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Reaction of 5-Allenyl-2,3,5-trichloro-4,4-dimethoxy-2-cyclopentenone and Its Derivative with Iodine*

N. A. Ivanova, A. M. Shainurova, A. A. Khusainova, O. V. Shitikova, and M. S. Miftakhov

Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia
bioreg@anrb.ru

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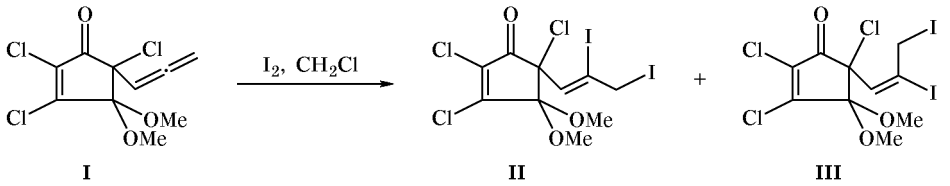
Abstract—5-Allenyl-2,3,5-trichloro-4,4-dimethoxy-2-cyclopentenone and 5-allenyl-2,3,5-trichloro-4,4-dimethoxy-1-(2-propynyl)-2-cyclopentenol react with iodine in methylene chloride at room temperature to give the corresponding 5-[(*E*)-2,3-diiodo-1-propenyl] derivatives.

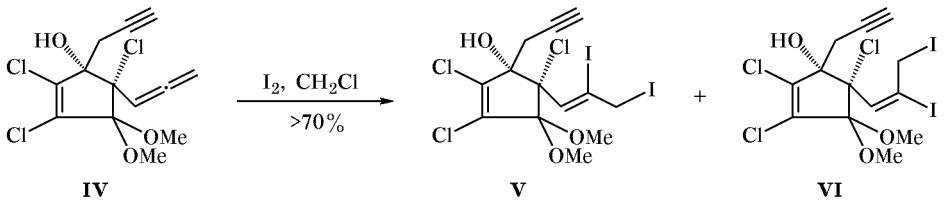
While searching for derivatives of allenylcyclopentenone **I** [1], capable of undergoing intramolecular cyclizations [2, 3], we examined the reaction of **I** with iodine. Allenyl ketone **I** smoothly reacted with an equimolar amount of iodine in methylene chloride at room temperature, yielding adduct **II** with a small admixture (7–10%) of minor isomer **III**. By single recrystallization of the product mixture from ethyl acetate we obtained pure compound **II** in 56% yield (Scheme 1). Isomeric diiodo derivatives **II** and **III** were identified on the basis of the CH_2I signals in the ^{13}C NMR spectra. The more upfield signal was observed for *E* isomer **II**. Heating of crystalline compound **II** at 50°C for 30 min led to its isomerization and formation of a mixture of isomers **II** and **III** at a ratio of 6:4 (according to the intensities of the olefinic protons in the ^1H NMR spectra; δ 6.50 and 6.60 ppm for compounds **II** and **III**, respectively).

Compound **IV** [4], which was obtained from cyclopentenone **I** [2], reacted with iodine in a similar way. As a result, an oily mixture of *E* and *Z* isomers **V** and **VI** (ratio 9:1; ^1H NMR data) was isolated in more

Scheme 1.



Scheme 2.



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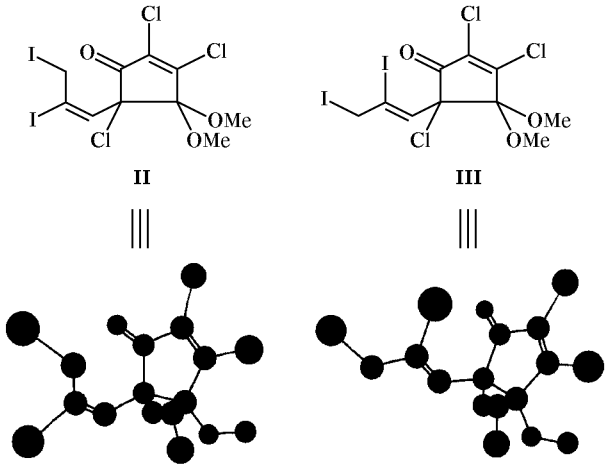
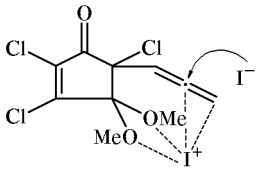


Low-energy conformers of compounds **II** and **III**. Hydrogen atoms are not shown.

than 70% yield (Scheme 2). The high stereoselectivity of formation of *E* isomers **II** and **V** in the iodination of compounds **II** and **III** seems to be surprising. In keeping with published data [5, 6], such electrophilic reactions, e.g., of Br_2 in CCl_4, $Hg(OAc)_2$ in MeOH, and I_2 in MeOH or CCl_4, with substituted allenes follow the stereoselective *trans*-addition scheme yielding mainly the corresponding *trans*-adducts. Computer modelling of low-energy conformers of **II** and **III** (using Chem 3D software) showed that *Z* isomer **III** is more energetically favorable (cf. ΔH_f values given in figure). However, according to our experimental data, less thermodynamically favorable *E* isomer **II** is mainly formed. The observed easy transformation of compound **II** into a mixture of isomers **II** and **III** on heating for a short time also indicates greater thermodynamic stability of compound **III**.

Presumably, the stereoselectivity of iodination is determined by effective internal control in transition state A, which involves coordination of iodonium cation to oxygen atoms of the methoxy groups and fixed spatial orientation of the allene moiety. As a result, the subsequent attack by I^- ion is directed preferentially at the more electrophilic central carbon atom of the allene fragment.



A

EXPERIMENTAL

The IR spectra were recorded on UR-20 and Specord M-80 spectrometers from samples prepared as thin films or dispersions in mineral oil. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-300 instrument at 300.13 and 75.47 MHz, respectively; $CDCl_3$ was used as solvent and internal reference (δ_H 7.27, δ_C 77.00 ppm). The mass spectra (20 and 70 eV) were run on an MKh-1306 mass spectrometer; ion source temperature 75–100°C. The progress of reactions was monitored by TLC on Silufol plates using hexane–ethyl acetate as eluent; spots were visualized by treatment with an alkaline solution of potassium permanganate [7].

Reaction of allenyl ketone I with iodine. A solution of 2.69 g (1.06 mmol) of iodine in 30 ml of CH_2Cl_2 was added dropwise with stirring to a solution of 3 g (1.06 mmol) of ketone **I** in 20 ml of CH_2Cl_2. The mixture was stirred for 6 h at 20°C, washed with saturated solutions of $Na_2S_2O_3$ and NaCl, dried over $CaCl_2$, and evaporated. The residue was recrystallized from ethyl acetate.

2,3,5-Trichloro-5-[(*E*)-2,3-diiodo-1-propenyl]-4,4-dimethoxy-2-cyclopentenone (II). Yield 3.3 g (56%). Colorless crystals, mp 114–114.5°C. IR spectrum, ν, cm^{-1}: 1616, 1636, 1712, 1724, 1736. ^1H NMR spectrum, δ, ppm: 3.45 s (3H, OMe), 3.49 s (3H, OMe), 4.36 d (1H, CH_AI, J = 10.7 Hz) and 4.7 d (1H, CH_BI, J = 10.7 Hz), 6.50 s (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 14.45 (CH_2I), 52.03 (OMe), 52.32 (OMe), 73.23 (C^5), 101.74 (C^4), 113.16 ($C^{2'}$), 131.81 ($C^{1'}$), 133.22 (C^2), 157.11 (C^3), 183.74 (CO). Found, %: C 22.50; H 1.81; Cl 19.68; I 47.47. $C_{10}H_9Cl_3I_2O_3$. Calculated, %: C 22.35; H 1.69; Cl 19.79; I 47.23.

2,3,5-Trichloro-5-[(*Z*)-2,3-diiodo-1-propenyl]-4,4-dimethoxy-2-cyclopentenone (III). ^1H NMR spectrum, δ, ppm: 3.44 s (3H, OMe), 3.49 s (3H, OMe), 4.48 d (1H, CH_AI, J = 10.5 Hz) and 4.54 d (1H, CH_BI, J = 10.5 Hz), 6.60 s (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 19.81 (CH_2I), 51.83 (OMe), 51.62 (OMe), 73.34 (C^5), 102.86 (C^4), 108.63 ($C^{2'}$), 132.0 ($C^{1'}$), 134.48 (C^2), 156.24 (C^3), 183.22 (CO).

The reaction of compound IV with iodine was carried out in a similar way. Purification by column chromatography on silica gel (hexane–ethyl acetate, 7:3) gave an oily mixture of isomers **V** and **VI** at a ratio of 9:1. Yield 73%. IR spectrum, ν, cm^{-1}: 1600, 1640, 1960, 2100, 3160, 3550. Found, %: C 26.91; H 2.18; Cl 18.58; I 44.19. $C_{13}H_{13}Cl_3I_2O_3$. Calculated, %: C 27.04; H 2.27; Cl 18.42; I 43.96.

2,3,5α-Trichloro-5β-[(*E*)-2,3-diiodo-1-propenyl]-4,4-dimethoxy-1β-(2-propynyl)-2-cyclopentenol

(**V**). ^{1}H NMR spectrum, δ, ppm: 2.13 t (1H, ≡CH, J = 2.5 Hz), 2.70 m (2H, CH_2), 3.30 s (3H, OMe), 3.40 s (3H, OMe), 4.35 d.d (1H, CH_AI, J = 10.5, 4.2 Hz) and 5.08 d.d (1H, CH_BI, J = 10.5, 4.2 Hz), 6.76 d (1H, HC=, J = 4.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 15.65 (CH_2I), 50.19 (OMe), 52.53 (OMe), 72.57 (≡CH), 78.18 (C≡), 82.33 (C^5), 83.38 (C^1), 106.05 (C^4), 110.50 ($C^{2'}$), 130.47 (C^3), 134.71 ($C^{1'}$), 137.92 (C^2).

2,3,5α-Trichloro-5β-[(*Z*)-2,3-diiodo-1-propenyl]-4,4-dimethoxy-1β-(2-propynyl)-2-cyclopentenol (VI). ^{1}H NMR spectrum, δ, ppm: 2.10 t (1H, ≡CH, J = 7 Hz), 2.68 m (2H, CH_2), 3.33 s (OMe), 3.43 s (OMe), 4.40 d (1H, CH_AI, J = 10.5 Hz) and 4.62 d (1H, CH_BI, J = 10.5 Hz), 6.98 s (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 21.93 (CH_2I), 29.55 (CH_2), 50.34 (OMe), 52.40 (OMe), 78.18 (≡CH), 79.57 (C≡), 81.86 (C^5), 82.86 (C^1), 106.50 ($C^{2'}$), 131.42 ($C^{1'}$), 139.01 (C^2).

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