ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 1, pp. 82–97. © Pleiades Publishing, Ltd., 2010.
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Reactions of Arylacetylenic Compounds with Arenes in the Presence of Aluminum Halides

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Received April 8, 2009

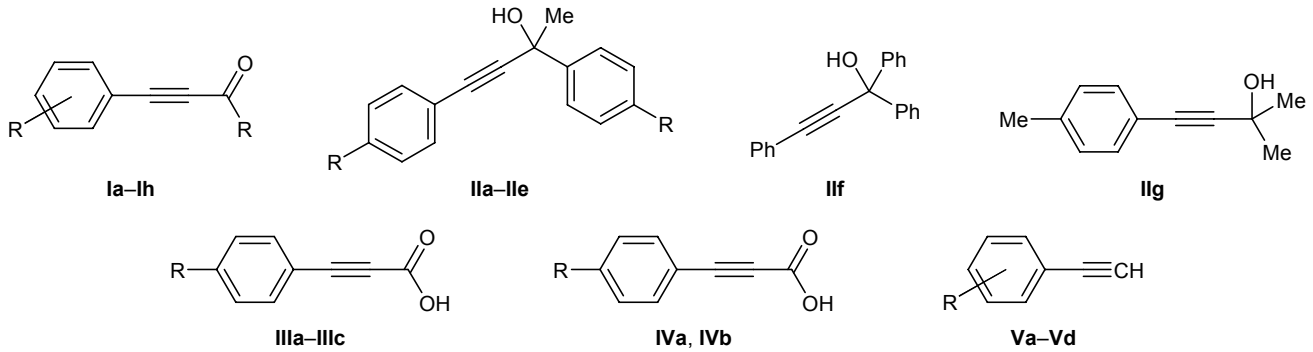
Abstract—Conjugated arylacetylenic ketones and aldehydes, propargyl-type alcohols, and arylacetylenes reacted with arenes in the presence of $AlBr_3$ or $AlCl_3$ as catalyst to give substituted indenes. 3-Arylpropynoic acids under analogous conditions gave rise to 3,3-diarylindan-1-ones, while the corresponding methyl esters were converted into methyl 3,3-diarylprop-2-enoates. The key intermediates in the transformations of acetylenic ketones and aldehydes and propargyl-type alcohols into indene derivatives are resonance-stabilized propargyl–allenyl cations $–C{\equiv}C–C^+ \leftrightarrow –C^+{=}C{=}C$ which reacted with one of the resonance structures to give isomeric indenes, depending on the substituent nature.

DOI: 10.1134/S1070428010010082

Since XIXth century various Lewis acids were extensively used for the preparation of organic compounds on both laboratory and industrial scales [1, 2]. Lewis acids are now used in organic synthesis as reagents and catalysts in numerous processes involving formation of carbon–carbon and carbon–heteroatom bonds, oxidation, reduction, polymerization, etc. [3–11]. Various Lewis acids have also found wide application in the chemistry of alkynes [12]. However, until recently the use of such common Lewis acids as aluminum halides $AlBr_3$ and $AlCl_3$ for direct activation of triple carbon–carbon bond was fairly limited and occasional [13–15]. Effective participation of aluminum halides in electrophilic activation of acetylenic compounds was demonstrated by us only recently [16–18].

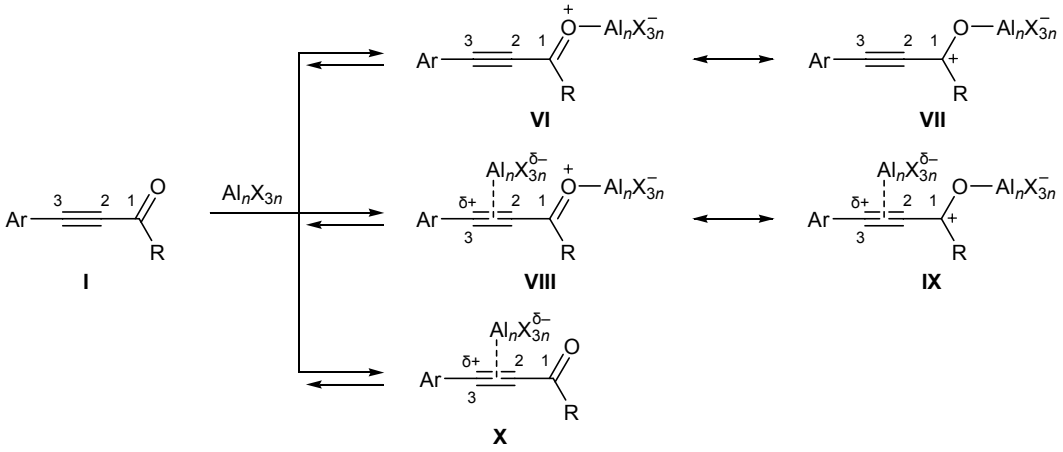
The goal of the present work was to study transformations and reactivity of arylacetylenic compounds in their reactions with arenes catalyzed by $AlBr_3$ or $AlCl_3$. As substrates we used α,β-acetylenic carbonyl compounds **Ia**–**Ih**, alcohols **IIa**–**IIg**, 3-arylpropynoic acids **IIIa**–**IIIc**, methyl 3-arylpropynoates **IVa** and **IVb**, and arylacetylenes **Va**–**Vd**.

Aluminum halides AlX_3 are capable of coordinating at two electron-donor centers in the $–C^3{\equiv}C^2–C^1{=}O$ fragment of compounds **I**, at the carbonyl oxygen atom and at the $C^3{\equiv}C^2$ bond (Scheme 1). As a result, three types of cationic species may be formed. Cation **VI** is formed via coordination at the carbonyl oxygen atom, cation **VIII** involves coordination at both carbonyl oxygen atom and triple carbon–carbon bond, and struc-



I, R = R′ = H (**a**), R = Me, R′ = H (**b**), 4-Me (**c**), 2,4-Me_2 (**d**), 2,4,6-Me_3 (**e**), 4-MeO (**f**), 4-F (**g**); R = Ph, R′ = H (**h**); **II**, R = R′ = H (**a**); R = H, R′ = Me (**b**); R = Me, R′ = H (**c**); R = F, R′ = H (**d**), Me (**e**); **III**, R = H (**a**), F (**b**), Me (**c**); **IV**, R = H (**a**), Me (**b**); **V**, R = H (**a**), 2-F (**b**), 4-F (**c**), 4-Cl (**d**).

Scheme 1.



X = Cl, Br.

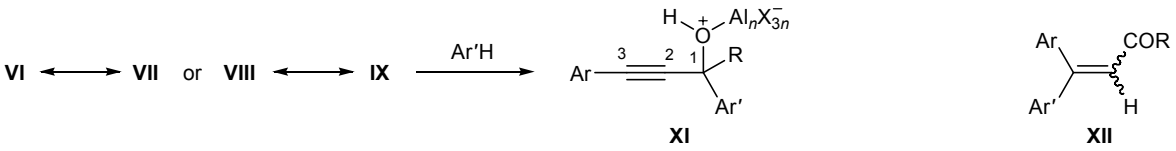
ture **X** corresponds to coordination only at the triple bond. Taking into account that the interaction between AlX_3 and carbonyl oxygen atom is much more energetically favorable than coordination of AlX_3 at the acetylenic bond π-system [19, 20], the formation of species **X** should be regarded as hardly probable. The most probable is generation of intermediate cations **VI** and **VIII** which can also be represented by canonical structures **VII** and **IX**, respectively.

Cationic species **VI**↔**VII** and **VIII**↔**IX** possess two electrophilic centers, C^1 and C^3 (Scheme 1), which can be involved in subsequent reactions with arenes according to aromatic electrophilic substitution pattern leading to structures **XI** and **XII**, respectively (Scheme 2). However, 3,3-diarylprop-2-en-1-ones **XII** did not react with aromatic compounds in the presence of aluminum halides. For example, 1,3,3-triphenylprop-2-en-1-one failed to react with benzene in the presence of $AlCl_3$ and HCl [21]. Moreover, in the present work we also found that a ~1:1 mixture of (*E*)- and (*Z*)-4-(4-methylphenyl)-4-phenylbut-3-en-2-ones [22] remained unchanged after heating for 0.5 h at 60°C in benzene in the presence of $AlBr_3$ (according to the general procedure for the reaction of acetylenic compounds with arenes; see Experimental) and was quantitatively recovered from the reaction mixture. No structures like **XII** were detected in analogous reactions of acetylenic compounds **Ia**–**Ih** (see below). These data indicate that initial addition of aromatic compounds occurs at the C^1 rather than C^3 atom of intermediate **VI**↔**VII** or **VIII**↔**IX** with formation of structure **XI** (Scheme 2).

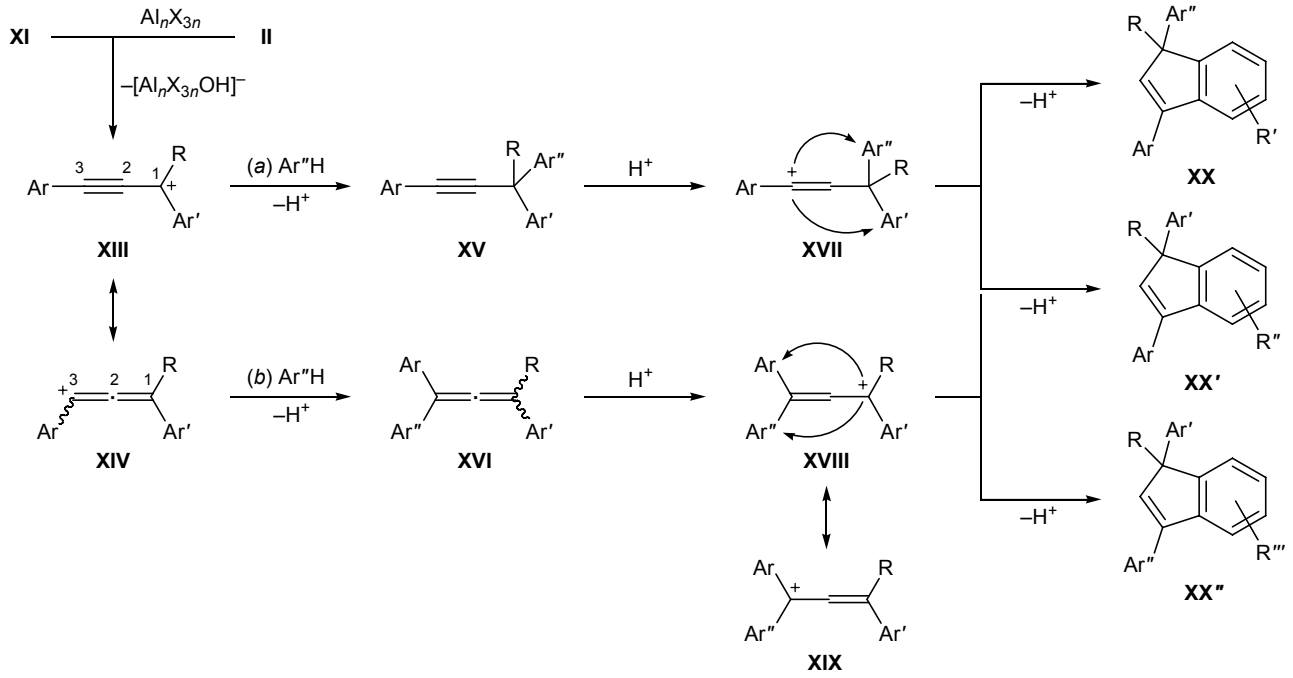
Acetylenic carbonyl compounds **Ia**–**Ih** and alcohols **IIa**–**IIg** reacted with benzene and 1,2-dichlorobenzene in the presence of $AlBr_3$ or $AlCl_3$ to give substituted indenes **XXa**–**XXq**. Scheme 3 illustrates the most probable paths of formation of final products **XX** in the examined reactions. The structures of reactive intermediates **XIIIa**–**XIIIm**, **XIVa**–**XIVm**, **XVa**–**XVn**, **XVIa**–**XVIk**, **XVIn**, **XVIIa**, **XVIIb**, **XVIId**–**XVIIn**, **XVIIIa**–**XVIIIk**, **XVIIIn**, **XIXa**–**XIXi**, **XIXk**, and **XIXn** and indenes **XXa**–**XXq** are shown in table; the corresponding reaction paths (*a* and *b*; Scheme 3) are also indicated.

The structure of indenes **XXa**–**XXq**, **XXVa**–**XXVc**, and indanones **XXIIa**–**XXIId** (Schemes 4, 5, 8) was determined by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and mass spectrometry [16–18] with account taken of the GC–MS data obtained by us previously [16]. The substitution pattern in the indene system and aromatic fragments was established by detailed analysis of spin–spin couplings in the ^1H NMR spectra of **XXa**–**XXq** and **XXVa**–**XXVc** (see Experimental and the data reported in [16–18]).

Scheme 2.



Scheme 3.



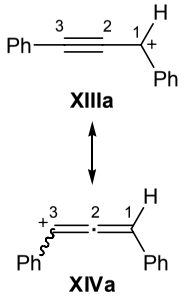
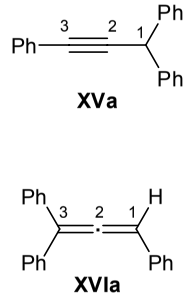
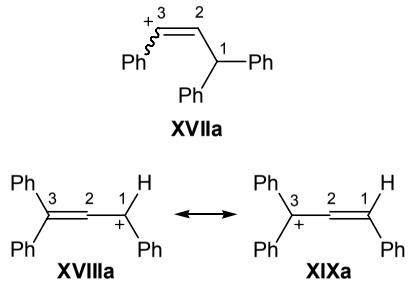
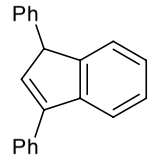
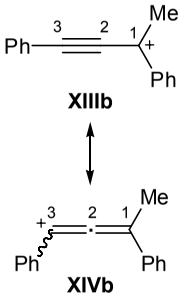
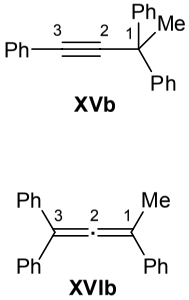
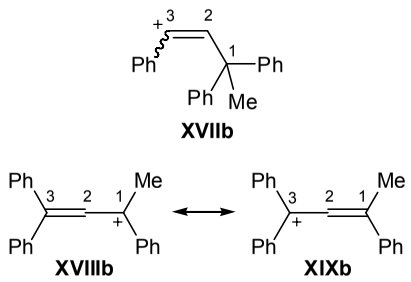
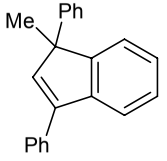
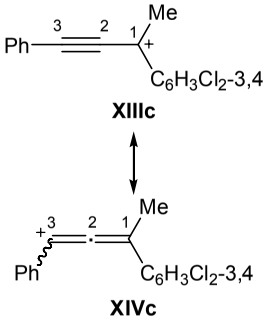
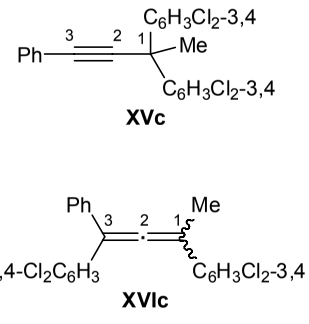
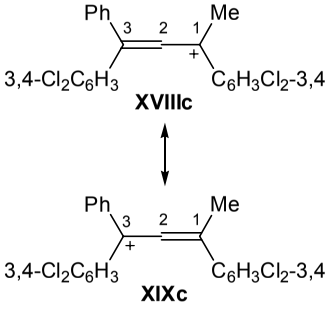
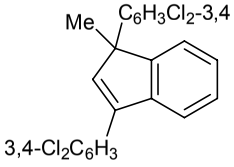
Propargyl-type alcohols **II** are synthetic equivalents of species **XI** (Scheme 2). By the action of various Lewis and Brønsted acids alcohols **II** give rise to propynyl (alkynylcarbenium) cations **XIII** [23–27] that may also be represented as allenyl cations **XIV** (Scheme 3). Resonance-stabilized cationic intermediates **XIII**↔**XIV** are capable of reacting with arenes along two pathways. The first of these involves attack by the electrophilic C^1 carbon atom in structure **XIII** (path *a*), and the second implies addition at the C^3 atom in structure **XIV** (path *b*). Path *a* gives alkyne **XV** which is then protonated at the triple bond to produce vinyl-type cation **XVII**, and intramolecular cyclization of the latter finally yields indene structure **XX** or **XX′**. Following alternative path *b*, cation **XIV** is converted into allene **XVI** which is protonated at the central carbon atom in the C=C=C allene triad [28] to form resonance-stabilized allyl-type cations **XVIII**↔**XIX** and finally indenes **XX′** and **XX″**.

Intermediate formation of structures **XV** and **XVI** is confirmed by the transformation of 1,1,3,3-tetraphenylpropadiene (tetraphenylallene) into 1,1,3-triphenylindene (**XXI**) in acid medium [29], as well as by the synthesis of the latter from 1,3,3,3-tetraphenylprop-1-yne (**XXI**) in a solution of $AlBr_3$ in methylene chloride (see Experimental). In addition, allyl-type alcohols in H_2SO_4 or HSO_3F give rise to substituted indenes **XX** as a result of cyclization of cations **XVIII**↔**XIX** [30].

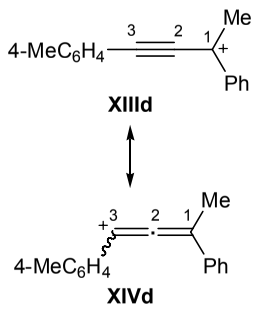
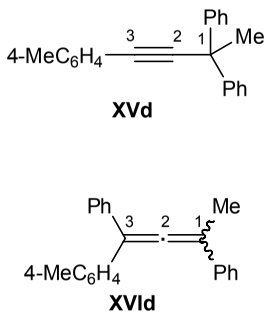
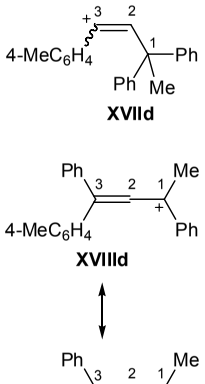
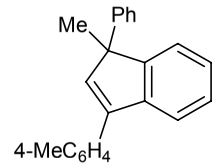
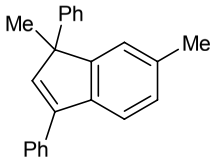
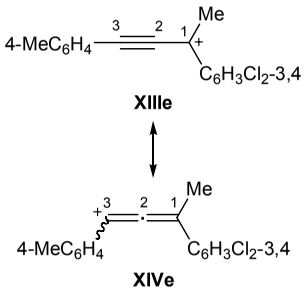
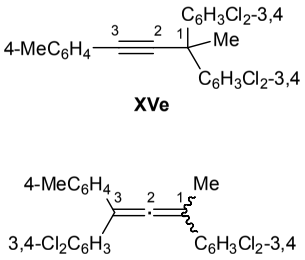
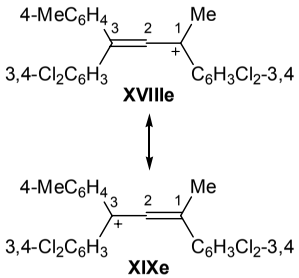
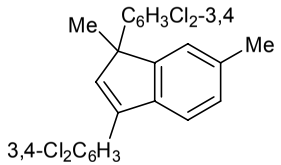
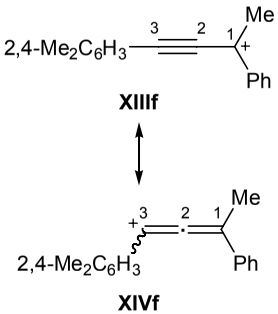
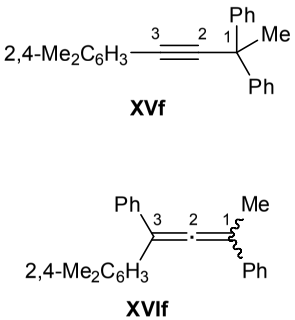
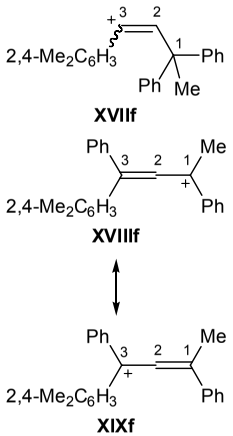
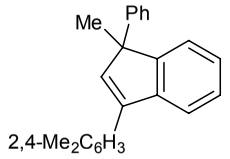
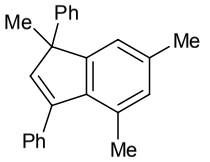
With a view to elucidate the effect of electronic properties of the Ar, Ar′, and R substituents on distribution of the positive charge in structures **XIII**↔**XIV** and direction (*a* or *b*; Scheme 3) of their further reactions with arenes (π-nucleophiles), we examined transformations of a series of arylacetylenic compounds **Ia**–**Ih** and **IIa**–**IIg** (see table). In many cases, the structure of indene **XX** formed as final product unambiguously indicated the path of its formation. For example, compound **XXc** can be formed only along path *b* through intermediates **XIVc**, **XVIc**, and **XVIIIc** (see table, run no. 3). Alternative path involving structures **XIIIc** and **XVc** cannot lead to indene **XXc**. Likewise, indenes **XXe**, **XXf**, **XXh**, and **XXq** are formed from alkynes **Ic**, **Id**, **IIc**, and **IIg** according to path *b* (run nos. 4–6, 14, 18), while compounds **XXm**–**XXo** originate from alkynes **IIb** and **IIe** following path *a* (run nos. 12, 13, 16).

Comparison of the reactions of cations **XIII**↔**XIV** with aromatic π-nucleophiles showed that electron-donating substituents Ar, Ar′, and R (see table) capable of essentially delocalizing positive charge (aromatic systems), favor activation of the neighboring electrophilic center, C^1 in structure **XIII** or C^3 in structure **XIV**. Analogous conclusions were drawn previously [24–26] on the basis of ^1H and ^{13}C NMR studies on positive charge distribution in resonance stabilized propargyl–allenyl cations. Other examples illustrating

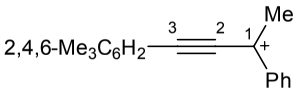
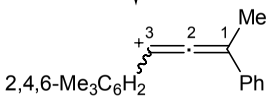
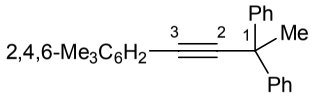
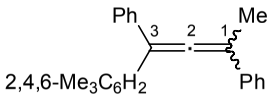
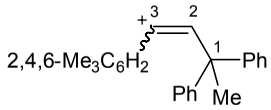
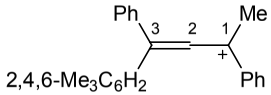
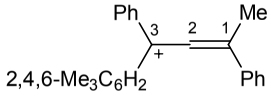
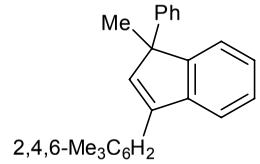
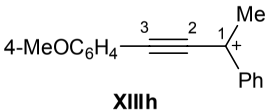
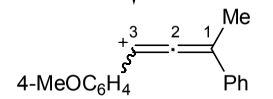
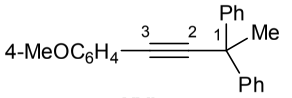
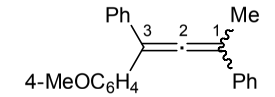
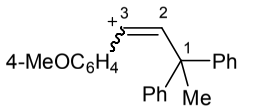
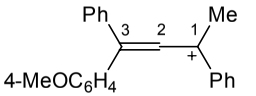
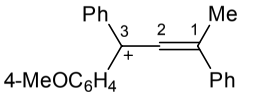
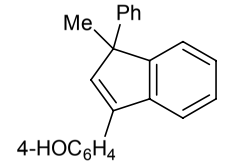
Structures of intermediates **XIII**↔**XIV**, **XV**–**XVII**, and **XVIII**↔**XIX** in the reactions of acetylenic carbonyl compounds **Ia**–**Ih** and alcohols **IIa**–**IIg** with benzene and 1,2-dichlorobenzene in the presence of $AlBr_3$ and $AlCl_3$, leading to indenes **XXa**–**XXq**

Run no.	Initial compounds	Intermediates			Products (yield, %), reaction path[a]
		XIII↔**XIV**	**XV**, **XVI**	**XVII**, **XVIII**↔**XIX**	
1	**Ia** + C_6H_6	 **XIIIa** **XIVa**	 **XVa** **XVIa**	 **XVIIa** **XVIIIa** **XIXa**	 **XXa** (21), *a* or *b*
2	**Ib** + C_6H_6	 **XIIIb** **XIVb**	 **XVb** **XVIb**	 **XVIIb** **XVIIIb** **XIXb**	 **XXb** (38), *a* or *b*
3	**Ib** +1,2-$Cl_2C_6H_4$	 **XIIIc** **XIVc**	 **XVc** **XVIc**	 **XVIIIc** **XIXc**	 **XXc** (31), *b*

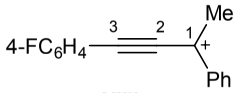
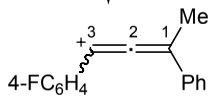
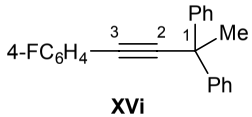
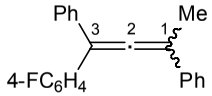
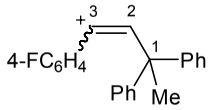
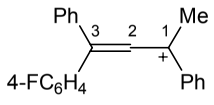
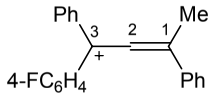
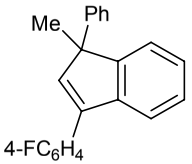
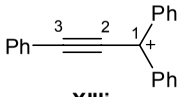
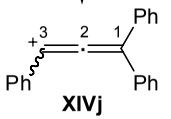
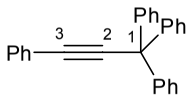
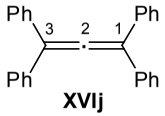
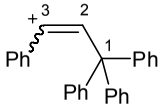
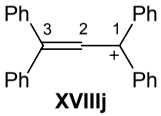
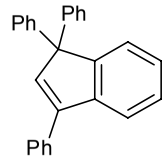
(Contd.)

Run no.	Initial compounds	Intermediates			Products (yield, %), reaction path[a]
		XIII↔XIV	**XV, XVI**	**XVII, XVIII↔XIX**	
4	**Ic** + C_6H_6	 **XIIId** ↔ **XIVd**	 **XVd** **XVId**	 **XVIId** ↔ **XVIIId** ↔ **XIXd**	 **XXd** (14), *a* or *b*  **XXe** (46), *b* **XXb** (10), aryl group exchange
5	**Ic** + $1,2\text{-}Cl_2C_6H_4$	 **XIIIe** ↔ **XIVe**	 **XVe** **XVIe**	 **XVIIIe** ↔ **XIXe**	 **XXf** (40), *b*
6	**Id** + C_6H_6	 **XIIIf** ↔ **XIVf**	 **XVf** **XVIf**	 **XVIIf** ↔ **XVIIIf** ↔ **XIXf**	 **XXg** (10), *a* or *b*  **XXh** (57), *b*

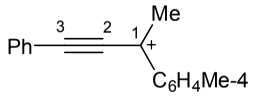
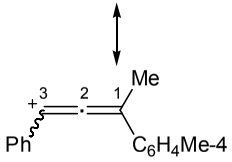
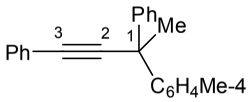
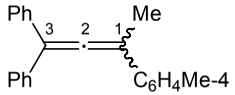
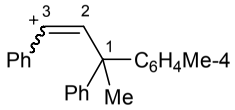
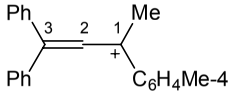
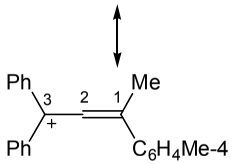
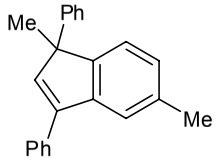
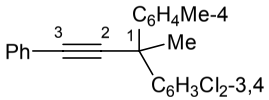
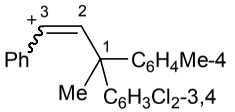
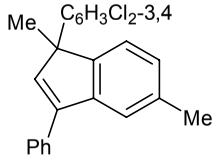
(Contd.)

Run no.	Initial compounds	Intermediates			Products (yield, %), reaction path[a]
		XIII↔XIV	**XV, XVI**	**XVII, XVIII↔XIX**	
7	**Ie** + C_6H_6	 **XIIIg** ↕  **XIVg**	 **XVg**  **XVIg**	 **XVIIg**  **XVIIIg** ↕  **XIXg**	 **XXi** (56), *a* or *b*
8	**If** + C_6H_6	 **XIIIh** ↕  **XIVh**	 **XVh**  **XVIh**	 **XVIIh**  **XVIIIh** ↕  **XIXh**	 **XXj** (94), *a* or *b*

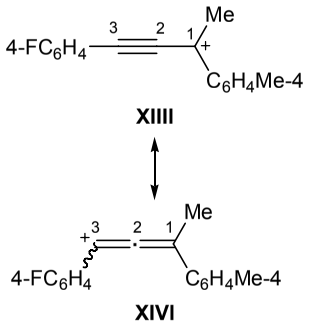
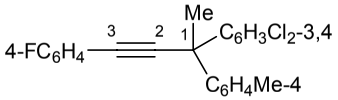
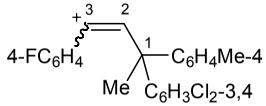
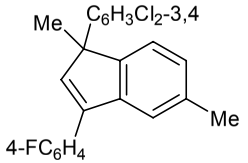
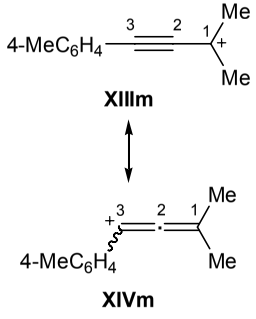
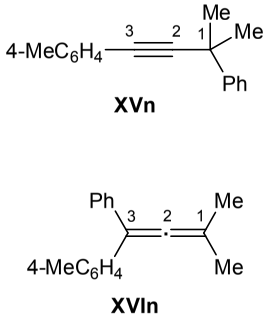
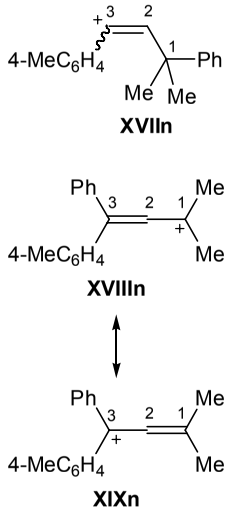
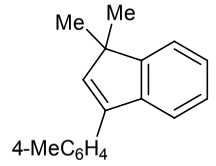
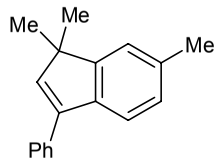
(Contd.)

Run no.	Initial compounds	Intermediates			Products (yield, %), reaction path[a]
		XIII↔XIV	**XV, XVI**	**XVII, XVIII↔XIX**	
9	**Ig** + C_6H_6	 **XIIIi**  **XIVi**	 **XVi**  **XVIi**	 **XVIIi**  **XVIIIi**  **XIXi**	 **XXk** (26), *a* or *b*
10	**Ih** + C_6H_6	 **XIIIj**  **XIVj**	 **XVj**  **XVIj**	 **XVIIj**  **XVIIIj**	 **XXl** (12), *a* or *b*
11	**IIa** + C_6H_6	**XIIIb↔XIVb**	**XVb, XVIb**	**XVIIb, XVIIIb↔XIXb**	**XXb** (53), *a* or *b*

(Contd.)

Run no.	Initial compounds	Intermediates			Products (yield, %), reaction path[a]
		XIII↔XIV	**XV, XVI**	**XVII, XVIII↔XIX**	
12	**IIb** + C_6H_6	 **XIIIk**  **XIVk**	 **XVk**  **XVIk**	 **XVIIk**  **XVIIIk**  **XIXk**	 **XXm** (21), *a* **XXb** (34), aryl group exchange
13	**IIb** +1,2-$Cl_2C_6H_4$	**XIIIk↔XIVk**	 **XVI**	 **XVIII**	 **XXn** (51), *a*
14	**IIc** + C_6H_6	**XIIId↔XIVd**	**XVg, XVIg**	**XVIId, XVIIId↔XIXd**	**XXd** (21), *a* or *b*; **XXe** (46), *b*
15	**IId** + C_6H_6	**XIIIi↔XIVi**	**XVi, XVIi**	**XVIIi, XVIIIi↔XIXi**	**XXk** (65), *a* or *b*

(Contd.)

Run no.	Initial compounds	Intermediates			Products (yield, %), reaction path[a]
		XIII↔XIV	**XV, XVI**	**XVII, XVIII↔XIX**	
16	**IIe** +1,2-$Cl_2C_6H_4$	 **XIIIl** ↔ **XIVl**	 **XVm**	 **XVIIm**	 **XXo** (40), *a*
17	**IIf** + C_6H_6	**XIIIj↔XIVj**	**XVj, XVIj**	**XVIIj, XVIIIj**	**XXl** (50), *a* or *b*
18	**IIg** + C_6H_6	 **XIIIm** ↔ **XIVm**	 **XVn** ↔ **XVIn**	 **XVIIn** ↔ **XIXn**	 **XXp** (7), *a* or *b*  **XXq** (23), *b*

[a] See Scheme 3. Paths *a* and *b* were identified on the basis of the structure of indene **XX**.

dual reactivity of ions **XIII**↔**XIV** were reported in [23, 27]. Some results of quantum-chemical calculations of charge and orbital parameters of resonance-stabilized cations were reviewed in [23].

Although the observed empirical relation does not allow us to estimate the contribution of hybridization of the C^1 (sp^2) and C^3 atoms (sp) to the overall electrophilicity of these reaction centers in the series of cations **XIIIa**↔**XIV** without special theoretical calculations, the above simple rule rationalizes formation of many indene structures **XXa**–**XXq**. For instance, indene **XXq** is formed from alcohol **IIg** according to path *b* only (run no. 18) through allenyl structure **XIVm** in which the electrophilic center is the C^3 atom conjugated with the *p*-tolyl group. Alternative path *a* involves propargyl-type cation **XIIIm** in which the C^1 atom bears two methyl groups that delocalize positive charge less effectively.

The presence of a stronger electron-donating 2,4-dimethylphenyl substituent on the C^3 atom in **XIIIf**↔**XIVf** (as compared to methyl and phenyl groups on C^1) determines formation of indene **XXh** along path *b* through allenyl cation **XIVf** (run no. 6). The formation of indene **XXc** (run no. 3) according to path *b* suggests better stabilization of the cationic center by phenyl group on C^3 in allenyl cation **XIVc** as compared to methyl and 3,4-dichlorophenyl substituents on C^1 in structure **XIIIc**. On the other hand, the formation of indenes **XXm** and **XXn** exclusively along path *a* (run nos. 12, 13) indicated that the reaction involved propargyl-type cation **XIIIk** where the C^1 atom bears methyl and *p*-tolyl groups which better stabilize positive charge than does phenyl substituent on C^3.

In terms of the above approach we can predict formation of indenes **XX** even when their structure does not indicate unambiguously the path of their formation (*a* or *b*; Scheme 3). Thus compound **XXl** (run nos. 10, 17) is most likely to be formed according to path *a* through propargyl-type cation **XIIIj** in which the electrophilic C^1 center is activated by the presence of two phenyl groups, whereas only one phenyl group is attached to C^3. Likewise, it may be presumed that indenes **XXi** and **XXj** are formed along path *b* (run nos. 7, 8) since the corresponding allenyl cations **XIVg** and **XIVh** are stabilized by strong electron-donating 2,4,6-trimethylphenyl and 4-methoxyphenyl substituents, respectively, on C^3.

In some cases it is impossible to identify the path leading to indenes **XX**, for it is difficult to estimate electron-donor effects of similar substituents Ar, Ar′, and R in intermediates **XIII**↔**XIV**. For example, both cations **XIIIa**↔**XIVa** (run no. 1) contain phenyl groups on C^1 and C^3; therefore, indene **XXa** can be formed along paths *a* and *b* with approximately equal probabilities. The same applies to indenes **XXb** and **XXk** which may be formed through intermediate cations **XIIIb**↔**XIVb** and **XIIIi**↔**XIVi**, respectively (run nos. 2, 9, 11, 15), where substituents on the C^1 and C^3 atoms are characterized by comparable electron-donor properties.

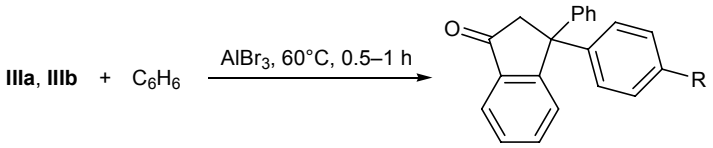
In the final step of path *b*, only allylic cations **XVIII** (Scheme 3, see table) undergo intramolecular cyclization to indenes **XX**. The reactive electrophilic center in **XVIII** is localized on the C^1 atom bearing less electron-donor substituents R and Ar′ than Ar′ and Ar″ on C^3 (cf. cations **XVIIIa**–**XVIIIi**, **XVIIIk**, and **XVIIIn** with the corresponding structures **XIXa**–**XIXi**, **XIXk**, and **XIXn** in table). This is consistent with the previously reported data on the reactivity of allyl-type cations (cyclization into substituted indenes in acid medium through the most stable indanyl cations) [30, 31].

We also observed aryl group exchange in the course of formation of indene **XXb** from ketone **Ic** (run no. 4) or alcohol **IIb** (run no. 12) in benzene (see Experimental). In both cases, the *p*-tolyl fragment was replaced by phenyl group. Heating of a 1:1.4:4.6 mixture of indenes **XXb**, **XXd**, and **XXe** (obtained from ketone **Ic**; run no. 4) in excess benzene at 60°C over a period of 1 h in the presence of 5 equiv of $AlBr_3$ did not result in increased fraction of substitution product **XXb**, and the initial indene mixture was quantitatively recovered. These findings could indicate aryl group exchange at intermediate steps. Apart from aryl group exchange, $AlBr_3$ and $AlCl_3$ promoted demethylation of the methoxy group in the reaction leading to indene **XXj**.

The synthetic potential of the examined reactions is limited to reactions of acetylenic compounds **Ia**–**Ih** and **IIa**–**IIg** with benzene and 1,2-dichlorobenzene (see table). The reactions with other arenes are not selective, and they lead to complex mixture of products. Thus the reaction of acetylenic ketone **Ib** with toluene according to the general procedure gave a mixture of five isomeric indenes with different positions of methyl groups in the indene system and aromatic rings on C^1 and C^3 (according to the ^{1}H NMR and GC–MS data). Analogous reaction of ketone **Ib** with 1,2-dimethylbenzene produced a mixture of more than 10 isomeric indenes (GC–MS data).

Indenes **XXa**–**XXq** were isolated in 12 (run no. 10) to 94% yield (run no. 8). On the average, the yields of

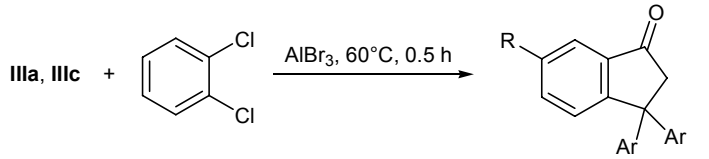
Scheme 4.



XXIIa (30%), **XXIIb** (18%)

R = H (**a**), F (**b**).

Scheme 5.



XXIIc (5%), **XXIId** (6%)

Ar = 3,4-$Cl_2C_6H_3$; R = H (**c**), Me (**d**).

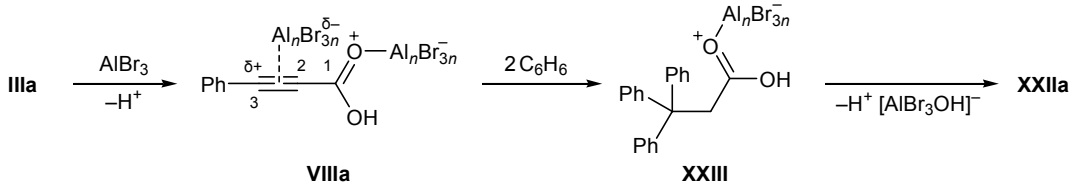
XXa–**XXq** were 30–60% (see table). As a rule, aluminum bromide ensured higher yields than did $AlCl_3$. For example, the yields of indene **XXj** obtained in the presence of $AlCl_3$ and $AlBr_3$ were 50 and 94%, respectively (see Experimental and the data of [18]).

Unlike acetylenic ketones **Ia**–**Ih** and alcohols **IIa**–**IIg**, 3-arylprop-2-ynoic acids **IIIa** and **IIIb** reacted with benzene (Scheme 4) to give 3,3-diarylindan-1-ones **XXIIa** and **XXIIb**, respectively. Analogous ketones **XXIIc** and **XXIId** were obtained by reactions of acids **IIIa** and **IIIc**, respectively, with 1,2-dichlorobenzene (Scheme 5). In all cases, the yields were fairly poor (5–30%).

The most probable mechanism of formation of indanones **XXII** is shown in Scheme 6 with acid **IIIa** as an example. Addition of two benzene molecules at the triple bond of compound **IIIa** involves the C^3 atom as electrophilic center activated by $AlBr_3$ (structure **VIIIa**). The subsequent intramolecular acylation through intermediate **XXIII** yields final product **XXIIa**. An alternative path involving initial acylation of benzene with acid **IIIa** to give 1,3-diphenylprop-2-yn-1-one (**Ih**) cannot be operative, for ketone **Ih** should react with benzene under analogous conditions with formation of indene **XXl** (run. no. 12) which was not detected (Scheme 4; cf. [21]). Indanone **XXIIa** was also formed from acid **IIIa** and benzene in trifluoromethanesulfonic acid [32].

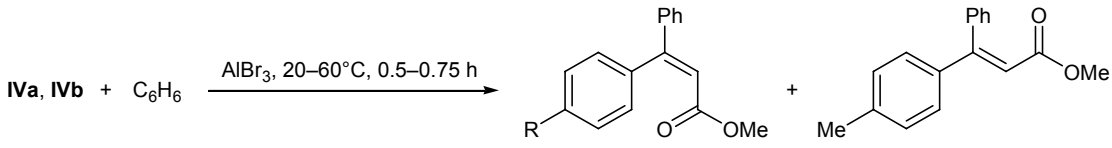
Aluminum bromide does not activate the carbonyl carbon atom (C^1) in methyl 3-arylprop-2-ynoates **IVa** and **IVb**, and the latter react with benzene to give the corresponding alkenylation products **XXIVa** and

Scheme 6.



VIIIa **XXIII**

Scheme 7.



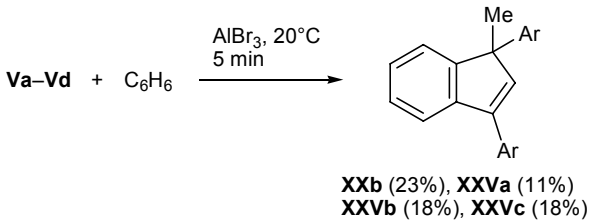
XXIVa (18%), *Z*-**XXIVb** (25%) *E*-**XXIVb** (20%)

R = H (**a**), Me (**b**).

XXIVb (Scheme 7), as in the reactions of esters **IVa** and **IVb** in HSO_3F [33]. Presumably, the positive charge on C^1 in intermediates **VI**↔**VII** or **VIII**↔**IX** (R = OMe, Scheme 1) derived from **IVa** and **IVb** is insufficient due to electron-donating effect of the methoxy group.

Arylacetylenes **Va**–**Vd** reacted with benzene in the presence of $AlBr_3$ to afford indenes **XXb** and **XXVa**–**XXVc** in 11–23% yield (Scheme 8), and the reaction time was as short as 5 min at 20°C. It was found previously that indene **XXb** is formed in 17 and 43% yield in the reaction of phenylacetylene (**Va**) with benzene in the presence of H_3PO_4–BF_3 [34] or CF_3SO_3H [35], respectively. The authors [34, 35] postulated initial formation of 1,1-diphenylethene whose subsequent protonation yields 1,1-diphenylethan-1-yl cation Ph_2C^+Me. Reaction of the latter with initial acetylene **Va**, followed by intramoleclar cyclization of intermediate cationic species, leads to indene **XXb** as final product. Presumably, analogous mechanism is typical of reactions catalyzed by $AlBr_3$ (Scheme 8).

Scheme 8.



XXV, Ar = RC_6H_4; R = 2-F (**a**), 4-F (**b**), 4-Cl (**c**).

Thus the results of our study demonstrated the efficiency of aluminum halides, $AlBr_3$ and $AlCl_3$, in electrophilic activation of various acetylenic compounds. These reactions underlay simple preparative procedures for the synthesis of indene derivatives that attract interest as potential biologically active substances [36], components of catalytic complexes for polymerization of alkenes [37], and materials for other important applications [38, 39].

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded on a Bruker AM-500 spectrometer at 500 and 470 MHz, respectively. The chemical shifts were determined relative to the residual solvent signals ($CHCl_3$, δ 7.25 ppm; acetone-d_5, δ 2.05 ppm) or $CFCl_3$ (δ_F 0.0 ppm). The IR spectra were measured from solutions in chloroform on a Specord 75IR spectrophotometer. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1321 instrument with direct sample admission into the ion source; vaporizer temperature 100–120°C. Gas chromatographic–mass spectrometric analysis was performed on an Agilent Technologies G 2570A GC/MSD instrument (electron impact, 70 eV; separator temperature 250°C, ion source temperature 280°C; Ultra-2 capillary column, 30000 × 0.25 mm, stationary phase 95% of methylsilicone–5% of phenylmethylsilicone, film thickness 0.25 μm; oven temperature programming from 100 to 270°C at a rate of 5 deg/min; carrier gas helium, flow rate 1 ml/min; sample volume 1 μl, 3–5% solution).

3-Phenylprop-2-ynal (**Ia**), phenylethyne (**Va**), 2-fluorophenylethyne (**Vb**), 4-fluorophenylethyne (**Vc**), 4-chlorophenylethyne (**Vd**), and 3-phenylpropynoic acid (**IIIa**) were commercial products (from Sigma–Aldrich). The syntheses and properties of the other acetylenic substrates, 4-(4-methylphenyl)but-3-yn-2-one (**Ic**), 4-phenylbut-3-yn-2-one (**IIb**), 4-(2,4-dimethylphenyl)but-3-yn-2-one (**Id**), 4-(4-methoxyphenyl)but-3-yn-2-one (**If**) [40], 4-(2,4,6-trimethylphenyl)-but-3-yn-2-one (**Ie**) [22]; 1,3-diphenylprop-2-yn-1-one (**Ih**) [41]; 2,4-diphenylbut-3-yn-2-ol (**IIa**), 1,1,3-triphenylprop-2-yn-1-ol (**IIf**), 2-methyl-4-(4-methylphenyl)but-3-yn-2-ol (**IIg**) [17], 3-(4-fluorophenyl)-propynoic acid (**IIIb**), 3-(4-methylphenyl)propynoic acid (**IIIc**) [42], methyl 3-phenylpropynoate (**IVa**), and methyl-3-(4-methylphenyl)propynoate (**IVb**) [43] were reported previously.

4-(4-Fluorophenyl)but-3-yn-2-one (Ig) was synthesized by acylation of lithiated 4-fluorophenylacetylene according to the procedure described in [44]. Yield 20%, oily substance. ^1H NMR spectrum (acetone-d_6), δ, ppm: 2.41 s (3H, Me), 7.27 t (2H, H_{arom}, J = 8.9 Hz), 7.71 d.d (2H, H_{arom}, J = 8.9, 5.3 Hz). Found, %: C 74.09; H 4.40. $C_{10}H_7FO$. Calculated, %: C 74.07; H 4.35.

Acetylenic alcohols **IIb**–**IIe** were synthesized as reported in [45] by reaction of the corresponding lithiated arylacetylenes with substituted acetophenones.

2-(4-Methylphenyl)-4-phenylbut-3-yn-2-ol (IIb). Yield 25%, oily substance [46]. IR spectrum, ν, cm^{-1}: 3600 (OH), 3500–3200 (OH_{assoc}), 2250 (C≡C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.87 s (3H, Me), 2.37 s (3H, Me), 2.56 br.s (1H, OH), 7.20 d (2H, H_{arom}, J = 8.1 Hz), 7.32–7.35 m (3H, H_{arom}), 7.47–7.50 m (2H, H_{arom}), 7.63 d (2H, H_{arom}, J = 8.1 Hz).

4-(4-Methylphenyl)-2-phenylbut-3-yn-2-ol (IIc). Yield 28%, oily substance. IR spectrum, ν, cm^{-1}: 3580 (OH), 3500–3200 (OH_{assoc}), 2230 (C≡C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.86 s (3H, Me), 2.85 s (3H, Me), 2.50 br.s (1H, OH), 7.13 d (2H, H_{arom}, J = 8.0 Hz), 7.29–7.44 m (5H, H_{arom}), 7.73 d (2H, H_{arom}, J = 8.0 Hz). Found, %: C 86.47; H 6.85. $C_{17}H_{16}O$. Calculated, %: C 86.40; H 6.82.

4-(4-Fluorophenyl)-2-phenylbut-3-yn-2-ol (IId). Yield 20%, oily substance. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.86 s (3H, Me), 2.48 br.s (1H, OH), 7.01 t (2H, H_{arom}, J = 8.8 Hz), 7.31 t.t (1H, H_{arom}, J = 7.4, 1.5 Hz), 7.39 t (2H, H_{arom}, J = 7.4 Hz), 7.45 d.d (2H, H_{arom}, J = 8.8, 5.4 Hz), 7.71 d.t (2H, H_{arom}, J = 7.4, 1.5 Hz). Found, %: C 79.94; H 5.52. $C_{16}H_{13}FO$. Calculated, %: C 79.98; H 5.45.

4-(4-Fluorophenyl)-2-(4-methylphenyl)but-3-yn-2-ol (IIe). Yield 23%, oily substance. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.84 s (3H, Me), 2.36 s (3H, Me), 2.42 br.s (1H, OH), 7.01 t (2H, H_{arom}, J = 8.7 Hz), 7.19 d (2H, H_{arom}, J = 8.2 Hz), 7.45 d.d (2H, H_{arom}, J = 8.7, 5.4 Hz), 7.59 d (2H, H_{arom}, J = 8.2 Hz). Found, %: C 80.19; H 5.88. $C_{17}H_{15}FO$. Calculated, %: C 80.29; H 5.95.

1,3,3,3-Tetraphenylpropyne (XXI) was synthesized according to the procedure reported in [47] from phenylethynylmagnesium bromide and chloro(triphenyl)methane. Yield 10%, mp 137–139°C; published data [47]: mp 138–141°C. IR spectrum: ν 2300 cm^{-1}, w (C≡C). ^1H NMR spectrum ($CDCl_3$): δ 7.24–7.51 ppm, m (20H, H_{arom}).

Substituted indenes XXa–XXq, XXVa–XXVc, indanones XXIIa–XXIId, and methyl 3,3-diarylprop-2-enoates XXIVa and XXIVb (*general procedure*). Acetylenic compound **Ia–Ih**, **IIa–IIg**, **IIIa–IIIc**, **IVa**, **IVb**, or **Va–Vd**, 0.17–1.5 mmol, was added under vigorous stirring to a solution of 0.85–7.5 mmol of aluminum halide ($AlBr_3$ or $AlCl_3$) in 0.7–10 ml of benzene or 1,2-dichlorobenzene, maintained at 20–70°C. The mixture was stirred for 5–90 min, poured into 30–50 ml of water, and extracted with chloroform (3×30 ml). The extracts were combined, washed with a saturated solution of sodium hydrogen carbonate and water, and dried over sodium sulfate, the solvent was distilled off under reduced pressure, and the residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate as eluent. The yields of final products **XXa–XXq**, **XXVa–XXVc**, **XXIIa–XXIId**, **XXIVa**, and **XXIVb** were determined by weighing the corresponding fractions isolated by chromatography. The synthesis and properties of indenes **XXa–XXf**, **XXi**, **XXk**, **XXl**, **XXn**, **XXo**, and **XXq** were reported in [16–18].

1-Methyl-1,3-diphenylindene (XXb). *a*. The synthesis of **XXb** from compounds **Ib** and **IIa** was reported in [16, 17].

b. Compound **XXb** was obtained from 61 mg (0.6 mmol) of phenylacetylene (**Va**) in a solution of 0.8 g (3 mmol) of aluminum bromide in 2 ml (22.4 mmol) of benzene at 20°C (reaction time 5 min). Yield 39 mg (23%).

3-(2,4-Dimethylphenyl)-1-methyl-1-phenylindene (XXg) and 1,4,6-trimethyl-1,3-diphenylindene (XXh) were obtained as an oily isomer mixture from 31 mg (0.18 mmol) of compound **Id** in a solution of 0.29 g (1.1 mmol) of $AlBr_3$ in 0.8 ml (9.1 mmol) of benzene at 60°C (reaction time 0.5 h).

Compound **XXg**. Yield 5 mg (10%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.81 s (3H, Me), 2.27 s (3H, Me), 2.38 s (3H, Me), 6.39 s (1H, 2-H), 7.07 br.d (1H, H_{arom}, J = 7 Hz), 7.13 br.s (1H, H_{arom}), 7.15–7.42 m (10H, H_{arom}). Mass spectrum (GC–MS), m/z (I_{rel}, %): 310 (100) $[M]^+$, 295 (60), 279 (12), 265 (10), 203 (11), 202 (17).

Compound **XXh**. Yield 32 mg (57%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.77 s (3H, Me), 1.98 s (3H, Me), 2.28 s (3H, Me), 6.28 s (1H, 2-H), 6.80 s (1H, H_{arom}), 6.88 s (1H, H_{arom}), 7.15–7.42 m (10H, H_{arom}). Mass spectrum (GC–MS), m/z (I_{rel}, %): 310 (100) $[M]^+$, 295 (61), 279 (12), 265 (10), 203 (10), 202 (16). Found (for isomer mixture), %: C 92.96; H 7.21. $C_{24}H_{22}$. Calculated, %: C 92.86; H 7.14. M 310.17.

4-(1-Methyl-1-phenylinden-3-yl)phenol (XXj). *a*. The reaction of 50 mg (0.29 mmol) of compound **If** with a solution of 0.38 g (1.45 mmol) of $AlBr_3$ in 5 ml (58 mmol) of benzene at 60°C (reaction time 0.5 h) gave 80 mg (94%) of **XXj**.

b. Compound **XXj** was obtained from 30 mg (0.17 mmol) of **If** in a solution of 0.37 g (2.55 mmol) of $AlCl_3$ in 1 ml (11.2 mmol) of benzene at 70°C (reaction time 1 h). Yield 26 mg (50%), oily substance. IR spectrum, ν, cm^{-1}: 3600 (OH), 3500–3200 (OH_{assoc}), 1605 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.79 s (3H, Me), 5.20 br.s (1H, OH), 6.51 s (1H, 2-H), 6.91 d (2H, H_{arom}, J = 8.6 Hz), 7.17–7.33 m (8H, H_{arom}), 7.53 d (3H, H_{arom}, J = 8.6 Hz). Mass spectrum, m/z (I_{rel}, %): 298 (100) $[M]^+$, 283 (73), 221 (10), 77 (8). Found, %: C 88.62; H 6.11. $C_{22}H_{18}O$. Calculated, %: C 88.56; H 6.08. M 298.14.

1,1,3-Triphenylindene (XXl). *a*. The synthesis of **XXl** from compounds **Ih** and **IIf** was reported in [16, 17].

b. Compound **XXl** was obtained from 30 mg (0.09 mmol) of 1,3,3,3-tetraphenylpropyne (**XXI**) in a solution of 0.12 g (0.45 mmol) of $AlBr_3$ in 4 ml of methylene chloride at 20°C (reaction time 1 h), following the general procedure for the synthesis of substituted indenes. Yield 14 mg (47%).

1,5-Dimethyl-1,3-diphenylindene (XXm) was obtained from 64 mg (0.27 mmol) of compound **IIb** in a solution of 0.36 g (1.35 mmol) of $AlBr_3$ in 1 ml (11.2 mmol) of benzene at 60°C (reaction time 0.5 h). The product was isolated as a mixture with compound **XXb** [yield 26 mg (34%)].

Compound **XXm**. Yield 17 mg (21%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.79 s (3H, Me), 2.39 s (3H, Me), 6.57 s (1H, 2-H), 7.04–7.40 m (9H, H_{arom}), 7.44–7.48 m (2H, H_{arom}), 7.62–7.65 m (2H, H_{arom}). Mass spectrum (GC–MS), *m*/*z* (I_{rel}, %): 296 (100) $[M]^+$, 281 (73), 265 (20), 202 (15). Calculated: *M* 296.16.

1-(3,4-Dichlorophenyl)-3-(4-fluorophenyl)-1,5-dimethylindene (XXo) was obtained from 60 mg (0.24 mmol) of compound **IIe** in a solution of 0.32 g (1.2 mmol) of $AlBr_3$ in 1 ml (9.6 mmol) of 1,2-dichlorobenzene at 70°C (reaction time 10 min). Yield 36 mg (40%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.74 s (3H, Me), 2.39 s (3H, Me), 6.43 s (1H, 2-H), 7.06 br.d (1H, H_{arom}, *J* = 7.5 Hz), 7.07 d.d (1H, H_{arom}, *J* = 8.4, 2.2 Hz), 7.11 d (1H, H_{arom}, *J* = 7.5 Hz), 7.15 t (2H, H_{arom}, *J* = 8.8 Hz), 7.28 d (1H, H_{arom}, *J* = 8.4 Hz), 7.29 br.s (1H, H_{arom}), 7.37 d (1H, H_{arom}, *J* = 2.2 Hz), 7.57 d.d (2H, H_{arom}, *J* = 8.8, 5.4 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –110.58 ppm, m. Mass spectrum, *m*/*z* (I_{rel}, %): 382 (100) $[M]^+$, 367 (50), 297 (14), 237 (7), 220 (11), 147 (14). Found, %: C 71.96; H 4.51. $C_{23}H_{17}Cl_2F$. Calculated, %: C 72.07; H 4.47. *M* 382.07.

3,3-Diphenylindan-1-one (XXIIa) was obtained from 188 mg (1.29 mmol) of compound **IIIa** in a solution of 1.72 g (6.44 mmol) of $AlBr_3$ in 5 ml (56 mmol) of benzene at 60°C (reaction time 1 h). Yield 108 mg (30%), mp 127–128°C; published data [48]: mp 128–130°C. IR spectrum: ν 1700 cm^{-1} (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.48 s (2H, CH_2), 7.15–7.30 m (10H, H_{arom}), 7.36 d (1H, H_{arom}, *J* = 7.9 Hz), 7.42 t (1H, H_{arom}, *J* = 7.4 Hz), 7.59 t (1H, H_{arom}, *J* = 7.5 Hz), 7.79 d (1H, H_{arom}, *J* = 7.7 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 284 (92) $[M]^+$, 207 (95), 178 (94), 167 (32), 152 (28), 105 (100), 77 (90), 51 (45).

3-(4-Fluorophenyl)-3-phenylindan-1-one (XXIIb) was obtained from 100 mg (0.61 mmol) of compound **IIIb** in a solution of 0.81 g (3 mmol) of $AlBr_3$ in 2 ml (22.5 mmol) of benzene at 60°C (reaction time 0.5 h). Yield 33 mg (18%), mp 123–125°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.49 s (2H, CH_2), 7.17 d (3H, H_{arom}, *J* = 7.7 Hz), 7.20–7.30 m (6H, H_{arom}), 7.37 d (1H, H_{arom}, *J* = 7.6 Hz), 7.42 t (1H, H_{arom}, *J* = 7.6 Hz), 7.59 t (1H, H_{arom}, *J* = 7.6 Hz), 7.81 d (1H, H_{arom}, *J* = 7.6 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –112.79 ppm, m. Mass spectrum, *m*/*z* (I_{rel}, %): 302 (100) $[M]^+$, 167 (32), 105 (94), 77 (90), 51 (35). Found, %: C 83.35; H 5.04. $C_{21}H_{15}FO$. Calculated, %: C 83.42; H 5.00. *M* 302.11.

3,3-Bis(3,4-dichlorophenyl)indan-1-one (XXIIc) was obtained from 300 mg (2 mmol) of compound **IIIa** in a solution of 2.7 g (10 mmol) of $AlBr_3$ in 3 ml (27 mmol) of 1,2-dichlorobenzene at 60°C (reaction time 0.5 h). Yield 43 mg (5%), mp 128–130°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.39 s (2H, CH_2), 6.97 d.d (2H, H_{arom}, *J* = 8.5, 2.0 Hz), 7.20 d (2H, H_{arom}, *J* = 2.0 Hz), 7.31 d (1H, H_{arom}, *J* = 7.6 Hz), 7.37 d (2H, H_{arom}, *J* = 8.5 Hz), 7.49 t (1H, H_{arom}, *J* = 7.6 Hz), 7.66 t (1H, H_{arom}, *J* = 7.6 Hz), 7.83 d (1H, H_{arom}, *J* = 7.6 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 420 (48) $[M]^+$, 385 (24), 361 (8), 322 (10), 275 (100), 212 (50), 176 (48), 143 (47), 125 (29). Found, %: C 59.82; H 2.67. $C_{21}H_{12}Cl_4O$. Calculated, %: C 59.75; H 2.87. *M* 419.96.

3,3-Bis(3,4-dichlorophenyl)-6-methylindan-1-one (XXIId) was obtained from 155 mg (0.97 mmol) of compound **IIIc** in a solution of 1.29 g (4.84 mmol) of $AlBr_3$ in 2 ml (11 mmol) of 1,2-dichlorobenzene at 60°C (reaction time 0.5 h). Yield 25 mg (6%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (3H, Me), 3.36 s (2H, CH_2), 6.97 d.d (2H, H_{arom}, *J* = 8.5, 2.3 Hz), 7.19 d (1H, H_{arom}, *J* = 8.0 Hz), 7.20 d (2H, H_{arom}, *J* = 2.3 Hz), 7.37 d (2H, H_{arom}, *J* = 8.5 Hz), 7.47 d.d (1H, H_{arom}, *J* = 8.0, 1.5 Hz), 7.61 br.s (1H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 434 (50) $[M]^+$, 419 (4), 399 (25), 289 (100), 226 (18), 189 (25). Found, %: C 60.71; H 3.20. $C_{22}H_{14}Cl_4O$. Calculated, %: C 60.58; H 3.24. *M* 433.98.

Methyl 3,3-diphenylprop-2-enoate (XXIVa) was obtained from 50 mg (0.31 mmol) of compound **IVa** in a solution of 0.415 g (1.55 mmol) of $AlBr_3$ in 1 ml (11.2 mmol) of benzene at 60°C (reaction time 0.5 h). Yield 14 mg (18%), oily substance; its properties were reported in [33].

Methyl (*E*)-3-(4-methylphenyl)-3-phenylprop-2-enoate (*E*-XXIVb) and methyl (*Z*)-3-(4-methylphen-

yl)-3-phenylprop-2-enoate (*Z*-XXIVb) (mixture of isomers**)** were obtained from 47 mg (0.27 mmol) of compound **IVa** in a solution of 0.36 g (1.35 mmol) of $AlBr_3$ in 0.8 ml (9.1 mmol) of benzene at 20°C (reaction time 0.75 h). Oily substance. Yield 14 mg (20%) (*E* isomer), 17 mg (25%) (*Z* isomer). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E* isomer: 2.40 s (3H, Me), 3.63 s (3H, OMe), 6.33 s (1H, 2-H), 7.10–7.40 m (9H, H_{arom}); *Z* isomer: 2.36 s (3H, Me), 3.60 s (3H, OMe), 6.36 s (1H, 2-H), 7.10–7.40 m (9H, H_{arom}). Mass spectrum (isomer mixture), *m*/*z* (I_{rel}, %): 252 (95) $[M]^+$, 237 (5), 221 (100), 193 (33), 178 (52), 165 (18), 119 (23), 115 (34). Found (for isomer mixture), %: C 80.95; H 6.43. $C_{17}H_{16}O_2$. Calculated, %: C 80.93; H 6.39. *M* 252.12.

1,3-Bis(2-fluorophenyl)-1-methylindene (XXVa) was obtained from 69 mg (0.58 mmol) of 2-fluorophenylacetylene (**Vb**) in a solution of 0.77 g (2.9 mmol) of $AlBr_3$ in 2 ml (22.5 mmol) of benzene at 20°C (reaction time 5 min). Yield 10 mg (11%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.82 d (3H, Me, *J* = 1.4 Hz), 6.81 t (1H, 2-H, *J* = 1.4 Hz), 7.00 d (1H, H_{arom}, *J* = 7.7 Hz), 7.01–7.04 m (1H, H_{arom}), 7.14–7.17 m (1H, H_{arom}), 7.20 t.d (2H, H_{arom}, *J* = 7.4, 1.1 Hz), 7.27–7.31 m (2H, H_{arom}), 7.31–7.34 m (1H, H_{arom}), 7.34–7.37 m (2H, H_{arom}), 7.45 d.d (1H, H_{arom}, *J* = 7.0, 1.6 Hz), 7.52 t.d (1H, H_{arom}, *J* = 7.4, 1.8 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –109.57 m (1F), –107.12 m (1F). Mass spectrum, *m*/*z* (I_{rel}, %): 318 (100) $[M]^+$, 303 (56), 283 (13), 209 (23). Found, %: C 83.12; H 5.00. $C_{22}H_{16}F_2$. Calculated, %: C 83.00; H 5.07. *M* 318.12.

1,3-Bis(4-fluorophenyl)-1-methylindene (XXVb) was synthesized from 60 mg (0.5 mmol) of 4-fluorophenylacetylene (**Vc**) in a solution of 0.67 g (2.5 mmol) of $AlBr_3$ in 1.2 ml (13.5 mmol) of benzene at 20°C (reaction time 5 min). Yield 15 mg (18%), oily substance. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.78 s (3H, Me), 6.68 s (1H, 2-H), 7.02 t (2H, H_{arom}, *J* = 8.9 Hz), 7.23–7.28 m (3H, H_{arom}), 7.31–7.34 m (2H, H_{arom}), 7.38 d.d (2H, H_{arom}, *J* = 8.9, 5.4 Hz), 7.53 d (1H, H_{arom}, *J* = 7.5 Hz), 7.72 d.d (2H, H_{arom}, *J* = 8.9, 5.4 Hz). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: –116.59 m (1F), –113.84 m (1F). Mass spectrum, *m*/*z* (I_{rel}, %): 318 (100) $[M]^+$, 303 (82), 301 (17), 220 (11). Found, %: C 82.99; H 5.11. $C_{22}H_{16}F_2$. Calculated, %: C 83.00; H 5.07. *M* 318.12.

1,3-Bis(4-chlorophenyl)-1-methylindene (XXVc) was obtained from 62 mg (0.46 mmol) of 4-chlorophenylacetylene (**Vd**) in a solution of 0.61 g (2.3 mmol) of $AlBr_3$ in 1.4 ml (15.8 mmol) of benzene at 20°C (reaction time 5 min). Yield 14 mg (18%), oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.77 s (3H, Me), 6.51 s (1H, 2-H), 7.20 s (4H, H_{arom}), 7.21–7.24 m (2H, H_{arom}), 7.28–7.32 m (1H, H_{arom}), 7.42 d (2H, H_{arom}, *J* = 8.5 Hz), 7.48 d (1H, H_{arom}, *J* = 7.6 Hz), 7.55 d (2H, H_{arom}, *J* = 8.5 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 350 (100) $[M]^+$, 335 (71), 315 (11), 299 (18), 265 (26), 202 (22), 131 (29). Found, %: C 75.10; H 4.67. $C_{22}H_{16}Cl_2$. Calculated, %: C 75.22; H 4.59. *M* 350.06.

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