Reactions of diazoalkanes with unsaturated compounds
16.* Catalytic reactions of diazomethane with 2-alkenyl-1,3-oxazolidines and 2-alkenyl-1,3-oxathiolanes

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The influence of 1,3-oxazolidine and 1,3-oxathiolane fragments in substituted alkenes on the direction of their catalytic reaction with diazomethane has been investigated. The olefins bearing an oxazolidine substituent in the α- or γ-position and an oxathiolane substituent in the γ-position relative to the C=C bond react with diazomethane in the presence of $Pd(acac)_2$ selectively resulting in cyclopropanation products. The use of $Cu(OTf)_2$ does not result in cyclopropanation; however $Cu(OTf)_2$ catalyzes the reaction of diazomethane with 2-(alk-1-enyl)-1,3-oxathiolanes yielding 2,3,5,6-tetrahydro-1,4-oxathiocines formed through the [2,3]-sigmatropic rearrangement of the intermediate sulfonium ylides.

Key words: 1,3-oxazolidines, 1,3-oxathiolanes, diazomethane, cyclopropanation, [2,3]-sigmatropic rearrangement, sulfonium ylides, oxathiocines

The intermolecular rearrangement of oxonium, ammonium and sulfonium ylides formed in the catalytic reaction of diazo compounds with 1,3-diheteracyclopentanes is a convinient method for the preparation of 1,3-dioxane, morpholine and oxathiane derivatives,[2—7] which are promising as synthons for the preparation of physiologically active polyfunctional compounds. Recently,[1] we have shown, that the yield of catalytic cyclopropanation products of unsaturated acetals bearing α- or γ-positioned acetal function is higher compared to the same reaction of parent unprotected alkenes. This reaction is an efficient approach to cyclopropane-containing carbaldehydes. Also, an example of successful synthesis of optically active 2-phenylcyclopropane carbaldehyde[8] is well known, where the key step is the reaction of a substituted 2-vinyl-1,3-oxazolidine, obtained from cinnamaldehyde and ephedrine, with a 10-fold excess of gaseous diazomethane in the presence of $Pd(OAc)_2$. However, it has been shown that insertion of carbenes into C—N or C—S bonds (see Refs 4, 5, 9—11) rather than cyclopropanation of a double bond occurs in the reactions of diazo compounds with allylamines and allyl sulfides in the presence of copper, palladium and rhodium compounds. This fact provides the evidence of a possible change in the reaction pathway when the substrate bears such bonds.

In this work, we have investigated the behavior of 2-alkenyl-1,3-oxazolidines **1a,b** and 2-alkenyl-1,3-oxathiolanes **2a-c** under conditions of catalytic decomposition of diazomethane. The reaction has been carried out in the presence of $Pd(acac)_2$ or $Cu(OTf)_2$, since it is these catalysts that are the most efficient in catalytic cyclopropanation of unsaturated compounds, bearing *e.g.* 1,3-dioxolane fragment.[1] Thus the cyclopropanation of 2-(*trans*-styryl)-1,3-dioxolane in the presence of $Pd(acac)_2$ and $Cu(OTf)_2$ proceeded with 99 and 49% yield, respectively.

However, the very first experiments showed a distinctive feature of heterocycles **1** and **2** in comparison with earlier studied 2-alkenyl-1,3-dioxolanes. If the reaction was performed using standard procedure[1] *viz.*, by addition of diazomethane to a solution of an olefin and a catalyst, virtually no products of transformation of the starting unsaturated compounds **1** and **2** were observed, although diazomethane decomposition was rather intensive. Therefore, we have changed the reaction conditions. Ethereal solutions of an unsaturated compound and CH_2N_2 were simultaneously added to

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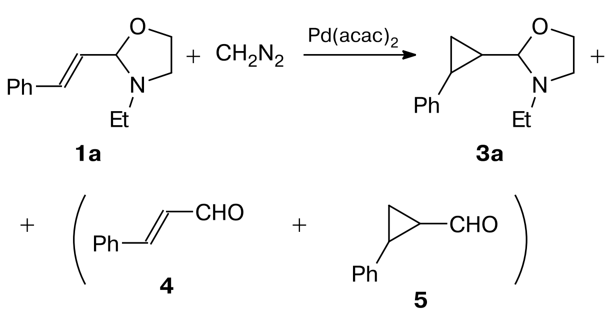
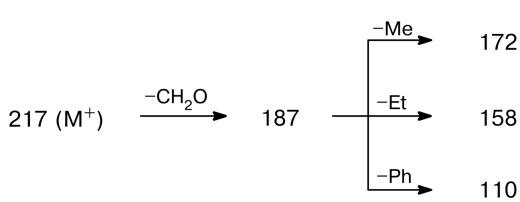
the solution of a catalyst containing some starting unsaturated compound in ether or CH_2Cl_2 at 5-10 °C (overall molar ratio olefin:CH_2N_2:catalyst was 1 : 3 : 0.02). Under these conditions, the reaction of oxazolidine **1a** with diazomethane in the presence of $Pd(acac)_2$ led to a mixture of 2-(*trans*-2-phenylcyclopropyl)-3-ethyl-1,3-oxazolidine (**3a**), the starting oxazolidine **1a** and aldehydes **4** and **5** (Scheme 1) according to data from ^1H NMR spectroscopy. Column chromatography on neutral alumina allowed us to isolate oxazolidine **3a** in 50—55% yield, however the use of silica gel for chromatography considerably increased the yield of **4** and **5**, which suggests efficient removal of the oxazolidine protecting group on this adsorbent.

Scheme 1



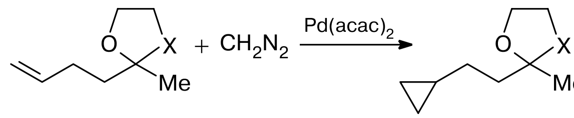
The relatively low efficiency of cyclopropanation of β-styryloxazolidine **1a** is probably related to a weak interaction of the C=C bond with a palladium catalyst, and as a consequence, predominant transformation of diazomethane to ethylene.[12] It is worth noting that the use of $Cu(OTf)_2$ as a catalyst in this reaction does not give cyclopropanation products at all. However, it accelerates cleavage of the oxazolidine protecting group of the aldehyde, and after column chromatography of the mixture, pure aldehyde **4** was isolated in virtually quantitative yield.

The structure of cyclopropyloxazolidine **3a** isolated by column chromatography on neutral alumina was estimated on the basis of mass, ^1H, ^{13}C NMR and $^1H—^1H$ COSY и $^1H—^{13}C$ NOESY spectra. The substituents in cyclopropane ring have *trans*-orientation ($^3J_{trans}$ ≈ 3.8 Hz). Mass spectrum (EI) of the obtained compounds have a molecular ion peak and a set of peaks of fragmentation ions, the most abundant of which are due to the elimination of CH_2O, methyl, ethyl and phenyl groups. The following fragmentation sequence of oxazolidine **3a** was registered, as proved by the peaks of metastable ions:



The cyclopropanation with diazomethane of 2-(but-3-enyl)-1,3-oxazolidine **1b** and (but-3-enyl)-1,3-oxathiolane **2a**, which contain monosubstituted C=C bonds, in the presence of $Pd(acac)_2$ proceeds more effectively than of oxazolidine **1a**, and leads to the formation of cyclopropanes **3b** and **6a** in 97 and 53% yields, respectively (Scheme 2). In contrast to cyclopropanation of **1a**, the obtained results are in good agreement with the fact that palladium catalysts are most effective in the cyclopropanation of unsaturated compounds capable of catalyst complexation; first of all, this is true for terminal and constrained cyclic double bonds.[12]

Scheme 2



1b, 2a **3b, 6a**

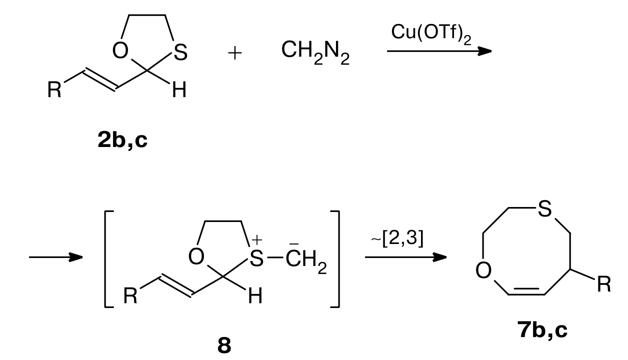
X = S (**a**), NEt (**b**)

As for oxazolidine **1a**, attempted use of $Cu(OTf)_2$ as a catalyst for cyclopropanation of unsaturated compounds **1b** and **2a** with diazomethane was unsuccessful. In the case of **1b**, the filtration of the reaction mixture through a pad of silica gel was accompanied by the removal of the oxazolidine group and the formation of allylacetone was observed, while in the case of oxathiolane **2a** there was no reaction at all.

In contrast to oxathiolane **2a**, the disubstituted double bond of oxathiolanes **2b,c** did not undergo cyclopropanation with diazomethane in the presence of $Pd(acac)_2$, probably, due to the coordination of palladium on the sulfur atom. However, we succeeded to make these oxathiolanes react with CH_2N_2 in the presence of $Cu(OTf)_2$ and obtained 2,3,5,6-tetrahydro-1,4-oxathiocines **7b,c** (^1H and ^{13}C NMR spectra), although in low yields (25 and 8% respectively). The latter likely to the reaction of oxathiolane **2c** with methyl diazoacetate in the presence of $Rh_2(OAc)_4$ (see Ref. 13) are formed as a result of [2.3]-sigmatropic rearrangement of allylsulfonium ylides **8** (Scheme 3) produced by the reaction of a carbene complex with heterocycle sulfur atom. In contrast to oxathiolane **2a**, the reaction of the copper carbene complex with oxathiolanes **2b,c** is likely feasible due to the lower steric interactions with substituents on the C(2) atom. The low yield of tetrahydrooxathiocines **7b,c** is attributed to the parallel catalytic reaction of diazomethane decomposition devoid of substrate participation, which is likely observed for copper-assisted catalysts.[12]

It is worth noting that the intermediate formation of ylides **8** could be associated with both the addition of the carbene complex [CH_2=CuX] to the sulfur atom of oxathiolanes and diazomethane reaction with a pre-

Scheme 3



R = Me (**b**), Ph (**c**)

formed complex of copper(II) triflate with oxathiolanes **2b,c** through Cu—S binding. At least, a remarkable shift of S—O (1120 cm^{-1}) stretching vibration band relative to that in free Cu(OTf)$_2$ (1032 cm^{-1}) is observed in the IR spectrum of an equimolar mixture of oxathiolane **2b** and Cu(OTf)$_2$. This shift is characteristic of the coordination of a metal ion to the sulfur atom of a substrate.[14]

The structures of eight-membered heterocycles **7b,c** were determined by the IR, ^{1}H, ^{13}C NMR and mass spectra. In the ^{1}H NMR spectrum of oxathiocine **7b**, the olefin protons resonate at δ 6.02 (^3J = 6.8, ^4J = 1.5 Hz) and δ 4.84 (^3J = 5.5, ^3J = 6.8 Hz) and, in contrast to the starting unsaturated compounds **2b**, **7b** has *cis* spin-spin coupling constants equal to 6.8 Hz. In the ^{1}H-^{1}H COSY NMR, the methine signal at δ 2.92 has a correlation with geminal protons at δ 2.65 and δ 2.40, which, with account of their chemical shifts, proved the insertion of a methylene fragment into the C—S bond of heterocycle. The retention of the isolated fragment OCH$_2$CH$_2$S and above-mentioned facts point to the presence of a tetrahydro-1,4-oxathiocine ring.

In conclusion, the product yield and composition of the catalytic reaction of diazomethane with 2-alkenyl-substituted 1,3-oxazolidines and 1,3-oxathiolanes are dependent on the nature of both the heterocyclic fragment and the catalyst. It was found that unsaturated compounds bearing an oxazolidine fragment in α- and γ-positions and an oxathiolane substituent in the γ-position relative to the C=C bond react with diazomethane in the presence of Pd(acac)$_2$ resulting in the formation of cyclopropanation products. The reaction of 2-(alk-1-enyl)-1,3-oxathiolanes with diazomethane proceeds through the intermediate formation of sulfonium ylides that undergo [2,3]-sigmatropic rearrangement resulting in 2,3,5,6-tetrahydro-1,4-oxathiocines.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.47 MHz respectively) in CDCl$_3$, internal standard — SiMe$_4$. IR spectra were obtained on a Specord M82-63 spectrometer in a thin layer. GC analyses of reaction mixtures were performed on a Chrom-5 chromatograph with a flame-ionization detector (column, 1200×5 mm with 5% SE-30 on Inerton N-AW DMCS (0.125—0.160 mm)), as helium gas carrier. TLC analyses were performed using Silufol, the separation of compounds was performed by column chromatography on silica gel 60 (0.040—0.063 mm) or neutral Al$_2$O$_3$ (Brockmann, 150 mesh). Mass spectra were obtained on a Thermo Finnigan MAT 95 XP spectrometer (EI, 70 eV, temperature of the ionization chamber 250 °C, temperature programming 50—250 °C, heating rate 10 deg • min^{-1}) and MX-1300 (cell temperature — 100 °C, ionizing potential 12 and 70 eV). The known oxathiolanes **2b,c** were synthesized according to reported procedures,[15] oxazolidines **1a,b** (see Ref. [16]) and oxathiolanes **2a** (see Ref.[15]) were obtained analogously with other derivatives of corresponding heterocyclic structures. Solvents were purified according to standard techniques.[17]

2-(*trans*-Styryl)-3-ethyl-1,3-oxazolidine (1a) was prepared analogously to the procedure.[16] Yield 65%, yellow liquid, b.p 124—125 °C (1 Torr). Found (%): C, 77.16; H, 8.33; N, 6.35. C$_{13}$H$_{17}$NO. Calculated (%): C, 76.81; H, 8.43; N, 6.89. IR, ν/cm^{-1}: 696, 752, 968, 1060, 1128, 1200, 1680, 2808, 2888, 2936, 2952, 2968. ^{1}H NMR (CDCl$_3$): δ 1.16 (t, 3 H, Me, ^3J = 7.3 Hz); 2.33 and 2.77 (both dq, each 1 H, C$\underline{H}_2$Me, ^2J = 11.9 Hz, ^3J = 7.3 Hz); 2.57 (ddd, 1 H, H$_a$C(4), ^2J = 8.4 Hz, ^3J = 7.8 Hz, ^3J = 7.9 Hz); 3.32 (ddd, 1 H, H$_b$C(4), ^2J = 8.4 Hz, ^3J = 7.8 Hz, ^3J = 7.9 Hz); 3.99 (m, 2 H, H$_2$C(5)); 4.43 (d, 1 H, HC(2), ^3J = 6.9 Hz); 6.15 (dd, 1 H, HC(1´), ^3J = 6.9 Hz, ^3J = 15.9 Hz); 6.67 (d, 1 H, HC(2´), ^3J = 15.9 Hz); 7.23—7.48 (m, 5 H, Ar). ^{13}C NMR (δ): 13.9 (Me); 46.0 ($\underline{C}$H$_2$Me); 51.3 (C(4)); 65.0 (C(5)); 96.6 (C(2)); 126.7, 127.7, 128.4 (5 CH, Ar); 127.8 (C(1´)); 134.3 (C(2´)); 136.1 (C, Ar).

2-(But-3-enyl)-2-methyl-3-ethyl-1,3-oxazolidine (1b) was prepared analogously to the procedure.[16] Yield 42%, yellow oil, b.p. 75—77 °C (20 Torr). Found (%): C, 70.03; H, 12.00; N, 8.52. C$_{10}$H$_{19}$NO. Calculated (%): C, 70.96; H, 11.31; N, 8.28. ^{1}H NMR (CDCl$_3$): δ 1.10 (s, 3 H, Me); 1.13 (t, 3 H, Me, ^3J = 7.3 Hz); 1.60 (m, 2 H, H$_2$C(2´)); 2.12 (dq, 1 H, C$\underline{H}_2$Me, ^2J = 12.3 Hz, ^3J = 7.3 Hz); 2.19 (dq, 1 H, C$\underline{H}_2$Me, ^2J = 12.3 Hz, ^3J = 7.3 Hz); 2.39 (ddd, 1 H, H$_a$C(1´), ^2J = 10.0 Hz, ^3J = 6.6 Hz, ^3J = 8.2 Hz); 2.53 (ddd, 1 H, H$_b$C(1´), ^2J = 10.0 Hz, ^3J = 6.6 Hz, ^3J = 8.2 Hz); 2.73 (ddd, 1 H, H$_a$C(4), ^2J = 8.0 Hz, ^3J = 7.5 Hz, ^3J = 7.8 Hz); 3.12 (ddd, 1 H, H$_a$C(5), ^2J = 3.5 Hz, ^3J = 7.5 Hz, ^3J = 7.8 Hz); 3.83 (ddd, 1 H, H$_b$C(4), ^2J = 8.0 Hz, ^3J = 7.5 Hz, ^3J = 7.8 Hz); 3.91 (ddd, 1 H, H$_b$C (5), ^2J = 3.5 Hz, ^3J = 7.5 Hz, ^3J =7.8 Hz); 4.91 (dd, 1 H, H$_a$C (4´), ^2J = 2.0 Hz, $^3J_{cis}$ = 10.2 Hz); 5.00 (dd, 1 H, H$_b$C (4´), ^2J = 2.0 Hz, $^3J_{trans}$ = 17.1 Hz); 5.83 (ddt, 1 H, CH (3´), ^3J = 6.6 Hz, ^3J = 10.2 Hz, ^3J = 17.1 Hz). ^{13}C NMR (δ): 14.8 (CH$_2\underline{Me}$); 19.8 (Me); 28.0 (C(2´)); 36.9 (C(1´)); 42.70 ($\underline{C}$H$_2$Me); 49.2 (C(4)); 63.9 (C(5)); 95.5 (C(2)); 113.7 (=CH$_2$); 139.3 (=CH).

2-(But-3-enyl)-2-methyl-1,3-oxathiolane (2a) was prepared analogously to the procedure.[15] Yield 60%, colourless oil, b.p. 130—132 °C (30 Torr). Found (%): C, 61.12; H, 9.02; S, 20.93. C$_8$H$_{14}$OS. Calculated (%): C, 60.71; H, 8.92; S, 20.26. ^{1}H MNR (CDCl$_3$): δ 1.55 (s, 3 H, Me); 1.88 (m, 2 H, H$_2$C(2´)); 2.12 (dd, 1 H, H$_a$C (1´), ^2J = 10.0 Hz, ^3J = 6.4 Hz, ^3J = 8.2 Hz); 2.20 (dd, 1 H, H$_b$C (1´), ^2J = 10.0 Hz, ^3J = 6.4 Hz, ^3J = 8.2 Hz); 3.02 (m, 2 H, H$_2$C (4)); 4.07 (ddd, 1 H, H$_a$C (5), ^2J = 5.6 Hz, ^3J = 6.9 Hz, ^3J = 9.2 Hz); 4.17 (ddd, 1 H, H$_b$C (5), ^2J = 5.6 Hz, ^3J = 5.1 Hz,

^3J = 9.2 Hz); 4.92 (dd, 1 H, $H_aC(4')$, ^2J = 1.8 Hz, $^3J_{cis}$ = 10.1 Hz); 5.00 (dd, 1 H, H_bC (4´), ^2J = 1.8 Hz, $^3J_{trans}$ = 17.1 Hz); 5.81 (ddt, 1 H, HC (3´), ^3J = 6.4 Hz, ^3J = 10.1 Hz, ^3J = 17.1 Hz). ^{13}C NMR (δ): 28.9 (Me); 29.6 (C(2´)); 33.9 (C(4)); 42.2 (C(1´)); 70.2 (C(5)); 94.8 (C(2)); 114.4 (=CH_2), 138.1 (=CH).

Catalytic reaction of unsaturated compounds 1 and 2 with diazomethane (general procedure). To a stirring solution of unsaturated compounds **1** or **2** (1.0 mmol) and Pd(acac)$_2$ (0.042 g, 0.14 mmol) in ether (20 mL) (or Cu(OTf)$_2$ in 20 mL CH_2Cl_2) an ethereal solution 0.45—0.47 *M* CH_2N_2 (45 mL, ~21 mmol) and the corresponding 2-alkenyl-1,3-oxazolidine **1** (6.0 mmol) or 1,3-oxathiolane **2** were added at 5—10 °C. The mixture was stirred for 30—40 min and then filtered through a thin layer of Al_2O_3, the solvent was evaporated in *vacuo* distillation and the residue was chromatographed on Al_2O_3 or SiO_2.

2-(*trans*-2-Phenylcyclopropyl)-3-ethyl-1,3-oxazolidine (3a). The product was isolated using column chromatography on neutral Al_2O_3, R_f 0.72 (eluent was petroleum ether—AcOEt, 20 : 1), yield 50—55%. Found (%): C, 76.93; H, 8.90; N, 6.92. $C_{14}H_{19}NO$. Calculated (%): C, 77.38; H, 8.81; N, 6.45. IR, ν/cm^{-1}: 696, 752, 968, 1060, 1128, 1200, 1680, 2808, 2888, 2936, 2952, 2968. ^{1}H NMR ($CDCl_3$): δ 1.09 (t, 3 H, Me, ^3J = 7.1 Hz); 1.32 (m, 1 H, HC (1´), of cyclopropane); 1.38 (m, 1 H, H_aC (3´), of cyclopropane); 1.59 (m, 1 H, H_bC (3´), of cyclopropane); 2.06 (м, 1 H, HC(2´), of cyclopropane); 2.66 (q, 2 H, C$\underline{H_2}$Me, ^3J = 7.1 Hz); 2.74 (t, 2 H, $H_2C(4)$, ^3J = 6.2 Hz); 3.56 (t, 2 H, $H_2C(5)$, ^3J = 6.2 Hz); 5.10 (d, 1 H, CH(2), ^3J = 11.3 Hz); 7.23—7.48 (m, 5 H, Ph). ^{13}C NMR (δ): 4.3 (CH_2 of cyclopropane); 11.8 and 15.2 (2 CH of cyclopropane); 12.5 (Me); 48.1 ($\underline{C}H_2$Me); 58.5 (C(4)); 69.3 (C(5)); 98.4 (C(2)); 126.7, 127.7, 128.4 (5 CH, Ph); 137.1 (C, Ph).

2-(2-Cyclopropylethyl)-3-ethyl-2-methyl-1,3-oxazolidine (3b). The product was obtained as an yellow oil after the solvent evaporation, yield 97%. Analytically pure sample was obtained upon column chromatography on SiO_2, R_f 0.81 (eluent was petroleum ether—AcOEt, 20 : 1). Found (%): C, 71.63; H, 11.88; N, 7.83. $C_{11}H_{21}NO$. Calculated (%): C, 72.08; H, 11.55; N, 7.64. IR, ν/cm^{-1}: 736, 756, 916, 960, 1060, 1152, 1192, 1304, 1380, 1456, 1552, 1632, 1712, 2856, 2936, 2952, 3080. ^{1}H NMR ($CDCl_3$): δ 0.02 and 0.37 (both m, each 2 H, CH_2CH_2 of cyclopropane); 0.62 (m, 1 H, CH of cyclopropane); 1.06 (bs, 3 H, Me); 1.10 (t, 3 H, Me, ^3J = 7.3 Hz); 1.27 (m, 2 H, $H_2C(1')$, ^2J = 10.0 Hz, ^3J = 8.2 Hz); 1.60 (m, 2 H, $H_2C(2')$); 2.39 and 2.52 (both dq, each 1 H, $\underline{CH_2}$Me, ^2J = 12.0 Hz, ^3J = 7.3 Hz); 2.72 (dt, 1 H, $H_aC(4)$, ^2J = 8.2 Hz, ^3J = 7.5 Hz); 3.08 (ddd, 1 H, $H_bC(4)$, ^2J = 8.2 Hz, ^3J = 7.0 Hz, ^3J = 3.7 Hz); 3.80 (ddd, 1 H, $H_aC(5)$, ^2J = 7.7 Hz, ^3J = 7.0 Hz, ^3J = 7.5 Hz); 3.88 (ddd, 1 H, $H_bC(5)$, ^2J = 7.7 Hz, ^3J = 7.5 Hz, ^3J = 3.7 Hz). ^{13}C NMR (δ): 4.3 (CH_2CH_2 of cyclopropane)); 11.1 (Me); 14.7 (CH); 19.6 (Me); 28.8 и 37.5 (H_2CCH_2); 42.7 (NCH_2); 49.2 (C(4)); 63.7 (C(5)); 95.5 (C(2)).

2-(2-Cyclopropylethyl)-2-methyl-1,3-oxathiolane (6a). The product was isolated using column chromatography SiO_2, R_f 0.88 (eluent was petroleum ether—AcOEt, 20 : 1), yield 53%, yellow oil. Found (%): C, 63.01; H, 9.21; S, 18.93. $C_9H_{16}SO$. Calculated (%): C, 62.74; H, 9.36; S, 18.61. IR, ν/cm^{-1}: 760, 832, 1016, 1064, 1224, 1268, 1376, 1444, 2856, 2928, 3080. ^{1}H NMR ($CDCl_3$): δ 0.20 and 0.39 (both m, each 2 H, CH_2CH_2 of cyclopropane); 0.66 (m, 1 H, CH); 1.79 (m, 2 H, CH_2); 1.55 (s, 3 H, Me); 2.02 (m, 2 H, CH_2); 2.96—3.11 (m, 2 H, $H_2C(4)$); 4.10—4.22 (m, 2 H, $H_2C(5)$). ^{13}C NMR (δ): 4.2 (CH_2CH_2 of cyclopropane); 10.9 (CH); 28.9 (Me); 30.5 and 33.7 (H_2CCH_2); 43.1 (C(4)); 70.1 (C(5)); 95.1 (C(2)).

6-Methyl-2,3,5,6-tetrahydro-1,4-oxathiocine (7b). The product was isolated by vacuum distillation, yield 25%, yellowish liqiud, b.p. 95—97 °C (10 Torr). Mass spectrum (EI) *m/z* (I_{rel} (%)): 144 $[M]^+$ (54); 129 (8); 116 (22); 99 (43); 83 (13); 71 (100). Found (%): C, 58.79; H, 8.84; S, 22.14. $C_7H_{12}SO$. Calculated (%): C, 58.29; H, 8.39; S, 22.23. IR, ν/cm^{-1}: 760, 976, 1056, 1064, 1088, 1208, 1248, 1304, 1360, 1512, 1656, 2872, 2920, 2960. ^{1}H NMR ($CDCl_3$): δ 1.07 (d, 3 H, Me, ^3J = 7.1 Hz); 2.40 (dd, 1 H, $H_aC(5)$, ^2J = 14.1 Hz, ^3J = 10.0 Hz); 2.69 (dd, 1 H, $H_bC(5)$, ^2J = 14.1 Hz, ^3J = 2.0 Hz); 2.72 (dt, 1 H, $H_aC(3)$, ^2J = 12.0 Hz, ^3J = 3.7 Hz); 2.90 (dddd, 1 H, HC(6), ^3J = 7.1 Hz, ^3J = 2.0 Hz, ^3J = 10.0 Hz, ^4J = 1.5 Hz); 2.92 (dt, 1 H, $H_bC(3)$, ^2J = 12.0 Hz, ^3J = 7.1 Hz); 3.88 (dd, 2 H, $H_2C(2)$, ^3J = 7.1 Hz, ^3J = 3.7 Hz); 4.84 (dd, 1 H, HC(7), ^3J = 5.5 Hz, ^3J = 6.8 Hz); 6.02 (dd, 1 H, HC(8), ^3J = 5.5 Hz, ^4J = 1.5 Hz). ^{13}C NMR (δ): 21.0 (Me); 31.4 (C(3)); 33.6 (C(6)); 39.5 (C(5)); 71.7 (C(2)); 124.3 (C(7)); 142.4 (C(8)).

6-Phenyl-2,3,5,6-tetrahydro-1,4-oxathiocine (7c). The product was isolated by vacuum distillation, yield 8%, yellow oil, b.p. 144—146 °C (1 Torr). Mass spectrum (EI), *m/z* ($I_{отн}$ (%)): 206 $[M]^+$ (5); 146 (7); 131 (23); 115 (20); 102 (100); 89 (10). Found (%): C, 70.16; H, 7.04; S, 16.13. $C_{12}H_{14}SO$. Calculated (%): C, 69.86; H, 6.84; S, 15.54. ^{1}H NMR ($CDCl_3$): δ 2.45 and 2.52 (both dt, each 1 H, $H_2C(3)$, ^2J = 13.2 Hz, ^3J = 6.8 Hz); 2.60 and 2.62 (both d, each 1 H, $H_2C(5)$, ^3J = 7.1 Hz); 3.50 (m, 1 H, HC(6)); 3.70 and 3.87 (both m, each 1 H, $H_2C(2)$); 4.95 (dd, 1 H, HC(7), ^3J = 6.8 Hz, ^3J = 5.6 Hz); 5.90 (dd, 1 H, HC(8), ^3J = 5.6 Hz, ^4J = 1.5 Hz); 7.00—7.19 (m, 5 H, Ph). ^{13}C NMR (δ): 31.7 (C(3)); 39.8 (C(5)); 46.3 (C(6)); 72.0 (C(2)); 122.1 (C(7)); 143.0 (C(8)), 126.5; 126.7 and 128.8 (5 CH, Ph); 135.7 (C, Ph).

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