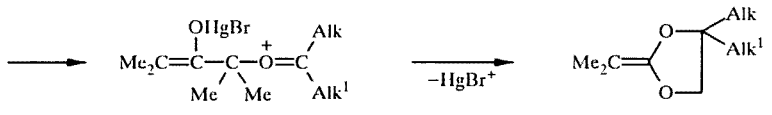


LXXX LXXXI

The authors of [56] explain the formation of dioxolanes (LXXXIV) from α,α^1-dibromoketone (LXXXII) and ketones (LXXXIII) as follows. The dibromoketone reacts with ultrasonically dispersed mercury (150 W), forming cation (A), which reacts with the ketones LXXXIII; this leads to the oxonium ions (LXXXV), undergoing ring closure to form dioxolanes LXXXIV in 25-59% yields (reaction time, 1-2 days).

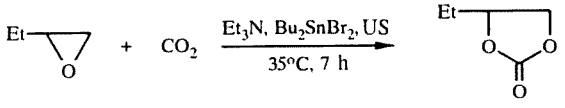


LXXXII A



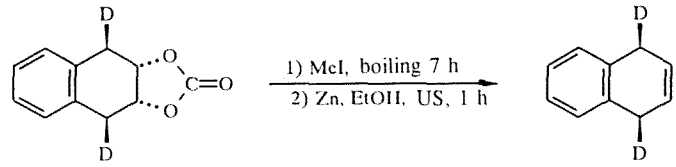
LXXXV LXXXIV

The anhydride (LXXXVI) is synthesized in 70% yield by reaction of ethyloxirane with CO_2 gas in the presence of Et_3N with ultrasonic treatment [57]:



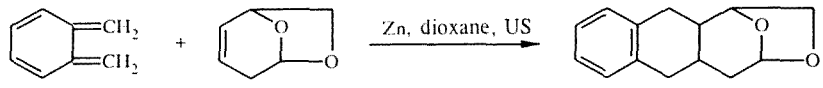
LXXXVI

The product of reaction of compound (LXXXVII) with MeI upon treatment with zinc under sonolysis conditions is stereoselectively converted to *cis*-1,4-dideutero-1,4-dihydronaphthalene in 59% yield [58]:



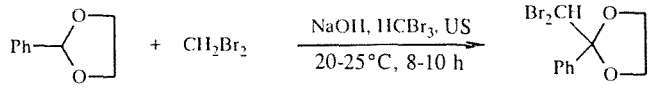
LXXXVII

The dimethylidene derivative, obtained when 1,2-di(bromomethyl)benzene is subjected to ultrasonic treatment (50 kHz) in the presence of zinc, reacts *in situ* with the cycloalkene (LXXXVIII), which leads to the compound (LXXXIX) [50]:

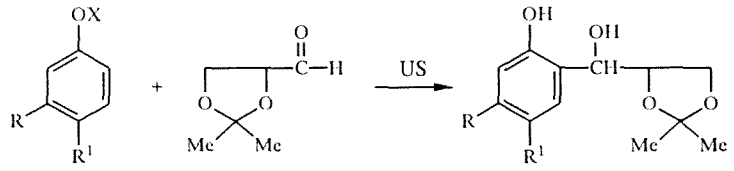


LXXXVIII LXXXIX

The unusual reaction of haloalkylation is observed upon reaction of 2-phenyldioxolane with CH_2Br_2 under sonochemical reaction conditions (22 kHz, 150 W) [59]:



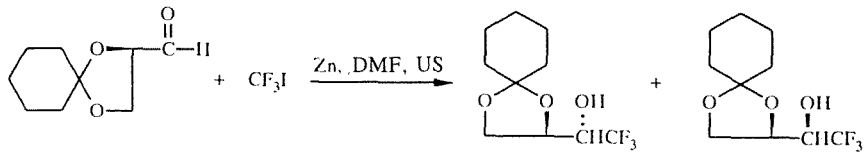
Upon ultrasonic treatment (50 kHz), the reaction of phenol derivatives (XC) with 2,2-dimethyl-4-formyl-1,3-dioxolane occurs highly stereoselectively and regioselectively with formation of the condensation products (XCI), 61-76% yields [60]:



XC XCI

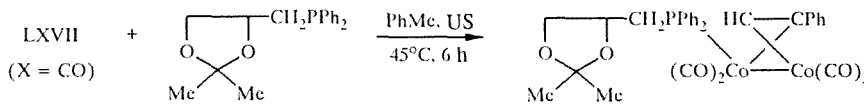
R, R^1, X = H, Me_3C, $MgBr^+$; H, Me_3C, $Ti(OCHMe_2)_3^+$; H, H, $MgBr^+$; H, H, $Ti(OCHMe_2)_3^+$; OMe, H, $MgBr^+$; OMe, H, $Ti(OCHMe_2)_3^+$

The reaction of the aldehyde (CXII) with CF_3I in the presence of zinc in an ultrasonic bath leads to a 3:2 mixture of diastereomers (XCIII) and (XCIV) with overall yield 70% [49]:



XCII XCIII XCIV

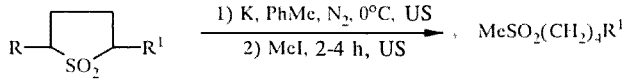
Under sonolysis conditions, upon reaction of the complex LXVII (X = CO) with the dioxolane derivative (XCV), one CO group is substituted by the XCV residue and the complex (XCVI) is formed in 31% yield [61]:



XCV XCVI

3.3. Sulfur-Containing Heterocycles

In an ultrasonic bath (50 kHz, 150 W) potassium in toluene cleaves the C–S bond in sulfolanes (XCVII), and if the reaction is carried out in the presence of MeI, then the sulfones (XCVIII) are formed in 82-94% yields. We note that the bond between sulfur and the most highly substituted carbon atom is preferentially cleaved [23]:

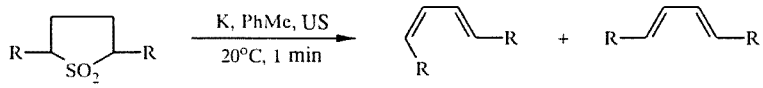


XCVII XCVIII

R, R^1 = H, H; H, Me; H, CHMe2; H, C_6H_{13}; H, $PhCH_2$; Me, Me

In the case of the sulfolane XCVII (R = H, R^1 = Me), the sulfone XCVIII with R^1 = $CHMeCH_2CH_2Me$ is also formed in 8% yield [23].

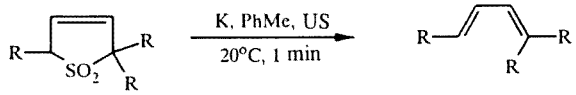
Trans-2,5-dialkyl-3-sulfolenes (XCIX) upon treatment with potassium in an ultrasonic bath (50 kHz, 150 W) is rapidly converted to a mixture of (E, E)- and (E, Z)-dienes (C) and (CI) in 84-86% and 10-11% yields respectively [23]:



XCIX C CI

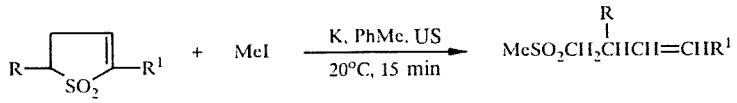
Under the same conditions, the diene CI (R = C_6Hd_{13}) is formed in 92% yield form (Z)-2,5-dihexyl-3-sulfolene [23]. Without ultrasonic treatment, the analogous conversion of 3-sulfolenes takes 2 h at 100-150°C [62]. When the reaction is carried out under a nitrogen atmosphere, the overall yield of dienes C and CI is reduced down to 80% and the reaction time is increased to 30 min, while the selectivity increases: the ratio (E, Z):(E, E) becomes equal to 20:1 [62].

Upon treatment of 2,2,5-trialkyl-3-sulfolenes (CII) with potassium in a Branson 220 ultrasonic bath, only the *trans* dienes (CIII) are formed in 90-91% yields [63]:



CII CIII

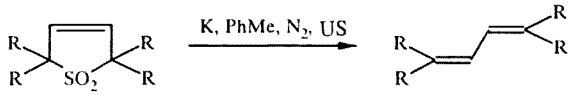
In the same ultrasonic bath, the reaction of 2-sulfolnes (CIV) with potassium in the presence of MeI leads to the unsaturated sulfone (CV) in 40-72% yields [63]:



CIV CV

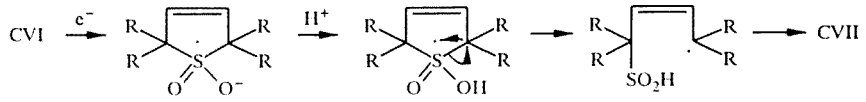
Upon treatment of monosubstituted 2-sulfolenes CIV (R = H) with potassium without ultrasonic treatment, the reaction occurs over the course of 20 h and only with 5% yield [63].

The authors of [62] noted that 2,2,5,5-tetrasubstituted 3-sulfolenes are not cleaved by potassium in an ultrasonic bath even at 60°C over the course of 4 h. However, later it was established that upon treatment with potassium in a T 570/H ultrasonic bath in the presence of proton donors (H_2O, Me_3COH), 2,2,5,5-tetrasubstituted 3-sulfolenes (CVI) are converted to dienes (CVII) with 49-92% yields [64]:

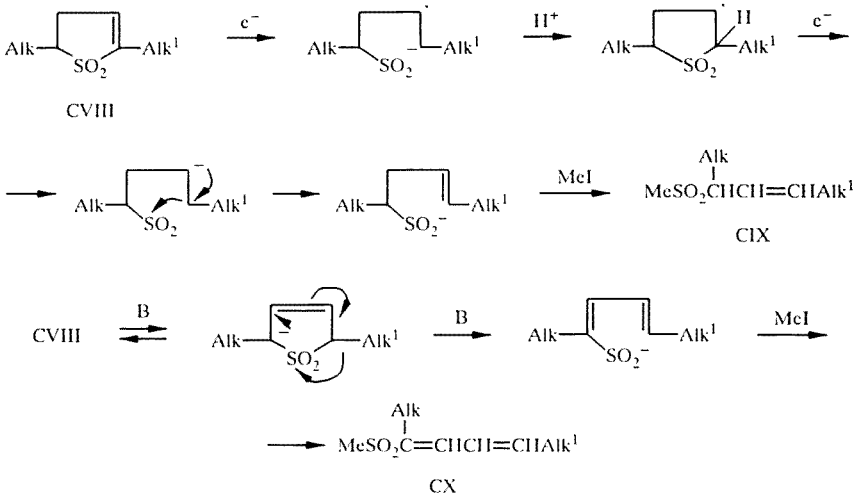


CVI CVII

The authors of [64] present the following scheme for the formation of dienes CVII:

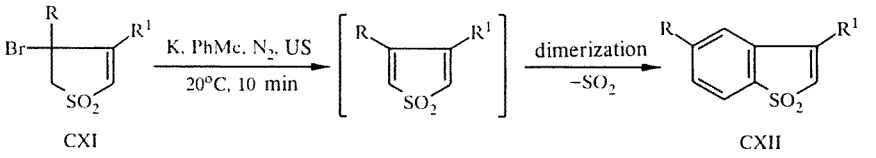


In another paper [65], the same authors showed that upon treatment with potassium in a T 570/H ultrasonic bath in the presence of MeI and proton donors (H_2O, MeOH, Me_3COH, PhOH, AcOH), the 3-sulfolenes (CVIII) are converted to unsaturated sulfones (CIX) and (CX) in 20-88% and 40-72% yields respectively, and they proposed a different scheme for their formation:



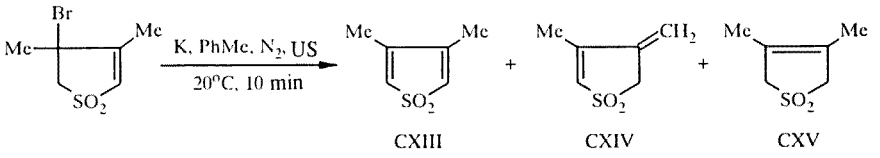
In cases when Alk = Alk^1 = Bu or Alk = Alk^1 = C_7H_{15}, in addition to the products CIX and CX, the corresponding dienes AlkCH=CHCH=CHAlk^1 are also formed in 10.2% and 8.5% yields respectively [65].

4-Bromo-2-sulfolenes (CXI) upon treatment with potassium in an ultrasonic bath (50 kHz, 150 W) are converted to the bicyclic compounds (CXII) [66]:



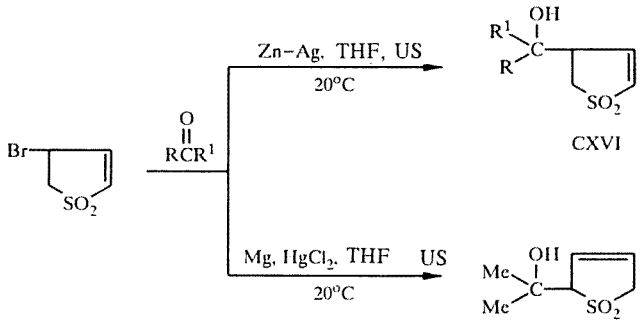
R, R^1, yield in %: H, H, 52; H, Me, 33; H, Cl, 46

If R = R^1 = Me in the sulfolene CXI, then a mixture of three compounds (CXIII), and (CXIV), and (CXV) is formed with 83%, 2%, and 4% yields respectively [66]:

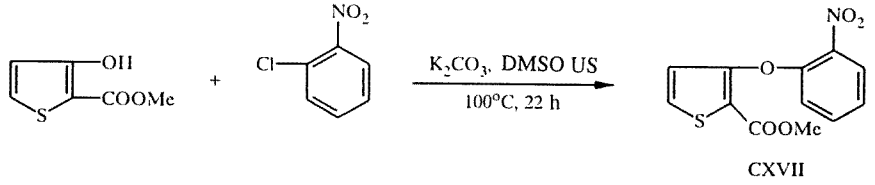


It is interesting that upon treatment of 2,3-dibromo-2-methylsulfolane with potassium under sonolysis conditions, only the reaction of debromination occurs and 2-methyl-2-sulfolene is formed in 85% yield [66].

Using a ultrasonic bath (30-50 kHz, 120 W) and different metals, we can regulate the regioselectivity of the reaction of 4-bromo-2-sulfolene with carbonyl compounds. Thus in the presence of Zn–Ag, the substituents add at the 4 position and the compounds (CXVI) are formed in 35-97% yields. In the presence of Mg and $HgCl_2$, the hydrogen in the 2 position is substituted with isomerization of the double bond, and 2-(1-methyl-1-hydroxyethyl-3-sulfolene is formed in 31% yield [67]:



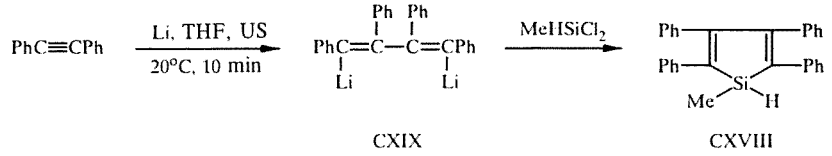
3-Hydroxy-2-methoxycarbonylthiophene reacts with 2-chloronitrobenzene in a Branson ultrasonic bath (350 W) in the presence of potassium carbonate with formation of 34% ether (CXVII) [68]:



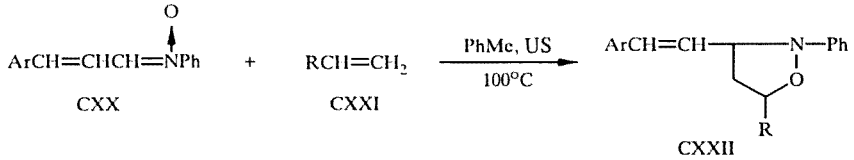
Under the same conditions but without ultrasound, the ether CXVII is synthesized in only 17% yield [68].

3.4. Other Heterocycles

The reaction of $MeHSiCl_2$ with the dilithium derivative (CXIX) has been used to synthesize 1-methyl-2-3,4,5-tetraphenylsilacyclopenta-2,4-diene (CXVIII). Sixteen hours is required to obtain CXIX under standard conditions (with stirring) [69]. The use of ultrasonic treatment (50-60 kHz, 150 W) makes it possible to obtain the dilithium derivative CXIX over the course of 10 min [70]:

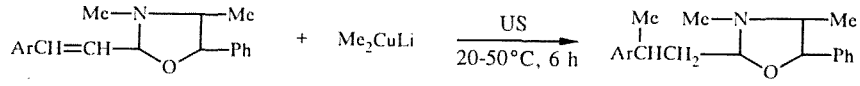


Delocalization of the charges in the conjugated nitrones (CXX) is the reason for their low activity in reactions of 1,3-dipolar cycloaddition with inactivated alkenes (CXXI). With ultrasonic treatment, these reactions proceed significantly faster: the reaction time is shortened from 34-48 h (with stirring and without ultrasonic treatment) down to 50-180 min; the yield of cycloaddition products (CXXII) is 45-81% [71]:



R, Ar: Ph, Ph; furyl -2, Ph; Ph, 4-MeC_6H_4; Ph, 4-ClC_6H_4

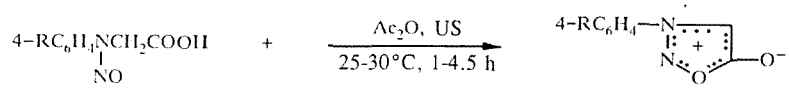
Under sonolysis conditions, the reaction of oxazolidines (CXXIII) with lithium dimethylcuprate occurs in the solid phase, the yields of compounds (CXXIV) are 33-85% [72]:



CXXIII CXXIV

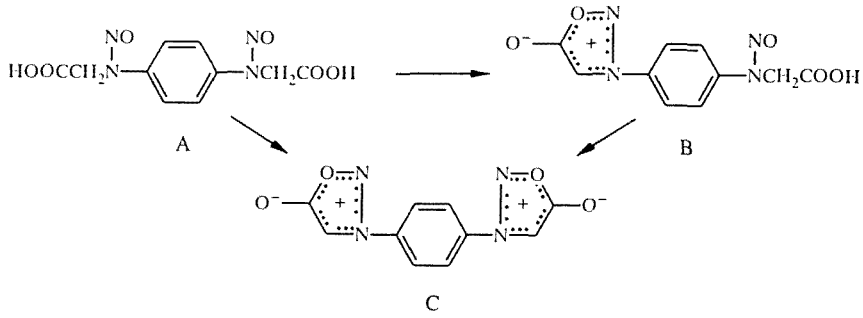
Ar: Ph, 2-ClC_6H_4, 2-$MeOC_6H_4$, 4-MeC_6H_4

Ultrasound significantly accelerates cyclization of N-nitroso derivatives (CXXV) to sydnones (CXXVI) [73]:



CXXV CXXVI

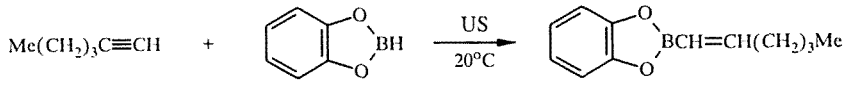
Below we present the results of treatment of compound CXXV (R = $N(NO)CH_2COOH$) with Ac_2O at 20°C under sonolysis conditions and without ultrasound [73]:



Indicated: conversion, treatment time and yields without and without ultrasound: A → B, 5 h, 98%, 9 days, low; B → C, 2 h, 90%, 5 days, 17% A → C, 7 h, 98%, 5 days, 17%.

In [74], the use of ultrasound is described for debromination of 4-bromo-3-substituted sydnones, occurring with 60-96% yield, and also for conversion of 3-substituted sydnones upon treatment with acetic anhydride to their 4-acetyl-3-substituted derivatives in 17-68% yields.

Ultrasound substantially accelerates the reaction of hydrobromination. While addition of catechoborane (CXXVII) to hex-1-yne under standard conditions takes 24 h, upon ultrasonic treatment the addition product (CXXVIII) was obtained in 6 h in 98% yield [75]:

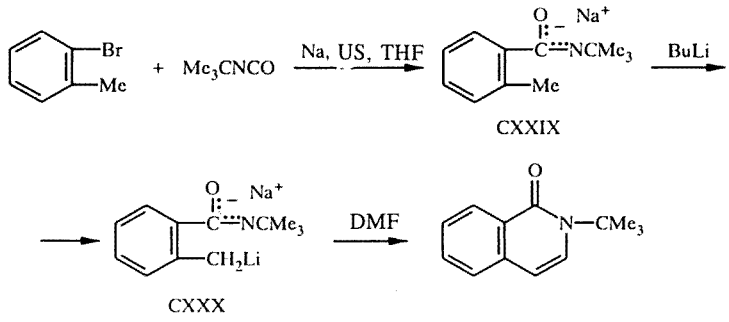


CXXVIII

4. SIX-MEMBERED HETEROCYCLIC COMPOUNDS

4.1. Nitrogen-Containing Heterocycles

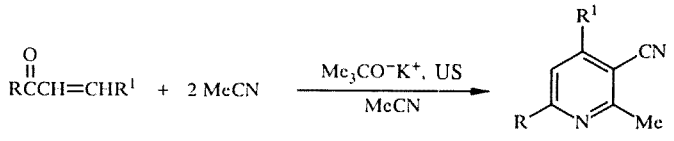
2-Bromotoluene under sonolysis conditions reacts with Me_3CNCO and sodium with formation of the salt (CXXIX), yielding with butyllithium the salt (CXXX), the reaction of which with DMF leads to N-*tert*-butylisoquinol-1-one in 40% yield [27]:



CXXIX

CXXX

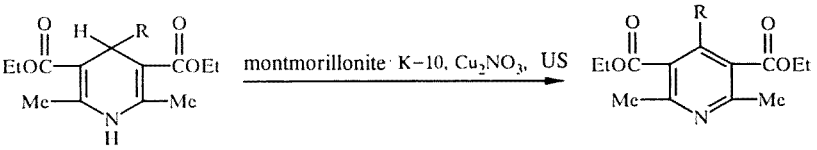
As a result of reaction of chalcones with acetonitrile in the presence of potassium *tert*-butylate with ultrasonic treatment (47 kHz, 150 W), a large number of pyridine derivatives (CXXXI) were obtained, containing aryl, hetaryl, or ferrocenyl radicals in the 4 and 6 position [76, 77]:



CXXXI

In the opinion of the authors of [76], the reaction begins with Michael addition of the acetonitrile dimer to the chalcone followed by dehydration and dehydrogenation.

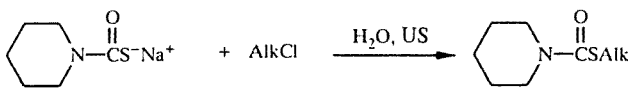
Hantzsch bases (CXXXII) containing aromatic radicals or a hydrogen atom in the 4 position are converted to pyridine derivatives (CXXXIII) under standard conditions (with stirring) over the course of 1.5-11 h in 40-93% yields. When this reaction is carried out under sonolysis conditions (VC 375 Ultrasonic Processor), the reaction time is shortened down to 5-10 min, while the yields of reaction products CXXXIII are 78-98% [78]:



CXXXII CXXXIII

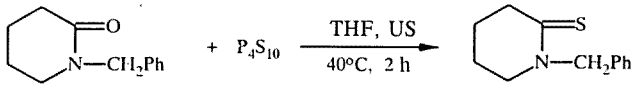
We should note that if alkyl radicals are in the 4 position of compounds CXXXII, then aromatization does not proceed either under standard conditions or upon ultrasonic treatment [78].

The use of ultrasonic treatment is of fundamental importance in alkylation of slats of thiocarbamic acids. Usually this reaction is carried out at elevated temperatures, but the salts formed are thermally unstable and the yields of alkylation products (CXXXIV) after 3 h at 70°C are 30-53%. When alkylation is carried out with ultrasonic treatment (22 kHz, 45.8 ± 0.1 W), we can obtain the same products in 97.9-99.4% yields at 50-70°C after 10-20 min [79]:



CXXXIV

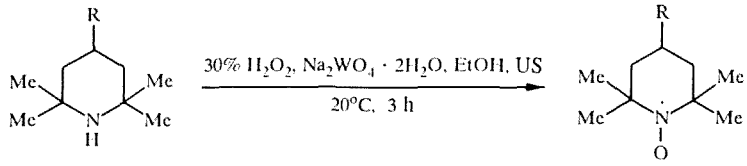
Under sonolysis conditions (80 kHz), substitution of the oxygen atom by a sulfur atom occurs easily upon treatment of amides (CXXXV) with P_4S_{10}; yield of reaction product, 77% [80].



CXXXV

Upon treatment of 2,2,6,6-tetramethylpiperidine with BuLi under sonochemical reaction conditions (50 kHz, 60 W) at 20°C for 15-30 min,the corresponding N-Li derivative is formed [47].

Usually difficulties arise when obtaining N-oxyl radicals by oxidation of sterically hindered amines with lengthy lipophilic substituents by hydrogen peroxide under standard condition. Using ultrasound makes it possible to overcome these difficulties [81]:

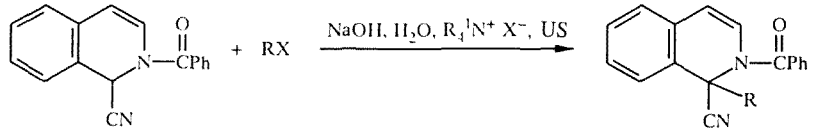


Yield in %: $C_{17}H_{35}COO$, 84; 4-$C_8H_{17}C_6H_4COO$, 38; 4-$C_8H_{17}C_6H_4CONH$, 63

Sonolysis significantly facilitates introduction of a methyl group into the 1 position of isoquinoline by treatment with DMSO in the presence of NaH; the yield of 1-methylisoquinoline is 72-76% for a reaction temperature of 20°C and a reaction time of 2 h [82]. Without ultrasonic treatment, in order to obtain the same product in 65-70% yield it is necessary to vigorously stir the reaction mixture at 70°C for 4 h [82].

The use of ultrasound in alkylation of the Reissert compound (CXXXVI) in the presence of phase-transfer catalysts makes it possible to shorten the reaction time from 2 h down to 20-25 min and to increase the product yields (CXXXVIII) from 24-80% up to 45-88% [83].

When carrying out the reaction with ultrasonic treatment, an exception is the reaction of the compounds CXXXVI with XCH_2COOEt (24% yield),obviously due to saponification of the ester group [84]:

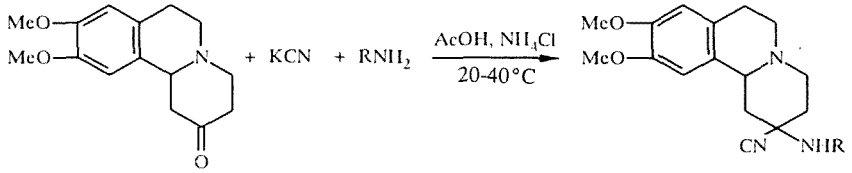


CXXXVI CXXXVII

R: $PhCH_2$, 2-$ClC_6H_4CH_2$, 4-$ClC_6H_4CH_2$, 2,4-$(O_2N)_2C_6H_3$, CH_2COOEt; $R_4^1N^+$, X^-: Et_3NCH_2Ph, Cl; $Me_3NC_{16}H_{33}$, Br; X = Cl, Br

6-Nitroquinoline under sonolysis conditions is quantitatively converted to 6-aminoquinoline upon treatment with hydrazine and sulfur [85].

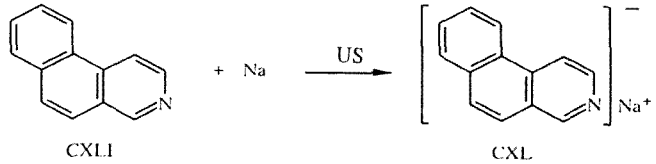
The substantial effect of ultrasound on the Strecker–Zelinsky reaction has been established. Thus, upon reaction of the ketone (CXXXVIII) with KCN and ammonia or amines with ultrasonic treatment (50-55 kHz, 150 W), the process time is shortened from 12-13 days (under standard conditions) down to 20-35 h, and the product yields (CXXXIX) are increased from 60-80% up to 81-100% [86]:



CXXXVIII CXXXIX

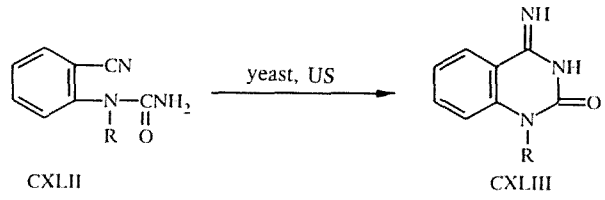
While under standard (thermal) conditions quaternary salts can be obtained from 1-(phenoxycarbonyl)acridine only with MeX of EtX, with ultrasonic treatment the analogous salts can also be obtained with PrX, Me_2CHX, and $PhCH_2X$ [87].

The salt of the radical anion (CXL) under sonolysis conditions is formed from isobenzoquinoline (CXLI) and Na in 15 min, instead of 4 h when the reaction is carried out without ultrasound [88]:



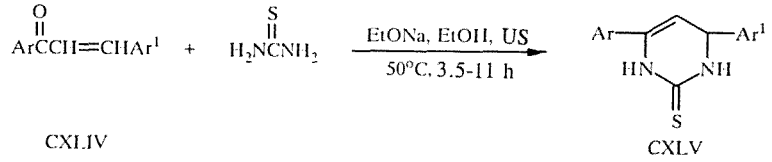
CXLI CXL

In the presence of baker's yeast with ultrasonic treatment (Branson Sonifier B-30 ultrasonic bath), o-substituted benzonitriles (CXLII) undergo ring closure to form the bicyclic compounds (CXLIII) in 82-93% yields [89]:



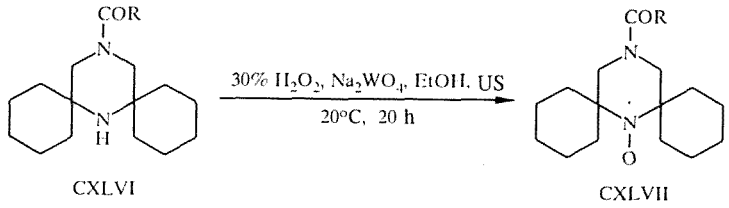
CXLII CXLIII

Usually upon reaction of chalcones with thiourea, strong saponification is observed and a mixture of products is formed which is difficult (often impossible) to separate. It has been found that carrying out this reaction under sonolysis conditions (25 kHz, 160 W) makes it possible to avoid these difficulties and to synthesize derivatives of pyrimidine-2-thione (CXLV) in 58-79% yields from chalcones (CXLIV) and thiourea [90]:



CXLIV CXLV

Upon oxidation of piperazine derivatives (CXLVI) by H_2O_2 in the presence of Na_2WO_4 with ultrasonic treatment (20 kHz, 160 W), the N-oxyl radicals (CXLVII) are formed in 58-86% yields [81]:

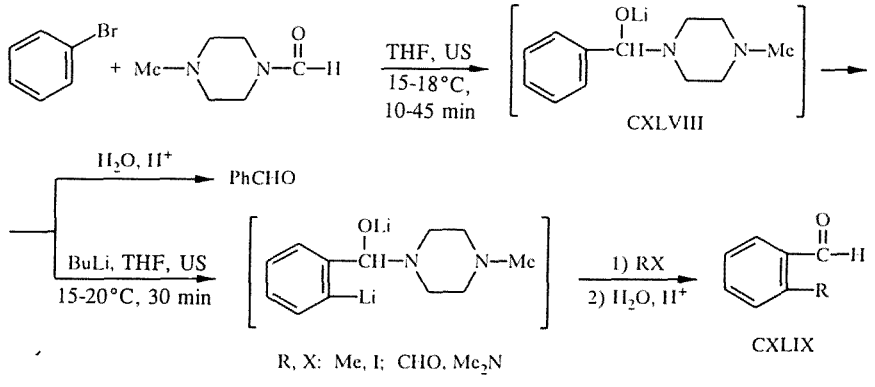


CXLVI CXLVII

R: C_8H_{17}, $C_{17}H_{35}$, 4-$C_8H_{17}OC_6H_4$

Without ultrasound, only traces of radicals CXLVII are formed even after several weeks [81].

Bromobenzene reacts with N-methyl-N^1-formylpiperazine and lithium under sonolysis conditions (in THF or tetrahydropyran, 50 kHz; in Et_2O, 500 kHz), forming the lithium alcoholate (CXLVIII), which upon hydrolysis is converted to benzaldehyde in 75-80% yield. If the alcoholate CXLVIII before hydrolysis is treated with BuLi and then with electrophilic reagents, when o-substituted benzaldehyde (CXLIX) is obtained [91, 92]:

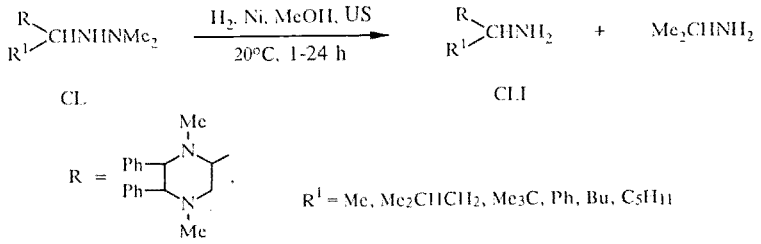


CXLVIII

CXLIX

R, X: Me, I; CHO, Me_2N

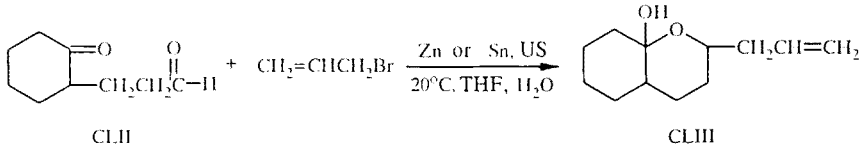
The effect of ultrasonic treatment has been studied on the reaction of cleavage of hydrazine derivatives (CL) in the presence of Raney nickel catalyst. When using ultrasonic treatment, the reaction occurs significantly faster and in higher yields (than under standard conditions), there is no need to operated under pressure (usually H_2 is used at a pressure of 3-50 atm), racemization does not occurs when using enantiomers as the starting compounds, and debenzylation or hydrogenation of the aromatic rings does not occur; the yields of reaction products (CLI) are 66-85% [93]:

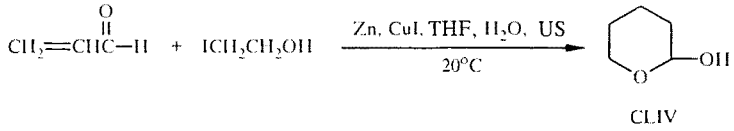


Upon ultrasonic treatment (50 kHz, 120 W), the reaction of cyanuric acid with formaldehyde is significantly accelerated and the yields of mono- and dihydroxymethyl derivatives are increased. Thus is pyridine at 17°C after 3 h, the yield of 1-hydromethylcyanuric acid was 95%, while without ultrasonic treatment with stirring at 20°C, after 16 h the yield was 64%. The yield of 1,3-di(hydroxymethyl)cyanuric acid with ultrasonic treatment (17°C, 3 h) was 97%, while simple stirring (20°C, 15 h) the yield was 85%. Conversion of the monohydroxymethyl derivative to the dihydroxymethyl derivative occurs without ultrasonic treatment at 20°C with 96% yield after 20 h; with ultrasonic treatment at 17°C, the conversion is complete after 3 h with 97% yield [94].

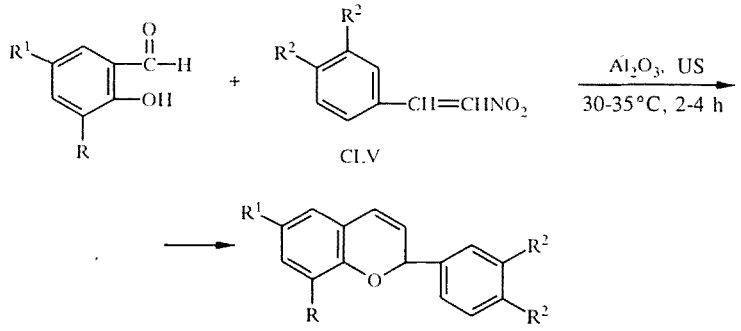
4.2. Oxygen-Containing Heterocycles

In condensation of ketoaldehyde (CLII) with allylbromide [95] or 2-iodoethanol with acrolein [96], the cyclization products (CLIII) (yield 55% with Zn and 70% with Sn) or (CLIV) (yield 70%) respectively are obtained; in both cases, the reactions were carried out with ultrasonic treatment (50 kHz, 240 W):

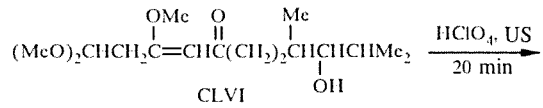




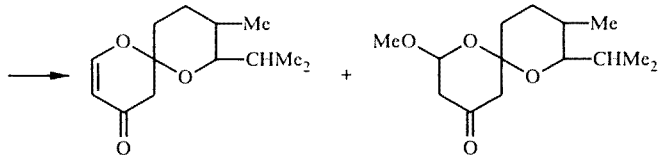
The reaction of nitroethylene derivatives (CLV) with salicylic aldehyde or its derivatives in the presence of Al_2O_3 is significantly accelerated in an ultrasonic bath; the yields of reaction products are 36-85% [97].



Under sonolysis conditions in the presence of $HClO_4$, the compound (CLVI) undergoes ring closure with formation of a 4:1 mixture of two compounds (CLVII) and (CLVIII) with overall yield 63% [98]:

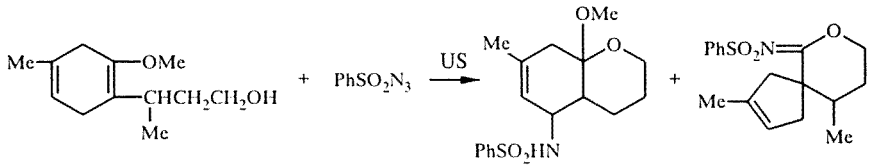


CLVI



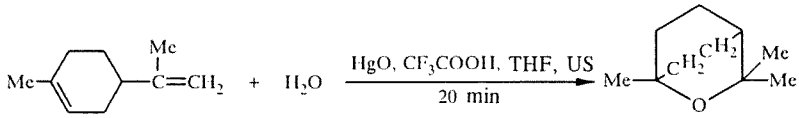
CLVII CLVIII

Two products (CLIX) and (CLX) were also obtained with ultrasonic treatment (ME 4.6 ultrasonic bath) of a mixture of the cyclohexa-1,4-diene derivative (CLXI) and $PhSO_2N_3$ [99]:



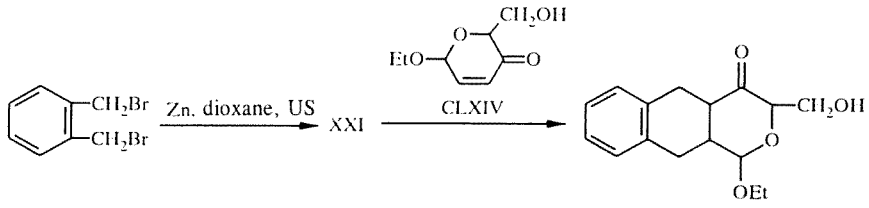
CLXI CLIX CLX

In the sonochemical reaction (HE 2500 ultrasonic bath) of limonene and water, among other compounds the bicyclic product (CLXII) is formed (15% yield) [100]:

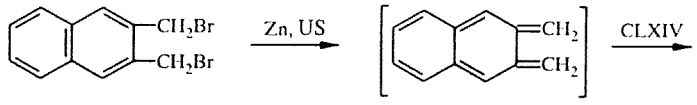


CLXII

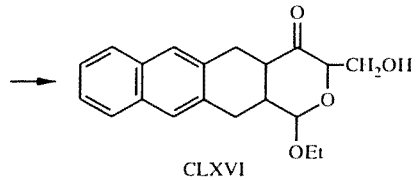
1,2-Di(bromomethyl)benzene or 2,3-di(bromomethyl)naphthalene with ultrasonic treatment (50 kHz) are converted to o-di(methylidene) derivatives LXXI or (CLXIII), which react *in situ* with the compound (CLXIV) to form cyclization products (CLXV) or (CLXVI); yields 20-30% [101]:



CLXV

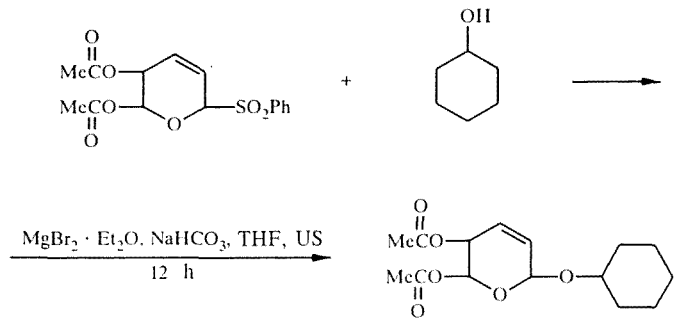


CLXIII



CLXVI

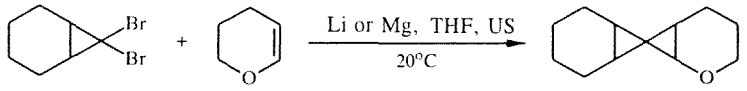
Upon reaction of 2-phenylsulfonyl-5,6-di(methoxycarbonyl)-5,6-dihydropyran with cyclohexanol under sonolysis conditions, the $PhSO_2$ group is substituted by a cyclohexyloxy group and compound (CLXVII) is obtained in 77% yield (without ultrasound, the yield is 20%) [102]:



CLXVII

In an ultrasonic bath (125 W), the reaction of 5,6-dihydro-4H-pyran with CH_2Br_2 is accomplished in the presence of Cu–Zn alloy and the compound 2-oxabicyclo[4.1.0]heptane is synthesized in 41% yield [103].

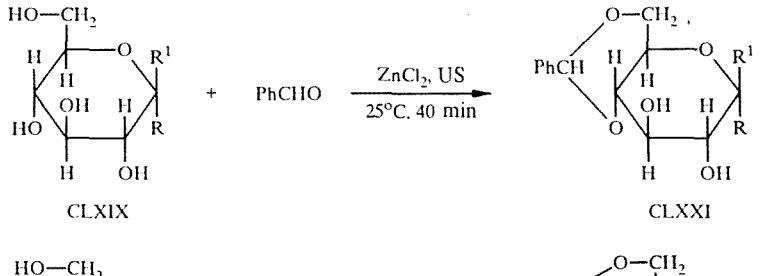
The spiro compound (CLXVIII) is synthesized as a result of sonochemical reaction (20 kHz) of 7,7-dibromobicyclo[4.1.0]heptane with 5,6-dihydro-4H-pyran [10]:



CLXVIII

With ultrasonic treatment, the reaction of acetalization of sugars is considerably simplified: side reactions are significantly suppressed, the reaction time of sugars with carbonyl compounds is significantly shortened, the yields of target products are increased, and the reaction is well controlled.

α-D- and β-D-Glucopyranosides (CLXIX) or α-D- and β-D-galactopyranosides (CLXX) easily react with benzaldehyde in the presence of $ZnCl_2$ under sonolysis conditions (50-60 Hz) with formation of the corresponding cyclic acetals (CLXXI) or (CLXXII) [105]:

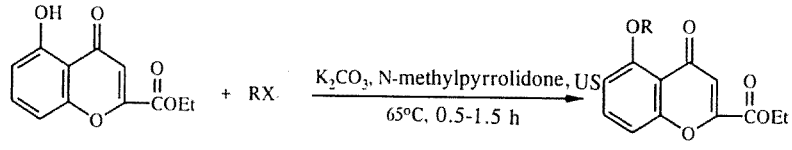


R, R^1, yield (%): MeO, H, 71 and 73; H, **MeO**, 64 and 74

The ketalization of D-glucose, D-galactose, and D-mannose upon their treatment with acetone or cyclohexane in the presence of concentrated H_2SO_4 also proceeds significantly better with ultrasonic treatment; the corresponding diketals are formed in 43-86% yields over the course of 50-60 min (without ultrasound, the reaction time increases to 18 h) [106].

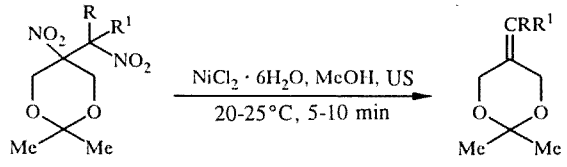
In the reaction of 2-hydroxytetrahydropyran with allylbromide in the presence of Zn with ultrasonic treatment (50 kHz), ring opening occurs and oct-1-ene-4,8-diol is formed in 79% yield (38].

In an ultrasonic bath (225 W), the O-alkylation of esters (CLXXIII) by alkyl halides occurs smoothly in the presence of potassium carbonate; the yields of alkylation products are 88-100% [107]:



CLXXIII

With ultrasonic treatment (50 kHz, 20-40 W), for compounds with two vicinal nitro groups (CLXXIV) in the presence of nickel chloride, both nitro groups are cleaved and the 2,2-dimethyl-1,3-dioxolane derivatives (CLXXV) are formed in 89-95% yields [108]:



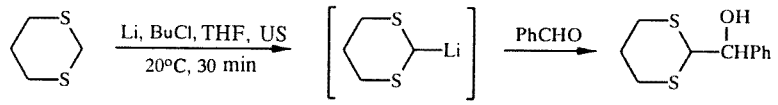
CLXXIV CLXXV

The iodine in 4-(2-iodomethyl)-2-phenyl-1,3-dioxane upon reaction with $PhSe^-Na^+$ under sonolysis conditions (55 kHz, 100 W) is substituted by the $PhSe^-$ group; the yield of substitution product is 84% [12].

4.3. Sulfur-Containing Heterocycles

Methylpentylsulfone is synthesized in 91% yields by treatment of pentamethylenesulfone with potassium in toluene in the presence of MeI with ultrasonic treatment (45 kHz, 100 W) [23].

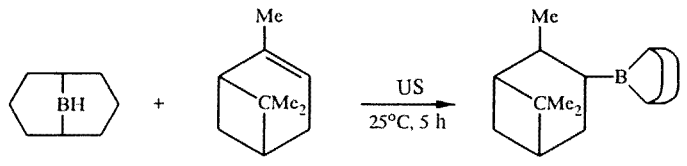
In an ultrasonic bath (HE 2500), 1,3-dithiane reacts with BuLi and is converted to 2-lithium-1,3-dithiane, which reacts with benzaldehyde; the condensation product (CLXXVI) is formed in 98% yield [47]:



CLXXVI

4.4. Other Heterocycles

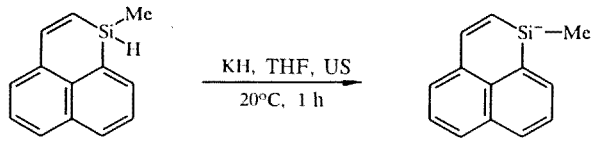
With ultrasonic treatment, 9-borobicyclo[3.3.1]nonane (CLXXVII) is added to pinene; the addition product (CLXXVIII) is formed in 99% yield [75]:



CLXXVII CLXXVIII

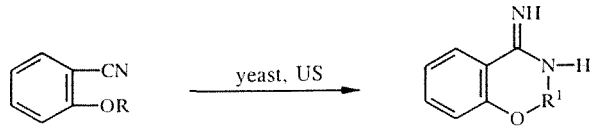
Earlier it was noted that upon treatment of dimethyldichlorosilane with Li under sonolysis conditions (50-60 kHz, 150 W), dodecamethylcyclohexasilane is obtained in 70% yield [24]. This reaction was studied in more detail with ultrasonic treatment (22 kHz, 50 W, 20°C, 1 h, argon atmosphere); the indicated product was synthesized in 73.4% yield (without ultrasonic treatment, the yield was 65.8%).

Under sonolysis conditions (55 kHz, 150 W, ≈20°C), 1-methyl-1-silaphenalene (CLXXIX) forms the anion (CLXXX) upon treatment with potassium hydride [110]:



CLXXIX CLXXX

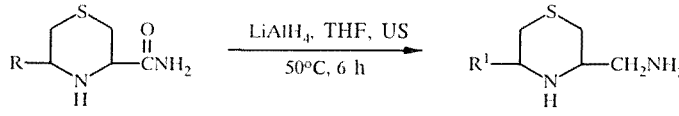
Cyclization of nitriles (CLXXXI) to bicyclic compounds (CLXXXII) in the presence of baker's yeast in a phosphate buffer solution is accelerated by ultrasonic treatment (Branson Sonifier B-30 bath); the cyclization products yields are higher than 80% [88]:



CLXXXI CLXXXII

R, R^1: $CONH_2$, CO; SO_2NH_2, SO_2

Reduction of the $CONH_2$ groups in tetrahydro-1,3-thiazine derivatives (CLXXXIII) by $LiAlH_4$ is difficult to accomplish due to the poor solubility of such compounds in conventionally used solvents. Carrying out reduction with ultrasonic treatment (55 kHz, 125 W) makes it possible to carry out this reaction in THF and to obtain the reduction products (CLXXXIV) in 60-79.5% yields [111]:

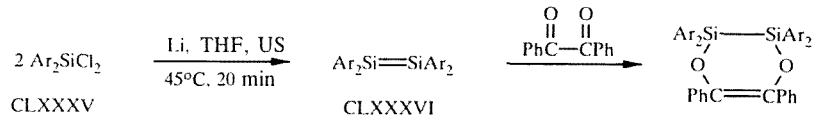


CLXXXIII CLXXXIV

R, R^1: H, H; $CONH_2$, CH_2NH_2

As noted above, the derivatives of 6H-1,3,4-thiadiazine XLIV (X = S) or 6H-1,3,4-selenodidiazine XLIV (X = Se) under sonolysis conditions (25 kHz) are converted to pyrazole derivatives XLV in 81-90% yields [34].

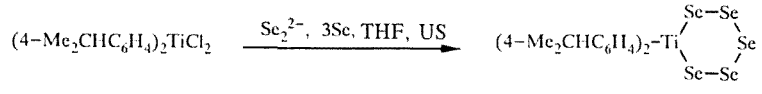
According to the data in [112], upon treatment of dimesityldichlorosilane (CLXXXV) with lithium in an ultrasonic bath (50-60 kHz, 150 W) in THF, tetramesitylsilene (CLXXXVI) is formed in 90% yield. Formation of the compound CLXXXVI was confirmed by obtaining the cycloaddition product (CLXXXVII) from it in 38% yield:



CLXXXV CLXXXVI CLXXXVII

Ar = 2, 4, 6-$Me_3C_6H_2$

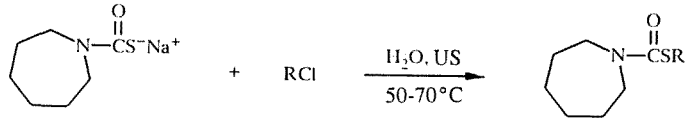
Ultrasonic treatment accelerate mass transfer on the surface of electrodes, and as result the electrolysis rate is increased. Using this phenomenon, the authors of [113] accomplished the synthesis of compound (CLXXXVIII), containing a heterocycle consisting of a titanium atom and five selenium atoms, under electrolysis conditions with ultrasonic treatment; yield, 82% [113]:



CLXXXVIII

5. COMPOUNDS CONTAINING MORE THAN SIX ATOMS IN THE HETEROCYCLE

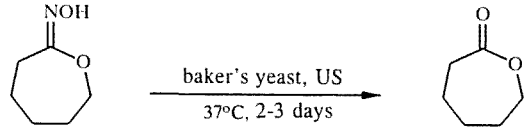
Under sonolysis conditions, S-alkylation of the sodium salt of hexamethylenecarbamic acid (CLXXXIX) occurs faster and in higher yields. Thus upon alkylation of CLXXXIX by C_2H_5Cl with ultrasonic treatment (22 kHz, 45.8 ± 0.1 W), compounds CXC (R = C_2H_5) is formed in 98.4% yield in 20 min; without ultrasonic treatment (with stirring under homogenenous conditions), the yield of the same product was 53.5% after 2.5 h at 70-75°C [79]:



CLXXXIX CXC

The use of ultrasound in polymerization of ε-caprolactam in the presence of promoters (amino acids) at 95-270°C over the course of 3-8 h makes it possible to obtain nylon-6 with higher molecular mass and with lower variance in the degree of polymerization than under standard conditions [114].

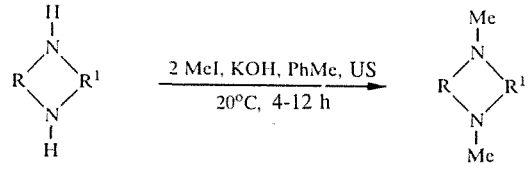
Oxime (CXCI) with ultrasonic treatment in the presence of baker's yeast in a phosphate buffer solution (pH 7.2) over the course of 3 days is converted to caprolactone in 94% yield [115]:



CXCI

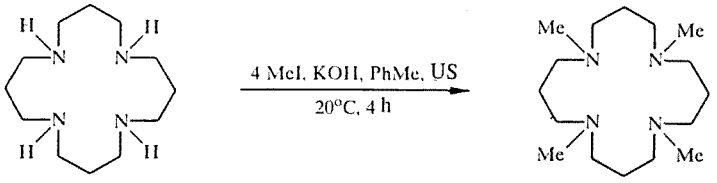
Without ultrasonic treatment, the same oxime is converted to caprolactone in 63% yield [115].

Under sonolysis conditions, N-methylation of diazacoronands (CXCII) and cyclam (CXCIII) is facilitated; the yields of the corresponding alkylation products (CXCIV) and (CXCV) are 92-98% [116]:



CXCII CXCIV

R, R¹: $(CH_2)_2O(CH_2)_2$, $(CH_2)_2O(CH_2)_2$; CH_2CH_2, $(CH_2)_2O(CH_2)_2$; *o*-phenylene, $(CH_2)_2O(CH_2)_2$; $(CH_2)_2OCH_2CH_2O(CH_2)_2$, $(CH_2)_2OCH_2CH_2O(CH_2)_2$; 1,2-$C_6H_4(OCH_2CH_2)_2$, 1,2-$C_6H_4(OCH_2CH_2)_2$



CXCIII CXCV

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