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Reactions of Some Alken-1-yl and Cycloalken-1-yl Bromomethyl Sulfones with Dimethyl Malonate and Malononitrile

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Abstract—Bromomethyl cyclopent-1-enyl sulfone and bromomethyl cyclohex-1-enyl sulfone reacted with dimethyl malonate and malononitrile sodium salts in THF at 20–50°C to give products of Michael-induced Ramberg–Bäcklund reaction, functionalized derivatives of methylidenecyclopentane and methylidenecyclohexane. Reactions of bromomethyl hex-1-en-1-yl sulfone and bromomethyl hept-1-en-1-yl sulfones with the same sodium enolates followed the Michael-induced ring closure pattern with formation of tetrahydrothiophene 1,1-dioxide derivatives containing allylmalonic acid derivatives as impurities. Factors responsible for the different reaction pathways of cyclic and acyclic bromomethyl sulfones are discussed.

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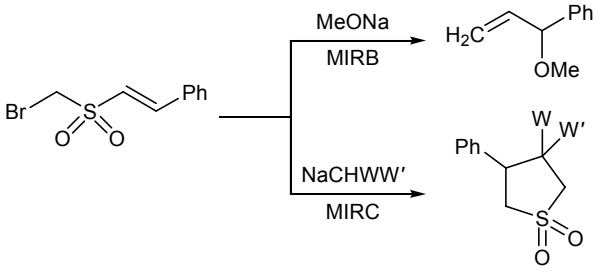
We previously showed that bromomethyl (*E*)-styryl sulfone reacts with a hard base (nucleophile), sodium methoxide, according to the Michael-induced Ramberg–Bäcklund (MIRB) pattern with formation of allyl derivative [1] and that its reaction with soft bases (nucleophiles), such as sodium salts of malononitrile and malonic, cyanoacetic, and acetoacetic acid esters, leads to tetrahydrotiophene 1,1-dioxide derivatives via Michael-induced ring closure (MIRC) [2] (Scheme 1).

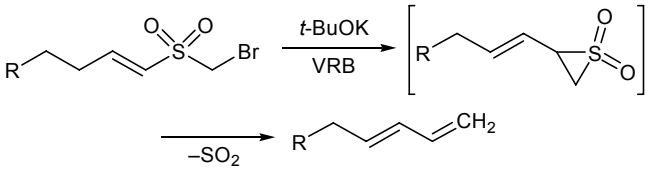
Scheme 1.



W, W′ = CN, CO_2Me; Ac, CO_2Me.

Unlike bromomethyl (*E*)-styryl sulfone, bromomethyl (*E*)-alk-1-en-1-yl sulfones having activated hydrogen atoms in the γ-position with respect to the sulfonyl group react with hard nucleophiles (alkali metal alkoxides) to give products of vinylogous Ramberg–Bäclund (VRB) reaction, conjugated dienes [3] (Scheme 2). Reactions of these sulfones with soft nucleophiles were not reported in the literature.

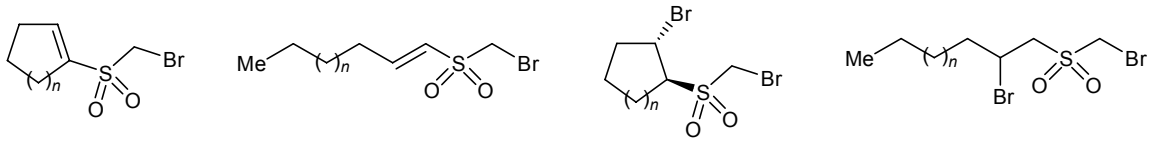
Scheme 2.



In the present work we examined reactions of unsaturated cyclic and acyclic bromomethyl sulfones **I**–**IV** with sodium enolates derived from dimethyl malonate and malononitrile with a view to reveal factors responsible for chemoselectivity of reactions initiated by Michael addition.* Initial unsaturated sulfones **I**–**IV** were prepared in two steps including UV-initiated addition of bromomethanesulfonyl bromide to the corresponding cycloalkene or terminal alkene in methylene chloride at 20°C and dehydrobromination of adducts **V**–**VIII** by the action of sodium carbonate in aqueous dioxane at 50°C.

The addition of bromomethanesulfonyl bromide to cyclic alkenes **I** and **II** was *trans*-stereoselective, which is consistent with published data [5–8], and the dehydrobromination of **V**–**VIII** was strictly regioselec-

* For preliminary communication, see [1].

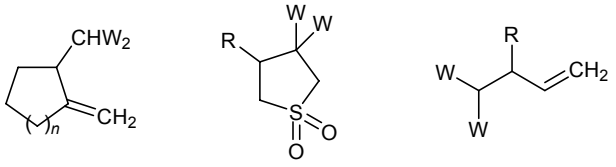


I, **II** **III**, **IV** **V**, **VI** **VII**, **VIII**

I, **III**, **V**, **VII**, $n = 1$; **II**, **IV**, **VI**, **VIII**, $n = 2$.

tive. Adducts **V**–**VIII** and their dehydrobromination products **I**–**IV** were isolated by column chromatography on silica gel and/or recrystallization. The structure of **I**–**VIII** was determined by IR spectroscopy, ^{1}H and ^{13}C NMR, and mass spectrometry. In particular, *E* configuration of the double bond in unsaturated sulfones **I** and **II** followed from the vicinal coupling constant for the olefinic protons ($^3J = 15$ Hz) [9].

Cycloalkenyl and alkenyl sulfones **I**–**IV** were brought into reactions with CH acid sodium salts (taken in a slight excess) at 20–50°C under dry argon by stirring over a period of 20–30 h. From cyclopentenyl and cyclohexenyl sulfones **I** and **II** we obtained MIRB reaction products **IXa**, **IXb**, **Xa**, and **Xb** in 20–34% yield. Acyclic unsaturated sulfones **III** and **IV** reacted with dimethyl malonate and malononitrile sodium salts to give mixtures of cyclic sulfones **XIa**, **XIb**, **XIIIa**, and **XIIIb** and allylmalonic acid derivatives **XIIa**, **XIIb**, **XIVa**, and **XIVb**, the former prevailing (according to the ^{1}H NMR data, the ratio was ~4 : 1 and 3 : 1, respectively). The yield in the MIRC reaction was 24–32%, and in the MIRB reaction, 8–23%.



IXa, **IXb**, **Xa**, **Xb** **XIa**, **XIb**, **XIIIa**, **XIIIb** **XIIa**, **XIIb**, **XIVa**, **XIVb**

IX, $n = 1$; **X**, $n = 2$; W = CO_2Me (**a**), CN (**b**); **XI**, **XII**, R = C_4H_9; **XIII**, **XIV**, R = C_5H_{11}.

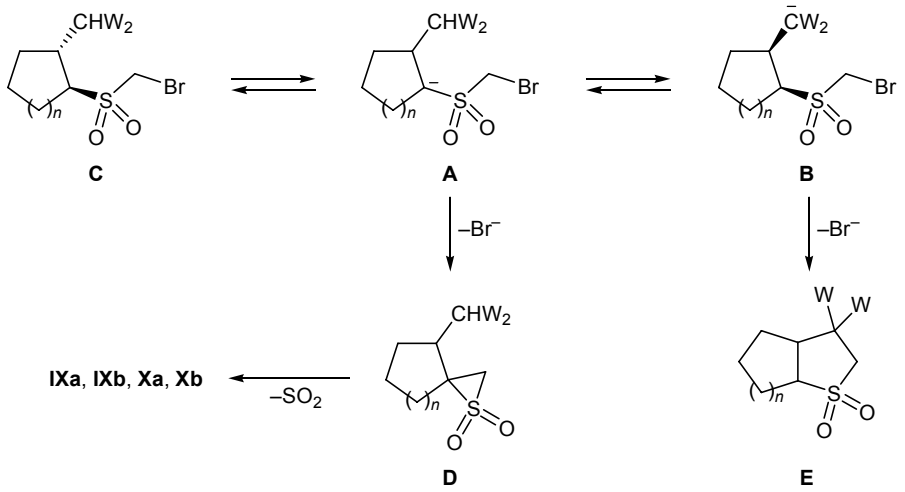
Compounds **IX**–**XIV** were isolated by column chromatography on silica gel, and their structure was determined on the basis of their IR, ^{1}H and ^{13}C NMR, and mass spectra (GC–MS). For example, compounds **XI** and **XIII** displayed in the IR spectra characteristic absorption bands due to stretching vibrations of the sulfonyl group at ~1130 (ν_s) and ~1310 cm^{-1} (ν_{as}). The ^{1}H NMR spectra of methylidene derivatives **IXa** and **IXb** contained two poorly resolved downfield doublets, whereas compounds **Xa** and **Xb** were characterized by two broadened singlets from olefinic protons. In addition, compounds **IXa** and **Xa** gave rise to separate singlets from diastereotopic CO_2Me groups. In the ^{13}C NMR spectra of **IXa**, **IXb**, **Xa**, and **Xb** two downfield signals with strongly different intensities reliably characterized 1,1-disubstituted ethylene fragment; in addition, separate carbon signals from diastereotopic groups W were observed. Likewise, in the ^{13}C NMR spectra of allylic derivatives **XIIa**, **XIIb**, **XIVa**, and **XIVb** we identified diastereotopic groups W, as well as vinyl groups and CH carbon atom linked to W. Cyclic sulfones **XIa**, **XIb**, **XIIIa**, and **XIIIb** characteristically showed in the ^{1}H NMR spectra two doublets at δ 3.6–3.9 ppm from diastereotopic protons on C^2 with a geminal coupling constant ^2J of ~14 Hz. Like other compounds considered above, the ^{13}C NMR spectra of **XIa**, **XIb**, **XIIIa**, and **XIIIb** contained separate signals of diastereotopic groups W and were very consistent with the assumed structures.

Thus our experimental results revealed differences in the behavior of cyclic (**I**, **II**) and acyclic (**III**, **IV**) unsaturated bromomethyl sulfones toward dimethyl malonate and malononitrile sodium salts. We believe that these differences are related to specific structure of carbanionic intermediates, which determines their stability and reactivity. Michael addition to cycloalkenyl sulfones initially gives carbanion **A** which is capable of undergoing reversible isomerization into thermodynamically more stable (due to better delocalization of negative charge over two electron-withdrawing groups W) carbanions **B** and **C** (Scheme 3).

Obviously, for steric reasons, 1,5-cyclization product **E** can be formed only from carbanion **B** with *cis* orientation of the substituents. Carbanion **B** is less stable than its *trans* isomer **C**, so that its concentration in the reaction mixture may be insignificant. Therefore, the main reaction direction is 1,3-elimination from carbanion **A**, leading to episulfone **D** which loses SO_2 molecule with formation of methylidene derivative **IX** or **X**.

Carbanions generated from open-chain unsaturated sulfones **III** and **IV** are stabilized by two electron-withdrawing substituents. In this case, there are no such rigorous steric limitations to 1,5-cyclization, and tetrahydrothiophene 1,1-dioxide derivatives **XI** and

Scheme 3.



XIII are formed as the major products. The composition of the equilibrium carbanion mixture is likely to be affected by the nature of electron-withdrawing group W. In particular, this is indicated by considerably higher yield of 1,5-cyclization product in the reaction of **III** and **IV** with malononitrile as compared to dimethyl malonate. In addition, the reaction mixtures obtained from sulfones **I** and **II** and malononitrile contained small impurities (5–8%; according to the GLC and ^{1}H NMR data) which may be identified as the corresponding MIRC reaction products.

Undoubtedly, concurrent pathways in the reactions of cyclic and acyclic unsaturated bromomethyl sulfones with CH acids require additional study.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker AMX-400 spectrometer at 400.1 and 100.6 MHz, respectively; the chemical shifts were determined relative to the residual proton signal and carbon signal of the solvent. The IR spectra were measured from thin films or KBr pellets on an InfraLYuM FT-02 spectrometer with Fourier transform. The elemental compositions were determined on a Vario MICRO CHN analyzer. Analytical thin-layer chromatography was performed on Silufol UV-254 plates using light petroleum ether–ethyl acetate (3:1) as eluent; spots were visualized by treatment with iodine vapor. Silica gel L40/60 μm was used for column chromatography (eluent light petroleum ether–ethyl acetate, 7:1). Photochemical reactions were carried out under irradiation with a DRT-400 mercury lamp.

Bromomethanesulfonyl bromide was prepared according to the procedure described in [3]; its purity was 97%.

Reactions of cyclopentene, cyclohexene, hex-1-ene, and hept-1-ene with bromomethanesulfonyl bromide (*general procedure*). Cold (0°C) solutions of 20 mmol of the corresponding alkene in 10 ml of anhydrous methylene chloride and of 5 g (21 mmol) of bromomethanesulfonyl bromide in 10 ml of the same solvent were mixed, 0.2 g of anhydrous sodium carbonate was added,** and the the mixture was irradiated with UV light in a tightly capped quartz test-tube at 20°C over a period of 28–30 h. The solvent was distilled off under reduced pressure, and the solid residue (in the reactions with acyclic alkenes) was washed with diethyl ether (3×2 ml), dried in air, and recrystallized from appropriate solvent. The oily residue obtained from cyclic alkenes was subjected to column chromatography on silica gel.

***trans*-1-Bromo-2-(bromomethylsulfonyl)cyclopentane (V).** Yield 60%, mp 45–46°C (from diethyl ether–pentane). IR spectrum, ν, cm^{-1}: 3036 m, 2967 m, 1304 v.s, 1269 m, 1246 m, 1138 v.s, 575 m, 494 m. ^{1}H NMR spectrum, δ, ppm: 1.83–1.95 m (1H), 1.96–2.07 m (1H), 2.11–2.34 m (3H), and 2.35–2.47 m (1H) [$(CH_2)_3$]; 4.14–4.23 m (1H, $CHSO_2$), 4.48 q (2H, $BrCH_2SO_2$, *AB*, $\Delta\nu_{AB}$ = 40.3, J_{AB} = 12.0 Hz), 4.57–4.63 m (1H, CHBr). ^{13}C NMR spectrum, δ_C, ppm: 23.8, 25.5, 38.6, 41.2, 46.3, 67.3. Found, %: C 23.50; H 3.38. $C_6H_{10}Br_2O_2S$. Calculated, %: C 23.55; H 3.29.

***trans*-1-Bromo-2-(bromomethylsulfonyl)cyclohexane (VI).** Yield 67%, R_f 0.62, mp 59–60°C (from

** The reaction with cyclohexene may start spontaneously and be accompanied by strong exothermic effect.

diethyl ether–hexane). IR spectrum, ν, cm^{-1}: 3032 w, 2948 m, 2928 w, 2863 w, 1447 m, 1327 m, 1312 s, 1134 s, 1127 v.s, 1100 m, 845 m. ^1H NMR spectrum, δ, ppm: 1.35–1.55 m (2H), 1.64–1.84 m (2H), 1.87–2.05 m (2H), and 2.37–2.61 m (2H) [$(CH_2)_4$]; 3.77–3.90 m (1H, $CHSO_2$), 4.36–4.47 m (1H, CHBr), 4.51 d and 4.92 d (1H each, $BrCH_2SO_2$, J = 11.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.7, 24.8, 25.1, 37.0, 43.9, 47.8, 62.9. Found, %: C 26.10; H 3.68. $C_7H_{12}Br_2O_2S$. Calculated, %: C 26.27; H 3.78.

2-Bromohexyl bromomethyl sulfone (VII). Yield 85%, mp 48–49°C (from diethyl ether–hexane). IR spectrum, ν, cm^{-1}: 3032 m, 2959 s, 2928 s, 1300 v.s, 1154 s, 1134 s, 930 m, 876 m, 586 m, 494 s. ^1H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, J = 7.2 Hz), 1.29–1.62 m (4H) and 1.86–2.06 m (2H) [$(CH_2)_3$], 3.55 d.d (1H, J = 5.3, 15.2 Hz) and 4.00 d.d (1H, J = 7.7, 15.2 Hz) (CH_2SO_2), 4.38–4.45 m (overlapped by the doublet at δ 4.42 ppm, 1H, CHBr), 4.42 d and 4.63 d (1H each, SO_2CH_2Br, J = 11.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.7, 21.7, 29.0, 38.1, 42.9, 45.0, 57.6. Found, %: C 25.98; H 4.47. $C_7H_{14}Br_2O_2S$. Calculated, %: C 26.11; H 4.38.

2-Bromoheptyl bromomethyl sulfone (VIII). Yield 77%, mp 50–51°C (from diethyl ether–hexane). IR spectrum, ν, cm^{-1}: 3032 m, 2955 m, 2928 m, 1466 w, 1300 v.s, 1157 m, 1130 m, 887 w, 582 w, 482 w. ^1H NMR spectrum, δ, ppm: 0.91 t (3H, CH_3, J = 6.9 Hz); 1.29–1.41 m (4H), 1.44–1.54 m (1H), 1.54–1.65 m (1H), and 1.89–2.07 m (2H) [$CH_2)_4$]; 3.54 d.d.d (1H, J = 1.3, 5.3, 15.3 Hz) and 4.02 d.d (1H, J = 7.7, 15.3 Hz) (SO_2CH_2), 4.38–4.47 m (1H, CHBr), 4.40 d.d (1H, J = 1.3, 11.9 Hz) and 4.64 d (1H, J = 11.9 Hz) (SO_2CH_2Br). ^{13}C NMR spectrum, δ_C, ppm: 13.9, 22.4, 26.7, 30.8, 38.5, 42.9, 45.0, 57.7. Found, %: C 28.43; H 4.68. $C_8H_{16}Br_2O_2S$. Calculated, %: C 28.59; H 4.80.

Dehydrobromination of adducts V–VIII (*general procedure*). A solution of 2.54 g (24.0 mmol) of sodium carbonate in 15 ml of water was added to a solution of 20.0 mmol of compound **V–VIII** in 15 ml of dioxane, and the mixture was stirred at 50°C for 20 h (**VII**, **VIII**) or 50 h (**V**, **VI**) and diluted with 150 ml of water. Compounds **I** and **II** gradually precipitated and were filtered off, dried in air, and recrystallized. Compounds **III** and **IV** containing ~5% of the corresponding *Z* isomer (according to the GLC and ^1H NMR data) were extracted into chloroform (3×30 ml), the combined extracts were washed with water, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography on silica gel.

1-(Bromomethylsulfonyl)cyclopentene (I). Yield 76%, R_f 0.42, mp 44–45°C (from diethyl ether–pentane). IR spectrum, ν, cm^{-1}: 3036 m, 2959 m, 1613 m, 1373 w, 1308 v.s, 1142 v.s, 1069 w, 745 m, 594 m, 505 s. ^1H NMR spectrum, δ, ppm: 2.15 quint (2H, 4-H, J = 7.6 Hz), 2.62–2.68 m and 2.69–2.75 m (2H each, 3-H, 5-H), 4.34 s (2H, CH_2Br), 6.92–6.94 m (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 23.7, 31.7, 33.1, 41.8, 139.5, 149.6. Found, %: C 32.10; H 3.68. $C_6H_8BrO_2S$. Calculated, %: C 32.16; H 3.60.

1-(Bromomethylsulfonyl)cyclohexene (II). Yield 81%, R_f 0.45, mp 55–56°C (from diethyl ether–hexane). IR spectrum, ν, cm^{-1}: 3036 m, 2959 m, 2936 m, 1640 m, 1439 m, 1308 s, 1300 s, 1142 v.s, 764 m, 606 m, 594 m, 521 m. ^1H NMR spectrum, δ, ppm: 1.62–1.74 m (2H), 1.76–1.88 m (2H), and 2.32–2.41 m (4H) [$(CH_2)_4$]; 4.32 s (2H, CH_2Br), 7.08 br.s (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 20.6, 21.8, 23.8, 25.7, 40.8, 134.9, 144.5. Found, %: C 35.10; H 4.68. $C_7H_{11}BrO_2S$. Calculated, %: C 35.16; H 4.64.

Bromomethyl (*E*)-hex-1-en-1-yl sulfone (III). Yield 81%, oily substance. IR spectrum, ν, cm^{-1}: 2959 m, 2932 m, 2874 w, 1636 m, 1323 s, 1142 v.s, 857 m, 667 w. ^1H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 7.3 Hz); 1.29–1.38 m, 1.43–1.50 m, and 2.29–2.34 m [2H each, $(CH_2)_3$]; 4.31 s (2H, CH_2Br), 6.37 d.t (1H, 1-H, J = 1.6, 15.2 Hz), 7.04 d.t (1H, 2-H, J = 6.9, 15.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.6, 22.0, 29.4, 31.4, 43.2, 124.5, 153.8. Found, %: C 34.88; H 5.38. $C_7H_{13}BrO_2S$. Calculated, %: C 34.87; H 5.43.

Bromomethyl (*E*)-hept-1-en-1-yl sulfone (IV). Yield 83%, oily substance. IR spectrum, ν, cm^{-1}: 2955 m, 2932 m, 2859 s, 1628 m, 1323 s, 1142 v.s, 864 m, 667 w. ^1H NMR spectrum, δ, ppm: 0.86–0.94 m (3H, CH_3); 1.28–1.37 m (4H) and 1.47–1.57 m (2H) [$(CH_2)_3$]; 2.35 q.d (2H, 3-H, J = 1.5, 7.1 Hz), 4.33 s (2H, CH_2Br), 6.37 d.t (1H, 1-H, J = 1.5, 15.2 Hz), 7.05 d.t (1H, 2-H, J = 6.8, 15.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.8, 22.2, 27.1, 31.0, 31.7, 43.2, 124.5, 153.9. Found, %: C 37.58; H 6.08. $C_8H_{15}BrO_2S$. Calculated, %: C 37.66; H 5.93.

Reactions of compounds I–IV with dimethyl malonate and malononitrile (*general procedure*). A 60% suspension of sodium hydride in mineral oil, 0.34 g (8.4 mmol), was washed with hexane. Most solvent was removed by decanting, and its residue was removed under reduced pressure. The remaining sodium hydride was de-evacuated with argon, and 5 ml of THF was added. A solution of 6.3 mmol of dimethyl

malonate or malononitrile in 10 ml of THF was added dropwise over a period of 15 min under stirring at 20°C, and the mixture was stirred for 1 h at 20°C. A solution of 4.2 mmol of compound **I**–**IV** in 10 ml of THF was added, and the mixture was stirred for 28–30 h at 20°C, diluted with 300 ml of water, neutralized with dilute (1:1) hydrochloric acid, and extracted with chloroform (3×15 ml). The combined extracts were washed with water, dried over $MgSO_4$, and evaporated under reduced pressure (water-jet pump), and the residue was analyzed by ^{1}H NMR and purified by column chromatography on silica gel.

Dimethyl 2-(2-methylidenecyclopentyl)malonate (IXa). Yield 19%, bp 88°C (1 mm), R_f 0.58. IR spectrum, ν, cm^{-1}: 2951 m, 1759 v.s, 1740 s, 1740 s, 1655 w, 1435 m, 1273 m, 1196 m, 1161 m, 1022 w, 891 w. ^{1}H NMR spectrum, δ, ppm: 1.51–1.66 m (2H), 1.67–1.76 m (1H), 1.83–1.93 m (1H), and 2.29–2.36 m (2H) [$(CH_2)_3$]; 3.05–3.13 m (1H, CH), 3.69 s and 3.70 s (3H each, OMe), 3.50 d [1H, C**H**$(CO_2Me)_2$, J = 8.6 Hz], 4.73 d and 4.88 d (1H each, =CH_2, J 1.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.7, 30.3, 32.8, 43.2, 52.1, 52.2, 55.0, 106.4, 152.6, 168.7, 169.0. Found, %: C 62.40; H 7.45. $C_{11}H_{16}O_4$. Calculated, %: C 62.25; H 7.60.

2-(2-Methylidenecyclopentyl)malononitrile (IXb). Yield 20%, bp 110°C (2 mm), R_f 0.5. IR spectrum, ν, cm^{-1}: 2971 s, 2948 m, 2936 m, 2253 w, 1655 w, 1435 m, 1273 m, 1196 m, 1161 m, 1022 w, 891 w. ^{1}H NMR spectrum, δ, ppm: 1.63–1.83 m (2H), 1.86–1.98 m (1H), 2.18–2.29 m (1H), and 2.43–2.50 (2H) [$(CH_2)_3$]; 2.99–3.08 m (1H, CH), 3.88 d [1H, $CH(CN)_2$, J = 5.6 Hz], 5.13 d and 5.25 d (1H each, =CH_2, J = 2.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.8, 27.2, 30.9, 33.1, 43.9, 110.0, 112.0, 112.4, 148.8. Found, %: C 73.74; H 6.85; N 19.06. $C_9H_{10}N_2$. Calculated, %: C 73.94; H 6.89; N 19.16.

Dimethyl 2-(2-methylidenecyclohexyl)malonate (Xa). Yield 30%, bp 102°C (1 mm). IR spectrum, ν, cm^{-1}: 2936 s, 1763 s, 1755 s, 1748 s, 1740 s, 1732 v.s, 1651 w, 1435 m, 1319 m, 1277 m, 1235 s, 1157 s, 1146 m, 895 w. ^{1}H NMR spectrum, δ, ppm: 1.41–1.68 m (6H), 2.05–2.14 m (1H), and 2.17–2.26 (1H) [$(CH_2)_4$]; 2.92–3.01 m (1H, CH), 3.66 s and 3.73 s (3H each, OMe), 3.71 d [1H, C**H**$(CO_2Me)_2$, J = 9.6 Hz], 4.57 br.s and 4.68 br.s (1H each, =CH_2). ^{13}C NMR spectrum, δ_C, ppm: 23.2, 28.2, 30.8, 34.0, 43.3, 52.3, 52.4, 54.0, 108.1, 148.9, 168.8, 168.9. Found, %: C 63.74; H 8.15. $C_{12}H_{18}O_4$. Calculated, %: C 63.70; H 8.02.

2-(2-Methylidenecyclohexyl)malononitrile (Xb). Yield 34%, bp 124°C (1 mm), R_f 0.70. IR spectrum, ν, cm^{-1}: 2940 v.s, 2932 s, 2867 m, 2257 w, 1651 m, 1451 m, 1327 m, 1316 m, 1134 m, 903 m. ^{1}H NMR spectrum, δ, ppm: 1.23–1.65 m (5H), 1.85–1.99 m (2H), and 2.08–2.17 m (1H) [$(CH_2)_4$]; 2.50–2.58 m (1H, CH), 3.80 d [1H, $CH(CN)_2$, J = 6.6 Hz], 4.61 s and 4.83 s (1H each, =CH_2). ^{13}C NMR spectrum, δ_C, ppm: 23.9, 25.8, 27.2, 30.8, 34.5, 44.1 109.8, 111.8, 112.3, 144.5. Found, %: C 74.84; H 7.61; N 17.36. $C_{10}H_{12}N_2$. Calculated, %: C 74.97; H 7.55; N 17.48.

Dimethyl 4-butyl-1,1-dioxotetrahydro-3*H*-1λ^6-thiophene 3,3-dicarboxylate (XIa). Yield 32%, mp 66–67°C (from ethyl acetate–hexane). IR spectrum, ν, cm^{-1}: 2966 m, 2935 m, 1747 s, 1732 s, 1315 v.s, 1273 s, 1261 s, 1219 s, 1146 s, 1126 v.s, 1061 m. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, J = 6.6 Hz); 1.22–1.44 m (5H) and 1.58–1.68 m (1H) [$(CH_2)_3$]; 3.03–3.13 m (2H) and 3.35 d.d.d (1H, J = 1.0, 10.8, 16.9 Hz) (4-H, 5-H), 3.56 d.d (1H, J = 1.0, 14.1 Hz) and 3.82 d (1H, J = 14.1 Hz) (2-H), 3.80 s (6H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 13.7, 22.1, 29.3, 30.0, 41.2, 53.3, 53.6, 54.5, 56.5, 60.0, 168.1, 168.5. Mass spectrum, m/z (I_{rel}, %): 264 (0.06), 263 (0.5), 145 (100), 113 (68.9). Found, %: C 49.38; H 7.01. $C_{12}H_{20}O_6S$. Calculated, %: C 49.30; H 6.90.

4-Butyl-1,1-dioxotetrahydro-3*H*-1λ^6-thiophene-3,3-dicarbonitrile (XIb). Yield 24%, R_f 0.35, mp 84–85°C (from ethyl acetate–hexane). IR spectrum, ν, cm^{-1}: 3029 m, 2967 m, 2944 m, 2257 w, 1331 v.s, 1316 s, 1269 m, 1142 s. ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, J = 7.1 Hz); 1.39–1.49 m (4H), 1.72–1.84 (1H), and 1.98–2.09 m (1H) [$(CH_2)_3$]; 2.91–3.01 m (1H, 4-H), 3.08 t (1H, J = 13.2 Hz) and 3.58 d.d (1H, J = 6.6, 13.2 Hz) (5-H), 3.70 d and 3.94 d (1H each, 2-H, J = 14.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.6, 22.2, 29.3, 30.2, 37.0, 45.0, 53.8, 58.7, 111.3, 112.3. Mass spectrum, m/z (I_{rel}, %): 226 (0.08) $[M]^+$, 161 (25.5), 147 (27.6), 134 (53.6), 133 (33.7), 120 (13.6), 119 (31.5), 107 (12.2), 106 (15.1), 105 (10.1), 94 (29.0), 93 (11.3), 84 (10.9), 83 (75.8), 82 (16.5), 81 (19.0), 80 (13.4), 79 (39.6), 69 (32.7), 57 (12.2), 56 (49.4), 55 (100), 54 (12.9), 53 (14.2), 52 (11.2), 43 (31.6), 42 (24.6), 41 (66.0). Found, %: C 53.28; H 6.20; N 12.44. $C_{10}H_{14}N_2O_2S$. Calculated, %: C 53.08; H 6.24; N 12.38.

Dimethyl 2-(hept-1-en-3-yl)malonate (XIIa). Yield 8%, bp 82°C (1 mm). IR spectrum, ν, cm^{-1}: 2955 m, 2931 m, 1755 s, 1740 v.s, 1643 w, 1435 m, 1265 m, 1242 m, 1146 m. ^{1}H NMR spectrum, δ, ppm: 0.86 t (3H, CH_3, J = 6.7 Hz), 1.16–1.36 m (5H) and 1.37–1.48 m (1H) [$(CH_2)_3$], 2.70–2.79 m (1H, CH), 3.36 d [1H, C**H**$(CO_2Me)_2$, J = 8.9 Hz], 3.67 s and

3.72 s (3H each, OCH_3), 5.03–5.11 m (2H, $=CH_2$), 5.56–5.67 m (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 13.9, 22.3, 29.1, 31.9, 44.1, 52.1, 52.3, 56.8, 117.3, 138.1, 168.5, 168.7. Mass spectrum, *m*/*z* (I_{rel}, %): 228 (0.17) $[M]^{+\cdot}$, 197 (10.1), 172 (10.2), 171 (100), 170 (10.9), 169 (93.0), 168 (12.1), 165 (31.2), 164 (12.5), 140 (11.3), 139 (86.2), 137 (16.8), 136 (11.2), 133 (33.6), 132 (75.1), 127 (14.1), 126 (59.7), 113 (52.4), 111 (21.3), 108 (13.6), 101 (28.8), 100 (34.9), 97 (20.9), 96 (22.5), 95 (17.4), 94 (12.3), 82 (11.4), 81 (47.9), 79 (15.6), 71 (12.3), 69 (20.7), 67 (24.9), 59 (23.5), 55 (45.6), 41 (27.4). Found, %: C 63.30; H 8.88. $C_{12}H_{20}O_4$. Calculated, %: C 63.14; H 8.83.

2-(Hept-1-en-3-yl)malononitrile (XIIb). Yield 23%, R_f 0.66, bp 112°C (1 mm). IR spectrum, ν, cm^{-1}: 3086 w, 2963 v.s, 2936 v.s, 2863 m, 2257 w, 1644 w, 1466 m, 1423 m, 992 m, 934 m. ^1H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, J = 6.8 Hz), 1.23–1.43 m (4H) and 1.54–1.75 m (2H) [$(CH_2)_3$], 2.58–2.68 m (1H, CH), 3.74 d [1H, $CH(CN)_2$, J = 5.4 Hz], 5.33–5.43 m (2H, $=CH_2$), 5.63–5.74 m (1H, =CH). ^{13}C NMR spectrum, δ, ppm: 13.7, 22.1, 28.5, 28.7, 31.2, 44.9, 111.6, 111.9, 121.2, 134.1. Mass spectrum, *m*/*z* (I_{rel}, %): 162 (0.05) $[M]^{+\cdot}$, 106 (12.6), 97 (15.0), 80 (11.5), 79 (19.0), 67 (14.1), 57 (30.9), 56 (69.5), 55 (100), 53 (11.1), 41 (47.1). Found, %: C 74.20; H 8.78; N 17.31. $C_{10}H_{14}N_2$. Calculated, %: C 74.03; H 8.70; N 17.27.

Dimethyl 1,1-dioxo-4-pentyltetrahydro-3*H*-1λ^6-thiophene-3,3-dicarboxylate (XIIIa). Yield 28%, R_f 0.31, mp 50–51°C (from diethyl ether–hexane). IR spectrum, ν, cm^{-1}: 2958 m, 2931 m, 1743 s, 1724 v.s, 1304 v.s, 1281 s, 1265 s, 1215 m, 1134 s, 1068 m. ^1H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, J = 6.9 Hz), 1.22–1.44 m (7H) and 1.57–1.68 m (1H) [$(CH_2)_4$], 3.03–3.13 m (2H) and 3.31–3.40 m (1H) 4-H, 5-H, 3.56 d and 3.83 d (1H each, 2-H, J = 14.3 Hz), 3.80 s (6H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 13.8, 22.3, 27.6, 29.6, 31.2, 41.3, 53.3, 53.6, 54.55 (C^5); 56.5, 60.0, 168.2, 168.5. Mass spectrum, *m*/*z* (I_{rel}, %): 278 (0.04), 277 (0.36), 145 (100), 113 (58.7). Found, %: C 50.83; H 7.28. $C_{13}H_{22}O_6S$. Calculated, %: C 50.96; H 7.24.

1,1-Dioxo-4-pentyltetrahydro-3*H*-1λ^6-thiophene-3,3-dicarbonitrile (XIIIb). Yield 27%, R_f 0.39, mp 93–94°C (from ethyl acetate–hexane). IR spectrum, ν, cm^{-1}: 3024 m, 2962 m, 2931 m, 2256 v.w, 1323 v.s, 1300 m, 1269 m, 1138 s, 1130 v.s, 933 w. ^1H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, J = 6.9 Hz); 1.32–1.52 m (6H), 1.73–1.84 m (1H), and 1.98–2.08 m (1H) [$(CH_2)_4$]; 2.91–3.01 m (1H, 4-H), 3.08 t (1H, J = 13.2 Hz) and 3.58 d.d (1H, J = 6.3, 13.2 Hz) (5-H), 3.70 d and 3.93 d (1H each, 2-H, J = 14.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.8, 22.2, 26.9, 30.5, 31.1, 37.0, 45.1, 53.8, 58.7, 111.2, 112.3. Mass spectrum, *m*/*z* (I_{rel}, %): 239 (0.39) $[M-1]^{+\cdot}$, 175 (20.1), 161 (36.5), 148 (33.8),147 (47.4), 134 (35.2), 133 (65.9), 132 (11.2), 120 (20.2), 119 (32.8), 108 (18.3), 107 (18.4), 106 (19.7), 97 (34.3), 96 (22.0), 95 (23.8), 94 (44.8), 93 (14.1), 83 (19.3), 82 (34.1), 81 (43.7), 80 (16.4), 79 (48.5), 70 (15.9), 69 (32.4), 68 (14.7), 67 (23.7), 57 (18.5), 56 (25.9), 55 (100), 54 (16.8), 53 (16.2), 52 (10.2), 43 (49.7), 42 (21.7), 41 (82.3). Found, %: C 54.80; H 6.78; N 11.51. $C_{11}H_{16}N_2O_2S$. Calculated, %: C 54.98; H 6.71; N 11.66.

Dimethyl 2-(oct-1-en-3-yl)malonate (XIVa). Yield 11%, R_f 0.63, bp 96°C (1 mm). IR spectrum, ν, cm^{-1}: 2958 s, 2931 m, 2858 m, 1763 s, 1740 v.s, 1646 w, 1435 m, 1261 s, 1142 s, 1018 m. ^1H NMR spectrum, δ, ppm: 0.86 t (3H, CH_3, J = 6.9 Hz), 1.15–1.36 m (7H) and 1.38–1.47 m (1H) [$(CH_2)_4$], 2.71–2.81 m (1H, CH), 3.38 d [1H, C**H**$(CO_2Me)_2$, J = 9.1 Hz], 3.68 s and 3.71 s (3H each, OCH_3), 5.04–5.11 m (2H, $=CH_2$), 5.57–5.67 m (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 14.0, 22.4, 26.6, 31.5, 32.2, 44.2, 52.2, 52.3, 56.9, 117.3, 138.1, 168.6, 168.7. Mass spectrum, *m*/*z* (I_{rel}, %): 242 (0.09) $[M]^{+\cdot}$, 183 (78.4), 179 (24.4), 172 (10.5), 171 (100), 151 (10.8), 140 (11.3), 139 (72.5), 133 (38.8), 132 (63.1), 127 (11.3), 126 (39.3) 123 (11.0), 113 (46.6), 112 (17.9), 111 (19.6), 110 (20.3), 109 (12.1), 108 (14.9), 101 (21.5), 100 (25.3), 95 (14.5), 82 (10.9), 81 (40.3), 79 (12.7), 69 (33.2), 68 (11.8), 67 (20.4), 59 (17.2), 55 (22.3), 54 (11.3), 53 (17.7), 43 (12.0), 41 (24.5). Found, %: C 64.30; H 9.18. $C_{13}H_{22}O_4$. Calculated, %: C 64.44; H 9.15.

2-(Oct-1-en-3-yl)malononitrile (XIVb). Yield 16%, oily substance, R_f 0.62, bp 125°C (1 mm). IR spectrum, ν, cm^{-1}: 3086 w, 2959 s, 2932 v.s, 2863 s, 2257 w, 1644 w, 1458 m, 1424 m, 992 m, 934 m. ^1H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, J = 6.7 Hz), 1.22–1.41 m (6H) and 1.54–1.74 m (2H) [$(CH_2)_4$], 2.58–2.69 m (1H, CH), 3.74 d [1H, $CH(CN)_2$, J = 5.4 Hz], 5.33–5.42 m (2H, $=CH_2$), 5.63–5.74 m (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 13.8, 22.3, 26.2, 28.5, 31.1, 31.5, 45.0, 111.6, 111.9, 121.2, 134.1. Mass spectrum, *m*/*z* (I_{rel}, %): 176 (0.19) $[M]^+$, 147 (12.0), 120 (17.9), 107 (10.8), 94 (12.1), 81 (18.8), 80 (15.7), 79 (17.2), 71 (18.0), 70 (81.4), 69 (100), 67 (19.3), 56 (12.7), 55 (72.2), 54 (13.1), 53 (12.6), 43 (71.0), 42 (22.7), 41 (52.7). Found, %: C 75.03; H 9.28; N 15.71. $C_{11}H_{16}N_2$. Calculated, %: C 74.96; H 9.15; N 15.89.

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