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REACTIONS OF ACETYLENIC CF_3-KETONES WITH MONO- AND BIDENTATE *N*-NUCLEOPHILES

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Chemo- and stereoselective addition of primary and secondary amines as well as N,N-, N,O- and N,S-binucleophiles to trifluoromethylated acetylenic ketones was studied. It was found that in all cases the corresponding aza-Michael adducts were obtained in good to excellent yields. Mono-adducts formed from diamines bearing two primary amino groups underwent intramolecular cyclization to give the diazepines. At the same time, when the same ketones were treated with diamines bearing only secondary amino groups, acyclic bis-β-aminoenones were obtained as a sole reaction product. Chemoselective addition of binucleophiles bearing various nucleophilic centers such as N-methylaminoethanol and 2-aminoethanethiol to CF_3-ynones was observed: the corresponding aza-Michael adducts were synthesized in good yield. In contrast to non-fluorinated analogues, trifluoromethylated acetylenic ketones react with both mono- and bidentate nitrogen nucleophiles to give the push-pull aminoenones as a single geometric isomer. Its configuration depends on the nature of amine moiety. In all cases, aminoenones bearing secondary amino group have *Z*-geometry due to the stabilizing effect of the intramolecular hydrogen bond while their analogues bearing tertiary amino group were obtained as *E*-isomer. The experimental data are in good agreement with quantum-chemical calculations. Refs 18.

Keywords: ynones, amines, bidentate nucleophiles, Michael addition.

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РЕАКЦИИ АЦЕТИЛЕНОВЫХ CF_3-КЕТОНОВ С МОНО- И БИДЕНТАТНЫМИ *N*-НУКЛЕОФИЛАМИ

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Трифторметил(алкинил)кетоны вступают в аза-реакцию Михаэля с первичными и вторичными аминами, а также N,N-, N,O- и N,S-бидентатными нуклеофилами, приводя к пушпульным аминоенонам. Моно-аддукты Михаэля, полученные из диаминов, с двумя первичными аминогруппами, претерпевают внутримолекулярную циклизацию, давая диазепины. Результатом взаимодействия симметрично замещённого N,N-диметилэтилендиамина с ацетиленовыми CF_3-кетонами являются бис-β-аминоеноны. Бинуклеофилы, содержащие различные по природе нуклеофильные центры — N-метиламиноэтанол и аминоэтантиол — хемоселективно присоединяются к изучаемым инонам, образуя исключительно аза-аддукты Михаэля. Аминоеноны, содержащие вторичную аминогруппу, имеют *Z*-конфигурацию благодаря стабилизирующему эффекту внутримолекулярной водородной связи, в то время как аминоеноны с третичной аминогруппой находятся в виде *E*-изомера. Полученные результаты были подтверждены квантово-химическими расчётами. Трифторметилированные ацетиленовые кетоны взаимодействуют с азотсодержащими нуклеофилами, образуя аза-аддукты Михаэля с высокой стереоселективностью. Библиогр. 18 назв.

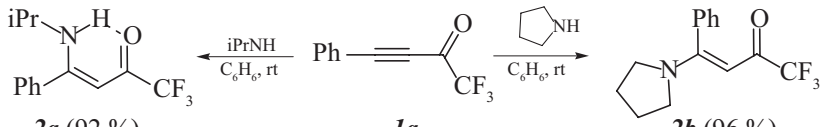
Ключевые слова: иноны, амины, бидентатные нуклеофилы, нуклеофильное присоединение.

Introduction. The term aminoenones became a part of world chemical society's lexicon by the last quarter of the 20th century [1, 2]. Nowadays these derivatives are considered to be a separate class of organic compounds. Being classic push-pull systems, β-aminoenones

possess a diverse reactivity and are widely used as valuable precursors for the synthesis of carbo- and heterocycles as well as analogues of natural compounds [3, 4].

The most common preparation method of β-aminoenones includes reactions of 1,3-diketones with nitrogen nucleophiles. However non-symmetrically substituted diketones react with amines affording inseparable mixtures of isomeric ketones. The problem of low selectivity can be successfully solved by another synthetic route based on aza-Michael addition of primary and secondary amines to acetylenic ketones [5–7]. Being atom-efficient, this method meets requirements of green chemistry and has some advantages over the previously published methods of synthesis of fluorinated aminoenones [8–11]. Herein we report a study of the chemical behaviour of easily available trifluoromethyl(alkynyl)ketones [12] with nitrogen mono- and bidentate nucleophiles. Chemoselectivity of addition of *N*, *O*- and *N*, *S*-binucleophiles is emphasized. Taking into account that aza-Michael adducts are of great interest as ligands bearing both nitrogen and oxygen chelating centers [13–16], we studied stereochemistry of aminoenones bearing secondary and tertiary amino group.

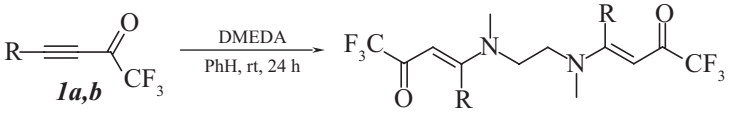
Preparation of CF_3-containing aminoenones. Trifluoromethyl(alkynyl)ketones ***1*** as bielectrophiles are able to react with nucleophiles giving products of 1,2- or 1,4-addition. We found that, similarly to non-fluorinated analogues, ynone ***1a*** readily reacts with primary and secondary amines to give push-pull aminoenones with nearly quantitative yields (Scheme 1).



2a (92 %) ***1a*** ***2b*** (96 %) (1)

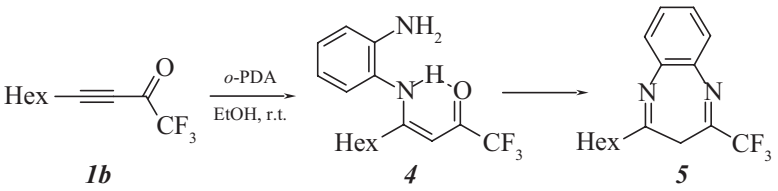
Isolated aza-Michael adducts bearing secondary (in the case of ***2a***) or tertiary (in the case of ***2b***) amino group were used as standards for studying of stereochemistry of push-pull aminoenones.

When a nucleophile has two nucleophilic centers the formation of different acyclic and heterocyclic derivatives is possible. Thus, the use of symmetrically substituted dimethylethylenediamine (DMEDA) in the reaction with ynones ***1a,b*** leads to bis-β-aminoenones ***3a,b*** in high yield (Scheme 2) [17].



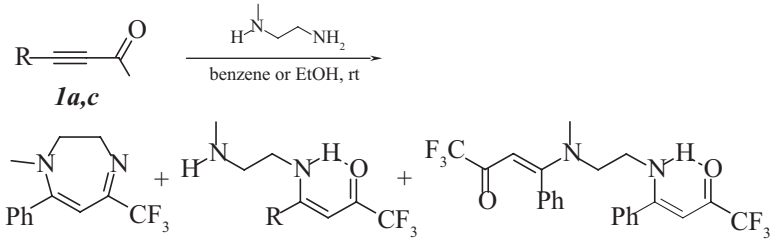
1a,b R = Ph (***a***), *n*-Hex (***b***) ***3a*** (67 %), ***3b*** (79 %) (2)

On the contrary, diamines bearing two primary amino groups form Michael monoadducts which subsequently undergo intramolecular cyclization giving corresponding heterocycles. For instance, *o*-phenylenediamine (***o***-PDA) reacts with ynone ***1b*** under the same conditions affording aminoenone ***4*** [18]. The presence of intramolecular hydrogen bond in the product provides its *Z*-configuration which is preferable for condensation of the second nucleophilic center with carbonyl group (Scheme 3). In fact, aminoenone ***4*** transforms into diazepine ***5*** under reaction conditions. The heterocyclic derivative ***5*** was obtained by the one-pot synthesis from the same starting materials.



1b *4* *5* (3)

The study of reaction of ynones with diamines containing both primary and secondary amino groups was of particular interest. *N*-methylethylendiamine used in the reaction with amine ***1a*** gave a mixture of diazepine ***6***, mono- ***7a***, and bis-adduct ***8*** (Scheme 4).

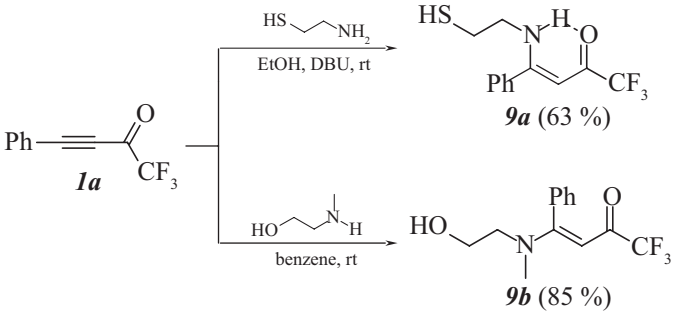


1a,c (4)

6 (33 %) ***7a*** (28 %), ***7b*** (87 %) ***8*** (15 %)

1: R = Ph (***a***), 4-ClC$_6$H$_4$ (***c***); ***7***: R = Ph (***a***), 4-ClC$_6$H$_4$ (***b***)

The data obtained indicate that reaction proceeds with low selectivity. The addition of *N*-methylethylenediamine to triple bond of ynone ***1a*** occurs via both primary and secondary amino group. In the case of attack by secondary amino group the forming intermediate undergoes intramolecular cyclization affording diazepine ***6*** or gives bis-β-aminoenone ***8*** via addition to triple bond of another molecule of ketone. On the contrary, the use of ynone ***1c*** in this reaction leads to aminoenone ***7b*** only. Chemoselectivity of AdN reactions of acetylenic ketones were studied using compounds bearing nucleophilic centers of different nature such as *N*-methylaminoethanol and aminoethanethiol. Thus, when ketone ***1a*** was treated with these binucleophiles the only aza-Michael adducts were formed (Scheme 5).



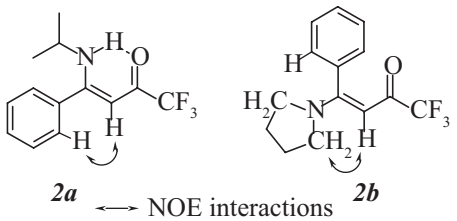
1a ***9a*** (63 %) ***9b*** (85 %) (5)

Chemoselective formation of aminoenones ***9a,b*** indicates the preferable attack of β-carbon atom of triple bond by nitrogen center of binucleophile.

Stereochemistry of CF$_3$-containing aminoenones. The previous stereochemical study of non-fluorinated aminoenones indicates that addition of primary amines to acetylenic bond proceeds with low stereoselectivity leading to mixtures of *E*- and *Z*-isomers with predominance of the latter while secondary amines give preferably *E*-aminoenones: the only traces of *Z*-isomer were observed in this case [7].

We found that in contrast to non-fluorinated analogues, trifluoromethyl(alkynyl)ketones react with mono- and bidentate nitrogen nucleophiles to give the only one stereoisomer. Its configuration strongly depends on the nature of nitrogen moiety.

Stereochemistry of push-pull β-aminoenones ***2a,b*** was defined with 2D NMR (NOESY) and IR spectroscopy. Thus, the presence of cross-peaks between olefinic proton and *ortho*-proton of benzene ring undoubtedly confirms *Z*-configuration of aminoenone ***2a***. Exclusive formation of *Z*-isomer in this case is due to presence of intramolecular hydrogen bond between carbonyl and secondary amino groups. Its formation is also confirmed by IR spectroscopy data. Thus, ν C=O (1607 cm^{-1}) and ν N−H (3205 cm^{-1}) are shifted to low-frequency area. On the contrary, moieties Ph and CH= of aminoenone ***2b*** are in *trans*-position which is indicated by the absence of their NOE interactions in NMR NOESY spectrum. Furthermore, there are intensive cross-peaks between olefinic proton and pyrrolidine moiety (Scheme 6).



2a ⟷ NOE interactions ***2b*** (6)

The data obtained were confirmed by quantum-chemical calculations with B3LYP//6-311+G level of theory. Thus, *Z*- and *E*-isomers for aminoenone ***2b*** are equally stable while the structure of compound ***2a*** possessing intramolecular hydrogen bond (*Z*-isomer) is 6 kcal/mol more stable.

Aminoenones ***2a,b*** were used as standards for studying of stereochemistry of aza-Michael adducts ***3–9***. As one expected, bis-β-aminoenones as products of addition of diamines bearing two secondary amino groups had *E*, *E*-configuration which was confirmed by NMR NOESY data. The absence of any cross-peaks between any olefinic proton and *o*-protons of phenyl substituents undoubtedly points out *E*, *E*-configuration. Analogous pattern is observed for bis-adduct ***8***. Its *E*, *Z*-configuration was unambiguously proved by spectral data 2D NMR (NOESY and HMBC experiments).

As for aminoenones ***4*** and ***7a,b***, they are formed as *Z*-isomers exclusively. Thus, in ^{1}H NMR spectrum, the signals of secondary amino group NH participating in intramolecular hydrogen bond formation are shifted to high-frequency field (δ = 12.07, 11.26 and 11.20 ppm for mono-adducts ***4***, ***7a***, and ***7b*** correspondingly) as well as low ν NH (3184, 3208, and 3196 cm^{-1}) in their IR spectra.

Considering stereochemistry of compounds ***2a*** and ***2b***, we expected that aminoenone ***9a*** has *Z*-configuration while aminoenone ***9b*** is in a form of *E*-isomer. In fact, intensive ν NH (3199 cm^{-1}) in IR spectrum of ketone ***9a*** confirms the presence of intramolecular hydrogen bond N−H...O=C and therefore its *Z*-configuration. For aminoenone ***9b***, broadened signals in ^{1}H NMR spectrum registered in $CDCl_3$ at room temperature indicate restricted rotation about the formal single bond C−N and decreasing of the rotation barrier around the double bond C=C which is a characteristic property of planar push-pull systems [19]. The use of DMSO-d_6 as a solvent in ^{1}H, ^{13}C, and ^{19}F NMR spectra leads to differentiation of signals between two rotational isomers of compound ***9b*** (the ratio is 5 : 1). Thus, in ^{1}H NMR spectrum olefinic proton resonates at 5.28 ppm (major rotamer) and 5.41 ppm (minor rotamer). In ^{13}C NMR spectrum the signals of corresponding carbon atoms C_α appear

at 86.4 and 85.8 ppm. It was found that *N*-methyl group showed the biggest distinction between spectral data of two rotamers: 3.17 and 2.78 ppm in ^{1}H NMR and 38.6 and 40.5 ppm in ^{13}C NMR correspondingly. In ^{19}F spectrum there are two singlets at −77.0 and −75.7 ppm being in 1 : 5 ratio.

Thus, the data obtained allow us to conclude that aminoenones bearing secondary amino group have exclusively *Z*-configuration due to stabilizing effect of intramolecular hydrogen bond while aminoenones bearing tertiary amino group were obtained as *E*-isomer. Therefore, the synthesis of trifluoromethylated aza-Michael adducts proceeds with high stereoselectivity that is a valuable advance in comparison with non-fluorinated analogues.

Experimental part.

General remarks. ^{1}H (400.1 MHz), ^{13}C (101.6 MHz), ^{19}F (376.5 MHz), and ^{15}N (40.6 MHz) NMR spectra were recorded on Bruker AVANCE 400 MHz spectrometer. Chemical shifts (δ) are given in ppm; residual signals of chloroform-*d* (7.24 for ^{1}H), acetone-d_6 (2.05 for ^{1}H), DMSO-d_6 (2.50 for ^{1}H) and trifluoroacetic acid (−76.0 for ^{19}F) were used as external references. The coupling constants (J) are given in Hertz. The concerted application of ^{1}H—^{1}H 2D homonuclear experiments NOESY as well as ^{1}H—^{13}C 2D heteronuclear experiments HMBC were used for the distinction of the carbon and proton resonances. The IR spectra were recorded with a Bruker Vertex 70 FT-IR spectrometer and with a portable Varian 3100 diamond ATR/FT-IR spectrometer. The GC/MS analyses were performed with a Shimadzu GCMS-QP5050A instrument (EI, 70 eV). The silica gel used for column chromatography was 230–400 Mesh. All reagents were of reagent grade and were used as such or distilled prior to use. All the solvents were dried according to standard procedures and freshly distilled prior to use.

General procedure. A mixture of corresponding acetylenic ketone ***1*** (1 mmol) and amine (1 mmol) in solvent (benzene or ethanol) (2 ml) was stirred at room temperature for 3 hours. In the case of aminoenones ***9a,b*** the sediment was filtered out, dried and weighed. In the case of aminoenones ***2a,b*** volatiles were evaporated *in vacuo*, residue ***2a*** was purified by column chromatography [silica gel, ether/hexane (1 : 1) or $CHCl_3$/MeOH (95 : 5)]. Aminoenones ***2a,b*** and ***9a,b*** were synthesized by given procedure. The synthesis of products ***3***–***8*** was reported earlier [17, 18].

(*Z*)-1,1,1-Trifluoro-4-isopropylamino-4-phenylbut-3-en-2-one (*2a*). Orange solid, mp 33 ℃ (m = 236 mg, 92 %). IR ($CDCl_3$, cm^{-1}): 1142, 1195, 1216 (C−F), 1571, 1583 (C=C, Ph), 1607 (C=O), 3205 (N-H). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.19, 1.21 (s, 6H, CH_3); 3.60–3.78 (m, ^{1}H, C^{6}H); 5.31 (s, ^{1}H, C^{3}H); 7.22–7.50 (m, 5H, Ph); 11.11 (s, ^{1}H, NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): 23.9 (Me_2); 47.2 (C6); 90.0 (c, C^3); 116.4 (q, J = 292.6 Hz, CF_3); 127.1, 128.9, 130.4, 134.3 (Ph); 169.7 (C^4); 175.8 (q, J = 32.6 Hz, C=O). ^{19}F NMR (376.5 MHz, $CDCl_3$): −76.7. ^{15}N NMR (40.6 MHz, $CDCl_3$): −235.7. Anal. Calcd for $C_{13}H_{14}F_3NO$: C 60.70; H 5.49; N 5.44. Found: C 60.81; H 5.68; N 5.27. MS (EI) m/z (relative intensity): m/z (%): 257 (48, M$^+$); 188 (100), 146 (70), 104 (73).

(*E*)-1,1,1-Trifluoro-4-phenyl-4-pyrrolidin-1-ylbut-3-en-2-one (*2b*). Yellow solid, mp 54 ℃ (m = 259 mg, 96 %). IR ($CDCl_3$, cm^{-1}): 1139, 1150, 1192 (C−F), 1530 (C=C), 1579 (Ph), 1657 (C=O). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.80–1.95, 2.05–2.15 (m, 4H, C^{7}H$_2$, C^{8}H$_2$); 3.15–3.25, 3.45–3.55 (m, 4H, C^{6}H$_2$, C^{9}H$_2$); 5.34 (s, ^{1}H, C^{3}H); 7.25–7.55 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): 24.7, 25.0 (C^7, C^8); 49.1, 50.6 (C^6, C^9); 87.4 (C^3); 117.9 (q, J = 293.0 Hz, CF_3); 126.5, 128.2, 128.7, 136.4 (Ph); 165.5 (C^4); 173.9 (q, J = 32.4 Hz, C=O). ^{19}F NMR (376.5 MHz, $CDCl_3$): −76.9. ^{15}N NMR (40.6 MHz, $CDCl_3$): −249.3. Anal. Calcd for $C_{14}H_{14}F_3NO$: C 62.45; H 5.24; N 5.20, F 21.17. Found: C 62.81; H 4.96; N 5.26, F 20.98. MS (EI) m/z (relative intensity): m/z (%): 270 (48, M$^+$+1); 200 (100).

1,1,1-Trifluoro-4-(2-mercaptoethylamino)-4-phenylbut-3-en-2-one (*9a*). White solid (m = 173 mg, 63 %). IR (KBr, cm^{-1}): 1129, 1150, 1157 (C−F), 1570 (C=C), 1590 (Ph), 1612 (C=O), 3199 (N−H). ^{1}H NMR (400.1 MHz, $CDCl_3$): 1.53 (s, ^{1}H, SH); 2.67 (m, 2H, C^7H_2); 3.56 (m, 2H, C^8H_2); 5.43 (s, ^{1}H, C^3H); 7.30–7.50 (m, 5H, Ph); 11.16 (s, ^{1}H, NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): 38.4, 43.8 (C^6, C^7); 91.0 (C3); 117.7 (q, J = 288.8 Hz, CF_3); 127.7, 129.2, 130.8, 133.8 (Ph); 170.8 (C^4); 177.0 (q, J = 33.2 Hz, C=O). ^{19}F NMR (376.5 MHz, $CDCl_3$): −76.6. ^{15}N NMR (40.6 MHz, $CDCl_3$): −259.4. Anal. Calcd for $C_{12}H_{12}F_3NOS$: C 52.36; H 4.39; N 5.09. Found: C 52.61; H 4.49; N 5.19.

1,1,1-Trifluoro-4-((2-hydroxyethyl)-methylamino)-4-phenylbut-3-en-2-one (*9b*).White solid (m = 232 mg, 85 %). IR ($CDCl_3$, cm^{-1}): 1167, 1186, 1215 (C−F), 1523 (C=C), 1552 (Ph), 1639, 1687 (C=O), 3406, 3640 (O−H). ^{1}H NMR (400.1 MHz, $CDCl_3$): 2.15–2.45 (b.s., ^{1}H, OH), 3.16 (s, 3H, NCH_3); 3.50 (s, 2H, C^6H2); 3.61 (b.s., 2H, C^7H_2), 5.41 (s, ^{1}H, C^3H); 7.00–7.55 (m, 5H, Ph). ^{13}C NMR (100.6 MHz, DMSO-d_6) (major rotamer): 38.7 (NCH_3); 54.5 (C^6); 58.5 (C^7), 86.5 (C^3); 117.8 (q, J = 294.5 Hz, CF_3); 127.6, 128.4, 128.6, 135.0 (Ph); 168.6 (C^4); 172.0 (q, J = 30.3 Hz, C=O). ^{19}F NMR (376.5 MHz, DMSO-d_6): −74.8. ^{15}N NMR (40.6 MHz, DMSO-d_6): −262.8. Anal. Calcd for $C_{13}H_{14}F_3NO_2$: C 57.14; H 5.16; N 5.13. Found: C 57.52; H 5.28; N 5.27.

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