ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 4, pp. 785–786. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © I.E. Andreev, Yu.A. Fomina, A.P. Kriven'ko, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 4, pp. 695–696.

LETTERS TO THE EDITOR

Bromination of Unsymmetrical Cross-Conjugated Dienones of Cyclohexane Series. Synthesis of Regioisomeric Dibromo Adducts

I. E. Andreev, Yu. A. Fomina, and A. P. Kriven'ko

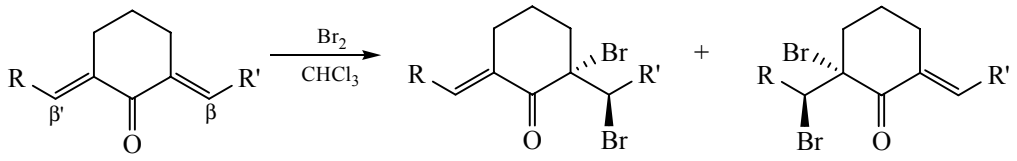
Chernyshevskii Saratov State University, ul. Astrakhanskaya 83, Saratov, 410012 Russia
e-mail: fominaya@mail.ru

Received March 25, 2010

DOI: 10.1134/S1070363211040335

Cross-conjugated dienone derivatives of alicyclic hydrocarbons (dienones) are widely used in the construction of various carbo- and heterocyclic systems, including the practically important ones [1]. Reactions of the dienones with nucleophilic reagents were previously discussed widely enough, while their electrophilic reactions, the bromination in particular, are poorly known. There is an information on the bromination of symmetrical dienones of cycloheptane and cyclohexane series [2]. However, their unsymmetrical counterparts have not been studied in these reactions.

In order to synthesize dibromo adducts and to reveal the reaction selectivity we studied the bromination of unsymmetrical dienones of cyclohexane series **I–III** containing terminal thienyl and aryl substituents (C_6H_5, 4-$MeOC_6H_4$, 3-$NO_2C_6H_4$). By keeping equimolar amounts of the reactants in chloroform at 0°C we obtained a mixture of regioisomeric dibromo adducts, 2-bromo-2-(bromophenylmethyl)-6-thienylmethylidene cyclohexanone **VIa** and 2-bromo-2-(bromothienylmethyl)-6-phenylmethylidene cyclohexanone **VIb** and their analogs **VIIa**, **VIIb**, **VIIIa**, **VIIIb** as a result of adding bromine to the exocyclic double bond. The total yield was 43–76% with the different ratio of regioisomers A:B depending on the nature of the substituents in the benzene ring.



I–V **VIa–Xa** **VIb–Xb**

R = Th, R' = Ph (**I, VI**), C_6H_5OMe-4 (**II, VII**), $C_6H_5NO_2$-3 (**III, VIII**), Th (**IV, IX**); R = R' = Ph (**V, X**).

In the absence of substituents in the benzene ring the major regioisomer is **VIa** (**VIa**:**VIb** = 3:1). The presence of an electron-donor group (4-OMe) increases the yield of the regioisomer **VIIa** (**VIIa**:**VIIb** = 5:1). The presence of an electron-withdrawing group (3-NO_2) leads to a decrease in the electron density at the reaction center β, resulting in prevalence of the alternative adduct **VIIb** (**VIIa**:**VII** = 1:3).

The IR spectra of dibromo adducts contain the absorption bands of the bonds C=C (1558–1561 cm^{-1}), C–Br (619–625 cm^{-1}), and the conjugated carbonyl group (1666–1670 cm^{-1}). In the ^1H NMR spectrum there are signals of methine protons at 6.06–6.15 (PhCHBr) and 6.31–6.40 ppm (ThCHBr), vinyl protons at 7.79–7.99 (=SHPh) and 8.09–8.46 ppm (=CHTh). For the assignment of the signals in the spectra we synthesized the dibromination products of some symmetric dienones such as 2,6-diphenylmethylidene and 2,6-dithienylmethylidene cyclohexanones **IV** and **V**: 2-bromo-2-(bromophenylmethyl)-6-phenylmethylidene cyclohexanone **IX** and 2-bromo-2-

(bromothienylmethy)-6-(2-thienylmethylidene)cyclohexanone **X**, respectively. The dibromo adduct **IX** has been obtained earlier [2], but its spectral data were not available. In the ^{1}H NMR spectra of the model compounds there are signals of methine protons (PhCHBr 6.10 ppm; ThCHBr 6.40 ppm) and vinyl protons (=CHPh 7.79 ppm; =CHTh 8.08 ppm), the assignment of regioisomers is made by referring to these data.

The data obtained are the first example of the electrophilic addition reactions of the unsymmetrical cross-conjugated dienone derivatives of cyclohexane.

Compounds **I**–**V** were described in [3].

2-Bromo-2-(bromophenylmethyl)-6-thienylidenecyclohexanone (VIa) and 2-bromo-2-(bromothienylmethyl)-6-phenylmethylidenecyclohexanone (VIb). To a solution of 0.5 g (1.8 mmol) of 2-thienylmethylidene-6-benzylidenecyclohexanone in 10 ml of chloroform was added dropwise a solution of 0.09 ml (1.8 mmol) of bromine in 5 ml of chloroform at cooling under stirring. The mixture was stirred for 1.5 h. After the solvent removal, the oily residue was triturated in hexane to give crystals. Yield 0.53 g (67%), mp 112–119°C (decomp.) (hexane). ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 2.00–3.18 m (6H, CH_2), 6.06 s (1H, PhCHBr), 6.31 s (1H, ThCHBr), 6.88–7.60 m (8H, Th+Ph), 7.79 s (1H, =CHPh), 8.09 s (1H, =CHTh). IR spectrum (KBr), ν, cm^{-1}: 625 (C–Br), 750–695 [C–S(Th)], 1561 (C=C), 1670 (C=O), 2951, 2854 (CH_2), 3084–3033 [CH(Ph+Th)]. Found, %: C 48.96; Br 36.36; S 6.55; H 4.63. $C_{18}H_{16}Br_2OS$. Calculated, %: C 49.09; Br 36.51; S 7.28; H 4.41.

2-Bromo-2-(bromo-4-methoxyphenylmethyl)-6-(2-thienylmethylidene)cyclohexanone (VIIa) and 2-bromo-(2-bromo-2-thienylmethyl)-6-(4-methoxyphenylmethylidene)cyclohexanone (VIIb) were obtained similarly from 0.5 g (1.6 mmol) of 2-thienylidene-6-(4-methoxyphenylmethylidene)cyclohexanone and 0.08 ml (1.6 mmol) of bromine. Yield 0.57 g (76%), mp 132–140°C (decomp.) (hexane). ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 2.02–3.00 m (6H, CH_2), 6.06 s (1H, PhCHBr), 6.40 s (1H, ThCHBr), 6.86–7.60 m (6H, Th+Ph), 7.99 s (=CHC_6H_4OMe-4), 8.09 s (1H =CHTh). IR spectrum (KBr), ν, cm^{-1}: 619 (C–Br), 721 [C–S(Th)], 1254 (C–O–C), 1460 (Me), 1558 (C=C), 1666 (C=O), 2955, 2854 (CH_2), 3098–3000 [CH (Ph+Th)]. Found, %: C 49.32; H 4.16; Br 33.74; S 7.10. $C_{19}H_{19}Br_2O_2S$. Calculated, %: C 48.83; H 3.86; Br 33.99; S 6.82.

2-Bromo-(2-bromo-3-nitrophenylmethyl)-6-(2-thienylidene)cyclohexanone (VIIIa) and 2-bromo-(2-bromo-2-thienylmethyl)-6-(3-nitrophenylmethylidene)-cyclohexanone (VIIIb) was synthesized similarly from 0.5 g (1.5 mmol) of 2-thienylidene-6-(3-nitrophenylmethylidene)cyclohexanone and 0.07 ml (1.5 mol) of bromine. Yield 0.31 g (43%), mp 145–147°C (decomp.) (hexane). ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 1.91–3.13 m (6H, CH_2CHPh), 6.15 s (1H, PhCHBr), 6.38 s (1H, ThCHBr), 6.98–7.61 m (6H, Th+Ph), 7.99 s (=$CHC_6H_4NO_2$-3), 8.46 s (1H, =CHTh). IR spectrum (KBr), ν, cm^{-1}: 632 (C–Br), 747–678 [C–S(Th)], 1346 (NO_{2s}), 1526 (NO_{2as}), 1569 (C=C), 1682 (C=O), 2931, 2872 (CH_2), 3073–3033 [CH(Ph+Th)]. Found, %: C 42.53; H 4.62; Br 32.39; S 5.98. $C_{18}H_{15}Br_2NO_3S$. Calculated, %: C 43.56; H 3.82; Br 32.94; S 6.61.

2-Bromo-2-(bromophenylmethyl)-6-benzylidenecyclohexanone (**IX**) was obtained by the known procedure [2]. Yield 0.66 g (77%), mp 122–128°C (decomp.) (hexane). ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 1.76–3.18 m (6H, CH_2), 6.10 s (1H, PhCHBr), 7.79 s (1H, –CH=), 6.93–7.54 m (10H Ph). IR spectrum (KBr), ν, cm^{-1}: 621 (C–Br), 1561 (C=C), 1680 (C=O), 2950, 2867 (CH_2), 3098–3010 [CH(Ph)]. Found, %: C 54.17; H 5.14; Br 36.16. $C_{20}H_{18}Br_2O$. Calculated, %: C 55.30; H 4.10; Br 36.80.

2-Bromo-2-(bromothienylmethyl)-6-(2-thienylidene)cyclohexanone (X) was synthesized similarly from 0.5 g (1.7 mmol) and 0.09 ml (1.7 mmol) of bromine. Yield 0.36 g (47%), mp 110–112°C (decomp.) (hexane). ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 1.96–3.21 m (6H CH_2), 6.40 s (1H, ThCHBr), 6.98–7.61 m (6H, Th), 8.08 s (1H, –CH=). IR spectrum (KBr), ν, cm^{-1}: 625 (C–Br), 1560 (C=C), 1678 (C=O), 2945, 2880 (CH_2), 3098–3010 [CH(Th)]. Found, %: C 43.32; H 3.87; Br 35.87; S 13.97. $C_{16}H_{14}Br_2OS_2$. Calculated, %: C 43.07; H 3.16; Br 35.81; S 14.37.

The reaction progress and individuality of the compounds obtained were monitored by TLC on Silufol UV-254 plates eluting with a hexane–diethyl ether–chloroform (3:1:1) and detecting with iodine vapor. The IR spectra were recorded on a IR Fourier-spectrometer FSM-1201 from KBr pellets. ^{1}H NMR spectra were registered on a Varian 400 spectrometer at 25°C in $CDC1_3$ operating at 400 MHz, internal reference TMS.

REFERENCES

1. Vatsadze, S.Z., Golikov, A.G., Kriven'ko, A.P., and Zyk, N.V.,*Usp. Khim.,* 2008, vol. 77, no. 8, p. 707.
2. Abd-Alla, M.A., Ismail, M.T., and El-Khawaga, A.M., *Revue Roumanie de Chimie,* 1985, vol. 30, no. 4, p. 343.
3. Fomina, Yu.A., Golikov, A.G., and Kriven'ko, A.P., *Zh. Org. Khim.,* 2008, vol. 44, no. 5, p. 715.