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Chemistry of 1,3-diarylpropynones in superacids

A. V. Vasilyev,[a] S. Walspurger,[b] M. Haouas,[b] J. Sommer,*[b] P. Pale*[c] and A. P. Rudenko[a]

[a] *Saint-Petersburg Forest Technical Academy, Institutsky per.5, Saint-Petersburg, 194021, Russia; Fax: 7 8125500815; Tel: 7 8125500698. E-mail: aleksvasil@hotmail.com*

[b] *Laboratoire de physico-chimie des hydrocarbures, associé au CNRS, Institut Le Bel, Université L. Pasteur, 67000, Strasbourg, France; Fax: 33 390241487; Tel: 33 390241486. E-mail: sommer@chimie.u-strasbg.fr*

[c] *Laboratoire de synthèse et réactivité organique, associé au CNRS, Institut Le Bel, Université L. Pasteur, 67000, Strasbourg, France; Fax: 33 390241517. E-mail: ppale@chimie.u-strasbg.fr*

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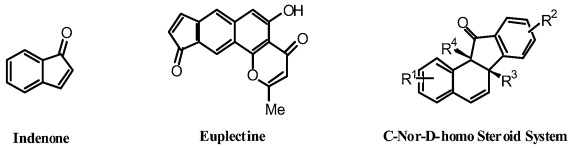
In superacids with $H_0 = -14$ to -20, it has been found that 1,3-diarylpropynones ArC≡CCOAr′ are either protonated on oxygen of carbonyl groups with the formation of stable ions ArC≡CC(O$^+$H)Ar′ or undergo further transformations when the highly conjugated system is electron-rich enough. In the latter case, 3-arylindenones are produced very rapidly and with high efficiency (up to 95% yield in less than 30 min). The influence of the substituents Ar, Ar′ and of the reaction conditions on the behavior of 1,3-diarylpropynones and on the intramolecular cyclisation have been studied. From the collected data, a mechanism has been proposed involving vinyl cations ArC$^+$=CHCOAr′ and/or dications ArC$^+$=CHC(O$^+$H)Ar′.

Introduction

Activation of organic compounds in superacids[1] such as HSO_3F or CF_3SO_3H has been widely used in order to generate and investigate various carbocations,[2,3] cation-radicals,[4] and other long-lived charged intermediates. Indeed, solvation in weakly nucleophilic superacids leads to the stabilization of highly electron-deficient species (electrophiles or superelectrophiles)[5] which can be then studied. Despite a large number of studies in this field,[6] there are only few data available on the behaviour of acetylenic derivatives in superacids. In original studies, Stang and Summerville[7] and Olah and Spear[8] have observed the addition of CF_3SO_3H (triflic acid) and HSO_3F to alkynes leading to the formation of vinyl triflates and vinyl fluorosulfonates. Transformation of some substituted acetylenes into cyclobutenyl cations with their subsequent oligomerization in HSO_3F was also monitored by NMR spectroscopy.[8,9] Although not directly observed, vinyl cations induced by the protonation of the triple bond were postulated as highly reactive intermediates. In fact, arylvinyl cations were observed as kinetically independent species and characterized by ^{1}H and ^{13}C NMR methods in the system HSO_3F–SbF_5 at −120 °C for the first time in 1992 by Siehl and coworkers.[10] Recently, Muller *et al*. have reported a fully characterized vinyl cation, stable at room temperature due to hyperconjugation with silicon atoms.[11] Nevertheless, the analysis of available literature reveals that the chemistry of acetylene compounds in superacids still remains little understood.

This report is a contribution from our research on 1,3-disubstituted propynones.[12] These compounds have been found to dimerize by oxidation with PbO_2 in acidic media *via* cation-radical intermediates leading to interesting polycarbonyl synthons.[13] Here we wish to report their behaviour in neat superacid (HSO_3F) by studying the protonation of 1,3-diarylpropynones by ^{1}H and ^{13}C NMR spectroscopy as well as their transformation into indenones in various superacidic media (HSO_3F and CF_3SO_3H). This reaction appears to be a new and efficient way to synthesize indenones.[14] The indenone pattern can be found in some natural products as euplectine [15] and in synthetic biologically active molecules such as C-nor-D-homosteroids (Scheme 1).[16]



Indenone Euplectine C-Nor-D-homo Steroid System

Scheme 1

Results and discussion

(a) 1,3-Diarylpropynones: behavior in superacids

When dissolved in fluorosulfonic or triflic acid, 1,3-diarylpropynones **1a–m** exhibit dramatic modifications of their NMR spectra. Formation of O-protonated ions **2a–m** from the acetylenic ketones **1a–m** in HSO_3F is evidenced by these modifications (Scheme 2). ^{1}H NMR spectra of these ions in HSO_3F at −80 °C are reported in Table 1, while ^{13}C NMR spectra of ions **2a**, **g**, **i**, **j** and **m** (HSO_3F, −80 °C and 0 °C) and their neutral precursors are collected in Table 2 (^{13}C–^{1}H decoupled spectra). Exact assignments of signals in ^{13}C NMR spectra have been made on the basis of multiplet analysis of ^{13}C–^{1}H coupled NMR spectra. Two-dimensional heteronuclear correlations HSQC, HMQC and HMBC [17] also confirmed these assignments.

In HSO_3F at −80 °C, ^{1}H NMR spectra of protonated forms **2a–m** clearly showed a new narrow singlet signal around 12–13.5 ppm corresponding to the proton bonded to carbonyl group. Integration of spectral signals confirmed that alkynones **1a–m** do exist in HSO_3F in completely O-protonated forms (Table 1). At 0 °C, the signal of this proton was not observed due to a fast exchange with the acidic medium. In HSO_3F, diynediones **1l,m** were present as dications **2l,m** after protonation of the two carbonyl groups (Scheme 2 and Table 1).

Under these conditions, no proton which could have been bonded to the electron-withdrawing groups R (NO_2, CN, COMe, CO_2Me) present in the ions **2d–k** could be detected. These results are in agreement with the fact that nitro and cyano groups are specifically solvated in HSO_3F[4] and that complete protonation is only observed in systems with higher acidity such as HSO_3F–SbF_5.[2] Although this can not be detected by

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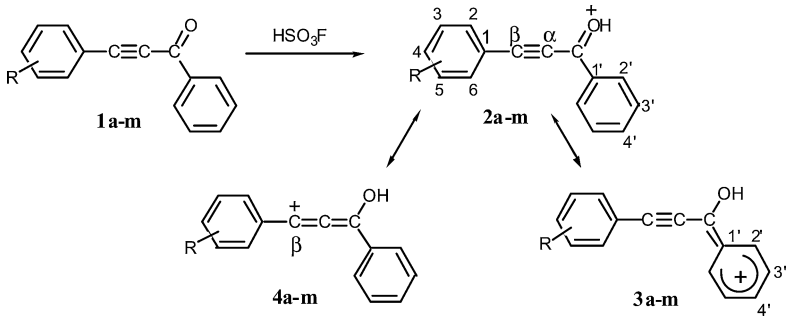


Scheme 2 Protonated 1,3-diarylpropynones. **1a–m**, **2a–i**, **3a–i**, **4a–i**, R = H (**a**), 4-Me (**b**), 2,4,6-Me_3 (**c**), 3-NO_2 (**d**), 4-NO_2 (**e**), 4-CN (**f**), 4-MeO-3-NO_2 (**g**), 2,4,5-Me_3-3-NO_2 (**h**), 2,3,5,6-Me_4-4-NO_2 (**i**), 4-COMe (**j**), 4-CO_2Me (**k**), 4-PhCOC≡C (**l**), 2,3,5,6-Me_4-4-PhCOC≡C (**m**); **2j–m**, **3j–m**, **4j–m**, R = 4-COH^+Me (**j**), 4-CO_2H^+Me (**k**), 4-PhCOH^+C≡C (**l**), 2,3,5,6-Me_4-4-PhCOH^+C≡C (**m**).

Table 1 NMR spectra of the protonated forms (**2a-m**) in HSO_3F at −80°, δ/ppm (J/Hz)

	Assignment of signals		
No. of ion	C=OH^+	H arom.	R
2a	12.75 s (1H)	7.58 s (2H), 7.78 s (3H), 7.98 s (2H), 8.16 s (1H), 8.51 s (2H)	—
2b	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)
2c	12.07 s (1H)	7.00 s (2H), 7.79 s (2H), 8.13s (1H), 8.35 s (1H), 8.45 s (1H); 8.50 s (1H), 8.53s (1H)	2.28 s (3H, Me) 2.62 s (6H, 2Me)
2d	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)	—
2e	13.24 s (1H)	7.89 s (1H), 7.96 s (1H), 8.35 s (3H), 8.65 s (3H), 8.84 s (1H)	—
2f	13.26 s (1H)	7.89 t (1H, *J* 6.5 Hz), 7.95 t (1H, *J* 6.5 Hz), 8.34 d (2H, *J* 6.2 Hz), 8.35 t (1H, *J* 6.5 Hz), 8.41 d (2H, *J* 6.2 Hz), 8.69 d (1H, *J* 6.5 Hz), 8.84 d (1H, *J* 6.5 Hz)	—
2g	12.87 (1H)	7.67 d (1H, *J* 8.7 Hz), 7.64 t (1H, *J* 7.0 Hz), 7.81 t (1H, *J* 7.0 Hz), 8.19 t (1H, *J* 7.0 Hz), 8.53 d (1H, *J* 7.0 Hz), 8.56 d (1H, *J* 8.7 Hz), 8.68 d (1H, *J* 7.0 Hz), 9.17 s (1H)	4.43 s (3H, Me)
2h	12.86 s (1H)	7.54 s (1H), 7.87 s (1H), 7.93 s (1H), 8.28 s (1H), 8.67 s (2H)	2.61s (3H, Me), 2.85s (6H, 2Me)
2i	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)
2j	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)
2k	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)
2l[a]	13.47 (2H)	7.90 s (4H), 8.33 s (6H), 8.69 s (2H), 8.85 s (2H)	—
2m[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] Diprotonated structure

^{1}H NMR, the acetyl group of the cation **2j** was also protonated according to the ^{13}C NMR spectrum. The carbonyl carbon of this group indeed appeared at δ 222.8 ppm (Table 2), that is 25.8 ppm higher than in the starting propynone **1j** and well in the range known (210–223 ppm) for protonated carbonyl groups of substituted acetophenones in HSO_3F and HSO_3F–SbF_5.[18] In a similar way, protonation of the ester group in ion **2k** was observed only *via* ^{13}C NMR.

Because of the relatively high viscosity of HSO_3F, the ^{1}H NMR signals of aromatic protons of ions **2a–m** were observed at −80 °C as broadened singlets with unresolved fine structure in most cases (Table 1). However, at 0 °C, the NMR spectra displayed well resolved multiplets typical for aromatic systems.

The NMR signals of the aromatic part reveal interesting features concerning the delocalization of positive charge in some of these ions. Due to the partial π-bond character of the carbonyl carbon–phenyl ring bond, the rotation around this bond is generally slow on the NMR time scale leading to non-equivalence on the *o,o′*-carbons or protons of the phenyl ring. Such temperature dependant phenomenon is well known for aromatic carbonyl compounds and strongly promoted by protonation of the carbonyl oxygen.[19]

Comparison between ^{13}C NMR spectra of the initial 1,3-diarylpropynones ($CDCl_3$, 25 °C) and their protonated forms (HSO_3F, −80 °C and 0 °C) in Table 2 showed that the positive charge of the protonated carbonyl group of ynone ions **2a**, **g**, **i**, **j**, and **m** was delocalized both on the phenyl ring adjacent to carbonyl substituent and on the arylacetylene part of molecule. Indeed, the signal of the β-acetylenic carbon of the ynone system (Scheme 2) was shifted downfield (about $\Delta\delta$ 23–32 ppm) in comparison with the signal of this atom in the neutral molecules (Table 2). This shift underlined the contribution of the resonance structures of type **4** (Scheme 2).

Significant shifts of the signals of the atoms $C^{2'}$, $C^{3'}$ and $C^{4'}$ between neutral ketones and their protonated forms also showed a substantial participation of the phenyl ring connected to the carbonyl group in the distribution of the positive charge (**3a–m** in Scheme 2). Thus, in HSO_3F, the signal of atom $C^{4'}$ in the ions **2a**, **g**, **i**, **j**, and **m** underwent a downfield shift (about $\Delta\delta$ 11–14 ppm) compared to the signal in the neutral molecule. At −80 °C, the two non-equivalent atoms $C^{2'}$ showed shifts about $\Delta\delta$ 2.5–4 ppm and $\Delta\delta$ 10–13 ppm higher than the signal $C^{2'}$ in neutral 1,3-diarylpropynone (Table 2).

(b) 1,3-Diarylpropynones: stability and reactivity in HSO_3F

The stability of 1,3-diarylpropynones depends on the nature of the substituents borne by the aryl group linked to the acetylenic end of the ynone system.

Compounds with groups R = hydrogen **1a** or electron withdrawing groups **1g–m** existed as stable protonated ions in HSO_3F **2a–m**. On the contrary, derivatives with R = methoxy group in the *para* position quickly underwent secondary transformations even at −80 °C. Derivatives with R = alkyl groups **1b, c** were stable at −80 °C, but showed similar transformations at 0 °C.

The presence of electron-donating groups in the arylalkynyl part of 1,3-diarylpropynones, specially at the *para* position, does increase the electron density on the ynone system, mainly on

Table 2 NMR spectra data of 1,3-diarylpropynones (**1a**, **g**, **i**, **j**, and **m**) ($CDCl_3$, 25 °C) and protonated forms (**2a**, **g**, **i**, **j**, and **m**) in HSO_3F

		Chemical shifts, δ/ppm[a]										
No. of compound	T/°C	C=O[b]	C^{α}	C^{β}	$C^{1'}$	$C^{2'}$[c]	$C^{3'}$	$C^{4'}$	C^{1}	C^{2} and C^{6}	C^{3} and C^{5}	C^{4}	R
1a[d]	25	177.92	86.87	93.03	136.89	129.52	128.57	134.04	120.11	133.00	128.64	130.73	—
2a[e]	−80	181.87	87.93	116.45	129.68	132.18 and 139.84	131.08	145.07	129.9	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	—
1g	25	177.53	87.32	90.01	136.55	129.53	128.73	134.38	112.31	130.27 and 138.72	139.53 and 114.00	154.53	56.87
2g	−80	183.38	86.73	119.56	130.19	133.16 and 141.44	131.45	146.84	112.48	138.31 and 151.18	131.57and 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 and 146.68	134.37 and 118.05	164.14	60.20
1i	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
2i	−80	183.08	93.96	120.79	130.58	132.83 and 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
1j	25	177.67	88.72	91.12	136.60	129.60	128.71	134.40	124.68	133.06	128.37	138.08	197.01 C=O 26.69 CH_3
2j	−80	184.35	87.71	118.11	130.16	133.71 and 142.30	131.66	147.81	130.30	136.60[f]	136.60[f]	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
1m	25	177.84	91.23	96.03	137.03	129.53	128.70	134.12	122.74	138.07	—	—	18.58
2m	−80	183.13	95.18	123.59	130.66	133.12 and 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] Numeration of carbons atoms see in Scheme 2. [b] In HSO_3F signal of protonated carbonyl group C=OH^+. [c] In HSO_3F at −80 °C two unequivalent signals of $C^{2'}$ atoms are observed (see text). [d] I : neutral compounds in $CDCl_3$. [e] II : protonated compounds in HSO_3F. [f] Coinciding signals.

the acetylenic bond. Such higher electron density would favour further reactions. This effect is clearly reflected in the calculated HOMO energies of selected 1,3-diarylpropynones **1a**, **b**, **n**, and **e**. Compared to the parent propynone **1a**, the *para* methyl- and methoxy-substituted **1b** and **1n** exhibit higher HOMO levels (−9.405 and −9.192 eV respectively *vs*. −9.636 eV). Such higher reactivity and electron density at the triple bond could even lead to further protonation in superacids. Dicationic intermediates have been recently suggested by Klumpp *et al*.[20] and Olah *et al*.[21] as a part of their work in superelectrophilic activation of phenylpropynoic acid.

If so, one could expect the formation of a vinyl cation either from the propynone **1** or from the protonated form **2** (Scheme 3, route a or b). Since one conformation of this cation would ideally place the carbocationic center close to the acylaryl group, one would expect a facile ring closure *via* a Friedel–Crafts type reaction. An indenone would thus be formed.

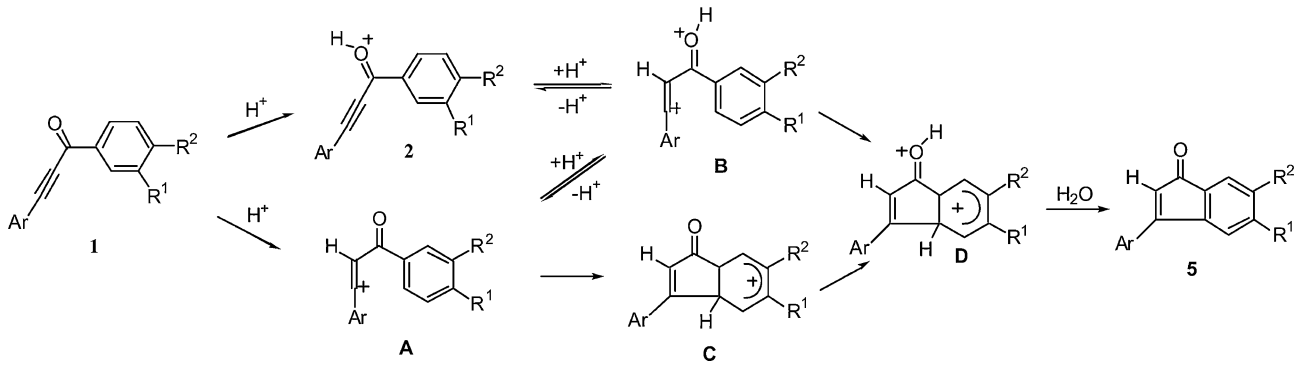
Calculations (MOPAC PM3) indicated an overall thermodynamically favourable process (Fig. 1). However, dicationic intermediates (**B** in Fig. 1 and Scheme 3) proved to be highly energetic species. Calculations also showed that the O-protonated forms of 1,3-diarylpropynones **2** are only slightly more stable that the corresponding C-protonated form (**A** in Fig. 1 and Scheme 3). It is therefore not possible to omit a pathway through such intermediates (Scheme 3, route b), since both forms could be in equilibrium.

Fig. 1 Calculation of the energy of some compounds and proposed intermediates.

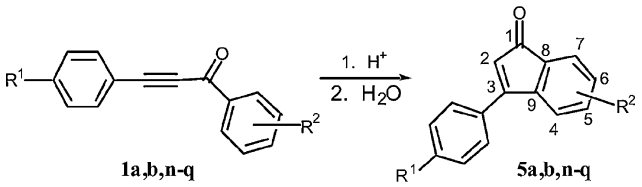
(c) Synthesis of indenones from 1,3 diarylpropynones.

In order to identify such transformations and characterize the corresponding products, preparative reactions starting with various 1,3-diarylpropynones were performed in superacids. Attempts to characterize products of reaction obtained in the presence of HSO_3F failed. Indeed, in most cases complex mixtures of products were obtained probably due to the sulfonation of the arene parts of the products. Thus investigations were performed in triflic acid which is 10 times weaker than fluorosulfonic acid but which is known to avoid sulfonation or oxidation as side reactions. Under these conditions, it was found that 1,3-diarylpropynones **1a, b, n–q** indeed gave 3-arylindenones **5a, b, n–q** as major products (Scheme 4 and Table 3).

As underlined above, the nature of the substituents carried by the aryl groups of 1,3-diarylpropynones play also a critical role on the formation of 3-arylindenones. Methoxy-substituted derivatives **1n–p** were easily transformed into the compounds **5n–p** under the action of CF_3SO_3H or HSO_3F at



Scheme 3 Proposed mechanism for formation of 3-arylindenones.



Scheme 4 Synthesis of 3-arylindenones. **1**, R^1 = MeO, R^2 = H (**n**), 3-MeO (**o**), 3,4-Me_2 (**p**), R^1 = H, R^2 = 3-MeO (**q**); **5**, R^1 = H, R^2 = H (**a**), R^1 = Me, R^2 = H (**b**), R^1 = MeO, R^2 = H (**n**), 6-MeO (**o**), 5,6-Me_2 (**p**), R^1 = H, R^2 = 6-MeO (**q**).

low temperatures (Table 3, entries 6–9). However, in the presence of less activating substituents **1a, b, q** transformation into the corresponding indenones occurred only when acidity was significantly enhanced by addition of a strong Lewis acid. For example, 17 mol% of SbF_5 in CF_3SO_3H ($H_0 \sim -19$)[1] promoted the cyclization of **1a, b, q** while in CF_3SO_3H ($H_0 = -14.1$) these propynones remained unchanged as O-protonated species (Table 3, entries 2, 4, 11 *vs.* 1, 3, 10). Analogously, the propynone **1b** gave the indenone **5b** in the system HF–SbF_5 (2 mol% SbF_5) ($H_0 \sim -20$)[1] (Table 3, entry 5). This difference in reactivity is clearly related to the electron density of the propynone system.

In order to investigate the regioselectivity of indenone formation, compounds **1o, q** with an unsymmetrical arrangement of methoxy substituent R^2 were synthesized. In triflic acid these compounds gave only one regioisomer **5o, q** formed after a cyclization occurring in *para*-position to the MeO-group (Scheme 4). In a similar way, only one isomeric indenone **5p** was formed from the propynone **1p**.

These results showed that in acids strong enough the β-acetylenic carbon (Scheme 2) becomes electrophilic enough to promote a Friedel–Crafts type reaction with the facing aromatic group (Scheme 3). This electophilic species can not be the O-protonated ynone **2**, usually stable (see section (b) above, Tables 1 and 2, and entries 1, 3, 10 in Table 3) and without any reactive conformation. It could be the C-protonated form **A** (Scheme 3) due to its proper geometry in one of its conformations and its probable equilibrium with the O-protonated form **2** (see calculations above). However, such species could not be detected by NMR. The fact that stronger acids promote the cyclization of stable O-protonated propynones (Table 3, entries 2, 4, 11) suggests a further protonation of the O-protonated form. Such species would be a highly reactive O,C-diprotonated propynone (**B** in Scheme 3). Although it was also not possible to directly observe it by spectroscopy, the intermediacy of such superelectrophilic species **B** can thus not be excluded.

Both pathways would lead to protonated indenones **D**, slightly more stable than the O- or C-protonated propynones **2** or **A** (Fig. 1), which upon work-up and isolation produce 3-arylindenones **5**.

Conclusion

1,3-diarylpropynones, unsubstituted or with electron withdrawing substituents exist as stable O-protonated ions in superacidic medium which have been characterised by ^1H and ^{13}C NMR at −80 °C and 0 °C. Enhancement of the basicity of the propynone system by introduction of alkyl or methoxy groups leads to intramolecular cyclization leading to 3-arylindenones. An increase of the acidity of the medium gives the same results, leading to a variety of 3-arylindenones in excellent yields (up to 95%). This new method offers a very efficient route (reaction time 15–30 min) to 3-arylindenones. Supported by some calculations and NMR studies, a mechanism have been proposed for this new reaction.

Table 3 Conditions of preparative synthesis of the 3-arylindenones (**5a, b, n–q**) from 1,3-diarylpropynones (**1a, b, n–q**) in various acidic systems

		Reaction conditions				
	No. of compounds	Initial/mmol	Superacidic system	Time/min	T/°C	Reaction product (yield (%))
1	**1a**	0.5	CF_3SO_3H, 30 eq.	30	25	**5a** (0)[a]
2	**1a**	0.5	CF_3SO_3H/SbF_5 (17 mol%), 20 eq.	30	25	**5a** (43)
3	**1b**	0.5	CF_3SO_3H, 30 eq.	30	25	**5b** (0)[a]
4	**1b**	0.5	CF_3SO_3H/SbF_5 (17 mol%), 20 eq.	30	25	**5b** (75)
5	**1b**	1.0	HF/SbF_5 (2 mol%), 250 eq.	30	0	**5b** (60)
6	**1n**	0.4	CF_3SO_3H, 20 eq.	15	−30	**5n** (54)
7	**1o**	0.4	CF_3SO_3H, 20 eq.	15	−30	**5o** (95)
8	**1p**	0.4	CF_3SO_3H, 20 eq.	15	−30	**5p** (95)
9	**1p**	1.0	HSO_3F, 90 eq.	120	−75	**5p** (71)
10	**1q**	0.5	CF_3SO_3H, 20 eq.	30	25	**5q** (0)[a]
11	**1q**	0.5	CF_3SO_3H/SbF_5, (17 mol%), 20 eq.	30	25	**5q** (61)

[a] No reaction occurred, starting material completely recovered.

Experimental

General

^{1}H and ^{13}C NMR spectra of compounds **1a–q** and **5a, b, n–q** were recorded on spectrometer Bruker AVANCE 300 (working frequencies 300 and 75 MHz respectively) or on spectrometer Bruker AM-500 (working frequencies 500 and 125 MHz respectively). The residual proton-solvent peaks: $CDCl_3$ (δ 7.25 ppm) and $(CD_3)_2CO$ (δ 2.05 ppm) for ^{1}H spectra, $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra were used as internal references. Spectral measurements in HSO_3F at −80 °C and 0 °C, and in CF_3SO_3H at −30 °C were performed on spectrometer Brucker AVANCE 400 (frequencies 400 for ^{1}H and 100 MHz for ^{13}C NMR spectra). Spectra in the superacids were referenced to the signal of CH_2Cl_2 added as internal standard (δ 5.32 ppm for ^{1}H and δ 53.84 ppm for ^{13}C NMR spectra). Mass spectra (electron impact, ionisation energy 70 eV) were measured on instrument TSQ 700 Finnigan MAT or on machine MKh-1321. IR spectra of solutions of the compounds in $CHCl_3$ were registered on instrument Specord 75IR.

Purity of the starting and obtained compounds was controlled by TLC on the plates Silufol UV-254. Preparative separation and purification of reaction productss were carried out by column chromatography on silica-gel Merck 60, eluted gradient with mixtures of ether-hexanes. Yields of products were determined after chromatography.

Synthesis of 1,3-diarylpropynones

Initial 1,3-diarylpropynones **1a–q** were synthesized according to the method[12] previously developed by ourselves by reaction of terminal arylacetylenes with aroyl chlorides in the presence of palladium catalysts.

1,3-Diphenylpropynone 1a. mp 46–48 °C previously obtained by ourselves.[12]

3-(4-Methylphenyl)-1-phenylprop-3-yn-1-one 1b. Yield 66%. Mp 57–59 °C, lit. 58.5–59 °C.[22] ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 2.41 (s, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.5 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 8.23 (d, J= 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.75, 86.81, 93.84, 116.96, 128.60, 129.50, 129.53, 133.12, 134.02, 136.96, 141.58, 178.00. IR : ν (cm^{-1}) 1630, 1635 (C=O), 2195 (C=C).

3-(2,4,6-Trimethylphenyl)-1-phenylprop-3-yn-1-one 1c Yield 72%. Mp 71–73 °C, lit. 72 °C.[23] ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 2.31 (s, 3H), 2.52 (s, 6H), 7.02 (s, 2H), 7.59–7.73 (m, 3H), 8.23-8.25 (m, 2H). IR : ν (cm^{-1}) 1620 (C=O), 2190 (C=C).

3-(3-Nitrophenyl)-1-phenylprop-3-yn-1-one 1d. Yield 73%. Mp 149–151 °C, lit. 151-152 °C.[23] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (t, J = 7.5 Hz, 2H), 7.61-7.67 (m, 2H), 7.97 (d, J = 7.5 Hz, 1H), 8.19 (d, J = 7.5 Hz, 2H), 8.31 (d, J= 8.2 Hz, 1H), 8.49 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 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. IR : ν (cm^{-1}) 1640 (C=O), 2205 (C=C).

3-(4-Nitrophenyl)-1-phenylprop-3-yn-1-one 1e. Yield 69%. Mp 146–148 °C, lit. 148-149 °C.[24] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (t, J = 7.4 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.83 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 7.4 Hz, 2H), 8.28 (d, J= 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 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-phenylprop-3-yn-1-one 1f. Yield 51%. Mp 151–152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (t, J = 7.8 Hz, 2H), 7.65 (t, J = 7.8 Hz, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 8.18 (d, J = 7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 89.33, 89.56, 113.99, 117.78, 124.87, 128.73, 129.55, 132.24, 133.20, 134.52, 136.40, 177.33. IR : ν (cm^{-1}) 1640 (C=O), 2210 (C=C), 2230 (C=N). MS : m/z = 231 M+. Anal. calcd for $C_{16}H_9NO$: C, 83.10; H, 3.92; N, 6.06. Found: C, 82.98; H, 4.00; N, 6.01.

3-(4-Methoxy-3-nitrophenyl)-1-phenylprop-3-yn-1-one 1g. Yield 57%. Mp 138–141 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 4.09 (s, 3H), 7.51 (d, J = 8.9 Hz, 1H), 7.60 (t, J = 7.5 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1H), 8.05 (dd, J = 8.9, 2.0 Hz, 1H), 8.25 (d, J = 7.5 Hz, 2H), 8.28 (d, J = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.87, 87.33, 90.01, 112.31, 114.00, 128.73, 129.53, 130.27, 134.38, 136.55, 138.72, 139.53, 154.53, 177.53. IR : ν (cm^{-1}) 1630 (C=O), 2195 (C=C). MS : m/z = 281 M+. Anal. calcd for $C_{16}H_{11}NO_4$: C, 68.33; H, 3.94; N, 4.98. Found: C, 68.19; H, 4.08; N, 5.12.

3-(2,4,5-Trimethyl-5-nitrophenyl)-1-phenylprop-3-yn-1-one 1h. Yield 24%. Mp 137–139 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.50 (s, 3H), 2.56 (s, 3H), 7.06 (s, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 8.18 (d, J = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 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. IR : ν (cm^{-1}) 1645 (C=O), 2200 (C=C). MS : m/z = 293 M+. Anal. calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.85; H, 5.11; N, 4.82.

3-(2,3,5,6-Tetramethyl-4-nitrophenyl)-1-phenylprop-3-yn-1-one 1i. Yield 40%. Mp 159–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.16 (s, 6H), 2.54 (s, 6H), 7.52 (t, J = 7.5 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 8.20 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.51, 18.52, 89.69, 95.52, 122.31, 124.85, 128.74, 129.50, 134.24, 136.87, 140.03, 153.69, 177.67. IR : ν (cm^{-1}) 1625 (C=O), 2195 (C=C). MS : m/z = 307 M+. Anal. calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.27; H, 5.58; N, 4.60.

3-(4-Acetylphenyl)-1-phenylprop-3-yn-1-one 1j. Yield 46%. Mp 115–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.61 (s, 3H), 7.51 (t, J = 7.3 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.98 (d, J = 8.3 Hz, 2H), 8.19 (d, J = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.69, 88.72, 91.12, 124.68, 128.37, 128.71, 129.60, 133.06, 134.40, 136.60, 138.08, 177.67, 197.01. IR : ν (cm^{-1}) 1630 (C=O), 1685 ($(CH_3)C$=O), 2200 (C=C). MS : m/z = 248 M+. Anal. calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.19; H, 4.86.

3-(4-Methoxycarbonylphenyl)-1-phenylprop-3-yn-1-one 1k Yield 60%. Mp 98–100 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.51 (t, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.72 (d, J = 8.2 Hz, 2H), 8.06 (d, J = 8.2 Hz, 2H), 8.19 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 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. IR : ν (cm^{-1}) 1640 (C=O), 1725 ($(CH_3O)C$=O), 2210 (C=C). MS : m/z 264 M+. Anal. calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.40; H, 4.32.

1,4-Bis(phenylcarbonylethynyl)benzene 1l. Yield 52%. Mp 183-185 °C, lit.[2] 183–184 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 7.51 (t, J = 6.2 Hz, 4H), 7.63 (t, J = 6.2 Hz, 2H), 7.70 (s, 4H), 8.20 (d, J= 6.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 88.91, 91.18, 122.37, 128.74, 129.60, 133.05, 134.41, 136.61, 177.62. IR : ν (cm^{-1}) 1620 (C=O), 2200 (C=C).

2,3,5,6-Tetramethyl-1,4-Bis(phenylcarbonylethynyl)benzene 1m. Yield 41%. Mp 222–225 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.54 (s, 12H), 7.25 (t, J = 7.5 Hz, 4H), 7.64 (t, J = 7.5 Hz, 2H), 8.22 (d, J = 7.5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.58, 91.23, 96.03, 122.74, 128.70, 129.53, 134.12, 137.03, 138.07, 177.84. IR : ν (cm^{-1}) 1620 (C=O), 2190 (C=C). MS : m/z = 390 M+. Anal. calcd for $C_{28}H_{22}O_2$: C, 86.13; H, 5.68. Found: C, 85.97; H, 5.64.

3-(4-Methoxyphenyl)-1-phenylprop-3-yn-1-one 1n Yield 53%. Mp 79–81 °C, lit. 81 °C.[25] ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 3.89 (s, 3H), 7.07 (d, J = 8.7 Hz, 2H), 7.60 (t, J = 7.4 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.75 (d, J = 8.7 Hz, 2H), 8.24

(d, $J = 7.4$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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)prop-3-yn-1-one 1o. Yield 55%. Mp 106–108 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H), 3.88 (s, 3H), 6.92 (d, $J = 8.8$ Hz, 2H), 7.16 (dd, $J = 8.1$, 1.9 Hz, 1H), 7.41 (t, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 2H), 7.69 (t, $J = 1.9$ Hz, 1H), 7.83 (dt, $J = 8.1$, 1.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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. MS : m/z (I_{rel},%) =266 (100) M+, 159 (42), 135 (29). Anal. calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.22; H, 5.27.

3-(4-Methoxyphenyl)-1-(3, 4-dimethylphenyl)prop-3-yn-1-one 1p. Yield 65%. Mp 103–104.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 6H), 3.84 (s, 3H), 6.92 (d, $J = 8.8$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 2H), 7.94-7.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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. MS : m/z (I_{rel},%)=264 (100) M+, 236 (35), 221 (22), 159 (14). Anal. calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.77; H, 6.05.

1-(3-Methoxyphenyl)-3-phenylprop-3-yn-1-one 1q Yield 72%. Mp 50–52 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 7.17 (dd, $J = 8.2$, 1.9 Hz, 1H), 7.38–7.51 (m, 4H), 7.66–7.69 (m, 3H), 7.83–7.87 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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. MS: m/z (I_{rel},%)=236 (100) M+, 129 (78). Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.32; H, 5.07.

NMR studies of 1,3-diarylpropynones

General technique for generation of the ions **2-m** in HSO_3F or CF_3SO_3H.

5-30 mg of substrate **1-m** were added to 0.8–1 ml of HSO_3F (mp −89°) frozen in an NMR tube at ~−110 °C (ethanol-liquid nitrogen). The temperature was raised up to −78 °C and a teflon capillary with internal diameter 1 mm was entered to the bottom of the NMR tube, passing through it a weak flow of argon during 5–15 min in order to obtain a homogeneous solution of ions (**1i–m**). The capillary was removed and internal standard CH_2Cl_2 was added. ^{1}H and ^{13}C NMR spectra of the ions **2–m** were recorded at −80 °C and 0 °C (Tables 1, 2).

Synthesis of indenones

General procedure for the cyclisation of 1,3-diarylpropynones **1a, b, n–q** into 3-arylindenones **5a, b, n–q** in superacids.

Substrate **1a, b, n–q** (0.4–1.0 mmol) was added to superacidic system (HSO_3F, CF_3SO_3H or CF_3SO_3H-SbF_5) with vigorous magnetic stirring at the temperature shown in Table 3. At this temperature the reaction mixture was stirred for 15 to 120 min (Table 3). Then the reaction mixture was slowly added dropwise to vigorously stirring ice–water mixture (~30 ml). Products **5a, b, n–q** were isolated ether after extraction with CH_2Cl_2 and subsequent washing of the CH_2Cl_2 solution with H_2O, aqueous $KHCO_3$, H_2O, drying over Na_2SO_4, and finally flash-chromatography on silica gel or after filtration of the solids formed after water quenching and recrystallization from MeOH–CH_2Cl_2. Yields of compounds **5a, b, n–q** are given in Table 3.

3-Phenylindenone 5a. Yield 43%. Red-orange oil, lit. oil.[26] ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.98 (s, 1H), 7.25–7.69 (m, 9H). NMR data of **5a** were comparable to those previously reported.[27]

3-(4-Methylphenyl)indenone 5b. Yield 75%. Orange crystals, mp 54–56 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 5.96 (s, 1H), 7.27-7.36 (m, 5H), 7.49-7.56 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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. MS : m/z (I_{rel},%)=220 (100) M+, 116 (40). Anal. calcd for C16H12O: C, 87.25; H, 5.49. Found: C, 86.51; H, 5.83.

3-(4-Methoxyphenyl)indenone 5n. Yield 54%. Red oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 5.95 (s, 1H), 7.02 (d, $J = 8.7$ Hz, 2H), 7.27-7.51 (m, 4H), 7.65 (d, $J = 8.7$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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. MS : m/z (I_{rel},%) = 236 (100) M+, 206 (17).

6-Methoxy-3-(4-methoxyphenyl)indenone 5o. Yield 95%. Red-orange crystals, mp 155–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3H), 3.86 (s, 3H), 5.84 (s, 1H), 6.77 (dd, $J = 8.1$, 2.5 Hz, 1H), 6.98 (d, $J = 8.9$ Hz, 2H), 7.08 (d, $J = 2.5$ Hz, 1H), 7.26 (d, $J = 8.1$ Hz, 1H), 7.62 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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. MS : m/z (I_{rel},%) = 266 (100) M+, 159 (72), 135 (59). Anal. calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.76; H, 5.27.

3-(4-Methoxyphenyl)-5,6-dimethylindenone 5p. Yield 95%. Yellow-orange crystals, mp 155–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 2.28 (s, 3H), 3.87 (s, 3H), 5.85 (s, 1H), 7.01 (d, $J = 8.6$ Hz, 2H), 7.13 (s, 1H), 7.27 (s, 1H), 7.63 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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. MS : m/z (I_{rel},%) = 264 (100) M+, 249 (25), 118 (8). Anal. calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.60; H, 6.16.

6-Methoxy-3-phenylindenone 5q. Yield 61%. Red crystals, mp 84–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H), 5.91 (s, 1H), 6.79 (dd, $J = 8.1$, 2.5 Hz, 1H), 7.12 (d, $J = 2.5$ Hz, 1H), 7.25 (d, $J = 8.1$ Hz, 1H), 7.48–7.50 (m, 3H), 7.64–7.67 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 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. MS : m/z (I_{rel},%)=236 (100) M+, 135 (26), 129 (83), 105 (12). Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 80.92; H, 5.01.

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