ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 12, pp. 1760–1764. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © V.P. Boyarskii, T.E. Zhesko, K.E. Tvorogov, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 12, pp. 1759–1764.

Carbonylation of Chlorobiphenyls Catalyzed by Modified Cobalt Carbonyl

V. P. Boyarskii[a], T. E. Zhesko[a], and K. E. Tvorogov[b]

[a] *VNIINeftekhim Public Corporation, Zheleznodorozhnyi pr. 40, St. Petersburg, 193148 Russia*
e-mail: vadimpb@yahoo.com

[b] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*

Received June 21, 2006; revised September 12, 2007

Abstract—Dichlorobiphenyls having both chlorine atoms in the same benzene ring undergo mild carbonylation in the presence of 1,2-epoxypropane-modified carbonyl cobalt complex to give biphenylcarboxylic acid esters. Monochlorobiphenyls fail to react under analogous conditions. The rate and selectivity of the reaction depend on the position of chlorine atoms. Carbonylation of dichlorobiphenyls having a chlorine atom in the *meta* position occurs preferentially at that position. 2,4-Dichlorobiphenyl gives rise mainly to the carbonylation product at the 2-position.

DOI: 10.1134/S1070428007120044

Polychlorinated biphenyls possess a number of unique physical and chemical properties which predetermine their wide applications as dielectrics in transformers and condensers, hydraulic liquids, heat-transfer materials, and refrigerants. On the other hand, polychlorobiphenyls are highly toxic substances which affect immune, endocrine, and nervous systems and exhibit carcinogenic properties [1]. Therefore, in the recent time much attention is given to the development of effective procedures for utilization of polychlorobiphenyls.

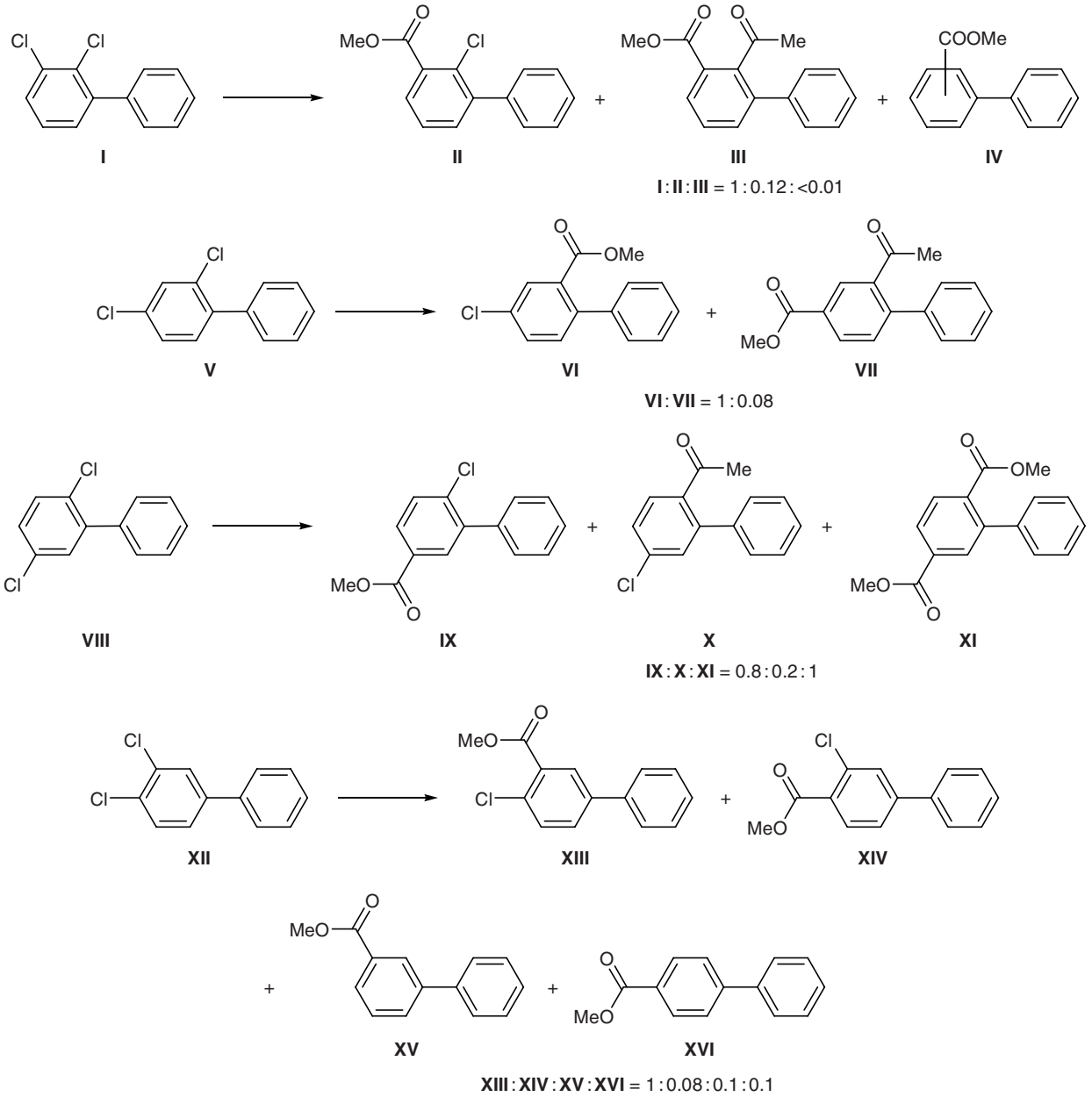
We recently described a procedure for utilization of commercial polychlorobiphenyl mixtures via catalytic carbonylation [2, 3]. As catalyst we used carbonyl cobalt complex modified by 1,2-epoxypropane [4]. The mechanism of carbonylation of aryl halides in the catalytic system $Co_2(CO)_8$–epoxide was described in [5]. It involves reversible opening of the oxirane ring with formation of intermediate anionic complex which is the true catalyst of carbonylation of aryl halides. This complex is strongly nucleophilic, and it activates aryl halides according to the $S_{RN}1$ mechanism.

There are some published data on the structure of polychlorobiphenyl carbonylation products obtained under conditions ensuring complete substrate conversion [3]. However, these data provide no information on the positional selectivity of carbonylation: the products contained on the average two carboxy groups per molecule, and it remained unclear which chlorine atom reacted first. Furthermore, at a high substrate conversion it is impossible to obtain monocarbonylation product, for methoxycarbonyl group that replaces chlorine accelerates the carbonylation process [5, 6].

Therefore, it was interesting to perform carbonylation of polychlorobiphenyls using specially synthesized individual compounds under specific conditions ensuring a low substrate conversion with a view to determine the structure of primary carbonylation products. Naturally, the simplest case should be the reaction with mono- and dichlorobiphenyls. Thus the goal of the present work was to analyze the structure of products formed in the first stage of carbonylation of low-chlorinated biphenyls.

The carbonylation in the presence of modified carbonyl cobalt complex was carried out under the conditions described in [2]: carbon(II) oxide pressure 760 mm, 60°C, methanol–potassium carbonate–potassium (tetracarbonyl)cobaltate, 1,2-epoxypropane as activator. Short reaction time and low concentrations of the reactant and catalyst ensured a low substrate conversion (15–30%). All monochlorobiphenyls, as well as 4,4′-dichlorobiphenyl, turned out to be inert under the given conditions. Dichlorobiphenyls having both chlorine atoms in the same ring underwent carbonylation to produce the corresponding biphenylcarboxylic acid esters (Scheme 1). The product structure was determined on the basis of their NMR and high-resolution mass spectra and GC–MS data.

Scheme 1.



The major carbonylation product obtained from 2,3-dichlorobiphenyl (**I**) was methyl 2-chlorobiphenyl-3-carboxylate (**II**). Its structure was determined by alkaline hydrolysis which resulted in the formation of known carboxylic acid **XVII** [7]. The latter was also identified by NMR spectroscopy. Acid **XVII** displayed in the ^{1}H NMR spectrum a doublet of doublets at δ 7.78 ppm, which is likely to belong to proton in the 6-position; the ^{13}C NMR spectrum contained a signal at δ_C 167.6 ppm corresponding to the carbonyl carbon atom. The two-dimensional ^{1}H–^{13}C NMR spectrum revealed an appreciable coupling between the C=O carbon atom and 6-H, while no couplings between the same carbon atom and other protons were observed. These data indicate interaction through three bonds, which should occur in 2-chlorobiphenyl-3-carboxylic acid but not in isomeric 3-chlorobiphenyl-2-carboxylic acid.

Another carbonylation product derived from 2,3-dichlorobiphenyl (**I**) was diester **III**. It was isolated from the second fraction after separation of the product mixture by column chromatography. In the ^{1}H NMR spectrum of **III** we observed two signals at δ ~3.9 and ~3.6 ppm, corresponding to protons of the methoxy

groups. The first of these is likely to belong to the ester group in the *meta* position, and the second, to that in the *ortho* position.

According to the GC–MS data, the product mixture (after isolation and methylation) contained a small amount (~0.5%) of ester **IV** ($[M]^+$ 212) resulting from hydrodechlorination of **II** or **III** (we failed to determine the position of the ester group in the benzene ring of compound **IV**).

In order to identify carbonylation products of 2,4-dichlorobiphenyl (**V**), the reaction mixture was subjected to hydrolysis. The ^{1}H NMR spectrum of carboxylic acid mixture thus obtained contained a signal at δ 7.73 ppm, which was assigned to 3-H in the major product. This signal is displaced appreciably downfield relative to the corresponding signal of initial 2,4-dichlorobiphenyl (δ 7.53 ppm), indicating that the carboxy group is attached to C^2. Otherwise (replacement of the 4-Cl atom), signals from protons in positions *3* and *5* should be displaced approximately equally. The signal at δ 7.52 ppm (d.d) was assigned to 5-H (*para* position with respect to the carboxy group); it was displaced only slightly ($\Delta\delta < 0.15$ ppm) relative to the 5-H signal in the spectrum of **V**. This spectral pattern corresponds to 4-chlorobiphenyl-2-carboxylic acid (**XVIII**). The downfield region of the spectrum contained signals from the minor product: broadened singlet and doublet were attributed to protons in positions *3* and *5* of biphenyl-2,4-dicarboxylic acid (**XIX**). We can conclude that the carbonylation of 2,4-dichlorobiphenyl (**V**) yields mainly ester **VI** and that diester **VII** is formed as minor product.

Gas chromatographic–mass spectrometric analysis of the reaction mixture obtained by carbonylation of 2,5-dichlorobiphenyl (**VIII**) showed the presence of three products, two of which were isomeric methyl chlorobiphenylcarboxylates **IX** and **X** ($[M]^+$ 246) and the third was diester **XI** ($[M]^+$ 270). Compound **XI** and one of the monoesters predominated in the product mixture. Our attempts to avoid formation of the dicarbonylation product were unsuccessful; taking into account low reactivity of 2,5-dichlorobiphenyl (**VIII**), the reaction rate considerably increases after replacement of the first chlorine atom. The product ratio in the carbonylation of **VIII** was determined from the GC–MS data. The ester mixture was separated by column chromatography. We isolated two fractions, the first of which contained esters **IX** and **X**, and the second, diester **XI**.

The chemical shifts of methoxy protons in the ^{1}H NMR spectrum of mixture **IX/X** were similar to those found for diester **XI**: about 3.9 and 3.6 ppm. The upfield signal in the spectrum of **IX/X** belonged to the minor product. Analogous signals were observed in the spectra of isomeric esters **II** and **III** (see above). Therefore, we assigned the signal at δ 3.6 ppm to the ester group in the *ortho* positions, and that at δ 3.9 ppm, to the ester group in the *meta* position (C^5). This means that the major monocarbonylation product of 2,5-dichlorobiphenyl (**VIII**) is methyl 2-chlorobiphenyl-5-carboxylate (**IX**) rather than methyl 5-chlorobiphenyl-2-carboxylate (**X**).

The ^{1}H NMR spectrum of mixture **IX/X** also contained doublets at δ 7.62 and 7.76 ppm corresponding to 3-H in the major and minor products, respectively. The downfield signal is likely to belong to a proton neighboring to the carboxy group, i.e., 3-H in **X**, while the 3-H proton neighboring to chlorine atom (isomer **IX**) resonates in a stronger field. These findings provide further support to the above conclusion.

GLC analysis of the product mixture obtained by carbonylation of 3,4-dichlorobiphenyl (**XII**) showed that the major product is a chlorobiphenylcarboxylic acid ester. Its structure was determined by comparing the ^{1}H NMR spectrum of the isolated substance with that of initial 3,4-dichlorobiphenyl (**XII**). The 2-H signal in the spectrum of the former (δ 8.01 ppm) was displaced by 0.26 ppm downfield relative to the corresponding signal of initial 3,4-dichlorobiphenyl (**XII**) (δ 7.75 ppm). The isolated product also displayed a broadened doublet at δ 7.76 ppm, which was assigned to 6-H; this signal also appears in a weaker field relative to the corresponding signal of **XII**. The 2-H and 6-H protons in molecule **XII** occupy, respectively, the *ortho* and *para* positions with respect to the chlorine atom in position *3*. The observed changes in their chemical shifts indicate that the ester group is located in the 3-position, i.e., the major carbonylation product is ester **XIII** rather than **XIV**. The product composition was determined from the GC–MS data.

The reaction mixtures obtained by carbonylation of 2,3-dichlorobiphenyl (**I**) and 3,4-dichlorobiphenyl (**XII**) also contained reductive hydrodechlorination products (compounds **IV**, **XV**, and **XVI**). The absence of monochlorobiphenyls, as well as their inertness in the carbonylation process, indicates that carbonylation of dichlorobiphenyls precedes hydrodechlorination. This means in turn that initial dichlorobiphenyls do not undergo hydrodechlorination, i.e. hydrodechlorination is not a concurrent pathway of transformation of intermediate dichlorobiphenyl radical anions. It should be noted that hydrodechlorination occurs when chlorine

atoms in initial dichlorobiphenyl are located in the *ortho* position with respect to each other, i.e., only chlorine atom in the *ortho* position with respect to the carboxy group undergoes reductive substitution. Analogous pattern was observed previously in the Co-catalyzed carbonylation of polyhalogenated benzenes and *o*-halobenzoic acids under UV irradiation [8] and in the carbonylation of *o*-halobenzoic acids catalyzed by cobalt carbonyl–methyl iodide [9].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer at 300.130 and 75.03 MHz, respectively, using CCl_4–DMSO-d_6 (2:1 by volume) as solvent and on a Bruker Avance DRX-500 instrument at 500 and 125 MHz, respectively, using acetone-d_6 as solvent. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1321 instrument with direct sample admission into the ion source (ion source temperature 200°C) or on a TOF Micromass LCT mass spectrometer (electrospray ionization, ESI-TOF MS). Gas chromatographic–mass spectrometric analysis was performed using an Agilent 5973 instrument (electron impact, 70 eV; ion source temperature 200°C; HP-5-MS capillary column, 0.25 mm× 30 m; injector temperature 260°C, detector temperature 250°C, oven temperature programming) or a Shimadzu QO-5000 instrument (SE-54 capillary column, 0.25 mm×60 m; injector temperature 260°C, detector temperature 250°C, oven temperature programming). Gas–liquid chromatography was performed on a Chrom-5 chromatograph equipped with a flame ionization detector [glass column, 3 mm×2.5 m, stationary phase 10% of SE-30 on Chromaton N-Super (80–100 mesh); carrier gas argon, flow rate 20–30 ml× min^{-1}; injector temperature 200°C, oven temperature 200°C]. The elemental compositions were determined on a Hewlett–Packard 185B analyzer.

Commercial inorganic reagents of chemically pure grade were used without preliminary purification. Potassium carbonate of analytical grade was calcined for 6 h at 150°C. Cobalt carbonyl was commercial product (from Merck). The solvents used were purified and dehydrated (if necessary) according to standard procedures. Commercial 4,4′-dichlorobiphenyl and 1,2-epoxypropane (analytical grade) were used without additional purification. Mono- and dichlorobiphenyls were synthesized by the Cadogan reaction according to the procedures described in [10, 11].

General procedure for carbonylation of dichlorobiphenyls. A glass jacketed reactor was charged with 2 g (14 mmol) of potassium carbonate, 10 ml of methanol, and 0.5 g (2 mmol) of dichlorobiphenyl **I**, **V**, **VIII**, or **XII**, and carbon(II) oxide preliminarily passed through methanol was bubbled through the mixture over a period of 0.5 h under stirring using a magnetic stirrer. A solution of 29 mg (0.133 mmol) of $KCo(CO)_4$ in 0.7 ml of methanol was then added with a syringe, the mixture was heated to 60°C, and 0.35 g (6 mmol) of 1,2-epoxypropane was added with a syringe. The needle was withdrawn from the septum to prevent gas exhaust from the reactor. The reaction was carried out until a conversion of 15–30% was reached, the conversion being monitored by the consumption of carbon(II) oxide. Gas supply was then terminated, 1 g of potassium hydroxide was added (to hydrolyze esters), and the mixture was stirred at 60°C or was left overnight at room temperature. When the hydrolysis was complete, the mixture was diluted with diethyl ether and extracted with water. The aqueous phase was acidified with concentrated hydrochloric acid and was left to stand for product crystallization. The precipitate was filtered off and dried.

Carbonylation of 2,3-dichlorobiphenyl (I). The mixture of acids obtained at a conversion of 30% was dissolved in 10 ml of methanol, the solution was cooled, and 0.6 g (5 mmol) of thionyl chloride was added with care. The mixture was left overnight, excess thionyl chloride and the solvent were removed under reduced pressure, and the residue (a mixture of methyl esters) was analyzed by GC–MS and separated by column chromatography using ethyl acetate–hexane (1:5) as eluent to isolate 80 mg (89%) of methyl 2-chlorobiphenyl-3-carboxylate (**II**) as an oily substance, R_f 0.38. ^{1}H NMR spectrum, δ, ppm: 3.91 s (3H), 7.37–7.50 m (7H), 7.67 d.d (1H). Found, %: C 68.17; H 4.50. $C_{14}H_{11}ClO_2$. Calculated, %: C 68.16; H 4.50.

A mixture of 80 mg of compound **II** and 0.4 g of potassium hydroxide in 10 ml of methanol was heated for 5 h under reflux. The solvent was removed, 10 ml of water was added to the residue, the mixture was acidified with hydrochloric acid to pH <1, and the precipitate was filtered off. Yield of 2-chlorobiphenyl-3-carboxylic acid (**XVII**) 60 mg (79%), mp 154°C; published data [7]: mp 156–158°C. ^{1}H NMR spectrum, δ, ppm: 7.37–7.53 m (7H, H_{arom}), 7.78 d.d (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 127.85, 128.83, 129.15, 129.26, 129.51, 130.38, 131.05, 134.56, 140.25, 143.23, 167.60. Found: $[M - H]^-$ 231.0219. $C_{13}H_9ClO_2$. Calculated: $[M - H]^-$ 231.0291.

The second fraction isolated by column chromatography contained dimethyl biphenyl-2,3-dicarboxylate

(**III**). Yield 10 mg (11%), oily substance, R_f 0.22. ^{1}H NMR spectrum, δ, ppm: 3.09 s (3H, CH_3), 3.36 s (3H, CH_3), 7.31–7.41 m (5H), 7.58–7.69 m (2H), 7.96 d.d (1H). Found, %: C 71.11; H 5.23. $C_{16}H_{14}O_4$. Calculated, %: C 71.10; H 5.22.

Carbonylation of 2,4-dichlorobiphenyl (V) (conversion 30%) gave 140 mg (97%) of a mixture of 4-chlorobiphenyl-2-carboxylic acid (**XVIII**) and biphenyl-2,4-dicarboxylic acid (**XIX**) at a ratio of 1:0.08. ^{1}H NMR spectrum, δ, ppm: **XVIII**: 7.29–7.47 m (6.5H), 7.52 d.d (1H), 7.73 d (1H); **XIX**: 7.94 d (0.08H), 8.04 s (0.08H).

Carbonylation of 2,5-dichlorobiphenyl (VIII). The mixture of acids obtained at a conversion of 15% was esterified with methanol as described above to obtain compounds **IX**–**XI** (GC–MS data).

Methyl 2-chlorobiphenyl-5-carboxylate (IX) (40%). Mass spectrum, *m*/*z* (I_{rel}, %): 248 (27.8) [M + 2]$^+$, 246 (78.1) [M]$^+$, 217 (36.1), 215 (100), 152 (92.1), 107 (9.65), 76 (23.7), 44 (7.89).

Methyl 5-chlorobiphenyl-2-carboxylate (X) (10%). Mass spectrum, *m*/*z* (I_{rel}, %): 248 (19.4) [M + 2]$^+$, 246 (54.8) [M]$^+$, 217 (37.6), 215 (100), 180 (3.2), 152 (69.9), 126 (5.4), 76 (12.9), 44 (19.4).

Dimethyl biphenyl-2,5-dicarboxylate (XI) (50%). Mass spectrum, *m*/*z* (I_{rel}, %): 270 (75.0) [M]$^+$, 239 (100), 207 (13.4), 180 (9.8), 152 (32.1), 112 (3.8), 76 (7.1), 44 (21.4).

Ester mixture **IX**–**XI** was subjected to column chromatography using ethyl acetate–hexane (1:5) as eluent. The first fraction contained mixture of esters **IX** and **X**. Yield 23 mg (4%), R_f 0.45. ^{1}H NMR spectrum, δ, ppm: **IX**: 3.88 m (3.0H), 7.61 d (1H); **X**: 3.59 s (0.6H), 7.76 d (0.2H); **IX**/**X**: 7.36–7.47 m (6.2H), 7.91–7.94 m (2.2H). The second fraction was pure diester **XI**. Yield 27 mg (5%), R_f 0.27, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 3.62 s (3H), 3.91 s (3H), 7.30 d (2H), 7.35–7.49 m (3H), 7.82 d (1H), 7.97 s (1H), 8.03 d (1H). Found, %: C 71.11; H 5.23. $C_{16}H_{14}O_4$. Calculated, %: C 71.10; H 5.22.

Carbonylation of 3,4-dichlorobiphenyl (XII). The mixture of acids obtained at a conversion of 30% was esterified with methanol as described above for the carbonylation products of **I**. According to the GC–MS data, the resulting ester mixture contained compounds **XIII**–**XVI**.

Methyl 4-chlorobiphenyl-3-carboxylate (XIII) (78%). Mass spectrum, *m*/*z* (I_{rel}, %): 248 (34.1) [M + 2]$^+$, 246 (91.8) [M]$^+$, 217 (36.9), 215 (100), 182 (1.6), 152 (94.5), 107 (3.6), 76 (6.5), 51 (1.0).

Methyl 3-chlorobiphenyl-4-carboxylate (XIV) (6.4%). Mass spectrum, *m*/*z* (I_{rel}, %): 248 (19.9) [M + 2]$^+$, 246 (53.8) [M]$^+$, 217 (36.8), 215(100), 186 (2.7), 152 (56.0), 107 (7.4), 76 (12.8), 51 (2.0).

Methyl biphenyl-3-carboxylate (XV) and methyl biphenyl-4-carboxylate (XVI) (7.8% each). Mass spectrum, *m*/*z* (I_{rel}, %): one isomer: 212 (100) [M]$^+$, 181 (88.6), 152 (50.9), 127 (3.5), 76 (13.2), 51 (1.8); another isomer: 212 (76.5) [M]$^+$, 181 (100), 152 (61.2), 127 (4.1), 76 (26.5).

Pure ester **XIII** was isolated by column chromatography using ethyl acetate–hexane (1:5) as eluent. Yield 102 mg, R_f 0.45, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 8.01 d (1H), 7.76 d.d (1H), 7.56–7.63 m (3H), 7.37–7.40 m (3H). Found, %: C 68.18; H 4.50. $C_{14}H_{11}ClO_2$. Calculated, %: C 68.16; H 4.50.

REFERENCES

1. Zanaveskin, L.N. and Aver'yanov, V.A., *Usp. Khim*., 1998, vol. 67, p. 788.
2. Zhesko, T.E., Boyarskii, V.P., Lanina, S.A., and Nikiforov, V.A., Russian Patent no. 2215729, 2002; *Byull. Izobret*., 2003, no. 31.
3. Boyarsky, V.P., Zhesko, T.E., Lanina, S.A., and Nikiforov, V.A., *Organohal. Compd*., 2001, vol. 54, p. 226; Nikiforov, V.A., Boyarsky, V.P., Zhesko, T.E., Lanina, S.A., Kolehmainen, E., and Virtanen, E., *Organohal. Compd*., 2002, vol. 56, p. 409; Lanina, S.A., Boyarsky, V.P., Zhesko, T.E., Nikiforov, V.A., Kolehmainen, E., and Virtanen, E., *Organohal. Compd*., 2003, vol. 63, p. 268.
4. Zhesko, T.E. and Boyarskii, V.P., *Kinet. Katal*., 1994, vol. 35, p. 320.
5. Boyarskii, V.P., Larionov, E.V., Polyakova, S.M., Boyarskaya, I.A., and Zhesko, T.E., *Russ. J. Gen. Chem*., 2007, vol. 77, p. 915.
6. Boyarskii, V.P., Zhesko, T.E., and Lanina, S.A., *Russ. J. Appl. Chem*., 2005, vol. 78, p. 1844.
7. Kikuchi, K., Yagi, M., and Takadaet, K., *Bull. Chem. Soc. Jpn*., 1968, vol. 41, p. 424.
8. Kashimura, T., Kudo, K., Mori, S., and Sugita, N., *Chem. Lett*., 1986, vol. 15, p. 299; Kashimura, T., Kudo, K., Mori, S., and Sugita, N., *Chem. Lett*., 1986, vol. 15, p. 483.
9. Miura, M., Itoh, K., and Nomura, M., *J. Mol. Catal*., 1990, vol. 59, p. 11.
10. Mullin, M.D., Pochini, C.M., McCrindle, S., Romkes, M., Safe, S.H., and Safe, L.M., *Environ. Sci. Technol*., 1984, vol. 18, p. 468.
11. Bolgar, M., Cunningham, J., Cooper, R., Kozloski, R., Hubball, J., Miller, D.P., Crone, T., Kimball, H., Janooby, A., Miller, B, and Fairless, B., *Chemosphere*, 1995, vol. 31, p. 2687.