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Bromo-Containing Oxadiazoles in Cross-Coupling Reactions

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New mesomorphic 1,2,4-oxadiazoles containing o-, m-, and p-bromo- substituents have been synthesized and used as starting compounds in cross-coupling reactions with arylboric acids. This procedure is widely used for synthesis of different biphenyls. For the first time we applied this method to the synthesis of heterocyclic compounds with five-membered oxadiazolic ring. As a result new liquid crystalline oxadiazoles of non linear structure were obtained and characterized by NMR and mesomorphic phase transitions.

The cross-coupling reaction with oxadiazoles containing a terminal p-Br-substituent easily provided as main products oxadiazole derivatives containing biphenyl fragments. On the contrary cross-coupling with m-bromo- and especially o-bromo-substituted oxadiazoles due to the steric hindrance was accompanied by a significant number of by-processes.

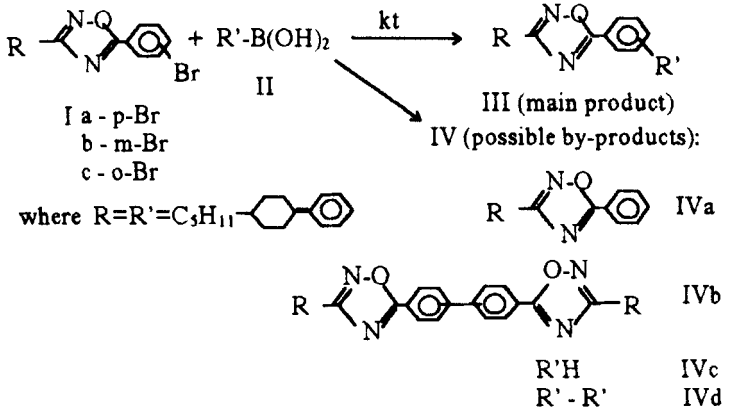
Keywords: oxadiazole; cross-coupling; mesomorphic transition

INTRODUCTION

Cross-coupling of phenylene fragments for obtaining various biphenyls in the last years is a classical method[1]. By this way mostly long chain liquid crystalline structures with biphenyl

central unit were synthesized[2]. Nevertheless many investigations at the last time were devoted to mesomorphic compound with non classical structure of the molecule: non linear, branched liquid crystals, discotics of different forms and others[3, 4]. Particularly liquid crystals with bent banana like shape of the molecule have a great theoretical and practical interest because the packing of bent molecules leads to the appearance of ferroelectric properties[5].

The mesomorphic heterocycles - 1,2,4-oxadiazoles, which we investigated[6] are also characterized by the asymmetrical structures. Non symmetric position of three heteroatoms defines in this case the orientation of exocyclic bonds and the angle between these bonds[7]. This is the reason of the nonlinear form of the whole molecule. It is possible to increase the curved shape of oxadiazolic molecule by the introduction of ortho- or meta-substituents into one of the aromatic rings at 3- or 5-C-atom of the 1,2,4-oxadiazole. Compounds constructed by this way are interesting not only as potential liquid crystals but also as potential ferroelectric materials. The cross-coupling reaction using p-, m-, and o-bromocontaining 1,2,4-oxadiazoles (I a-c) and aromatic boric acids (II) in the presence of the complex catalyst



was applied for the first time for the synthesis of this class of heterocyclic compounds.

The cross-coupling reaction represents a complicate series of oxydation - reduction - processes[8]. The structure and the ratio of its products depends on many factors including the structure of the starting reaction components.

EXPERIMENTAL

The starting bromides Ia-c were synthesized according to work[6]. 4-Amylcyclohexylphenyl boric acid was obtained according to the method[9].

Cross-coupling reaction:

Water solution of sodium hydrocarbonate (2M, 150-160 ml) was added to 0.33 mol of arylboric acid dissolved in an appropriated volume of DMF (in the case of the acid II - 270-300 ml) and then 270-300 ml of water was added. To the stirring mixture 0.8-1% mol of catalyst $PdCl_2[P(Ph)_3]_2$ and then an equimolecular amount (0.33 mol) of bromide I in 200-300 ml of DMF were added. The reaction mixture was stirred at the room temperature during 3-4 hours (till the starting bromide disappearance, checked by means of TLC and GLC). Then the reaction product was extracted and purified by crystallization and chromatography on the SiO_2. The hydrocarbonic by-products IVc, d were elueted with petroleum ether and the oxadiazolic main product III - with more polar benzene or toluene. The structures of all starting bromides I, by-product IVd and new oxadiazoles III were confirmed by elementary analysis data and the last ones also by NMR spectra (see structural formulae III a-c). NMR spectra were recorded on a Bruker WM-250 spectrometer, solvent $CDCl_3$.

Comp. IIIa (ppm): 8.27(2H,d,H-C); 8.10(2H, d, H-A); 7.76(2H, d, H-B); 7.59(2H, d, H-E); 7.41-7.31(4H, m, H-D+H-F); 2.52(2H, t,

CH cyclohexane); 1.9(8H, t, CH_2 cyclohexane); 1.7-1.0(26H, m, CH cyclohexane + CH_2 aliphat.); 0.9(6H, t, CH_3).

Comp.IIIb (ppm): 8.44(1H, s, H-F); 8.16(1H, d, H-C); 8.11(2H, d, H-B); 7.81(1H, d, H-E); 7.61(2H, d, H-G); 7.4-7.3(5H, m ,H-A+H-D+H-H); aliphatic part is equal to comp. III a.

Comp.IIIc (ppm): 8,07(1H, d, H-C): 7,95(4H, d, H-B); 7,61(1H, t, H-D); 7,50(1H, t, H-E); 7,3(5H, m, H-A+H-F+H-G); aliphatic part is equal to comp. III a.

Transition temperatures of the starting oxadiazole phenylbromides (I) and of the cross-coupling products (III a-c) were measured using Mettler-FP-5 apparatus with polarizing microscope.

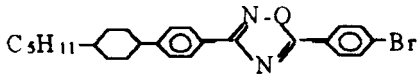
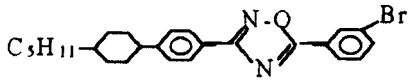
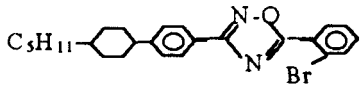
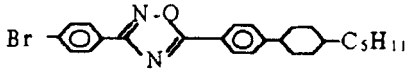
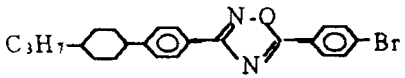
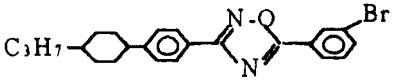
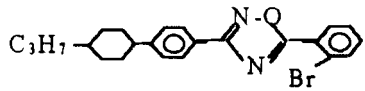
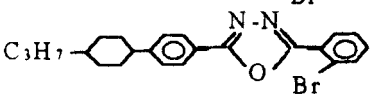
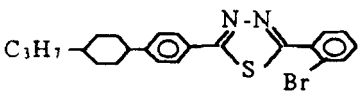
GLC analysis was fulfilled on "Tsvet-100" apparatus with flame-ionization detector, 2 m column with 5% SP-2100 on Chromaton N-Super, temperatures of analysis 100-270°C.

RESULTS AND DISCUSSION

The transition temperatures of the starting o-, m-, p- isomeric bromides I a-c and of their structure isomers, homologs and analogs (V) are presented in the Table.

The changement of the terminal p-Br-substituent (I a) to the lateral m-Br and o-Br leads to decreasing of clearing temperatures and to disappearance of the smectic phase. The similar picture is observed for the propyl homologs (V) too. It is necessary to note that also in this case the replacement of the asymmetric 1,2,4-oxadiazolic ring (compound V a) by the symmetric 1,3,4-oxadiazolic ring (the compound V d) leads to increase of the melting and clearing temperatures as well, especially by the change of heteroatom in the five-membered heterocycle.

TABLE Mesomorphic properties of starting bromides.

NN	Compound formula	Transition temperatures, °C
I a		C 113 S 120 N 215 I
I b		C 86 N 127 I
I c		C_1 42.6 C_2 51.3 N 97.2 I
I d		c 104 S 172 N 223 I
V a		C 110 S 120 N 228 I
V b		C 88 N 128 I
V c		C 67 N 85 I
V d		C 82.5 N 90 I
V e		C 93-95 N 158-160 I

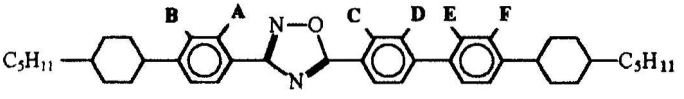
The introduction of the sulphur atom instead of the oxygen one (the compound Ve) causes the increase of molecular linearity and therefore the increase also of the transition temperatures. The similar alteration of mesomorphic parameters was observed in our work [7] concerning to p-Cl-containing oxadiazoles.

Cross-coupling of p-bromophenyl oxadiazole (Ia) with a high yield (~70%) leads to oxadiazole IIIa which demonstrated nematic and smectic phases as well.

The cross-coupling reaction of m-bromocontaining oxadiazole (I b) occurs with some steric difficulties, the main

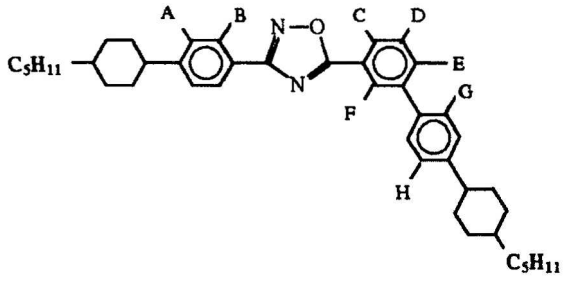
product III b was obtained with a yield near 50%. This mesogen demonstrated only nematic phase. There are great difficulties in proceeding cross-coupling reaction with o-Br-substituted compound Ic due to the steric hindrance in intermediates formation. The desired product (IIIc) was isolated only with a small yield (~5%); it was not mesomorphic. Probably it is due to the fact that the compound IIIc is too bended to give liquid crystalline properties.

Among the various by-products one high temperature liquid crystal was separated. It is identic to the biphenyl IVd obtained by the counter synthesis.



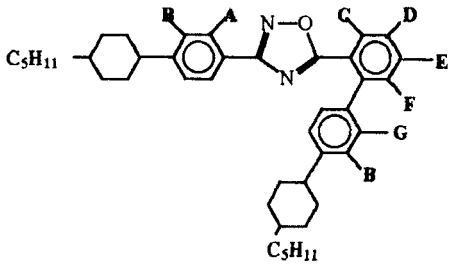
IIIa

C 163-164 S 275 N 307 I (with decomposition)



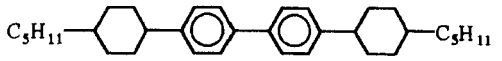
IIIb

C 107 N 178-179 I



IIIc

C 97.5 I (not mesomorphic)



IVd

C 227-229 S_A 243 N 261 I

The investigation of the non linear mesogens synthesized as a possible "banano form" structures with ferroelectric properties will be the subject of our future work..

CONCLUSION

1. The cross-coupling method was applied for the synthesis of new oxadiazolic mesogens. A series of bromophenyl-substituted 1,2,4-oxadiazoles with o-, m-, and p-Br-substituents were used as starting compounds. All bromo-containing compounds exhibit mesomorphic properties. In the case of terminal Br-substituent - both smectic and nematic phases, and in the case of lateral (ortho- and meta-) Br-substituent - only nematic phase were observed.
2. Reaction products were investigated by GLC and NMR methods. It was shown that the reaction with m- and especially

o-Br-substituted compounds has great steric hindrances and was accompanied by a large amount of by-products.

3. New non linear oxadiazoles - main products of cross-coupling reaction - were obtained, purified and characterized by mesomorphic phase transitions and NMR spectra.

ACNOLEDGEMENTS

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