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Protonation and Cyclization of 1,3-Diarylpropynones in Superacids

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Abstract—1,3-Diarylpropynones ArC≡CCOAr' in superacids with H_0 ranging from –20 to –14 undergo protonation at the carbonyl oxygen atoms to give stable ArC≡CC(O$^+$H)Ar' ions or at the acetylenic C^2 atom with formation of reactive ArC$^+$=CHCOAr' species. The effects of the Ar and Ar' substituents and reaction conditions on the intramolecular cyclization of ArC$^+$=CHCOAr' to 3-arylinden-1-ones are discussed.

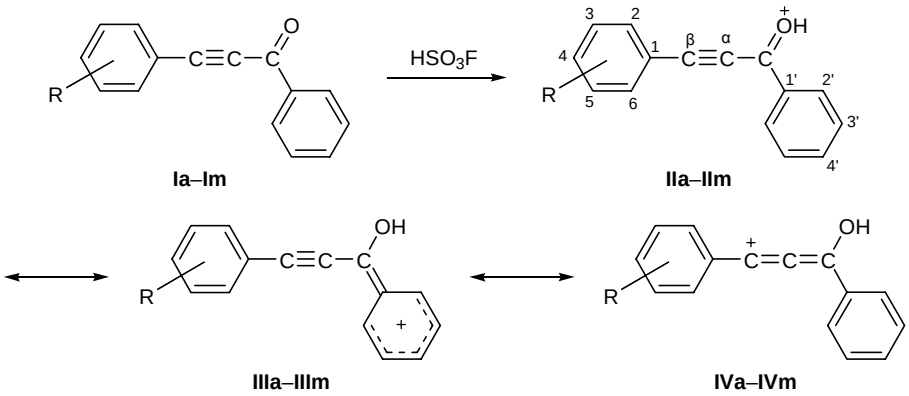
Superacids [1] are widely used as reaction medium for generation and study of various carbocations [2, 3], radical cations [4], and other long-lived charged intermediates [1]. Despite numerous publications on this topic [5], information on the behavior of acetylene derivatives in superacids is scanty. Stang [6] and Olah [7] showed that trifluoromethanesulfonic acid and fluorosulfonic acid add to alkynes with formation of the corresponding vinyl trifluoromethanesulfonates and fluorosulfonates. According to the NMR data, some substituted acetylenes in HSO_3F undergo transformation into cyclobutenyl cations with subsequent oligomerization of the latter [7, 8]. These reactions were postulated to involve generation of reactive vinyl-like cations via protonation of carbon atom at the triple bond. In 1992, Siehl *et al*. [9] were the first to detect arylvinyl cations as kinetically independent species in the system HSO_3F–SbF_5 and characterize them by ^{1}H and ^{13}C NMR spectra. Analysis of the available experimental data shows that the chemistry of acetylenic compounds in superacids still remains an unexplored area of organic chemistry.

The goal of the present work was to examine protonation of 1,3-diarylpropynones in superacids by ^{1}H and ^{13}C NMR spectroscopy, as well as to isolate and identify products of their transformations. Scheme 1 illustrates the formation of O-protonated species **IIa**–**IIm** from acetylenic ketones **Ia**–**Im** in HSO_3F. The ^{1}H NMR spectra of **IIa**–**IIm** in HSO_3F at –80°C are given in Table 1, and Table 2 contains the ^{13}C NMR spectra of cations **IIa**, **IIg**, **IIi**, **IIj**, and **IIm** (HSO_3F, –80 and 0°C) and their neutral precursors. The signals in the ^{13}C NMR spectra were unambiguously assigned on the basis of the proton-coupled spectra and using HSQC, HMQC, and HMBC two-dimensional heteronuclear correlation techniques [10]. The spectral data given in Table 2 were obtained from the proton-decoupled spectra.

The ^{1}H NMR spectra of protonated species **IIa**–**IIm** in HSO_3F at –80°C displayed a sharp singlet in the region δ 12–13.5 ppm, which corresponds to proton attached to the carbonyl oxygen atom. According to the signal intensities, alkynones **Ia**–**Im** in HSO_3F are protonated completely (Table 1). At 0°C, the above signal disappears due to fast exchange with the acidic medium. Diynediones **Il** and **Im** in HSO_3F undergo protonation at both carbonyl groups to give the corresponding dications **IIl** and **IIm** (Scheme 1, Table 1).

In the ^{1}H NMR spectra of compounds **Ia**–**Im** in HSO_3F we observed no signals assignable to protons attached to electron-acceptor groups R (NO_2, CN, COMe, CO_2Me). The NO_2 and CN groups in organic compounds are solvated by HSO_3F [4], and their protonation occurs in systems with higher acidity, e.g., in HSO_3F–SbF_5 [2, vol. 4, p. 1773]. As follows from the ^{13}C NMR spectrum of cation **IIj**, the acetyl group therein is protonated. The chemical shift of the carbonyl carbon atom in the acetyl group is δ_C 222.79 ppm at –80°C (Table 2), i.e., it falls into the δ_C range 210–223 ppm typical of protonated substituted acetophenones in HSO_3F and HSO_3F–SbF_5 [11]. The same applies to the substituent R = CO_2Me in **IIk**. The

Scheme 1.



Ia–**Im**, **IIa**–**IIi**, **IIIa**–**IIIi**, **IVa**–**IVi**, R = H (**a**), 4-Me (**b**), 2,4,6-Me_3 (**c**), 3-NO_2 (**d**), 4-NO_2 (**e**), 4-CN (**f**), 4-MeO-3-NO_2 (**g**), 2,4,6-Me_3-3-NO_2 (**h**), 2,3,5,6-Me_4-4-NO_2 (**i**), 4-COMe (**j**), 4-CO_2Me (**k**), 4-$PhCOC_2$ (**l**), 2,3,5,6-Me_4-4-$PhCOC_2$ (**m**); **IIj**–**IIm**, **IIIj**–**IIIm**, **IVj**–**IVm**, R = 4-$C(OH^+)$Me (**j**), 4-$C(O)(OH^+)$Me (**k**), 4-$PhC(OH^+)C{\equiv}C$ (**l**), 2,3,5,6-Me_4-4-$PhC(OH^+)C{\equiv}C$ (**m**).

different behaviors of the groups R in HSO_3F (NO_2 and CN in **IId–IIi** and COMe and CO_2Me in **IIj** and **IIk**) are reflected in Scheme 1.

Insofar as fluorosulfonic acid at –80°C is fairly viscous, signals from aromatic protons in the ^{1}H NMR spectra of ions **IIa**–**IIm** appear mostly as broadened singlets without fine structure (Table 1). At 0°C, we observed well resolved multiplets typical of aromatic systems.

The results of our NMR studies allowed us to draw some conclusions concerning the structure and positive charge delocalization in the examined species. The ^{1}H NMR spectra of **IIa**–**IIm**, recorded at –80°C, indicated that the *ortho*- (2'-H) and *meta*-protons (3'-H) in the

Table 1. ^{1}H NMR spectra of protonated species **IIa**–**IIm** in HSO_3F at –80°C

Ion no.	Chemical shifts δ, ppm (*J*, Hz)		
	$C{=}OH^+$	H_{arom}	R
IIa	12.75 s (1H)	7.58 s (2H), 7.78 s (3H), 7.98 s (2H), 8.16 s (1H), 8.51 s (2H)	–
IIb	12.30 s (1H)	7.44 s (2H), 7.77 s (1H), 7.80 s (1H), 7.92 s (2H), 8.28 s (1H)	2.47 s (3H, Me)
IIc	12.07 s (1H)	7.00 s (2H), 7.79 s (2H), 8.13 s (1H), 8.35 s (1H), 8.45 s (1H), 8.50 s (1H), 8.53 s (1H)	2.28 s (3H, Me), 2.62 s (6H, 2Me)
IId	13.15 s (1H)	7.89 s (1H), 7.97 s (1H), 8.07 s (1H), 8.34 s (1H), 8.58 s (1H), 8.69 s (1H), 8.82 s (1H), 8.88 s (1H), 9.13 s (1H)	–
IIe	13.24 s (1H)	7.89 s (1H), 7.96 s (1H), 8.35 s (3H), 8.65 s (3H), 8.84 s (1H)	–
IIf	13.26 s (1H)	7.89 t (1H, *J* = 6.5), 7.95 t (1H, *J* = 6.5), 8.34 d (2H, *J* = 6.2), 8.35 t (1H, *J* = 6.5), 8.41 d (2H, *J* = 6.2), 8.69 d (1H, *J* = 6.5), 8.84 d (1H, *J* = 6.5)	–
IIg	12.87 s (1H)	7.67 d (1H, *J* = 8.7), 7.64 t (1H, *J* = 7.0), 7.81 t (1H, *J* = 7.0), 8.19 t (1H, *J* = 7.0), 8.53 d (1H, *J* = 7.0), 8.56 d (1H, *J* = 8.7), 8.68 d (1H, *J* = 7.0), 9.17 s (1H)	4.43 s (3H, MeO)
IIh	12.86 s (1H)	7.54 s (1H), 7.87 s (1H), 7.93 s (1H), 8.28 s (1H), 8.67 s (2H)	2.61 s (3H, Me), 2.85 s (6H, 2Me)
IIi	13.36 s (1H)	7.83 s (1H), 7.90 s (1H), 8.23 s (1H), 8.63 s (1H), 8.67 s (1H)	2,26 s (6H, 2Me), 2.74 s (6H, 2Me)
IIj	13.50 s (1H)	7.90 s (1H), 7.96 s (1H), 8.37 s (3H), 8.72 s (3H), 8.87 s (1H)	3.51 s (3H, Me)
IIk	13.19 s (1H)	7.88 s (1H), 7.94 s (1H), 8.35 s (3H), 8.39 s (2H), 8.68 s (1H), 8.83 s (1H)	4.73 s (3H, Me)
III[a]	13.47 s (2H)	7.90 s (4H), 8.33 s (6H), 8.69 s (2H), 8.85 s (2H)	–
IIm[a]	12.84 s (2H)	7.87 s (2H), 7.92 s (2H), 8.28 s (2H), 8.67 s (2H), 8.71 s (2H)	2.77 s (12H, 4Me)

[a] Dication.

Table 2. ^{13}C NMR spectra of 1,3-diarylpropynones **Ia**, **Ig**, **Ii**, **Ij**, and **Im** ($CDCl_3$, 25°C) and their protonated forms **IIa**, **IIg**, **IIi**, **IIj**, and **IIm** in HSO_3F

Comp. no.	Solvent	Temperature, °C	Chemical shifts δ_C, ppm[a]											
			C=O[b]	C^{α}	C^{β}	$C^{1'}$	$C^{2'}$ [c]	$C^{3'}$	$C^{4'}$	C^{1}	C^{2}, C^{6}	C^{3}, C^{5}	C^{4}	R
Ia	$CDCl_3$	25	177.92	86.87	93.03	136.89	129.52	128.57	134.04	120.11	133.00	128.64	130.73	–
IIa	HSO_3F	–80	181.87	87.93	116.45	129.68	132.18, 139.84	131.08	145.07	129.90	137.1	130.21	137.85	–
		0	183.18	88.59	117.06	130.74	~136.5	131.47	145.34	131.16	137.38	130.54	138.12	–
Ig	$CDCl_3$	25	177.53	87.32	90.01	136.55	129.53	128.73	134.38	112.31	130.27, 138.72	139.53, 114.00	154.53	56.87
IIg	HSO_3F	–80	183.38	86.73	119.56	130.19	133.16, 141.44	131.45	146.84	112.48	138.31, 151.18	131.57, 118.28	165.16	61.12
		0	183.82	86.67	122.14	130.70	~136.0	131.72	146.68	111.53	137.56, 146.68	134.37, 118.05	164.14	60.20
Ii	$CDCl_3$	25	177.67	89.69	95.52	136.87	129.50	128.74	134.24	122.31	140.03	124.85	153.69	14.51, 18.52
IIi	HSO_3F	–80	183.08	93.96	120.79	130.58	132.83, 140.04	131.32	145.58	123.15	146.22	127.33	154.92	14.14, 18.76
		0	183.99	94.68	121.43	131.21	~137.0	131.84	146.41	124.81	146.53	127.99	156.02	14.24, 18.93
Ij	$CDCl_3$	25	177.67	88.72	91.12	136.60	129.60	128.71	134.40	124.68	133.06	128.37	138.08	197.0 (C=O), 26.69 (CH_3)
IIj	HSO_3F	–80	184.35	87.71	118.11	130.16	133.71, 142.30	131.66	147.81	130.30	136.60[d]		133.06	222.79 ($C=OH^+$), 26.39 (CH_3)
		0	185.06	88.22	118.54	130.81	~136.0	132.14	148.49	130.92	136.63	135.37	133.49	232.36 ($C=OH^+$), 26.47 (CH_3)
Im	$CDCl_3$	25	177.84	91.23	96.03	137.03	129.53	128.70	134.12	122.74	138.07	–	–	18.58
IIm	HSO_3F	–80	183.13	95.18	123.59	130.66	133.12, 140.42	131.49	146.13	124.50	143.78	–	–	18.75
		0	183.90	95.64	124.56	131.33	~136.0	131.86	146.51	125.01	143.96	–	–	18.71

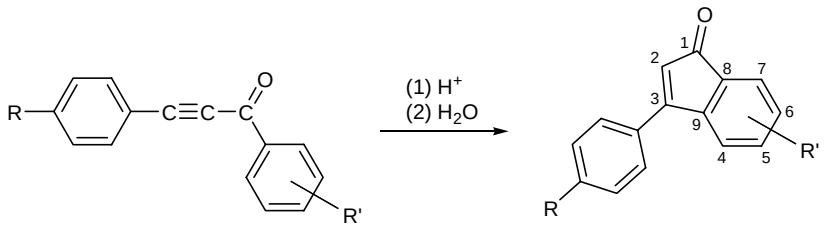
[a] For atom numbering, see Scheme 1.
[b] $C=OH^+$ in HSO_3F.
[c] Two $C^{2'}$ signals were observed in HSO_3F at –80°C (for details, see text).
[d] Merged signals..

phenyl ring neighboring to the carbonyl group are nonequivalent. For example, in the spectrum of **IIf** we observed two triplets at δ 7.89 and 7.95 ppm, belonging to the *meta*-protons (3'-H), and two doublets at δ 8.69 and 8.84 ppm, which correspond to the *ortho*-protons (2'-H) (Table 1). These data suggest that O-protonated species are contributed by structures **IIIa**–**IIIm** where rotation about the $C^{1'}$–C(O) bond is restricted at –80°C. No difference in the chemical shifts of the *meta*- and *ortho*-protons was found at 0°C: the spectrum contained a doublet at δ 8.74 ppm (2'-H) and a triplet at δ 7.91 ppm (3'-H). Analogous patterns were typical of the other cations.

Nonequivalence of the $C^{2'}$ nuclei in **IIIa**–**IIIm** was also revealed by ^{13}C NMR spectroscopy. The spectra of **IIa**, **IIg**, **IIi**, **IIj**, and **IIm** at –80°C contained two different signals from the *ortho*-carbon atoms, at δ 132–134 and 140–142 ppm. At 0°C, one broadened signal at δ 136–137 ppm was observed (Table 2). An analogous pattern was observed previously for acetophenone derivatives in superacids [11].

Comparison of the ^{13}C NMR parameters (Table 2) of the initial ketones ($CDCl_3$, 25°C) and their protonated forms (HSO_3F, –80 and 0°C) shows that both the phenyl ring conjugated with the carbonyl group and the arylacetylene moiety participate in delocaliza-

Scheme 2.



Ia, **Ib**, **In–Iq** **Va**, **Vb**, **Vn–Vq**

I, R = MeO, R' = H (**n**), 3-MeO (**o**), 3,4-Me_2 (**p**); R = H, R' = 3-MeO (**q**); **V**, R = H, R' = H (**a**); R = Me, R' = H (**b**); R = MeO, R' = H (**n**), 6-MeO (**o**), 5,6-Me_2 (**p**); R = H, R' = 6-MeO (**q**).

tion of the positive charge on the carbonyl oxygen atom in **IIa**, **IIg**, **IIi**, **IIj**, and **IIm**. The signal of the C^{β} atom (Scheme 1) in the protonated species is located ~23–32 ppm downfield relative to the corresponding signal in the spectra of the neutral precursors. This suggests that resonance structures like **IVa**–**IVm** (Scheme 1) also contribute to delocalization of the positive charge.

Considerable differences in the chemical shifts of $C^{2'}$, $C^{3'}$, and $C^{4'}$ between neutral ketones **I** and the corresponding protonated species indicate a considerable contribution of the phenyl ring conjugated with the carbonyl group to delocalization of the positive charge (structures **IIIa**–**IIIm** in Scheme 1). In going from ketones **Ia**, **Ig**, **Ii**, **Ij**, and **Im** to cations **IIa**, **IIg**, **IIi**, **IIj**, and **IIm** (HSO_3F), the signal from $C^{4'}$ shifts downfield by ~11–14 ppm. The chemical shifts of the two nonequivalent $C^{2'}$ nuclei in the cations (–80°C) are greater than that of $C^{2'}$ in the intitial ketone by 2.5–4 and 10–13 ppm, respectively (Table 2).

Ketones **I** in which the substituent R is a hydrogen atom (**Ia**), alkyl group (**Ib**, **Ic**), or electron-acceptor group (**Id**–**Im**) exist in HSO_3F as stable O-protonated species **IIa**–**IIm**, while methoxy derivatives (R = *p*-MeO) are rapidly converted into secondary ionic products even at –80°C. Substrates containing a *para*-methoxy group undergo protonation at the acetylenic C^{α} atom to give reactive vinyl cations which cannot be detected by NMR spectroscopy.

In order to elucidate transformation pathways of 1,3-diarylpropynones in superacids, some experiments were carried out on a preparative scale. We found that ketones **Ia**, **Ib**, and **In**–**Iq** are converted into the corresponding 3-arylinden-1-ones **Va**, **Vb**, and **Vn**–**Vq** as a result of intramolecular cyclization (Scheme 2, Table 3). Methoxy-substituted derivatives **In**–**Ip** were readily transformed into compounds **Vn**–**Vp** by the action of CF_3SO_3H (H_0 = –14.1 [1]) or HSO_3F (Table 3, run nos. 6–9), whereas analogous transformations of ketones **Ia**, **Ib**, **Iq** occurred only in CF_3SO_3H–SbF_5, 17 mol %; $H_0 \approx -19$) [1] (cf. run nos. 1 and 2, 3 and 4, and 10 and 11). Likewise, indenone **Vb** was formed from compound **Ib** in HF–SbF_5 (2 mol %, $H_0 \approx -20$) [1] (run no. 5).

Compounds **Io** and **Iq** having a methoxy group in the *meta* position (R' = 3-MeO) gave rise to only one regioisomer **Vo** and **Vq**, respectively; this means that the cyclization involves the *para*-position with respect to the methoxy group (Scheme 2). One isomer **Vp** was also obtained from ketone **Ip**.

Intramolecular cyclization of 1,3-diarylpropynones in superacids may be regarded as a new efficient procedure for the synthesis of 3-arylindenones (reaction time 15–30 min; yield up to 95%; Table 3). Other methods of synthesis of indenone derivatives from acetylenic compounds are based on coupling reactions which require expensive metal-complex catalysts [12] or on reactions of alkynes with aroyl chlorides in the presence of $AlCl_3$ [13].

We also examined by NMR spectroscopy the behavior of 3-arylindenones in superacids. According to the NMR data, both indenone **Vp** and the corresponding ketone **Ip** in CF_3SO_3H at –30°C give rise to the same species, O,C-diprotonated 3-arylindenone **VIp** (Scheme 3). Table 4 contains the spectral parameters of dications **VIp** and **VIo**. The latter was also generated *in situ* in CF_3SO_3H at –30°C in an NMR ampule in two ways, from diarylpropynone **Io** or indenone **Vo**. These data support the formation of O,C-diprotonated 3-arylindenone species. In the ^1H NMR spectra of **VIo** and **VIp**, a singlet was present at δ ~5.0 ppm which belongs to the CH_2 protons (Table 4). In the ^{13}C NMR spectra, characteristic signals appeared at δ 45–46 (C^2H_2), 183–186 (C^3 cationic center), and 214–217 ppm ($C{=}OH^+$) (Table 4). The observed spectral data resemble those reported for the corresponding structural

Table 3. Conditions of synthesis of 3-arylindenones **Va**, **Vb**, and **Vn–Vq** from 1,3-diarylpropynones **Ia**, **Ib**, and **In–Iq**, respectively, in different acid systems

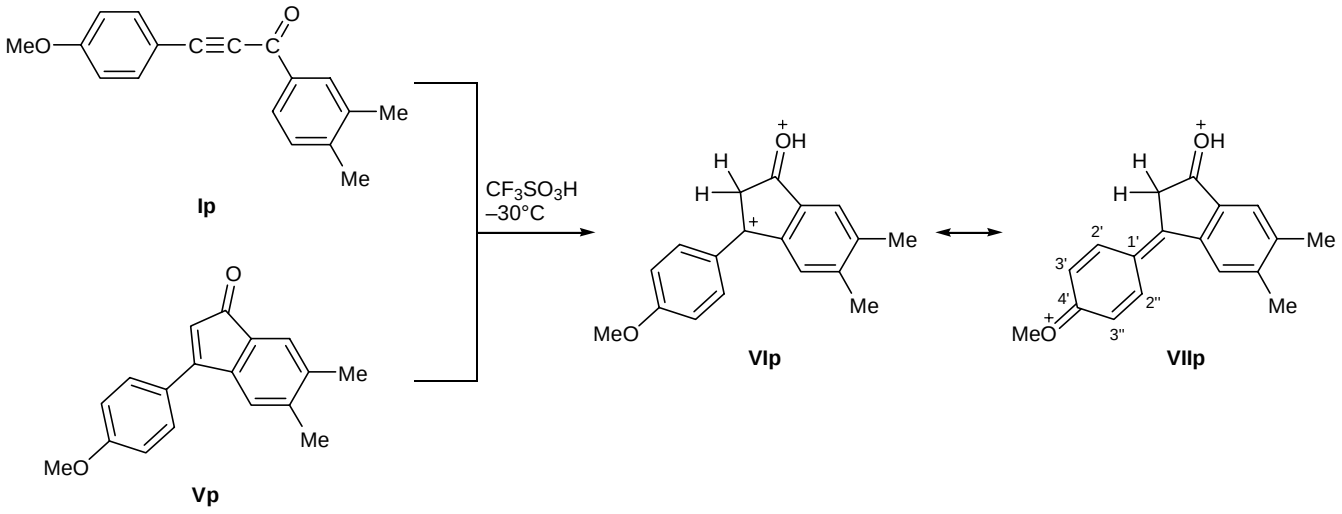
Run no.	Comp. no.	Amount of **I**, mmol	Acid system	Time, min.	Temperature, °C	Product (yield, %)
1	**Ia**	0.5	CF_3SO_3H (3 ml)	30	25	**Ia** (100)
2	**Ia**	0.5	CF_3SO_3H (2 ml)–SbF_5 (0.98 g, 17 mol %)	30	25	**Va** (43)
3	**Ib**	0.5	CF_3SO_3H (3 ml)	30	25	**Ib** (100)
4	**Ib**	0.5	CF_3SO_3H (2 ml)–SbF_5 (0.98 g, 17 mol %)	30	25	**Vb** (75)
5	**Ib**	1.0	HF (5 ml)–SbF_5 (1.1 g, 2 mol %)	30	0	**Vb** (60)
6	**In**	0.4	CF_3SO_3H (2 ml)	15	–30	**Vn** (54)
7	**Io**	0.4	CF_3SO_3H (2 ml)	15	–30	**Vo** (95)
8	**Ip**	0.4	CF_3SO_3H (2 ml)	15	–30	**Vp** (95)
9	**Ip**	1.0	HSO_3F (5 ml)	120	–75	**Vp** (71)
10	**Iq**	0.5	CF_3SO_3H (2 ml)	30	25	**Iq** (100)
11	**Iq**	0.5	CF_3SO_3H (2 ml)–SbF_5 (0.98 g, 17 mol %)	30	25	**Vq** (61)

fragments of O,C-diprotonated 4-phenyl-3-buten-2-one [14] and diprotonated naphthols [15]. In the ^1H NMR spectra of **VIo** and **VIp**, four aromatic protons, 2'-H, 2"-H, 3'-H, and 3"-H (Scheme 3) give four separate signals (Table 4), indicating a large contribution of structures **VIIo** and **VIIp**, where rotation about the C^3–$C^{1'}$ bond is restricted and the positive charge is delocalized over the methoxyphenyl fragment.

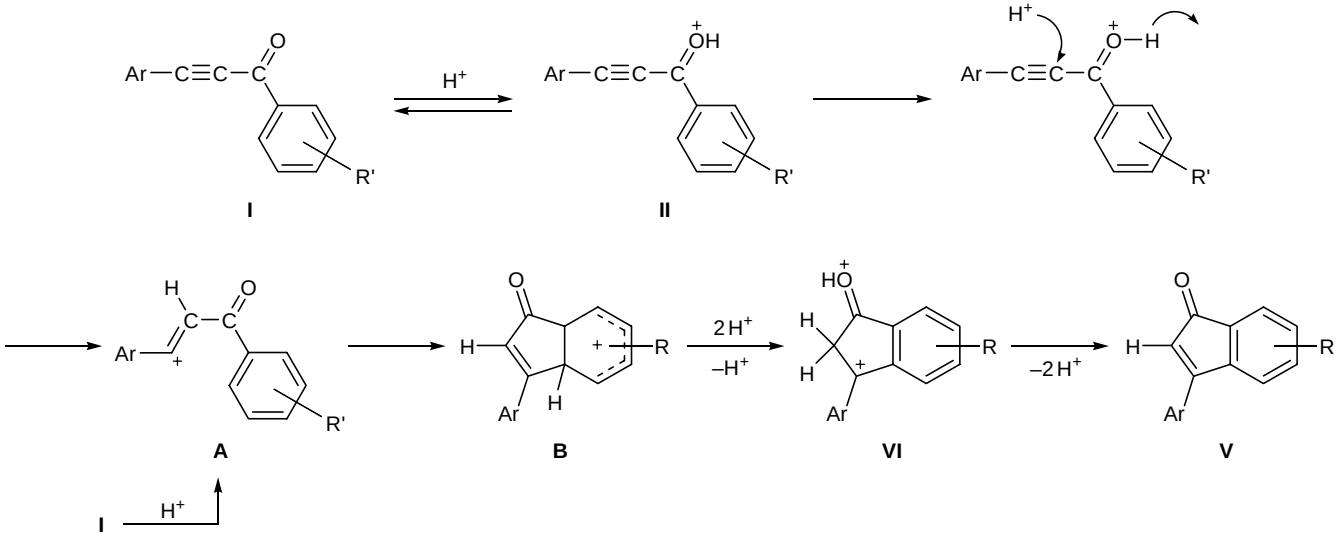
It should be noted that mixing of ketones **Io** and **Ip** with trifluoromethanesulfonic acid at –30°C in an NMR ampule gives rise to intensely colored solutions due to formation of stable dications **VIo** and **VIp**. According to the NMR data, these cations are quantitatively formed from compounds **Io** and **Ip** within several minutes.

On the basis of our experimental data on the protonation of 1,3-diarylpropynones and their transformations in superacids, we propose a mechanism for intramolecular cyclization of compounds **I** to 3-arylindenones **V** (Scheme 4). According to Scheme 4, the key intermediate is reactive vinyl cation **A** which can be formed either (1) by direct protonation of substrate **I** (which is present in a small concentration in the equilibrium mixture with cation **II)** at the C^{α} atom or (2) via slow second protonation of cation **II** with simultaneous deprotonation of the carbonyl group. Intramolecular electrophilic substitution in cation **A** gives cation **B** which is transformed (through a protonation–deprotonation sequence) into very stable dication **VI**; deprotonation of **VI** during treatment of the

Scheme 3.



Scheme 4.



reaction mixture leads to indenone **V** as final product. Reaction channel (2) is possible only in strongly acidic media like CF_3SO_3H–SbF_5 and for compounds with a sufficiently basic C^{α} atom. The basicity of the latter strongly depends on mutual arrangement of substituents in the aryl fragment, and it sharply increases in going to *para*-methoxy-substituted substrates. Taking into account the data on electrophilic reactions of 3-arylpropynoic acid esters in HSO_3F and intermolecular reactions of vinyl cations $ArC^+{=}CHCO_2R$ generated therefrom [16], it should be assumed that the transformation of acetylenic ketones **I** into indenones **V** in media with moderate acidity (such as CF_3SO_3H and HSO_3F) follows channel (1).

In order to detect by spectral methods exotic vinyl cations $ArC^+{=}CHCOX$ with an electron-acceptor group X (X = Ar, Alk, OAlk, CF_3) as kinetically independent species, special studies should be performed in superaicds at very low temperature using substrates with a weakly nucleophilic aromatic ring and spatially shielded charged C^{β} atom. Studies on the formation of such cations and their transformations in superacids will open new prospects in the chemistry of alkynes.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on Bruker AM-500 (500 and 125.76 MHz, respectively) and Bruker AVANCE-300 spectrometers (300 and 75 MHz, respectively) from solutions in chloroform-*d* and acetone-d_6. The proton chemical shifts were measured relative to the residual solvent signals [$CHCl_3$, δ 7.25 ppm; $(CHD_2)_2CO$, δ 2.05 ppm], and the ^{13}C chemical shifts were measured relative to the $CDCl_3$ signal (δ_C 77.0 ppm). The ^1H and ^{13}C NMR spectra in superacids (HSO_3F and CF_3SO_3H) were obtained on a Bruker AVANCE-400 spectrometer at 400 and 100 MHz, respectively, using CH_2Cl_2 as internal reference (δ 5.32 ppm, δ_C 53.84 ppm). The IR spectra of solutions in $CHCl_3$ were recorded on a Specord 75IR spectrometer. The mass spectra

Table 4. ^1H and ^{13}C NMR spectra of O,C-diprotonated 3-arylindenones **VIo** and **VIp** in CF_3SO_3H at –30°C

Ion no.	^1H NMR spectrum, δ, ppm	^{13}C NMR spectrum, δ_C, ppm
VIo	4.25 s (3H, OMe), 4.48 s (3H, OMe), 5.07 s (2H, CH_2), 7.52 s (1H, H_{arom}), 7.60 s (1H, H_{arom}), 8.10 s (2H, H_{arom}), 8.47 s (1H, H_{arom}), 8.84 s (1H, H_{arom}), 9.04 s (1H, H_{arom})[a]	45.71 (CH_2), 58.65, 60.93, 130.31, 134.07, 136.98, 142.42, 142.70, 145.48, 148.12, 171.73, 174.20, 183.71(C^3), 217.07 ($C{=}OH^+$)
VIp	2.72 s (3H, Me), 2.82 s (3H, Me), 4.56 s (3H, OMe), 5.05 s (2H, CH_2), 7.57 s (1H, H_{arom}), 7.64 s (1H, H_{arom}), 8.47 s (1H, H_{arom}), 8.51 s (1H, H_{arom}), 8.70 s (1H, H_{arom}), 9.19 s (1H, H_{arom})[a]	21.37, 22.70, 45.01 (CH_2), 61.90, 131.62, 132.88, 135.61, 136.23, 148.67, 145.90, 162.11, 174.22, 186.20 (C^3), 214.28 ($C{=}OH^+$)

[a] Signal from the acidic proton on the carbonyl oxygen atom is not observed owing to fast exchange with CF_3SO_3H.

(70 eV) were run on MKh-1321 and TSQ 700 Finigan MAT instruments.

The purity of the initial compounds and reaction products was checked by TLC on Silufol UV-254 plates. The reaction mixtures were separated by column chromatography on Silica gel 60 (40–63 μm, Merck) using gradient elution with diethyl ether–hexane mixtures. The yields were determined from the fractions isolated by column chromatography.

Initial 1,3-diarylpropynones (**Ia–Iq**) were synthesized by the procedure developed by us previously [17]; the data for 1,3-diphenylpropynone (**Ia**) were reported in [17].

3-(4-Methylphenyl)-1-phenylpropynone (Ib). Yield 66%, mp 57–59°C; published data [18]: mp 58.5–59°C. IR spectrum, ν, cm^{-1}: 1630, 1635 (C=O), 2195 (C≡C). ^{1}H NMR spectrum (500 MHz, acetone-d_6), δ, ppm: 2.41 s (3H, Me), 7.34 d (2H, H_{arom}, J = 8.0 Hz), 7.61 t (2H, H_{arom}, J = 7.5 Hz), 7.68 (2H, H_{arom}, J = 8.0 Hz), 7.72 t (1H, H_{arom}, J = 7.5 Hz), 8.23 d (2H, H_{arom}, J = 7.5 Hz). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 21.75, 86.81, 93.84, 116.96, 128.60, 129.50, 129.53, 133.12, 134.02, 136.96, 141.58, 178.00.

1-Phenyl-3-(2,4,6-trimethylphenyl)propynone (Ic). Yield 72%, mp 71–73°C; published data [19]: mp 69–70°C. IR spectrum, ν, cm^{-1}: 1620 (C=O), 2190 (C≡C). ^{1}H NMR spectrum (500 MHz, acetone-d_6), δ, ppm: 2.31 s (3H, Me), 2.52 s (6H, Me), 7.02 s (2H, H_{arom}), 7.59–7.73 m (3H, H_{arom}), 8.23–8.25 m (2H, H_{arom}).

3-(3-Nitrophenyl)-1-phenylpropynone (Id). Yield 73%, mp 149–151°C; published data [20]: mp 151–152°C. IR spectrum, ν, cm^{-1}: 1640 (C=O), 2205 (C≡C). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.53 t (2H, H_{arom}, J = 7.5 Hz), 7.61–7.67 m (2H, H_{arom}), 7.97 d (1H, H_{arom}, J = 7.5 Hz), 8.19 d (2H, H_{arom}, J = 7.5 Hz), 8.31 d (1H, H_{arom}, J = 8.2 Hz), 8.49 s (1H, H_{arom}). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 87.99, 89.01, 122.00, 125.24, 127.58, 128.80, 129.61, 129.92, 134.60, 136.39, 138.42, 148.16, 177.36.

3-(4-Nitrophenyl)-1-phenylpropynone (Ie). Yield 69%, mp 146–148°C; published data [20]: mp 148–149°C. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.54 t (2H, H_{arom}, J = 7.4 Hz), 7.66 t (1H, H_{arom}, J = 7.4 Hz), 7.83 d (2H, H_{arom}, J = 8.8 Hz), 8.19 d (2H, H_{arom}, J = 7.4 Hz), 8.28 d (2H, H_{arom}, J = 8.8 Hz). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 89.13, 89.82, 123.78, 126.74, 128.78, 129.58, 133.61, 134.60, 136.38, 148.51, 177.29.

3-(4-Cyanophenyl)-1-phenylpropynone (If). Yield 51%, mp 151–152°C. IR spectrum, ν, cm^{-1}:1640 (C=O), 2210 (C≡C), 2230 (C≡N). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.51 t (2H, H_{arom}, J = 7.8 Hz), 7.65 t (1H, H_{arom}, J = 7.8 Hz), 7.70 d (2H, H_{arom}, J 8.3 Hz), 7.75 d (2H, H_{arom}, J = 8.3 Hz), 8.18 d (2H, H_{arom}, J = 7.8 Hz). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 89.33, 89.56, 113.99, 117.78, 124.87, 128.73, 129.55, 132.24, 133.20, 134.52, 136.40, 177.33. Mass spectrum: m/z 231 $[M]^+$. Found, %: C 83.10; H 3.92; N 6.06. $C_{16}H_9NO$. Calculated, %: C 82.98; H 4.00; N 6.01. M 231.25.

3-(4-Methoxy-3-nitrophenyl)-1-phenylpropynone (Ig). Yield 57%, mp 138–141°C. IR spectrum, ν, cm^{-1}: 1630 (C=O), 2195 (C≡C). ^{1}H NMR spectrum (500 MHz, acetone-d_6), δ, ppm: 4.09 s (3H, MeO), 7.51 d (1H, H_{arom}, J = 8.9 Hz), 7.60 t (2H, H_{arom}, J = 7.5 Hz), 7.73 t (1H, H_{arom}, J = 7.5 Hz), 8.05 d.d (1H, H_{arom}, J = 8.9, 2.0 Hz), 8.25 d (2H, H_{arom}, J = 7.5 Hz), 8.28 (1H, H_{arom}, J = 2.0 Hz). Mass spectrum: m/z 281 $[M]^+$. Found, %: C 68.33; H 3.94; N 4.98. $C_{16}H_{11}NO_4$. Calculated, %: C 68.19; H 4.08; N 5.12. M 281.27.

1-Phenyl-3-(2,4,6-trimethyl-3-nitrophenyl)propynone (Ih). Yield 24%, mp 137–139°C. IR spectrum, ν, cm^{-1}: 1645 (C=O), 2200 (C≡C). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 2.30 s (3H, Me), 2.50 s (3H, Me), 2.56 s (3H, Me), 7.06 s (1H_{arom}), 7.51 t (2H, H_{arom}, J = 7.6 Hz), 7.63 t (1H, H_{arom}, J = 7.5 Hz), 8.18 d (2H, H_{arom}, J = 7.5 Hz). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 16.50, 17.67, 21.24, 88.19, 95.49, 119.70, 128.75, 129.46, 130.07, 131.68, 133.55, 134.29, 136.78, 144.44, 150.40, 177.55. Mass spectrum: m/z 293 $[M]^+$. Found, %: C 73.71; H 5.15; N 4.78. $C_{18}H_{15}NO_3$. Calculated, %: C 73.85; H 5.11; N 4.82. M 293.32.

1-Phenyl-3-(2,3,5,6-tetramethyl-4-nitrophenyl)-propynone (Ii). Yield 40%, mp 159–160°C. IR spectrum, ν, cm^{-1}: 1625 (C=O), 2195 (C≡C). ^{1}H NMR spec-trum (500 MHz, $CDCl_3$), δ, ppm: 2.16 s (6H, Me), 2.54 s (6H, Me), 7.52 t (2H, H_{arom}, J = 7.5 Hz), 7.64 t (1H, H_{arom}, J = 7.5 Hz), 8.20 d (2H, H_{arom}, J = 7.5 Hz). Mass spectrum: m/z 307 $[M]^+$. Found, %: C 74.25; H 5.58; N 4.56. $C_{19}H_{17}NO_3$. Calculated, %: C 74.27; H 5.58; N 4.60. M 307.35.

3-(4-Acetylphenyl)-1-phenylpropynone (Ij). Yield 46%, mp 115–117°C. IR spectrum, ν, cm^{-1}: 1630 (C=O), 1685 (CH_3C=O), 2200 (C≡C). ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 2.61 s (3H, Me), 7.51 t (2H, H_{arom}, J = 7.3 Hz), 7.63 t (1H, H_{arom}, J = 7.3 Hz), 7.74 d (2H, H_{arom}, J = 8.3 Hz), 7.98 d (2H, H_{arom}, J =

8.3 Hz), 8.19 d (2H, H_{arom}, J = 7.3 Hz). Mass spectrum: m/z 248 $[M]^+$. Found, %: C 82.24; H 4.87. $C_{17}H_{12}O_2$. Calculated, %: C 82.19; H 4.86. M 248.28.

3-(4-Methoxycarbonylphenyl)-1-phenylpropynone (Ik). Yield 60%, mp 98–100°C. IR spectrum, ν, cm^{-1}: 1640 (C=O), 1725 (C=O, ester), 2210 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 3.92 s (3H, Me), 7.51 t (2H, H_{arom}, J = 7.5 Hz), 7.63 t (1H, H_{arom}, J = 7.5 Hz), 7.72 d (2H, H_{arom}, J = 8.2 Hz), 8.06 d (2H, H_{arom}, J = 8.2 Hz), 8.19 d (2H, H_{arom}, J = 7.5 Hz). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 52.43, 88.52, 91.22, 124.57, 128.70, 129.60, 129.69, 131.73, 132.82, 134.36, 136.62, 166.04, 177.67. Mass spectrum: m/z 264 $[M]^+$. Found, %: C 77.26; H 4.58. $C_{17}H_{12}O_3$. Calculated, %: C 77.40; H 4.32. M 264.28.

1,4-Bis(3-phenyl-3-oxo-1-propynyl)benzene (Il). Yield 52%, mp 183–185°C; published data [20]: mp 183–184°C. IR spectrum, ν, cm^{-1}: 1620 (C=O), 2200 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.51 t (4H, H_{arom}, J = 6.2 Hz), 7.63 t (2H, H_{arom}, J = 6.2 Hz), 7.70 s (4H, H_{arom}), 8.20 d (4H, H_{arom}, J = 6.2 Hz). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 88.91, 91.18, 122.37, 128.74, 129.60, 133.05, 134.41, 136.61, 177.62.

2,3,5,6-Tetramethyl-1,4-bis(3-phenyl-3-oxo-1-propynyl)benzene (Im). Yield 41%, mp 222–225°C. IR spectrum, ν, cm^{-1}: 1620 (C=O), 2190 (C≡C). ^1H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 2.54 s (12H, Me), 7.25 t (4H, H_{arom}, J = 7.5 Hz), 7.64 t (2H, H_{arom}, J = 7.5 Hz), 8.22 d (4H, H_{arom}, J = 7.5 Hz). Mass spectrum: m/z 390 $[M]^+$. Found, %: C 86.13; H 5.68. $C_{28}H_{22}O_2$. Calculated, %: C 85.97; H 5.64. M 390.48.

3-(4-Methoxyphenyl)-1-phenylpropynone (In). Yield 53%, mp 79–81°C; published data [21]: mp 81°C. ^1H NMR spectrum (500 MHz, acetone-d_6), δ, ppm: 3.89 s (3H, MeO), 7.07 d (2H, H_{arom}, J = 8.7 Hz), 7.60 t (2H, H_{arom}, J = 7.4 Hz), 7.71 t (1H, H_{arom}, J = 7.4 Hz), 7.75 d (2H, H_{arom}, J = 8.7 Hz), 8.24 d (2H, H_{arom}, J = 7.4 Hz). ^{13}C NMR spectrum (125 Hz, $CDCl_3$), δ_C, ppm: 55.42, 86.89, 94.36, 111.82, 114.44, 128.57, 129.45, 133.91, 135.14, 137.03, 161.75, 178.00.

1-(3-Methoxyphenyl)-3-(4-methoxyphenyl)propynone (Io). Yield 55%, mp 106–108°C. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 3.85 s (3H, MeO), 3.88 s (3H, MeO), 6.92 d (2H, H_{arom}, J = 8.8 Hz), 7.16 d.d (1H, H_{arom}, J = 8.1, 1.9 Hz), 7.41 t (1H, H_{arom}, J = 8.1 Hz), 7.62 d (2H, H_{arom}, J = 8.8 Hz), 7.69 t (1H, H_{arom}, J = 1.9 Hz), 7.83 d.t (1H, H_{arom}, J = 8.1, 1.9 Hz). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 55.44, 55.48, 86.96, 94.21, 111.88, 112.80, 114.44, 120.72, 122.75, 129.58, 135.16, 138.44, 159.78, 161.76, 177.78. Mass spectrum: m/z 266 $[M]^+$. Found, %: C 76.68; H 5.30. $C_{17}H_{14}O_3$. Calculated, %: C 76.22; H 5.27. M 266.30.

1-(3,4-Dimethylphenyl)-3-(4-methoxyphenyl)-propynone (Ip). Yield 65%, mp 103–104.5°C. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 2.33 s (6H, Me), 3.84 s (3H, MeO), 6.92 d (2H, H_{arom}, J = 8.8 Hz), 7.25 d (1H, H_{arom}, J = 8.3 Hz), 7.62 d (2H, H_{arom}, J = 8.8 Hz), 7.94–7.97 m (2H, H_{arom}). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 19.77, 20.18, 55.41, 86.98, 93.60, 112.08, 114.38, 127.53, 129.83, 130.23, 135.03, 135.10, 136.97, 143.77, 161.60, 177.97. Mass spectrum: m/z 264 $[M]^+$. Found, %: C 81.79; H 6.10. $C_{18}H_{16}O_2$. Calculated, %: C 81.77; H 6.05. M 264.32.

1-(3-Methoxyphenyl)-3-phenylpropynone (Iq). Yield 72%, mp 50–52°C. ^1H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 3.88 s (3H, MeO), 7.17 d.d (1H, H_{arom}, J = 8.2, 1.9 Hz), 7.38–7.51 m (4H, H_{arom}), 7.66–7.69 m (3H, H_{arom}), 7.83–7.87 m (1H, H_{arom}). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 55.48, 86.98, 92.99, 112.87, 120.10, 120.94, 122.85, 128.71, 129.67, 130.83, 133.08, 138.26, 159.82, 177.74. Mass spectrum: m/z 236 $[M]^+$. Found, %: C 81.34; H 5.12. $C_{16}H_{12}O_2$. Calculated, %: C 81.32; H 5.07. M 236.27.

General procedure for generation of cations IIa–IIm in HSO_3F and cations VIo and VIp in CF_3SO_3H. Fluorosulfonic acid (mp –89°C), 0.8–1 ml, was placed in an NMR ampule and frozen at about –110°C (ethanol–liquid nitrogen), and 5–30 mg of 1,3-diarylprpynone **Ia**–**Im** was added. The mixture was allowed to warm up to –78°C, a Teflon capillary (1 mm i.d.) was immersed into the ampule up to its bottom, and a weak stream of argon was passed through the capillary over a period of 5–15 min to obtain a homogeneous solution. The capillary was withdrawn, and CH_2Cl_2 was added as internal reference. The ^1H and ^{13}C NMR spectra of ions **IIa**–**IIm** were recorded at –80 and 0°C (Tables 1, 2). Solutions containing dications **VIo** and **VIp** were prepared in a similar way from ketones **Io** and **Ip** or 3-arylindenones **Vo** and **Vp** by adding 5–30 mg of the substrate to 0.8–1 ml of CF_3SO_3H (mp –34°C) frozen at –78°C in an NMR ampule; the mixture was then homogenized at –30°C. The ^1H and ^{13}C NMR spectra of **VIo** and **VIp** were recorded at –30°C (Table 4).

General procedure for the transformation of 1,3-diarylpropynones Ia, Ib, and In–Iq into 3-aryl-

indenones Va, Vb, and Vn–Vq in superacids. Substrate **Ia**, **Ib**, or **In**–**Iq**, 0.4–1 mmol, was added under stirring to appropriate superacidic system (HSO_3F, CF_3SO_3H, CF_3SO_3H–SbF_5, or HF–SbF_5) at a temperature specified in Table 3. The mixture was stirred at that temperature for 15–120 min (Table 3). When the reaction was complete, the mixture was slowly poured under stirring onto 20–50 cm^3 of finely crushed ice. Compound **Vn** or **Vp** was filtered off, washed with water, dried in air, and recrystallized from MeOH–CH_2Cl_2. In the syntheses of compounds **Va**, **Vb**, **Vn**, and **Vq**, the mixture (after decomposition with ice) was extracted with methylene chloride (3×50 ml). The extracts were combined, washed with water (2× 30 ml), a saturated aqueous solution of $KHCO_3$ (2× 30 ml), and water again (2×30 ml), and dried over Na_2SO_4. The solvent was removed, and the residue was subjected to flash column chromatography using hexane–diethyl ether as eluent. The yields of **Va**, **Vb**, and **Vn**–**Vq** are given in Table 3. These products are sensitive to daylight, temperature, and nucleophilic reagents; therefore, all operations during their isolation should be performed avoiding unnecessary heating and exposure of their solutions to daylight for a long time.

3-Phenylinden-1-one (Va). Red–orange oily substance; published data [22]: orange oily substance [22]). ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 5.98 s (1H, =CH), 7.25–7.69 m (9H, H_{arom}) (cf. [22]).

3-(4-Methylphenyl)inden-1-one (Vb). Orange crystals, mp 54–56°C. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 2.42 s (3H, Me), 5.96 s (1H, =CH), 7.27–7.36 m (5H, H_{arom}), 7.49–7.56 m (3H, H_{arom}). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 21.53, 121.63, 122.34, 122.54, 127.40, 129.18, 129.64, 130.22, 132.55, 132.75, 141.01, 143.99, 162.81, 197.09. Mass spectrum, *m*/*z* (I_{rel}, %): 220 (100) $[M]^+$, 116 (40). Found, %: C 87.25; H 5.49. $C_{16}H_{12}O$. Calculated, %: C 86.51; H 5.83. *M* 220.27.

3-(4-Methoxyphenyl)inden-1-one (Vn). Red oily substance. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 3.88 s (3H, MeO), 5.95 s (1H, =CH), 7.02 d (2H, H_{arom}, *J* = 8.7 Hz), 7.27–7.51 m (4H, H_{arom}), 7.65 d (2H, H_{arom}, *J* = 8.7 Hz). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 55.55, 114.50, 122.56, 125.61, 127.10, 127.25, 128.32, 129.27, 132.76, 135.26, 144.03, 161.73, 162.58, 197.20. Mass spectrum, *m*/*z* (I_{rel}, %): 236 (100) $[M]^+$, 206 (17). Found, %: C 83.44; H 4.52. $C_{16}H_{12}O_2$. Calculated, %: C 80.92; H 5.01. *M* 236.27.

6-Methoxy-3-(4-methoxyphenyl)inden-1-one (Vo). Red–orange crystals, mp 155–157°C. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 3.82 s (3H, MeO), 3.86 s (3H, MeO), 5.84 s (1H, =CH), 6.77 d.d (1H, H_{arom}, *J* = 8.1, 2.5 Hz), 6.98 d (2H, H_{arom}, *J* = 8.9 Hz), 7.08 d (1H, H_{arom}, *J* = 2.5 Hz), 7.26 d (1H, H_{arom}, *J* = 8.1 Hz), 7.62 d (2H, H_{arom}, *J* = 8.9 Hz). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 55.44, 55.73, 110.24, 114.34, 115.32, 120.22, 122.60, 125.74, 129.13, 135.14, 135.53, 161.16, 161.63, 163.32, 196.67. Mass spectrum, *m*/*z* (I_{rel}, %): 266 (100) $[M]^+$, 159 (72), 135 (59). Found, %: C 76.68; H 5.30. $C_{17}H_{14}O_3$. Calculated, %: C 76.76; H 5.27. *M* 266.30.

5,6-Dimethyl-3-(4-methoxyphenyl)inden-1-one (Vp). Yellow–orange crystals, mp 135–137°C. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 2.26 s (3H, Me), 2.28 s (3H, Me), 3.87 s (3H, MeO), 5.85 s (1H, =CH), 7.01 d (2H, H_{arom}, *J* = 8.6 Hz), 7.13 s (1H, H_{arom}), 7.27 s (1H, H_{arom}), 7.63 d (2H, H_{arom}, *J* = 8.6 Hz). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 19.77, 20.53, 55.41, 114.31, 121.11, 123.52, 124.26, 125.82, 129.08, 130.84, 137.22, 141.19, 141.82, 161.42, 162.29, 197.47. Mass spectrum, *m*/*z* (I_{rel}, %): 264 (100) $[M]^+$, 249 (25), 118 (8). Found, %: C 81.79; H 6.10. $C_{18}H_{16}O_2$. Calculated, %: C 81.60; H 6.16. *M* 264.32.

6-Methoxy-3-phenylinden-1-one (Vq). Red crystals, mp 84–86°C. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 3.84 s (3H, MeO), 5.91 s (1H, =CH), 6.79 d.d (1H, H_{arom}, *J* = 8.1, 2.5 Hz), 7.12 d (1H, H_{arom}, *J* = 2.5 Hz), 7.25 d (1H, H_{arom}, *J* = 8.1 Hz), 7.48–7.50 m (3H, H_{arom}), 7.64–7.67 m (2H, H_{arom}). ^{13}C NMR spectrum (75 MHz, $CDCl_3$), δ_C, ppm: 55.77, 110.50, 115.57, 121.72, 122.59, 127.37, 128.90, 130.54, 133.29, 134.71, 135.60, 161.25, 163.74, 196.79. Mass spectrum, *m*/*z* (I_{rel}, %): 236 (100) $[M]^+$, 135 (26), 129 (83), 105 (12). Found, %: C 81.34; H 5.12. $C_{16}H_{12}O_2$. Calculated, %: C 80.92; H 5.01. *M* 236.27.

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