

SHORT
COMMUNICATIONS

New Example of Ramberg–Böcklund Reaction Initiated by Michael Addition

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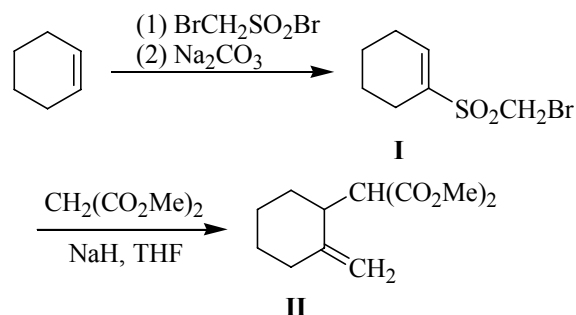
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Only isolated cases were reported [1–4] on the synthesis of functionalized olefins from α -haloalkyl vinyl sulfones through Ramberg–Böcklund reaction initiated by Michael addition. The limitations of this reaction evidently depend both on the structure of the initial substrate and on the nature of the used reagent. For instance, it was established in [5] that the treatment with potassium *tert*-butylate, a strong base but a weak nucleophile, of α -haloalkyl vinyl sulfones containing an allyl hydrogen atom promoted the so-called vinylogic Ramberg–Böcklund reaction leading to the formation of conjugated dienes. For instance, by this procedure nona-1,3-diene was obtained in 72% yield proceeding from 1-(bromomethylsulfonyl)oct-1-ene. We showed in [6] that the treatment with the typical Michael reagents, enolates of CH-acids, of bromomethyl β -styryl sulfone led to the cyclization initiated by Michael addition giving tetrahydrothiophene S,S-dioxide derivative.

We report here that at treating 1-(bromomethylsulfonyl)cyclohex-1-ene (**I**) with sodium dimethyl malonate (20°C, 17 h) from the three mentioned possible reaction routes proceeds the one consisting in the Ramberg–Böcklund reaction initiated by Michael addition: The functionalized derivative of methylenecyclohexane **II** is obtained.

Unsaturated sulfone **I** was obtained in a two-stage process involving the addition of BrCH₂SO₂Br to cyclohexene (CH₂Cl₂, 10°C, 24 h, no special initiation was required) and the debromination of the adduct in a water-dioxane solution of Na₂CO₃ at heating (50°C, 30 h).

The structure of compound **II** was confirmed by IR, ¹H and ¹³C NMR spectra. In particular, in the ¹H NMR spectrum two diastereotopic methoxycarbonyl groups were found with the signals at 3.65 and 3.71 ppm that in the ¹³C NMR spectrum gave rise to the signals at 52.3, 52.4 (OMe) and 168.7, 168.9 (C=O) ppm. The same groups appeared in the IR spectrum as four strong stretching vibrations bands $\nu_{C=O}$ at 1732, 1740, 1748, and 1755 cm⁻¹.



We are planning to establish in future whether this new example of the Ramberg–Böcklund reaction that we have discovered is of a general character in the series of 1-bromomethylsulfonylcycloalkenes.

1-(Bromomethylsulfonyl)cyclohex-1-ene (I). Yield 54%, mp 55–56°C (hexane–ether, 3:1). IR spectrum, ν , cm⁻¹: 3036 m, 2959 m, 2936 m, 1640 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), 2.32–2.41 m (4H), methylene protons of the ring; 4.32 s (2H, SO₂CH₂), 7.08 br.s (1H, CH=). ¹³C NMR spectrum, δ , ppm: 20.6, 21.8, 23.8, 25.7; 40.9 (SO₂CH₂); 134.9 and 144.5 (C=C). Found, %: C 35.10; H 4.68. C₇H₁₁BrO₂S.

Calculated, %: C 35.16; H 4.64.

Dimethyl (2-methylenecyclohexyl)malonate (II).

Yield 26%, oily substance. IR spectrum, ν , cm^{-1} : 2936 s, 1763 s, 1748 s, 1740 s, 1732 v.s, 1435 m, 1319 m, 1277 m, 1235 C, 1157 C, 1146 m. ^1H NMR spectrum, δ , ppm: 1.45–1.69 m (6H), 2.05–2.13 m (1H) and 2.17–2.26 m (1H), methylene protons of the ring; 2.92–3.01 m (1H, CHC=), 3.66 s and 3.73 s (6H, $2\text{CO}_2\text{Me}$), 3.71 d [1H, $\text{CH}(\text{CO}_2\text{Me})_2$, J 8.3 Hz], 4.57 s and 4.68 s (2H, $\text{CH}_2=$). ^{13}C NMR spectrum, δ , ppm: 23.2, 28.2, 30.8 and 34.0 (4 CH_2), 43.3 (CHC=), 52.4 and 52.5 (2 OMe), 54.1 [$\text{CH}(\text{CO}_2\text{Me})_2$], 108.1 ($\text{CH}_2=$), 148.9 (C=), 168.8 and 168.9 (2C=O). Found, %: C 63.74; H 8.15. $\text{C}_{12}\text{H}_{18}\text{O}_4$. Calculated, %: C 63.70; H 8.02.

IR spectra were recorded on a Fourier spectrophotometer InfraLYuM FT-02. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker AMX-400

(400.1 and 100.6 MHz respectively) from solutions of compounds in CDCl_3 . Elemental analyses were carried out on a CHN-analyzer HP-185B.

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