Synthesis of Polyalkylphenyl Prop-2-ynoates and Their Flash Vacuum Pyrolysis to Polyalkylcyclohepta[*b*]furan-2(2*H*)-ones

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Dedicated to *Manfred Hesse* on the occasion of his 65th birthday

A new method for the smooth and highly efficient preparation of polyalkylated aryl propiolates has been developed. It is based on the formation of the corresponding aryl carbonochloridates (*cf. Scheme 1* and *Table 1*) that react with sodium (or lithium) propiolate in THF at 25–65°, with intermediate generation of the mixed anhydrides of the arylcarbonic acids and prop-2-ynoic acid, which then decompose almost quantitatively into CO_2 and the aryl propiolates (*cf. Scheme 11*). This procedure is superior to the transformation of propynoic acid into its difficult-to-handle acid chloride, which is then reacted with sodium (or lithium) arenolates. A number of the polyalkylated aryl propiolates were subjected to flash vacuum pyrolysis (FVP) at 600–650° and 10^{-2} Torr which led to the formation of the corresponding cyclohepta[*b*]furan-2(2*H*)-ones in average yields of 25–45% (*cf. Scheme 14*). It has further been found in pilot experiments that the polyalkylated cyclohepta[*b*]furan-2(2*H*)-ones react with 1-(pyrrolidin-1-yl)cyclohexene in toluene at 120–130° to yield the corresponding 1,2,3,4-tetrahydrobenz[*a*]azulenes, which become, with the growing number of Me groups at the seven-membered ring, more and more sensitive to oxidative destruction by air (*cf. Scheme 15*).

1. Introduction. – In connection with our interest in thermally or photochemically induced double-bond shifts (DBS) in heptalenes as elements of potential molecular switches and data storage devices [1][2], we were interested in the synthesis of polyalkylated heptalene-1,2- and heptalene-4,5-dicarboxylates as starting materials for heptalenes substituted with chromogenic groups [2]. General observations allow the conclusion that the stability of heptalenes as [4*n*]annulenes will increase with the degree of twisting of the heptalene core that, in turn, is dependent on the number of substituents at the core, especially at the *peri*-positions (*cf.*, *e.g.*, [3]). Moreover, it can be expected that a buttressing effect of vicinally positioned alkyl groups at the heptalene skeleton will increase the thermal barriers that separate the DBS isomers[2]), as well as the two antipodes of the inherently chiral heptalenes [4][5].

Since heptalene-dicarboxylates are best prepared by thermal reaction of azulenes with dialkyl acetylenedicarboxylates, by a procedure originally developed by *Hafner et al.* [7] (see also [4][8]), we were interested in a practicable and variable synthesis of polyalkylated azulenes as precursors for the corresponding heptalene-dicarboxylates [9].

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[1]) Part of the diploma thesis of *M. N.*, University of Zurich, 1998.

[2]) For example, the establishment of the thermal equilibrium of dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate and dimethyl 1,6,8,10-tetramethylheptalene-4,5-dicarboxylate is characterized by $\tau_{1/2}(k_1 + k_{-1}) = 8.5$ min at 100° ((D_4)diglyme) [5]; with dimethyl 5,6,7,9,10-pentamethylheptalene-1,2-dicarboxylate and dimethyl 1,6,7,9,10-pentamethylheptalene-4,5-dicarboxylate with two pairs of vicinal Me groups, however, the same *peri*-substitution pattern shows $\tau_{1/2}(k_1 + k_{-1}) = 75$ min at 100° (toluene) [6].

Until now, practical syntheses of highly alkylated azulenes have not been published. In a broad and systematic study of the photoelectron (PE) spectra of alkylated azulenes, *Heilbronner*, *Hafner et al.* [10] have also investigated 1,4,5,6,7,8- and 2,4,5,6,7,8-hexamethylazulene. However, no details of their syntheses were given. One can speculate that a mixture of both azulenes was obtained by the established *Ziegler-Hafner* method (*cf.* [11]) from a pentamethylpyrylium salt and sodium methylcyclopentadienide. However, our own experience with the reaction between 4-ethyl-2,3,5,6-tetramethylpyrylium perchlorate [12] and sodium cyclopentadienide taught us that, in such cases, the cyclopentadienide attacks mainly C(4) of the pyrylium salt [13], perhaps due to maximum steric relief in the addition step, so that the formation of polyalkylated azulenes by the *Ziegler-Hafner* method is extremely inefficient[3]). *Alder* and *Whittaker* have introduced a versatile modification of the *Ziegler-Hafner* method, whereby 1-butylpyridinium salts are reacted with sodium cyclopentadienide in boiling DMF [18]. This variant is perfectly well-suited for the synthesis of azulenes without substituents at C(4) and C(8) (*cf.* also [19]), which are not available by the original pyrylium salt route (*cf.* [20]). However, the reaction of hexamethylpyridinium trifluoromethanesulfonate, which is accessible from pentamethylpyridine [16] and methyl trifluoromethanesulfonate, with sodium cyclopentadienide in boiling DMF gave yields of 4,5,6,7,8-pentamethylazulene in the range of 2% [17][4]). Therefore, the pyridinium-salt modification of the *Ziegler-Hafner* method is also not applicable to the synthesis of polyalkylated azulenes.

Fortunately, numerous further syntheses of azulenes, among them a number where cycloaddition reactions were utilized, have been exploited in recent years (*cf.* [21]). An interesting and variable synthesis of azulenes, based on the cycloaddition of cyclohepta[*b*]furan-2(2*H*)-ones and enamines or enol ethers, has been developed by *Nozoe et al.* (see, *e.g.*, [22]). The principle is shown in *Scheme 1*. Mainly, five-ring-substituted azulenes are conveniently prepared by this procedure, since it depends on the accessibility of the cyclohepta[*b*]furan-2(2*H*)-ones, for which *Nozoe et al.* (*loc. cit.*) have found a versatile synthesis in the base-catalyzed condensation reaction of tropolone derivatives with C–H acidic compounds such as alkyl carboxylates, cyanoacetates, malonates, or malononitrile. An example, starting with γ-thujaplicin as the tropolone component, is illustrated in *Scheme 2*.

However, a disadvantage is that the condensation reaction does not work well with alkylated tropolones such as 4,6,8-trimethyltropolone [23], as we have found [24]. In addition, the synthesis of variably substituted tropolones as precursors for the correspondingly substituted azulenes may become very tedious (*cf.* [25]). There is, however, an inspiring other way to synthesize substituted cyclohepta[*b*]furan-2(2*H*)-ones. More than 20 years ago, *Trahanovsky et al.* have investigated the flash vacuum pyrolysis (FVP; 650°/10^{-4} Torr) of phenyl propiolates **2** [26] and found that these

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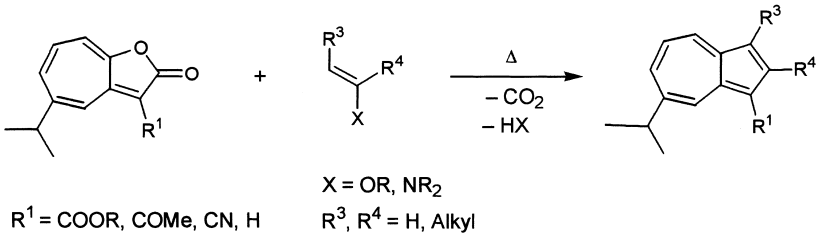
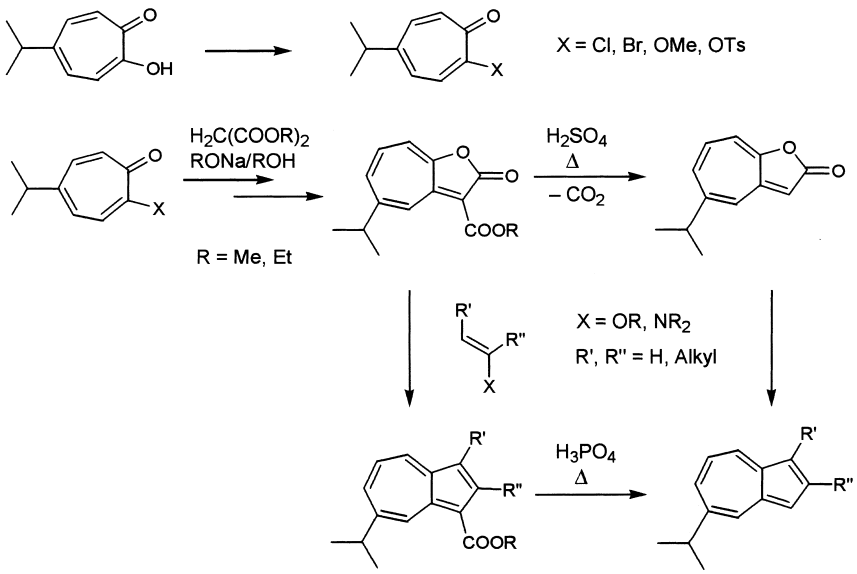
[3]) This is a general experience, as experiments by *Kurokawa* and *Anderson* [14], *Muth et al.* [15a], and *Porshnev et al.* [15b] reveal. Moreover, a systematic study of the reaction of pentamethylpyrylium methanesulfonate [16] with sodium cyclopentadienide showed that the maximum yields of 4,5,6,7,8-pentamethylazulene are well below 5% [17].

[4]) The pentamethylazulene is extremely sensitive to exposure to air [9]. Therefore, it cannot be excluded that some of the azulene, which is formed by no means in very low yield, is destroyed in the course of the tedious workup procedure.

Scheme 1



Scheme 2



compounds rearrange cleanly and in good yields into cyclohepta[*b*]furan-2(2*H*)-ones **3** (*Scheme 3*)[5]). By this way, the authors also obtained 4,6,8-trimethylcyclohepta[*b*]furan-2(2*H*)-one (**3c**) in yields up to 50%. The pyrolysis of *o*-cresyl propiolate led to the formation of a *ca.* 3:1 mixture of 4- and 8-methylcyclohepta[*b*]furan-2(2*H*)-one (4-Me-**3d**, $R^1 = Me$, $R^2 = R^3 = H$, and 8-Me-**3d**, $R^1 = R^2 = H$, $R^3 = Me$, resp.), an observation that indicates that the addition of the ethenylidene component of **2d** is slightly favored at the unsubstituted side of the *o*-cresyl part. Since highly alkylated phenols are commercially available or can easily be synthesized, *Trahanovsky*'s

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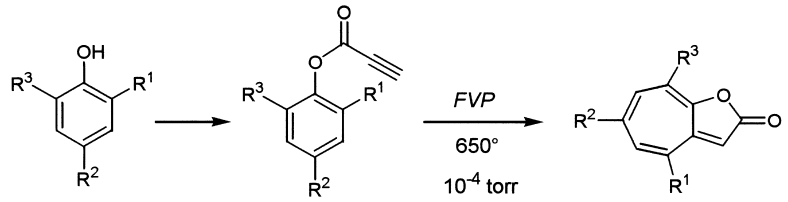
[5]) We will not go into the details of this remarkable high-temperature rearrangement. But it may be mentioned that it is crucially connected to the temperature dependence of the alkyne-ethenylidene equilibrium (–C≡C–H⇆–CH=C:), which lies at temperatures $< 600°$ completely on the side of the alkyne structure (see, *e.g.*, [27]), but is shifted towards the ethenylidene structure at temperatures $> 600°$ (*cf.* [28]). At 650°, the ethenylidene component of the phenyl propiolates **2** adds intramolecularly to the adjacent C=C bonds of the phenolic part, followed by ring enlargement of the norcaradiene → tropilidene type to the observed furan-2(2*H*)-ones **3**.

Scheme 3



1 **2** **3**

1, **2**, **3**	R^1	R^2	R^3	Yield **2** → **3** [%]
a	H	H	H	30–45
b	Me	H	Me	45–50
c	Me	Me	Me	45–50
d	Me	H	H	50–60 [b])
	H	H	Me	

[a]) According to *Trahanovsky et al.* [26].
[b]) A mixture of 4-Me-**3d** and 8-Me-**3d** is formed (see text).

procedure may open a variable and practical pathway to polyalkylated cyclohepta[*b*]-furan-2(2*H*)-ones **3** as attractive precursors for corresponding azulenes[6]).

In the following sections, we report a new esterification procedure for polyalkylated phenols with propiolic acid and on the general applicability of *Trahanovsky*'s method for the synthesis of highly substituted cyclohepta[*b*]furan-2(2*H*)-ones **3**.

2. Preparation of Aryl Propiolates. – The established procedure for the synthesis of these esters is the acylation of the corresponding phenolates with propynoyl chloride in a two-phase system in the presence of aqueous NaOH (*Schotten-Baumann* reaction; see, *e.g.*, [29]). *Jung* and *Buszek* described the formation of (2,6-dimethylphenyl) propiolate (**2b**) in 94% yield by deprotonation of **1b** with NaH in Et_2O, followed by the reaction with propynoyl chloride at $-78°$ [30]. The disadvantage of these procedures is that propynoyl chloride is not commercially available due to its instability[7]). It can be prepared from propiolic acid and PCl_5 at 4° in yields of 45–50% [31] (see also [32]). To remove $POCl_3$ as the second product, it has to be purified by trap-to-trap condensation. However, the thus-treated propynoyl chloride still contains some $POCl_3$ and also traces

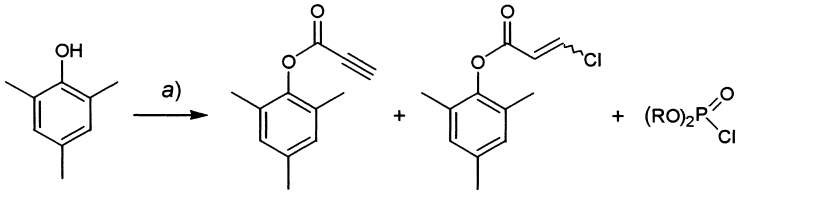
[6]) It is worthwhile to mention that, in the very first of our FVP experiments, *M. N.* sublimed a small quantity of crystalline **2c** through the red-hot zone, generated with the flame of a *Bunsen* burner, of a quartz tube (inner diameter *ca.* 5 mm) under vacuum (*ca.* $5 \cdot 10^{-2}$ Torr). The formation of **3c** was at once indicated by the development of an intensely yellow ring in the cold zone of the quartz tube. It was contaminated only with some starting material. This pilot experiment convinced us that, in principle, FVP of phenyl propiolates is an easy-to-handle procedure that should also be applicable to higher alkylated phenyl propiolates.

[7]) The acid chloride is a lachrymose, low-boiling compound (58–60°/760 Torr) that readily decomposes in air and daylight. It can be stored for some time in the dark at dry-ice temperature. It decarbonylates already at the boiling point under normal pressure to chloroacetylene, which, in turn, is a difficult-to-handle compound.

of HCl, which form with propynoyl chloride 3-chloroacryloyl chloride as the third component built in the chloride-formation reaction with PCl_5.

We tested the ester formation with mesitol (**1c**) in a number of runs. Following *Jung* and *Buszek*'s protocol, we obtained the phenyl ester **2c** in average yields of 70–80% (*Scheme 4*). Nevertheless, the raw propiolate had to be purified by chromatography on silica gel, because it was contaminated with the β-chloroacrylate **4** and diphenyl chlorophosphate **5** as a result of the presence of $POCl_3$ and HCl in the propynoyl chloride. The comparably expensive propiolic acid, the moderate yields of acid-chloride formation, and the difficulties obtaining really pure material led us to search for other ester-forming processes of propiolic acid and alkylated phenols.

Scheme 4



1c **2c** (70–80%) **4** (5–10%) **5** (10–12%)[a])

a) 1. 1.1 Mol-equiv. NaH, Et_2O, 20°; 2. Propynoyl chloride[b]), −80° → r.t.

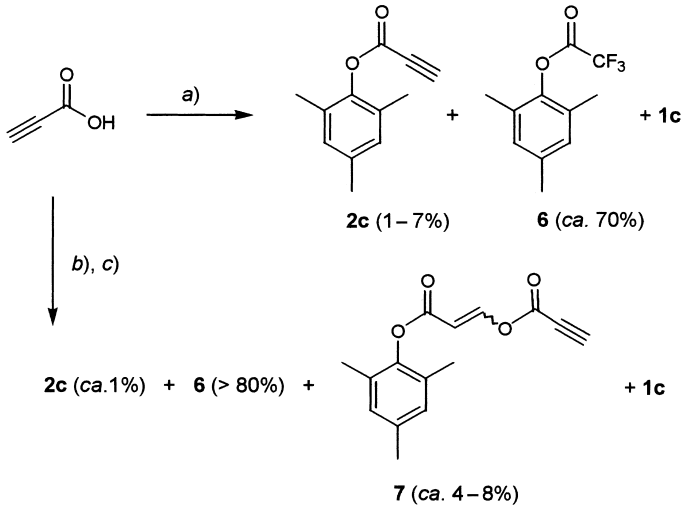
[a]) R = 2,4,6-Trimethylphenyl. [b]) From the reaction of propiolic acid with PCl_5 (see text).

Phenyl acrylates have been successfully prepared by reaction of phenols with the mixed anhydride of acrylic acid and CF_3COOH [33]. The latter compound is formed in an exothermic reaction from acrylic acid and $(CF_3CO)_2O$ (TFAA) [33]. Mixing of propiolic acid and TFAA showed no exothermicity (*cf.* [34]) and the reaction resulted mainly in the formation of 2,4,6-trimethylphenyl trifluoroacetate (**6**; *Scheme 5*). The addition of TFAA to lithium propiolate followed by addition of **1c** gave again mainly the trifluoroacetate **6**, accompanied by small amounts of **2c** and some enol ester **7**.

Brown and *Eastwood* prepared phenyl 2-butynoate from but-2-ynoic acid (tetrolic acid) and phenol in CH_2Cl_2 in the presence of dicyclohexylcarbodiimide (DCC) and catalytic amounts of 4-(dimethylamino)pyridine (DMAP) [35]. The same conditions applied to propiolic acid and **1c** led to an average turnover of 50–70% of **1c** (*Scheme 6*). The expected ester **2c** was formed in moderate yields, but, accompanied by appreciable amounts of (*E*)-**8** and (*Z*)-**8**, the *Michael* adducts of **1c** and **2c**.

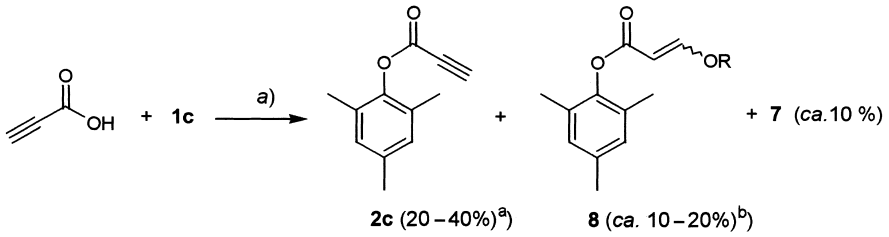
Phenyl carboxylates have also been prepared from carboxylic acids and phenols in the presence of Ph_3P/CCl_4 and a tertiary base [36]. However, all reactions performed with propiolic acid and **1c** led within minutes to a blackening of the reaction mixture and resin formation. *N*,*N*′-Carbonylbis[imidazol] has been similarly applied in phenyl-ester formation [37]. Indeed, the addition of propiolic acid to the coupling reagent, dissolved in THF, led to the expected CO_2 evolution, but, the reaction mixture turned yellow, and an insoluble gum-like material started to separate before any phenol **1c** could be added.

Scheme 5



a) 1. TFAA, 20°; **1c** in toluene, 20°, 36 h. *b*) 1. LiH, THF, 5°, 3 h; 2. TFAA, 20°, 1 h. *c*) **1c**, 20°, 12 h.

Scheme 6



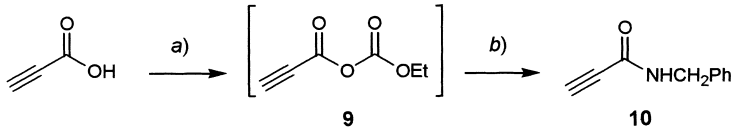
a) DCC + 1 mol-% DMAP, CH_2Cl_2, r.t.

[a]) 30–50% **1c** are recovered. [b]) R = 2,4,6-Trimethylphenyl.

In 1993, *Coppola* and *Damon* reported an elegant and efficient synthesis of *N*-benzylpropynamide (**10**), which otherwise is difficult to prepare (*Scheme 7*) [38]. The authors formed the mixed anhydride **9** of ethyl carbonic acid and propiolic acid in THF *in situ*, which was then reacted with $PhCH_2NH_2$ to give amide **10** in 77% yield.

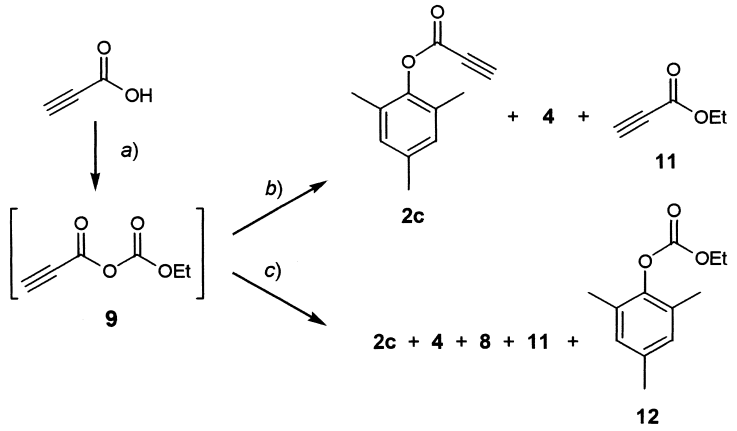
We tried to apply this procedure also to the formation of **2c** from propiolic acid and **1c**. The reaction of the *in situ* generated mixed anhydride **9** with **1c** led to a weak

Scheme 7



a) 1. LiH, THF, r.t., 18 h; 2. Ethyl carbonochloridate, –10° → r.t. *b*) $PhCH_2NH_2$, 5° → r.t., 4 h.

Scheme 8



a) See *a*) in *Scheme 7*. *b*) **1c**, THF, 20–45°, 5–24 h. *c*) 2,4,6-$Me_3C_6H_2OM$ (M = Li, Na), THF, 20–45°, 2–12 h.

evolution of CO_2, which could be enhanced by warming of the reaction mixture to 40–45°. However, the results of our first experiments were disappointing (*Scheme 8*). The expected ester **2c** could indeed be observed and obtained in yields of *ca.* 20%, but up to 50% of **1c** was still present. Interestingly, beside that we also found in the reaction mixture *ca.* 30% of a 1:1 mixture of the (*E*)- and (*Z*)-isomer of the β-chloroacrylate **4**. Moreover, appreciable amounts of ethyl propiolate (**11**) were finally identified[8]). The situation did not improve when we worked with the sodium salt of **1c** in order to utilize the enhanced nucleophilicity of the phenolate of **1c**. In addition to the discussed products, we found the (*E*)- and (*Z*)-isomer of the β-aryloxyacrylate **8**, which we had already identified in the DCC-mediated reaction of **1c** and propiolic acid (*Scheme 6*). At the end, the mixed carbonate **12** appeared also in the reaction mixture.

The adaptation of the *Coppola-Damon* procedure to the preparation of aryl propiolates was initially not very promising. Nonetheless, it was evident from a thorough review of the origin of all observed side products that most were secondary products from *Michael*-type addition of the initially formed **2c**. Only ethyl propiolate (**11**) and the mixed carbonate **12** were exceptions. The appearance of **11** in the reaction mixture finally proved to be the key step in the aryl-ester formation. At the moment when the mixed anhydride **9** is attacked by the phenolate of **1c** at the desired position under formation of **2c**, EtO^- ions enter the scene and become, during the course of the reaction, in an autocatalytic manner, competitors of the phenolate ions (*Scheme 9*). In other words and in view of earlier work on mixed anhydrides (see later), the reaction would be likely to run much cleaner if the EtO residue in the mixed anhydride were to be replaced by the corresponding aryloxy moiety of the phenol to be esterified with propiolic acid (*Scheme 10*). The only by-products that could also be formed in analogy

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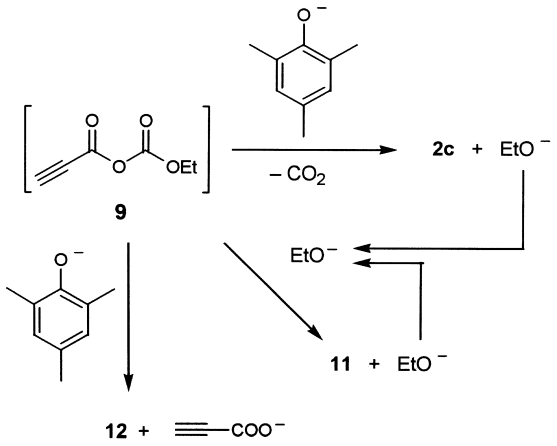
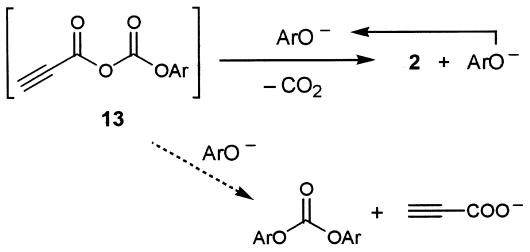
[8]) In our first experiments with the *Coppola-Damon* system, we had overlooked the formation of **11** due to its volatility (b.p. 117–120°/760 Torr). However, the mass balance of the identified products accounted only for *ca.* 60%. Thereafter, we observed that the THF, distilled off from the reaction mixture, exhibited a pugnant smell, which could finally be attributed to the ester **11** (for details of the analytical procedures see *Exper. Part*).

Scheme 9



Scheme 10



to **12** would be diaryl carbonates. The corresponding aryl carbonochloridates **14**, necessary for the mixed-anhydride formation, could be prepared in excellent yields from $COCl_2$ in toluene in the presence of *N*,*N*-dimethylaniline (*Scheme 11* and *Table 1*) (*cf.* [39][40]). When these carbonochloridates were added to a suspension of lithium propiolate, generated from propiolic acid and LiH in THF[9]), and the mixture was heated at 25 to 65°, a gentle CO_2 evolution took place, and the pure aryl propiolates **2** could be isolated in superb yields (*Scheme 11* and *Table 2*). In only one case did our procedure fail: [2,4,6-tri(*tert*-butyl)phenoxy]carbonyl chloride (**14k**) could be obtained in 75% yield (*cf.* [41]), but no reaction was observed with sodium propiolate[9]) in THF. The yield of the aryl propiolates dropped below 80% in three other cases (**2g**, **2h**, and **2l**) due to the accompanying formation of diaryl carbonate. These observations clearly indicate that propiolate formation from the mixed anhydrides **13** generated *in situ* is governed mainly by steric factors. However, the leaving group quality of the aryloxy

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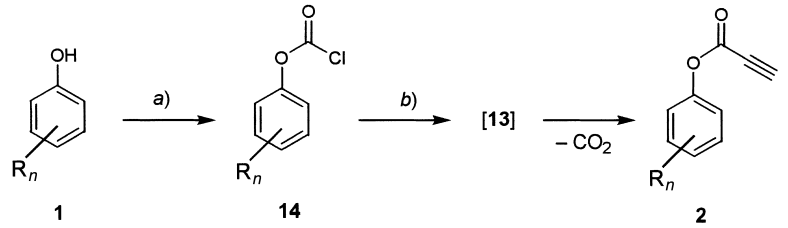
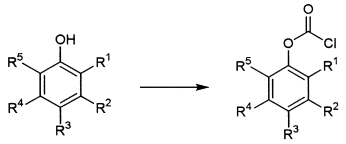
[9]) We found in later experiments that it is much easier to work with sodium propiolate, which can be prepared by neutralization of aqueous solutions of propiolic acid with concentrated aqueous NaOH. The removal of H_2O and drying in high-vacuum leads to a cream-colored salt whose color changes slowly to pale violet in the air and on exposure to daylight. However, an ivory color persists when the salt is protected against light and stored in the dark at –20°. The deprotonation of propiolic acid in THF with LiH has the disadvantage that the lithium propiolate forms as a suspension in THF, and 12–18 h are needed for the completion of the deprotonation reaction with the suspended LiH.

Scheme 11



a) 1. 1.3 Mol-equiv. $COCl_2$ (20% in toluene), r.t.; 2. 1 mol-equiv. *N,N*-dimethylaniline, $0 \rightarrow 5°$, 5 – 24 h. *b*) 1 Mol-equiv. HC≡C–COOM (M = Li, Na), THF, 25 – 65°, 2 – 12 h.

Table 1. *Preparation of Aryl Carbonochloridates* **14** [a])

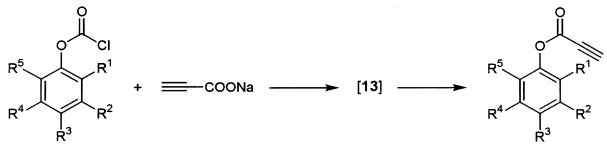


1, 14	R^1	R^2	R^3	R^4	R^5	Reaction time [h] [b])	Purification [c])	Yield [%]	Reference yield [%]
c	Me	H	Me	H	Me	18	*D*	93	95.5 [39]
e	Me	Me	Me	Me	Me	18	*C*	95	–
f	Me	Me	H	Me	Me	18	*D* + *C*	93	–
g	H	Me	Me	Me	H	15	*D*	90	–
h	H	Et	H	Et	H	8	*D*	77	–
i	i-Pr	H	H	H	i-Pr	24	*D* + *C* [d])	*ca.* 90	98 [39]
k	*t*-Bu	H	*t*-Bu	H	*t*-Bu	2.5	*C* [d])	75 [e])	*ca.* 50 [f]) [41a]
l	H	–C_4H_4– [g])		H	H	12	*D* + *C*	85	52 [39]

[a]) According to *Scheme 11.* [b]) After addition of *N,N*-dimethylaniline. [c]) *D* = bulb-to-bulb distillation, *C* = crystallization at 4°. [d]) Crystallization at −20°. [e]) Deprotonation with NaH in THF (*cf.* [41a]). Some not reacted **1k** could not be separated from **14k**. [f]) As intermediate; *via* the Li salt a quantitative yield of **14k** has been reported [41b]. [g]) Naphthalen-2-yl compound.

moiety in the mixed anhydrides, as expressed by the pk_A values of the corresponding phenols, seems to play a role, too. Otherwise, the enhanced carbonate formation in the case of naphthalen-2-ol (**1l**; $pk_A(H_2O, 25°) = 9.51$) in comparison with 3,4,5-trimethyl- or 3,5-diethylphenol (**1g** and **1h**, resp.; $pk_A(H_2O, 25°)$ of **1g** = 10.25), which all have non-substituted *o*-positions, is difficult to understand. All our observations are in agreement with a controlled autocatalytic decomposition of the mixed anhydrides **13** initiated by any nucleophile that attacks their carbonic part and liberates the corresponding aryloxides as chain reactants (*Scheme 10*). The nucleophilic chain reaction is interrupted by diaryl-carbonate formation. Nevertheless, propiolate ions are generated by this process that can ignite again the nucleophilic chain process. Moreover, according to our reaction protocol, the mixed anhydrides **13** are formed *in*

Table 2. *Preparation of Aryl Propiolates* **2** [a])



14 **2**

14, **2**	R^1	R^2	R^3	R^4	R^5	Reaction time [h] [b])	Reaction temp. [°]	Yield [%]
a	H	H	H	H	H	2	25 → 40	70 [c])
c	Me	H	Me	H	Me	18	25 → 45	90
e	Me	Me	Me	Me	Me	24	25 → 65	91
f	Me	Me	H	Me	Me	15	25 → 65	95
g	H	Me	Me	Me	H	2.5	25 → 40	75 [c])
h	H	Et	H	Et	H	2	30 → 55	72 [c])
i	i-Pr	H	H	H	i-Pr	18	25 → 65	85
k	*t*-Bu	H	*t*-Bu	H	*t*-Bu		no reaction	
l	H	$-C_6H_4-$ [d])		H	H	4	25 → 65	36 [e])

[a]) According to *Scheme 11*. [b]) After crystallization and/or distillation; not optimized. [c]) 20–30% of the corresponding diaryl carbonate was also isolated. [d]) Naphthalen-2-yl compound. [e]) 40% of di(naphthalen-2-yl) carbonate was also isolated.

situ from the corresponding (aryloxy)carbonyl chlorides and propiolate ions, and, hence, propiolate and chloride ions as nucleophiles are present during the whole reaction in molar proportion, whereby progressively propiolate ions are exchanged by chloride ions.

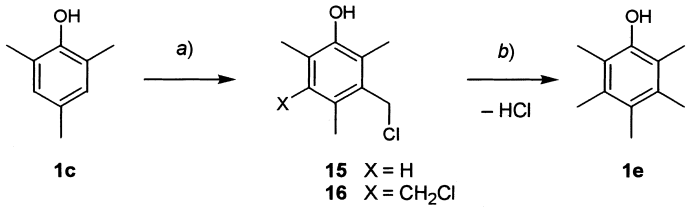
The mechanistic picture of the autocatalytic decomposition of the carboxylic carbonic anhydrides **13** that we have sketched here is in agreement with earlier investigations and observations (*cf.* [42])[10]), in particular with those of *Windholz* [44] and *Green* [45], who found that mixed anhydrides of type **9**, composed of carboxylic acids with electron-withdrawing groups, such as in cyano-, (*p*-nitrophenyl)- or trifluoroacetic acid, and alkylcarbonic acids give, on gentle heating, a nearly quantitative evolution of CO_2 with formation of the corresponding alkyl carboxylates in 80–95% yield. On the other hand, steric crowding in the α-position of the carboxylic part, *e.g.*, diphenylacetic acid, favors formation of the symmetric carboxylic anhydrides, and the corresponding esters are the minor part of the reaction mixtures [44]. Heating of pure mixed anhydrides of type **9** in the absence of external nucleophiles also reduces the ester formation in favor of the generation of the symmetric carboxylic anhydrides [44][46]. Added tertiary amines act as catalysts and lower the decomposition temperatures without markedly affecting the product composition [46b]. Moreover, *Tarbell* and *Longosz* [46b] have demonstrated that the purely thermal reaction of the mixed anhydride of benzoic and (*R*)-2-octylcarbonic acid takes place with complete retention of configuration with respect to the formed (oct-2-yl) benzoate as well as di(oct-2-yl) carbonate that was built as minor product. The observed retention of

[10]) The chemistry of mixed carboxylic carbonic anhydrides can be traced back to the time of *Alfred Einhorn* [43].

configuration excludes any intramolecular cyclic transition state for ester formation as has been proposed [44].

3. Preparation of Highly Alkylated Phenols. – A number of highly methylated phenols such as **1c**, **1f**, or **1g** are or have been commercially available (see *Exper. Part*). Others, such as pentamethylphenol (**1e**) are available in only small quantities at

Scheme 12



a) CH_2O (30% in H_2O)/HCl, AcOH, 55° [47] or $MeOCH_2Cl/SnCl_4$, CH_2Cl_2, r.t. [48]. *b*) H_2 (Pd/C), MeOH [47] or $LiAlH_4$/THF [49].

comparably high prices. The established procedure for the preparation of **1e** is the bis(chloromethylation) of mesitol (**1c**), followed by hydrogenolysis of the two Cl–C bonds (*Scheme 12*).

Wegler and *Regel* performed the chloromethylation reaction in glacial AcOH with HCHO in excess (30% aqueous solution) and gaseous HCl at 55° [47]. The authors reported yields of **16** of *ca.* 45% and mentioned no further detailed difficulties in the purification of **16**. Some years later, the chloromethylation reaction of **1c** has been described with chloromethyl methyl ether in CH_2Cl_2 and $SnCl_4$ as catalyst [48]. The bis(chloromethylated) phenol **16** was obtained in a yield of 65%.

The hydrogenolysis of **16** in MeOH in the presence of Pd/C as catalyst led to pentamethylphenol (**1e**) in a yield of 58%. However, the reductive cleavage of the Cl–C bonds in **16** with $LiAlH_4$ in THF seems to be more effective since a yield of **1e** of 95% has been reported by *H. Schmid* and co-workers [49].

We tried to substitute the gaseous HCl in the protocol of *Wegler* and *Regel* with 39% aqueous HCl. However, GC/MS analyses of the reaction mixture showed that, with increasing reaction time, growing amounts of several highly substituted benzyl phenyl ethers were also formed and could not be removed chromatographically in a satisfactory manner. Hydrogenolysis of the whole reaction mixture as such led to only small amounts of **1e**. Also the stepwise preparation of **1e** *via* the isolated 3-chloromethylated phenol **15** did not markedly improve the yields of **16**. Therefore, we searched for other procedures for the preparation of **1e** from **1c**.

Recently, the bromomethylation reaction of benzene derivatives has been rediscovered (*cf.* [50][51])[11]). The reaction is performed in glacial AcOH, containing HBr,

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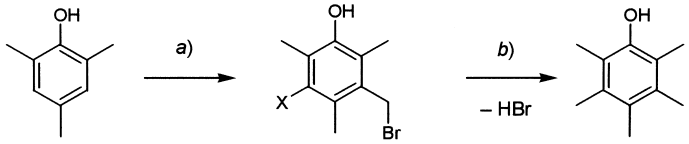
[11]) In a footnote *A. W.* and *R. H. Van der Made* [50] remarked that the bromomethylation reaction for benzene derivatives is not well-known very probably due to a mistranslation. *Darzens*, who was one of the first to investigate the bromomethylation of benzene derivatives already in 1936 [52], reported in French language that the yields are much better than in chloromethylations. *Fuson* and *McKeever* translated this statement incorrectly in their review entitled '*Chloromethylation of Aromatic Compounds*' [53], and from this time on, the wrong statement was perpetuated in the later literature.

with paraformaldehyde as the C_1 source. These conditions could also be applied for the bisbromomethylation of mesitol (*Scheme 13*). With dependence on the reaction time and temperature, the mono- or disubstituted phenol, **17** and **18**, respectively, is formed. We could not suppress the formation of up to 20% of the acetate of **1c**, which made the purification of the phenol **18** more difficult (see *Exper. Part*).

Scheme 13



1c **17** X = H **18** X = CH_2Br **1e**

a) $(CH_2O)_n$, HBr in AcOH, 50 → 85°, 7 h. *b*) H_2 (Pd/C), AcOH/AcONa (or *N,N*-dimethylaniline).

The hydrogenolysis of **18** could be performed in the presence of Pd/C in EtOH, AcOEt or AcOH. Without any further addition, the uptake of H_2 slowed distinctly after a third of the calculated volume of H_2 had been consumed. However, it could be started again by addition of AcONa[12]). Under these conditions, **1e** was obtained in 70–85% yield.

We also prepared **1e** in 65% yield by *Friedel-Crafts* alkylation of **1c** in boiling MeI in the presence of $AlCl_3$ (see *Exper. Part*). These conditions, however, could not be applied to the synthesis of 3,5-diethyl-2,4,6-trimethylphenol. The reaction of **1c** in EtBr in the presence of $AlCl_3$ at ambient temperature led after several hours to a reaction mixture from which a crystalline phenol with the expected mass was obtained. Nevertheless, the ^{1}H- as well as the ^{13}C-NMR spectrum of this compound exhibited three *s* signals for three Me groups, as well as signals for two non-equivalent Et groups, which, for symmetry reasons, excluded the structure of a 3,5-diethyl-2,4,6-trimethylphenol[13]).

4. Formation of Cyclohepta[*b*]furan-2(2*H*)-ones. – We performed the FVP reactions of the aryl propiolates as pilot experiments in an improvised apparatus consisting of an horizontally mounted, 40-cm-long quartz tube with an outer diameter of 10 mm and filled in its middle part to a length of 8–12 cm with quartz splinters, kept in place by loose plugs of quartz wadding at each end. One end of the quartz tube was linked to a small evaporation bulb and the other end to a cooling trap for the pyrolysate. The middle part of the quartz tube was heated with an oven for combustion analyses. The temperature in the hot zone of the filled quartz tube was controlled with an electronic digital thermometer and kept at 650–670° during the pyrolysis experiments. The pressure in the apparatus of *ca.* $5 \cdot 10^{-2}$ Torr was maintained with

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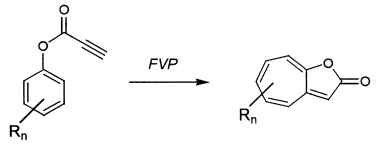
12) In later experiments, we used *N,N*-dimethylaniline as base for the neutralization of the HBr formed.

13) If we allow a complete permutation of the Me and Et substituents as the result of *Jacobsen*-type rearrangements four unsymmetrically substituted diethyltrimethylphenols are possible.

an oil pump. The dimensions of the apparatus allowed the pyrolysis of 0.5–2 g of the aryl propiolates.

The six cyclohepta[*b*]furan-2(2*H*)-ones that we prepared with this improvised FVP apparatus are shown in *Table 3*. All FVP reactions were performed several times, and the range of observed yields is also indicated in *Table 3*. The formation of furanones **3a**

Table 3. *Formation of Highly Alkylated Cyclohepta[*b*]furan-2(2*H*)-ones* **3** via *FVP* (at 650–670°/0.01 Torr)



2 **3**

R_n in **2**	No.	R_n in **3**	No.	Observed range of yields [%] [a])
None	**2a**	none	**3a**	35–50
2,4,6-Me_3	**2c**	4,6,8-Me_3	**3c**	30–50
2,3,4,5,6-Me_5	**2e**	4,5,6,7,8-Me_5	**3e**	15–40
2,3,4,6-Me_4	**2f**	4,5,7,8-Me_4	**3f**	25–45
3,4,5-Me_3	**2g**	5,6,7-Me_3	**3g**	30–45
3,5-Et_2	**2h**	5,7-Et_2	**3h**	35–45

[a]) After chromatography on silica gel and crystallization.

and **3c** has already been studied by *Trahanovsky et al.*, and yields of 30–50% have been reported (*Scheme 3*) [26]. We obtained similar yields with the simplified apparatus. The range of yields that we observed in the formation of the new cyclohepta[*b*]furan-2(2*H*)-ones can, therefore, be regarded as representative.

The general spectral features of a large number of simply substituted cyclohepta[*b*]furan-2(2*H*)-ones have already been reported by various authors (see, *e.g.*, [22][26][54][55]), but, to the best of our knowledge, not in a systematic and comparative way. Since we had new furanones **3** with an increasing number of alkyl substituents at the seven-membered ring in our hands, we studied their spectroscopic properties in greater detail.

4.1. *Structural and Spectroscopic Properties.* All furanones possess an almost planar structure, with the exception of the pentamethyl derivative **3e**. Its X-ray crystal-structure analysis revealed a slight deviation from planarity with ring-torsion angles of 7.4(4)°, −16.3(4)°, and 10.9(4)° at the fragment C(4)=C(5)−C(6)=C(7) [9]. Moreover, the bonds C(5)−C(6) and C(6)=C(7) represent with 146.2(3) and 138.7(3) pm, respectively, the longest σ and π bonds in the molecule, and also exhibit the largest bond-length deviations from the almost perfectly planar parent structure **3a** (C(5)−C(6): 142.4(3) pm and C(6)=C(7): 134.9(3) pm [9][14]).

4.1.1. *UV/VIS Spectra.* The spectra of the parent compound **3a** and its pentamethyl derivative **3e** in cyclohexane and in MeCN are displayed in *Figs. 1* and *2*. The absorbance data of all measured furanones **3** are collected in *Table 4*. The basal structure **3a** clearly exhibits in cyclohexane three spectral regions defined by a broad,

[14]) We have redetermined the X-ray crystal structure of **3a**, which was first published by *Saseda* in 1959 [56].

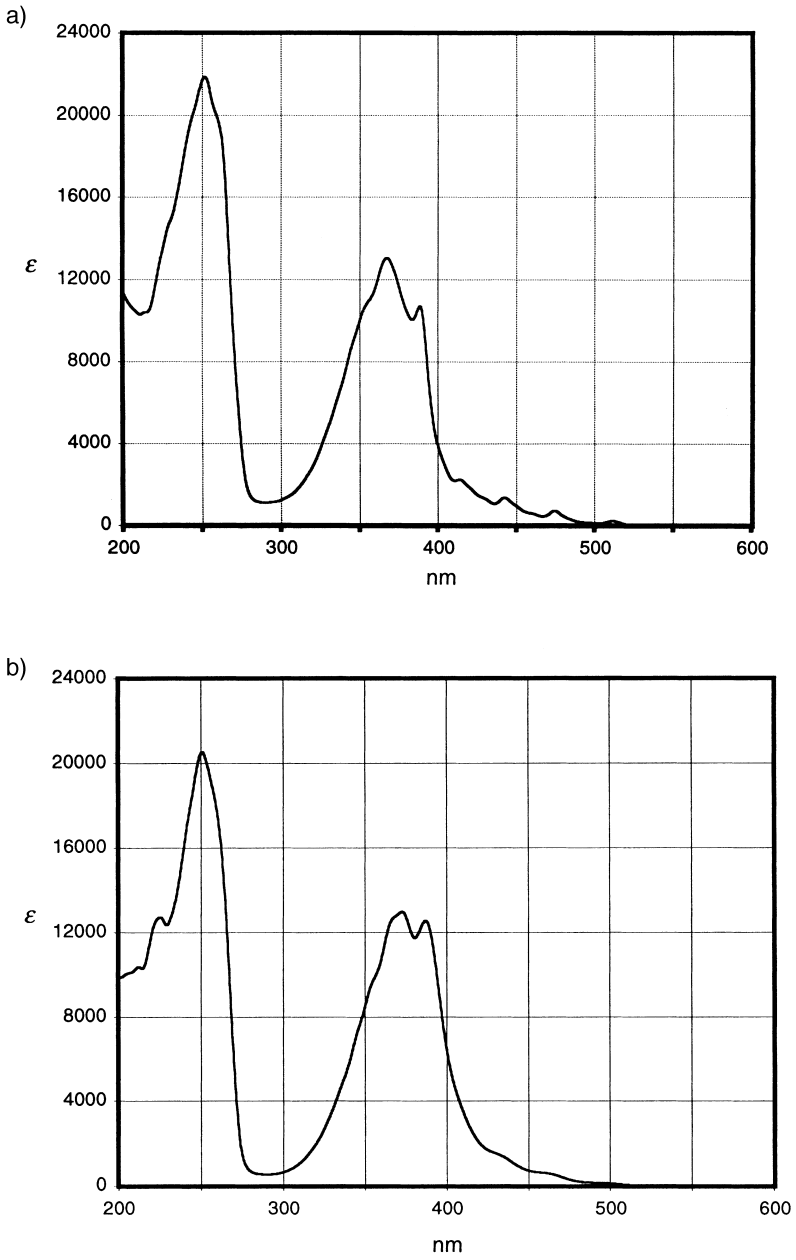


Fig. 1. *UV/VIS Spectrum of cyclohepta[*b*]furan-2(2*H*)-one* (**3a**): a) *in cyclohexane;* b) *in MeCN*

vibrationally structured absorption band in the range of 512 – 414 nm. This is followed by a strong and broad absorption band at 350 – 390 nm with a spectral half-width of *ca.* 60 nm, fully separated from a third strong absorption band at 252 nm. The spectral habitus of **3a** is markedly changed in MeCN. The broad and vibrationally structured

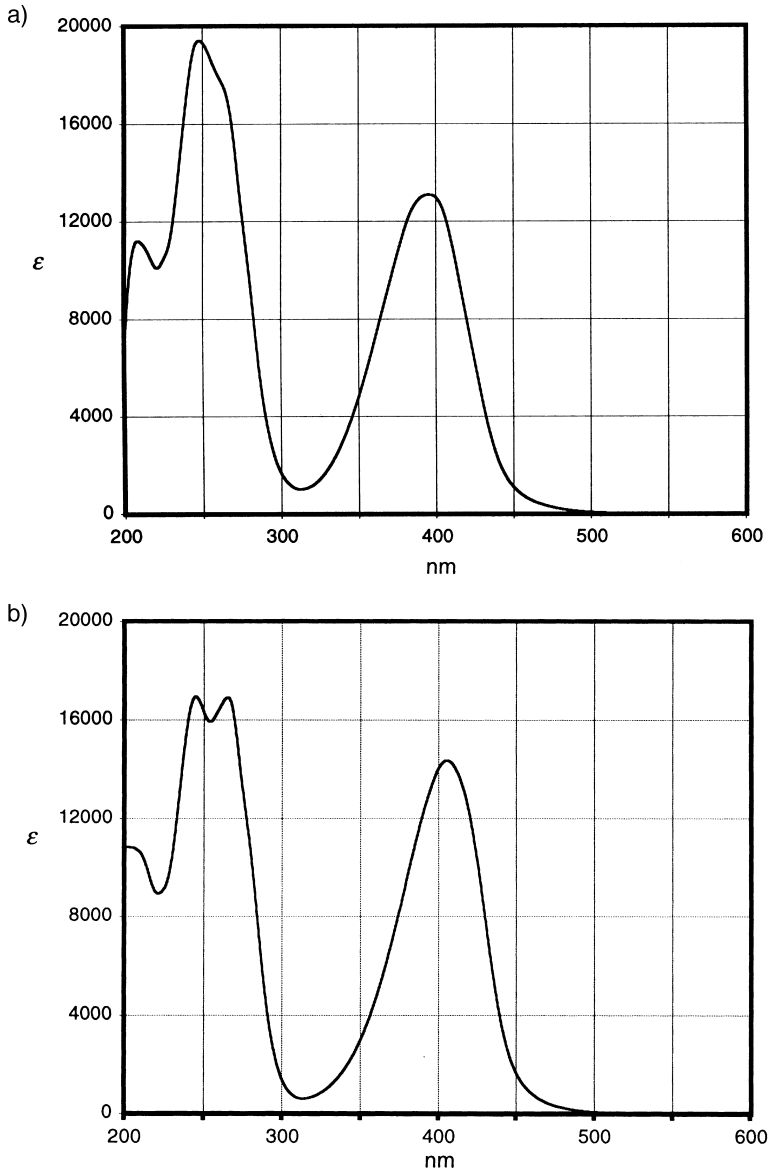


Fig. 2. *UV/VIS Spectrum of 4,5,6,7,8-pentamethylcyclohepta[*b*]furan-2(2*H*)-one* (**3e**): a) *in cyclohexane;* b) *in MeCN*

absorption band is hypsochromically shifted by *ca.* 23 nm, whereas the strong absorption band centered at *ca.* 370 nm has still a half-width of *ca.* 60 nm, but with a slight bathochromic shift of *ca.* 7 nm of the gravity of the band. The third and strongest absorption band appears more or less at the same place as in cyclohexane with almost no alteration in its habitus. The UV/VIS spectra of the pentamethyl form **3e** are much

simpler than those of **3a**. The vibrationally structured band at the longest wavelength region is no longer recognizable, neither in cyclohexane nor in MeCN. The second strong absorption band appears symmetrically centered and with a spectral half-width of 66 and 61 nm at 395 and 405 nm in cyclohexane and MeCN, respectively.

Table 4. *UV/VIS Data of the Cyclohepta[*b*]furan-2(2*H*)-ones* **3** [a])

Substituents in **3**	No.	Transitions			
		$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$ (1)	$\pi \rightarrow \pi^*$ (2)	Minima
None	**3a**	489 (sh, 150)	387 (12550)	256 (sh, 19160)	381 (11740)
		457 (sh, 610)	373 (12970)	251 (20520)	289 (520)
		430 (sh, 1500)	369 (sh, 12810)	225 (12720)	229 (12350)
			351 (sh, 8660)		
	3a [b])	488 (sh, 190)	387 (14700)	258 (sh, 20960)	380 (13650)
		453 (sh, 780)	373 (14660)	251 (23150)	289 (440)
		427 (sh, 1980)	370 (sh, 14340)	223 (14350)	230 (13300)
			351 (sh, 9220)		
	3a [c])	512 (220)	389 (10680)	259 (sh, 20130)	503 (100)
		474 (710)	367 (13030)	252 (21850)	467 (430)
		443 (1350)	362 (sh, 12030)	248 (sh, 20960)	436 (1050)
		414 (2240)	352 (sh, 10220)	238 (sh, 17570)	411 (2180)
					384 (10010)
					290 (1100)
					211 (10280)
4,6,8-Me_3	**3c**	– [d])	392 (16470)	266 (sh, 21320)	311 (1220)
			368 (sh, 12350)	256 (24360)	239 (16170)
				231 (18310)	
5,6,7-Me_3	**3g**	*ca.* 490 (sh, *ca.* 300)	396 (17400)	271 (sh, 15200)	300 (480)
			385 (sh, 15780)	260 (22680)	221 (11440)
		458 (sh, 1340)		236 (sh, 16300)	
4,5,7,8-Me_4	**3f**	– [d])	397 (15680)	272 (sh, 20600)	302 (410)
			384 (sh, 14000)	265 (24220)	243 (13570)
				232 (17120)	215 (10540)
4,5,6,7,8-Me_5	**3e**	430 (sh, 7700)	406 (14330)	277 (sh, 12000)	313 (590)
				265 (16900)	254 (15910)
				245 (16900)	221 (8930)
	3e [c])	–	395 (13080)	277 (sh, 11330)	312 (990)
			368 (8900)	261 (sh, 17830)	221 (10090)
				248 (19410)	

[a]) In MeCN if not otherwise stated; λ [nm]; in parentheses, ε. [b]) In MeOH. [c]) In cyclohexane. [d]) Weak tailing recognizable.

All these spectral features, which are also reflected in the UV/VIS spectra of the other furanones in MeCN (*cf. Table 4*), characterize the longest-wavelength absorption as an $n \rightarrow \pi^*$ transition at the C=O group. The vibrational splitting of *ca.* 1570 cm^{-1} corresponds quite well with the ground-state vibration of the C=O group of **3a** at 1747 cm^{-1} (*cf. Table 5*) and indicates the C=O bond weakening in the excited state. In agreement with this assignment is the negative solvatochromism of the absorption band and the dependence of its complete disappearance on the increasing degree of alkyl substitution at the seven-membered ring of **3** (*cf. Table 4*). The second strong absorption band has to be regarded as a $\pi \rightarrow \pi^*$ transition (1) with strong charge-

transfer character, *i.e.*, electron density from the C=O region, especially from C(3) (see later), is moved to the seven-membered ring in the excited state, in agreement with SCF calculations of **3a**. The expected positive solvatochromism for such an electronic transition is indeed observed. Moreover, the successive addition of Me groups at the seven-membered ring has no great influence on the position of this absorption band, which is in agreement with the observation that the hyperconjugative, electron-donating properties of the Me groups reduces the electron-accepting character of the seven-membered ring in the excited state. However, a bathochromic shift of *ca.* 10 nm is observed when the unsubstituted position at C(6) in **3f** is also occupied by a Me group, due to the already discussed non-planarity of the seven-membered ring in **3e** that raises the ground-state energy of **3e** in comparison to **3f** and the other furanones, so that **3e** profits more than the other furanones from the steric relief in the excited state caused by bond elongation. The magnitude of the absorption coefficients ε can serve as a second indicator for the change in the ground-state energy of the furanones in going from **3a** *via* **3c** to **3e**. It increases, especially for the third absorption band at *ca.* 250–260 nm, up to 24000 for **3c** and **3f**, but decreases to *ca.* 2/3 for the pentamethyl-furanone **3e**, an effect that can again be ascribed to the non-planarity of this compound affecting its optimal conjugation.

Table 5. *IR Data of the Cyclohepta[*b*]furan-2(2*H*)-ones* **3** [a])

Substituents in **3**	No.	$\tilde{\nu}$ [cm^{-1}]				
None	**3a**	1780*m* [b]) 1747*s* 1702*m* [b])	1604*s*	1540*s*	1513*s*	1262*s*
4,6,8-Me$_3$	**3c**	1732*s* 1702*s* [b])	1596*m*	1540*m*	1506*s*	1236*s*
5,6,7-Me$_3$	**3g**	1732*s* 1690*m* [b])	1599*s*	1518*m*	1473*s*	1277*m* 1223*m*
4,5,7,8-Me$_4$	**3f**	1738*s* 1715*s*	1571*m*	1490*m*	1481*m*	1230*m*
4,5,6,7,8-Me$_5$	**3e**	1732*s* [b]) 1716*s*	1556*m*	1502*w*	1454*s*	1240*m*

[a]) KBr pellets; only the most important bands in the region of 1800–1000 cm^{-1} are reported; *s* = strong, *m* = medium; *w* = weak. [b]) Shoulder.

Finally, the third absorption band can be regarded as being due to a more or less pure $\pi \rightarrow \pi^*$ transition (2). The negligible solvent dependence of this band speaks for this assumption.

4.1.2. *IR Spectra.* We recorded the IR spectra of the furanones in KBr pellets. The most intense bands for the spectral region of 1800–1000 cm^{-1} are collected in *Table 5*. The picture of this region is more or less the same, with the most intense band for $\tilde{\nu}$(C=O) at 1780–1716 cm^{-1}. The intensities of the other skeletal vibrations between 1600 and 1200 cm^{-1} may vary substantially with dependence on the pattern and degree of substitution at the seven-membered ring. The general trend is that all bands are shifted to lower wave numbers with the increase of the number of alkyl substituents at the seven-membered ring, whereby the unsubstituted **3a** and its pentamethyl derivative

3e can again be regarded as the two borderline cases. Also substitution at C(3) does not alter this vibrational pattern as is evident from the IR spectrum of 3-phenylcyclohepta[*b*]furan-2(2*H*)-one [24][57].

As a rule, all furanones show at least two vibrational bands in the $\tilde{\nu}$(C=O) region that may appear as two distinct bands as in the case of **3f** or the previously mentioned 3-phenylfuranone derivative. Already, *Nozoe et al.* pointed out [57] that this band-splitting resembles those for $\tilde{\nu}$(C=O) of α,β-unsaturated five-ring lactones [58]. However, this splitting has been ascribed to a *Fermi* resonance coupling with a vibration involving the α-C–H bond, because α-substituted α,β-unsaturated γ-lactones do not exhibit this splitting. Since the 3-phenylfuranone derivative displays also two separated bands at 1736 and 1716 cm^{-1}, the splitting in the furanones should have another cause. Nevertheless, the position of the main band is dependent on the degree of substitution and is shifted from 1747 cm^{-1} for **3a** to 1716 cm^{-1} for its pentamethyl form **3e**. Similar shifts are observed for the other reported bands, which should be due to skeletal vibrations of the cyclohepta[*b*]furanone-ring system.

Table 6. *^{1}H-NMR Data of the Cyclohepta[*b*]furan-2(2*H*)-ones* **3**

Substituents in **3**	No.	Chemical shift [ppm] [a])					
		H–C(3)	H/R–C(4)	H/R–C(5)	H/R–C(6)	H/R–C(7)	H/R–C(8)
None	**3a**	5.76 [b])	7.29	7.02	6.81	6.99	6.94
4,6,8-Me_3	**3c**	5.57	2.32	6.93	2.33	6.80	2.42
5,6,7-Me_3	**3g**	5.49 [c])	7.23	2.39	2.19	2.35	6.90 [d])
4,5,7,8-Me_4	**3f**	5.56 [d])	2.22	2.350	6.88	2.343	2.40
4,5,6,7,8-Me_5	**3e**	5.53	2.22	2.27	2.23	2.25	2.40
5,7-Et_2	**3h**	5.61 [f])	7.10	2.57/1.25	6.62	2.56/1.25	6.82 [g])

[a]) In $CDCl_3$ at 300 and 600 MHz (**3a**), respectively. [b]) As *d*, $^5J(3,8) = 1.2$ Hz; other couplings [Hz]: $^3J(4,5) = 11.4$, $^4J(4,6) = 1.2$; $^3J(6,7) = 10.2$, $^4J(6,8) = 1.2$; $^3J(7,8) = 9.0$. [c]) As *d*, $J = 0.6$ Hz. [d]) As *d*, $J = 1.3$ Hz. [e]) As *d*, $J = 0.6$ Hz. [f]) As *d*, $J = 1.4$ Hz. [g]) As *t*, $J = 1.4$ Hz.

Table 7. *^{13}C-NMR Data of Cyclohepta[*b*]furan-2(2*H*)-ones* **3**

Substituents in **3**	No.	Chemical shift [ppm] [a])								
		C(2)	C(3)	C(3a)	C(4)/ R–C(4)	C(5)/ R–C(5)	C(6)/ R–C(6)	C(7)/ R–C(7)	C(8)/ R–C(8)	C(8a)
None	**3a**	169.47	98.77	153.19	127.85	135.38	130.45	132.52	113.77	158.41
					–	–	–	–	–	
4,6,8-Me_3	**3c**	169.05	95.80	151.62	137.23	137.68	139.01	134.10	125.28	151.62
					24.40	–	27.49	–	19.85	
5,6,7-Me_3	**3g**	170.24	94.43	151.15	125.80	147.30	139.20	139.98	118.09	155.36
					–	28.78	21.32	27.23	–	
4,5,7,8-Me_4	**3f**	169.04	94.83	153.13	133.64	141.91	134.85	141.60	126.53	153.49
					20.21	26.42	–	26.42	16.85	
4,5,6,7,8-Me_5	**3e**	169.37	95.18	151.91	132.58	144.37	138.93	138.22	126.48	151.91
					20.77	23.75	23.94	21.04	18.08	
5,7-Et_2	**3h**	169.70	96.45	152.31	123.53	151.95	130.92	148.57	115.32	157.07
					–	34.77	–	34.29	–	
						15.23		15.11		

[a]) In $CDCl_3$ at 75 MHz; for data of **3a** see also [55].

4.1.3. *NMR Spectra*. The data of the ^{1}H- and ^{13}C-NMR spectra are assembled in *Tables 6* and *7*. All signal assignments were made by ^{1}H,^{13}C correlation spectra for each compound with the exception of 5,7-diethylfuranone **3h**, signal assignments of which were made by comparison with the chemical shifts of the other furanones. The high-field shift of the signal of H–C(3) is in agreement with the high electron density at C(3), which is also reflected in δ(C(3)) in the ^{13}C-NMR spectra. The increasing number of alkyl substituents at the seven-membered ring displaces the signals, as expected, to higher fields. The fact that all cyclohepta[*b*]furan-2(2*H*)-ones **3** that carry an H-atom at C(8) display ^5J(H–C(3),H–(8)) = 0.6–1.2 Hz is also of diagnostic value. The smallest shift differences are exhibited by the H-atoms or alkyl substituents at C(5) and C(7), and most obviously are demonstrated by the NMR spectra of **3f**. It can also be recognized that the resonance position of the C=O C-atom is not very sensitive to the alkyl substitution pattern at the seven-membered ring of the furanones.

4.2.4. *Mass Spectra*. We measured the mass spectra of the furanones **3** by GC/MS coupling. The most prominent signal is that of the $M^{+\cdot}$ ion in all spectra. Further characteristic signals and their relative intensities are listed in *Table 8*. As expected, the spectra are dominated by the successive loss of two CO molecules. The structure and further fate of the generated $[M-2\,CO]^{+\cdot}$ ions can only be speculated upon. However, it is remarkable that the most intense signal, after that of the $M^{+\cdot}$ peak, is found at the *m*/*z* value corresponding to $[M-2\,CO-R]^+$, whereby R represents Me, Et, or H, according to the given substituents of **3**. The intensity of this signal for all furanones speaks for the generation of stabilized cations, which may be represented by cyclopropenylium ions (see *Scheme 14*). The further fragmentation becomes more and more clouded. However, the loss of acetylene seems to play a role.

The loss of the first molecule of CO is in competition with the loss of $[H-C{=}O]^{\cdot}$, and it seems that this fragmentation plays a role when a Me group at C(4) can act as an H-atom donor, since this fragmentation pattern is not observed for **3a** and is also of no importance for **3g** and **3h** (*cf. Table 8*).

5. Formation of 1,2,3,4-Tetrahydrobenz[*a*]azulenes. – We reacted the furanones **3c**, **3e**, and **3f** with 1-(cyclohex-1-enyl)pyrrolidine (**19**) in toluene in order to test the azulene-forming propensity of these highly methylated cyclohepta[*b*]furan-2(2*H*)-ones (*Scheme 15*)[15]). Indeed, in all three cases the generation of the blue azulene color was recognized. The chromatographic isolation and purification of azulene **20c** created no specific problems. It was obtained in >50% yield. However, azulenes **20e** and **20f** turned out to be very sensitive to exposure to air, so that their chromatographic purification on Al_2O_3 was difficult. The blue color of purified samples of **20f** and especially of **20e** faded within hours when exposed to air.

Nevertheless, the new azulenes could be characterized by their ^{1}H- and ^{13}C-NMR spectra, as well as by their mass spectra (see *Table 9* and *Exper. Part*). Quite typical are the positions of the signals for H–C(10) which appear in the ^{1}H-NMR spectra as *s*s in the range of 7.07–6.86 ppm, and in the ^{13}C-NMR spectra as *d*s in the range of 112–115 ppm. The fragmentation behavior of **20c** and **20e** at 70 eV is distinctly different.

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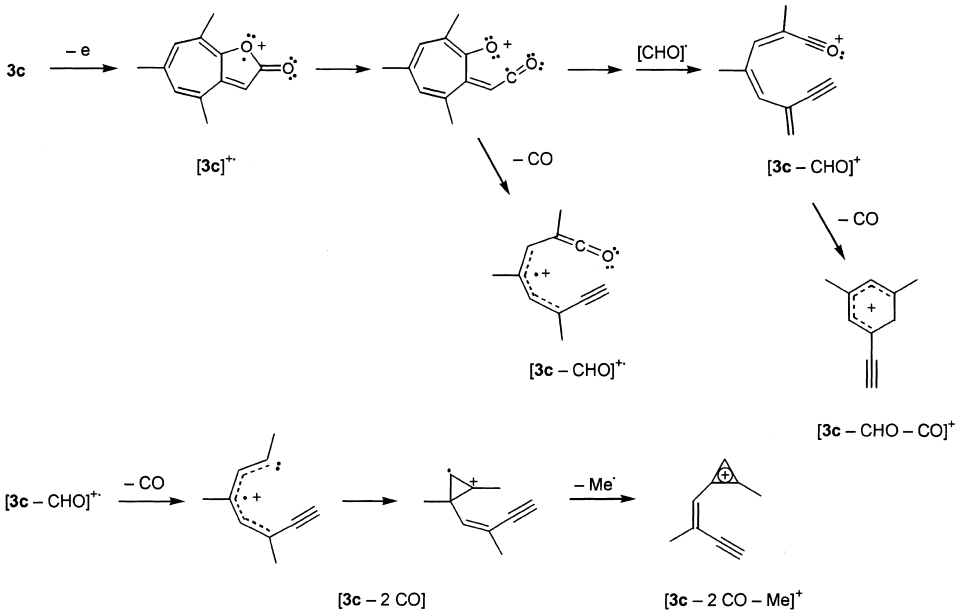
[15]) The new furanones **3** could also be transformed into azulenes with enol ethers at temperatures of 130–200°. We will report these results soon [9].

Scheme 14



[a]) Tentative fragmentation pattern, exemplified for **3c**.

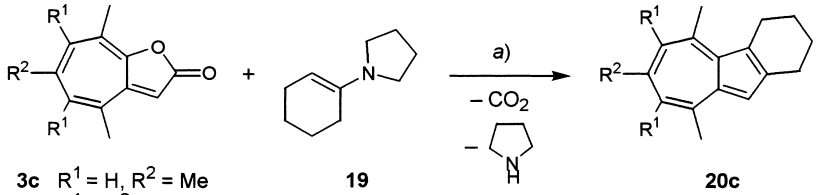
The spectrum of **20c** with $M^{+\cdot}$ at *m/z* 224 (90%) is dominated by the loss of ethene as the result of a *retro-Diels-Alder* fragmentation leading to the signal at *m/z* 196 (100%). The loss of a Me group is indicated by the signal at *m/z* 209 (50%). The loss of a second Me group does not play a role according to the weak signal at *m/z* 194 (<6%). The fragmentation behavior of **20e** is quite different. The $M^{+\cdot}$ signal at *m/z* 252 (100%) is

Table 8. *Mass Spectra of the Cyclohepta[*b*]furan-2(2*H*)-ones* **3** [a])

Substituents in **3**	No.	Ions [b])							
		$M^{+\cdot}$	$[M-CO]^{+\cdot}$	$[M-CHO]^+$	$[M-CO-Me]^+$	$[M-2\,CO]^+$	$[M-CO-CHO]^+$	$[M-2\,CO-R]^+$	$[M-X]^+$
None	**3a**	146 (100)	118 (25)	–	–	90 (85)	? [c])	89 (49)	63 (20)
4,6,8-Me_3	**3c**	188 (100)	160 (6)	159 (3)	145 (7)	132 (18)	131 (8)	117 (36) [d])	91 (13)
5,6,7-Me_3	**3g**	188 (100)	160 (12)	159 (4)	145 (12)	132 (18)	131 (13)	117 (47) [e])	91 (17)
4,5,7,8-Me_4	**3f**	202 (100)	174 (7)	173 (14)	159 (15)	146 (25)	145 (7)	131 (40) [f])	–
4,5,6,7,8-Me_5	**3e**	216 (100)	188 (5)	187 (17)	173 (20)	160 (22)	159 (5)	145 (27)	–
5,7-Et_2	**3h**	202 (100)	174 (8)	173 (2)	159 (15)	146 (2)	145 (9)	131 (22)	–
3-Ph [g])	**3m**	222 (100)	194 (9)	193 (7)	–	166 (61)	? [c])	165 (103)	139 (77)
3-Me [h])	**3n**	160 (100)	132 (21)	131 (92)	–	104 (27)	? [c])	103 (28)	77 (12)

[a]) If not otherwise stated, spectra were recorded by GC/MS; carrier gas He, EI at 70 eV. [b]) Ions in *m/z* (rel. %); R corresponds to substituents at the seven-membered ring in **3**; X = (2 CO + R + H–C≡C–H). [c]) *m/z* Values are identical for $[M-CO-CHO]^+$ and $[M-2\,CO-R]^+$ (R = H). [d]) Further signal at *m/z* 115 (19). [e]) Further signal at *m/z* 115 (25). [f]) Further signals at *m/z* 129 (7) and 128 (7). [g]) Taken from [24] and redetermined with GC/MS. [h]) Data taken from [54].

Scheme 15



3c R^1 = H, R^2 = Me **19** **20c**
3e R^1 = R^2 = Me **20e**
3f R^1 = Me, R^2 = H **20f**

a) Toluene, 120–130°, 9–12 h.

Table 9. *NMR Data of the 1,2,3,4-Tetrahydrobenz[a]azulenes* **20**

Substituents in **20** (solvent)	No.	^{1}H-NMR [a])				^{13}C-NMR [b])				
		H–C(10)	H–C(1–4)	H–C(6–8)	Me	C(10)	C(1–4)	C(6,7,8) [c])	Other C	Me
5,7,9-Me_3 ($CDCl_3$)	**20c**	7.07	3.37 [d]) 3.03 [e]) 1.93–1.80 [f])	6.83 (*s*) 6.82 (*s*)	2.96 2.76 2.51	114.7	28.8 27.1 24.8 22.8	128.2 126.2	146.2, 145.0, 143.9, 142.8, 135.4, 133.6, 126.1	28.3 27.7 25.4
5,7,9-Me_3 (C_6D_6)	**20c**	7.18	3.24–3.22 [d]) 3.03 [e]) 1.80–1.71 [f])	6.70 (br.*s*)	2.75 2.64 2.29	115.5	28.9 27.3 24.9 23.0	127.9 125.8	146.2, 144.2, 143.0, 142.2, 136.0, 134.4, 126.2	27.9 27.4 25.2
5,6,8,9-Me_4 ($CDCl_3$)	**20f**	7.07	3.34 [d]) 3.05 [e]) 1.80–1.92 [f])	7.40 (*s*)	2.83 2.71 2.51 2.50	112.1	29.9 27.0 25.1 22.9	139.1	[g])	27.2 26.2 23.2 21.1
5,6,7,8,9-Me_5 ($CDCl_3$)	**20e**	6.86	3.19 [d]) 2.93 [e]) 1.78–1.90 [f])	–	2.84 2.62 2.36 2.33 [h])					
5,6,7,8,9-Me_5 (C_6D_6)	**20e**	7.04	3.12 [d]) 3.01 [e]) 1.71–1.89 [f])	–	2.57 2.54 2.09 [h]) 2.08					

[a]) In the indicated solvent at 300 MHz. [b]) In the indicated solvent at 75 MHz; δ in ppm. [c]) *d* of H–C(X). [d]) Centered *m of* CH_2(1). [e]) Centered *m* of CH_2(4). [f]) *m* of CH_2(2,3). [g]) Signals of the quaternary C-atoms not recorded. [h]) Broad *s* of two Me groups.

here the reference signal, followed by the $[M^{+\cdot} - Me]$ signal at *m*/*z* 237 (77%) and the $[M^{+\cdot} - 2\,Me]$ signal at *m*/*z* 222 (21%). The *retro-Diels-Alder* fragmentation is of no importance according to the intensity of the signal at *m*/*z* 224 (7%).

We thank our NMR laboratory, in particular *Nadja Walch*, *Martin Binder*, and Dr. *Gudrun Hoppe*, for specific NMR measurements, Dr. *Philipp Ott* for UV/VIS measurements and presentations, and Dr. *Christophe Weymuth* for his helpful discussions. *H.-J. H.* thanks especially *Manfred Hesse* for a discussion on the fragmentation behavior of the furanones. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. TLC: glass plates pre-coated with silica gel *60* F_{254} from *Merck* or *Polygram Alox N/UV*$_{254}$ (*Macherey-Nagel*); visualization by UV light and/or I_2 vapor, respectively. Column chromatography (CC) and flash chromatography (FC): on silica gel *60* (40–63 μm), *Chemie Uetikon AG*, or aluminium oxide, *Fluka*, type *5016 A* basic, *Brockmann* grade IV, or Alox *ICN Alumina N* neutral, *Brockmann* grade III. UV/VIS Spectra: *Perkin-Elmer* spectrophotometer (model *Lambda 9*), λ in nm ($\log \varepsilon$). IR Spectra: *Perkin-Elmer* spectrophotometer (model *FT-IR 1600*), $\tilde{\nu}_{max}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker* instruments (*AC 300*, *ARX 300*, *AMX 600*); δ(^1H and ^{13}C) in ppm rel. to $CHCl_3$ and $CDCl_3$ as internal standard 7.26 and 77.00 ppm, resp.; J(H,H) in Hz; assignments by ^1H,^{13}C-correlation spectra (HSQC and HMBC technique). MS: GC/MS *Hewlett-Packard HP5890 Series II* (GC), *HP-5971 MSD* (mass-selective detector (EI, 70 eV)), *WCOT* cap. column *HP-5*, 25 m × 0.2 mm; carrier gas: He; GC conditions: injector temp. 280°, starting temp. 60° over 2 min, rate 20°/min, term. temp. 250° over 5 min.

1. Syntheses. – 1.1. *Reagents and Solvents*. If not otherwise stated, reagents and solvents are from *Fluka*. *2,4,6-Trimethylphenol* (mesitol; **1c**), 2,3,5,6-tetramethylphenol (**1f**), *Aldrich*, *purum*; *3,4,5-trimethylphenol* (**1g**), *EGA-Chemie*; *3,5-diethylphenol* (**1h**), *EGA-Chemie*; *2,6-diisopropylphenol* (**1i**), *EGA-Chemie*, *techn.* (90%); *2,4,6-tri(tert-butyl)phenol* (**1k**), *purum*; *2-naphthol* (**1l**), *purum*; *phenylcarbonochloridate* (**14a**), *purum*; $AlCl_3$, H_2O-free, *pract.*; HBr, 5.7M soln. in AcOH, *pract.*; cyclohexanone, *purum*; dicyclohexylcarbodiimide (DCC), *purum*; 4-(dimethylamino)pyridine (DMAP), *purum*; *N*,*N*-dimethylaniline (DMA), *purum*; formaldehyde soln. (30% in H_2O), *techn.*; HCl (33 wt.-%), *Merck*, *p.a.*; KOH, *Siegfried*, *puriss.*; MeI, *purum*; morpholine, *puriss.*; Pd/C (10%), *puriss.*; paraformaldehyde, *pract.*; $COCl_2$ in toluene (20%), *purum*; PCl_5, *purum*, *p.a.*; H_3PO_4 (85% in H_2O), *Merck*, *p.a.*; propiolic acid (= propynoic acid), *pract.*; trifluoroacetic anhydride (TFAA), *purum*; Ph_3P, *purum*. *Solvents*. Solvents of the grade '*puriss.*' were used without further purification. Solvents of the grade '*purum*' were distilled and, when necessary, dried (Et_2O and hexane over NaH; CH_2Cl_2 and AcOEt over P_2O_5) before distillation. THF, distilled from potassium ketyl; toluene and *o*-xylene, distilled from Na. Further solvents: *tert*-butyl methyl ether (TBME; *purum*), acetic acid (AcOH; Merck, *p.a.*), heptane fraction, *purum*, 1-methyl-2-pyrrolidone (NMP; *purum*).

1.2. *Aryl Propynoates* **2**. – 1.2.1. *2,3,4,5,6-Pentamethylphenol* (**1e**). 1.2.1.1. *3,5-Bis(bromomethyl)-2,4,6-trimethylphenol* (**18**). *Mesitol* (**1c**, 68.5 g, 0.5 mol) and paraformaldehyde (31 g, 1.0 mol) were suspended in 250 ml of AcOH, whereby the temp. of the mixture decreased. HBr/AcOH (200 ml, 1.14 mol HBr) was added rapidly with stirring and the resulting pink-colored mixture warmed to 40°. After *ca*. 10 min, a solid precipated from the reaction mixture (GC/MS indicated the predominant presence of *3-(bromomethyl)mesitol* (**17**; *m*/*z* 228/230 ($M^{+\bullet}$)). After heating to >60°, the solid dissolved again, and the soln. turned reddish brown. The reaction of **1c** → **17**, **18** was completed by further addition of paraformaldehyde (3.1 g, 0.1 mol) and stirring at 70–90° during 8 h (GC/MS control). The hot mixture was cautiously poured on to 1.5 l of ice and H_2O. The resulting greyish precipitate was vacuum-filtered and dissolved in Et_2O, washed 3 times with H_2O, and filtered through a silica-gel pad. After addition of hexane, a fine powder precipitated at −20° (158 g, >90%). It contained mainly **18**, but also some acetate of **18**, which could be removed only by several recrystallizations. However, the presence of **18**-acetate did not disturb the subsequent hydrogenolysis reaction.

Data of Purified **18**: colorless needles (felt). M.p. 162–164° (heptane). R_f(hexane/Et_2O 4:1; I_2) 0.4. ^1H-NMR ($CDCl_3$ + (D_6)acetone): 6.5 (br. *s*, OH); 4.59 (*s*, 2 CH_2Br); 2.38 (*s*, Me–C(4)); 2.32 (*s*, Me–C(2,6)). ^{13}C-NMR ($CDCl_3$ + (D_6)acetone): 151.1 (C(1)); 132.9 (C(3,5)); 128.8 (C(2,6)); 125.3 (C(4)); 30.52 (*t*, 2 CH_2); 14.5 (*q*, *Me*–C(4)); 12.2 (*q*, *Me*–C(2,6)). EI-MS (GC/MS): 324/322/320 (8/16/8, $M^{+\bullet}$), 243/241 (100, [M − HBr]$^{+\bullet}$), 162 (75, [M − 2 HBr]$^{+\bullet}$).

1.2.1.2. *2,3,4,6-Tetramethylphenol (***1o***)* via **17**. The reaction of **1c** with 1 mol-equiv. of paraformaldehyde and HBr/AcOH at <65° led after 2 h to almost pure **17** contaminated with *ca.* 10% of **17**-acetate (GC/MS). The crude compound was dissolved in a mixture of AcOEt/EtOH/AcOH (*ca.* 2:2:1) and hydrogenated in the presence of Pd/C (10%) (0.50 g of catalyst/100 g of **17**). For details see *1.2.1.3*. The phenol **1o** was obtained in yields of 75–85% (with respect to **1c**) as colorless needles.

Data of **1o**: M.p. 79–81°: ^1H-NMR ($CDCl_3$): 6.77 (*s*, H–C(5)); 4.45 (*s*, OH); 2.19, 2.18, 2.15 (3*s*, 4 Me). ^{13}C-NMR ($CDCl_3$): 150.0 (*s*, C(1)); 133.7 (*s*, arom. C); 129.1 (*d*, C(5)); 128.0, 121.9, 119.5 (3*s*, arom. C); 20.0 (*q*, Me); 15.7 (*q*, 2 Me); 12.1 (*q*, Me). EI-MS (GC/MS): 150 (70, $M^{+\bullet}$), 135 (100, [M − Me]$^+$).

1.2.1.3. *Hydrogenolysis of* **18**. Crude **18** was dissolved in AcOEt/EtOH/AcOH (*ca.* 2:2:1), and Pd/C (10%) was added (0.50 g/100 g **18**). Hydrogenation was performed with H_2 under normal pressure. At the beginning, the temp. increased to 30–35°. After ⅓ of H_2 had been consumed, an equimolar amount of conc. aq. AcONa was added. The two-phase mixture was stirred at r.t. until the total amount of H_2 had been taken up (after 12–24 h).

The mixture was filtered over sea sand/*Celite*/silica gel, and Et_2O was added to the filtrate. The org. layer was washed with H_2O and twice with sat. NaCl soln. The residue was recrystallized twice from hot heptane and provided pure **1e** in 70–85% yield with respect to **1c** in colorless crystals. Two times recrystallization from hot heptane delivered pure **1e** as colorless needles (purity according to GC: >98%).

Data of **1e**: M.p. 128–129° ([47]: 128°; [49]: 128–129°). R_f(hexane/Et_2O 4:1, I_2) 0.65. ^{1}H-NMR ($CDCl_3$): 4.50 (br. *s*, OH); 2.20, 2.18, 2.17 (3*s*, 5 Me). ^{13}C-NMR ($CDCl_3$): 149.5 (C(1)); 132.9, 126.9, 119.0 (3*s*, 5 arom. C); 16.4, 16.3 (2*q*, *Me*–C(3,4,5)); 12.5 (*q*, *Me*–C(2,6)). EI-MS (GC/MS): 164 (65, $M^{+\cdot}$), 149 (100, $[M-Me]^+$).

1.2.1.4. *2,3,4,5,6-Pentamethylphenol* (**1e**) *by* Friedel-Crafts *Reaction.* Mesitol (**1c**) (1.36 g, 10 mmol) and $AlCl_3$ (2.7 g, 20 mmol) were added to MeI (30 ml) and the suspension heated under reflux for 2 h. GC/MS Control revealed the presence of greater amounts of **1o**. After additional heating for 4 h, further MeI (5 ml) was added, and heating was continued for 18 h. The mixture was hydrolyzed with ice-water, and the formed **1e** was recrystallized twice from hot heptane: 1.07 g (65%) of **1e**.

1.2.2. *2,4,6-Trimethylphenyl Prop-2-ynoate* (**2c**) *with Prop-2-ynoyl Chloride.* 1.2.2.1. *Prop-2-ynoyl Chloride.* Prop-2-ynoic acid (5.0 g, 0.07 mol) was added dropwise to a small excess of PCl_5 (16.0 g, 0.0075 mol) at 5–10°. Vivid evolution of HCl was recognized. The prop-2-ynoyl chloride formed was separated from the mixture, kept at liquid N_2 temp., and then slowly thawed by evaporation and condensation at 12 Torr. In a first trap, kept at −78°, condensed mainly $POCl_3$. In a second trap, kept at *ca.* −130°, the chloride was collected. At temp. below −135°, the chloride was co-condensed with HCl, which partially reacted on thawing with the chloride to give 3-chloroprop-2-enoyl chloride. The procedure led to yields of the chloride in the range of 30–35%. ^{1}H-NMR ($CDCl_3$): 3.7 (*s*, H–C(3)). EI-MS (GC/MS): 90/88 (–/2, $M^{+\cdot}$), 62/60 (3/10, $[M-CO]^{+\cdot}$), 53 (100, $[M-Cl]^+$).

The thus prepared prop-2-ynoyl chloride contained always some 3-chloroprop-2-enoyl chloride (≤10%), as indicated by an *AB* system at 7.68 and 6.52 ppm with $J(AB)=13.6$ Hz (*cf.* [31]), as well as 10–20% $POCl_3$.

1.2.2.2. *Formation of* **2c**. Mesitol (**1c**) (4.22 g, 0.31 mmol) was added to a suspension of oil-free NaH (0.83 g, 35 mmol) in Et_2O (300 ml). The mixture was stirred until the evolution of H_2 had ceased, and then, after additional stirring for 0.5 h, cooled to −78°. Freshly prepared prop-2-ynoyl chloride (see above; 3.5 g, *ca.* 34 mmol) was added dropwise within 15 min. The cooling bath was removed after additional stirring for 30 min, and the mixture was allowed to warm up to r.t. H_2O (100 ml) was added, and **2c** formed was isolated by filtration over a short silica-gel column with hexane/Et_2O 4:1. The solvent mixture was removed from the almost colorless filtrate and the residue redissolved in hexane/Et_2O 9:1. Ester **2c** crystallized at −20°. Average yields of **2c** were 75–80%, which could be increased to 85–90% by workup of the mother liquors.

Data of **2c**: Colorless, transparent crystals. M.p. 58–60° ([26]: 57–58°). R_f(hexane/Et_2O 4:1, I_2) 0.65. IR (KBr): 3240*s* (≡C–H), 2130*s* (–C≡C–), 1725v*s* (C=O). ^{1}H-NMR ($CDCl_3$): 6.88 (*s*, H–(3′,5′)); 3.03 (*s*, H–C(3)); 2.27 (*s*, Me–C(4′)); 2.14 (*s*, Me–C(2′,6′)). ^{13}C-NMR ($CDCl_3$): 150.7 (C=O); 145.1 (C(1′)); 136.2 (C(4′)); 129.5 (C(2′,6′)); 129.4 (C(3′,5′)); 76.4 (C(3)); 74.2 (C(2)); 20.8 (*Me*–C(4′)); 16.1 (*Me*–C(2′,6′)). EI-MS (GC/MS): 188 (85, $M^{+\cdot}$), 173 (60, $[M-Me]^+$), 145 (65), 136 (100), 91 (90).

The by-products **4** and **5** in crude **2c** were identified by their GC/MS.

Also other products, *i.e.*, **6** and (*E*)-**7** and (*Z*)-**7** (*cf. Scheme 5*), **8** (*cf. Scheme 6*), **11** and **12** (*cf. Scheme 8*) that had been observed as by-products, were identified mainly by GC/MS. Moreover, *ethyl prop-2-ynoate* (**11**) was unequivocally identified by its ^{1}H-NMR ($CDCl_3$) with 2.97 (*s*, H–C(3)), and 4.28/1.32 (*q* and *t*, resp., $MeCH_2O$) as well as by comparison with an authentic sample.

1.2.3. *Aryl Prop-2-ynoates* **2** via *Mixed Anhydrides.* 1.2.3.1. *Aryl Carbonochloridates* **14**. *General Procedure:* $COCl_2$ in toluene (20%; 1.3–1.35 mol-equiv.) was added to the phenol (1 mol-equiv.), whereby the temp. decreased slightly without reaction. The mixture was cooled to 0°, and *N*,*N*-dimethylaniline (1 mol-equiv.) was added dropwise under stirring in a way that the temp. not surpassed 5°. The resulting creamy suspension was stirred for 2–22 h, whereby the temp. slowly reached r.t. The formation of the aryl carbonochloridates **14** was followed by GC/MS. Hydrolysis of the excess of $COCl_2$ was performed by dropwise addition of H_2O (20–30 ml) at 0°. After the precipitate of the anilinium hydrochloride had been dissolved, the org. phase was washed with 0.1N aq. HCl, and then with diluted NaOH and H_2O. The org. layer was dried ($MgSO_4$), and the residue was filtered over a short column of silica gel. The residues of the now colorless filtrates were dissolved in hexane, and **14** crystallized at 4° or −20°, or purified by bulb-to-bulb distillation *in vacuo*. (*cf. Table 1*).

Data of 2,4,6-Trimethylphenyl Carbonochloridate (**14c**). Colorless Oil. ^{1}H-NMR ($CDCl_3$): 6.85 (*s*, H–C(3′,5′)); 2.20 (*s*, Me–C(4′)); 2.08 (*s*, Me–C(2′,6′)). ^{13}C-NMR ($CDCl_3$): 149.3 (C=O); 145.8 (*s*, C(1′)); 135.3 (*s*, C(4′)); 130.4 (*s*, C(2′,6′)); 128.8 (*d*, C(3′,5′)); 20.0 (*q*, *Me*–C(4′)); 16.5 (*q*, *Me*–C(2′,6′)). EI-MS (GC/MS): 200/198 (17/50, $M^{+\cdot}$), 135 (100, $[M-COCl]^+$), 119 (45), 91 (35).

Data of 2,3,4,5,6-Pentamethylphenyl Carbonochloridate (**14e**). Colorless crystals. M.p. 60.5–62°. ^{1}H-NMR ($CDCl_3$): 2.20 (*s*, Me–C(2′,4′,6′)); 2.15 (*s*, Me–C(3′,5′)). ^{13}C-NMR ($CDCl_3$): 149.5 (C=O); 145.7 (*s*, C(1′));

134.1 (*s*, C(4′)); 134.0 (*s*, C(3′,5′)); 124.6 (*s*, C(2′,6′)); 16.7 (*q*, *Me*–C(4′)); 16.4 (*q*, *Me*–C(2′,6′)); 13.2 (*q*, *Me*–C(3′,5′)). EI-MS (GC/MS): 228/226 (27/80, $M^{+\bullet}$), 163 (100, $[M - COCl]^+$), 147 (45).

Data of 2,3,5,6-Tetramethylphenyl Carbonochloridate (**14f**). Colorless needles. M.p. 66.5–67.5°. ^{1}H-NMR ($CDCl_3$): 6.92 (*s*, H–C(4′)); 2.23 (*s*, Me–C(3′,5′)); 2.10 (*s*, Me–C(2′,6′)). ^{13}C-NMR ($CDCl_3$): 149.6 (C=O); 149.1 (*s*, C(1′)), 135.24 (*s*, C(3′,5′)); 130.1 (*d*, C(4′)); 125.1 (*s*, C(2′,6′)); 19.6 (*q*, *Me*–C(3′,5′)); 12.4 (*q*, *Me*–C(2′,6′)). EI-MS (GC/MS): 214/212 (20/60, $M^{+\bullet}$), 149 (70, $[M - COCl]^+$), 133 (100).

Data of 3,4,5-Trimethylphenyl Carbonochloridate (**14g**). Colorless oil, which solidified after several days standing at r.t. ^{1}H-NMR ($CDCl_3$): 6.83 (*s*, H–C(2′,6′)); 2.27 (*s*, Me–C(3′,5′)); 2.13 (*s*, Me–C(4′)). ^{13}C-NMR ($CDCl_3$): 149.8 (*s*, C=O); 149.0 (*s*, C(1′)); 138.2 (*s*, C(3′,5′)); 134.2 (*s*, C(4′)); 118.9 (*d*, C(2′,6′)); 20.7 (*q*, *Me*–C(3′,5′)); 15.0 (*q*, *Me*–C(4′)). EI-MS (GC/MS): 200/198 (35/100, $M^{+\bullet}$), 135 (70, $[M - COCl]^+$), 119 (80).

Data of 3,5-Diethylphenyl Carbonochloridate (**14h**). Colorless oil. ^{1}H-NMR ($CDCl_3$): 6.96 (*s*, H–C(4′)); 6.85 (*s*, H–C(2′6′)); 2.62 (*q*, 2 MeC*H*$_2$); 1.22 (*t*, 2 *Me*CH$_2$). ^{13}C-NMR ($CDCl_3$): 151.9 (C=O); 149.5 (s, C(1′)); 146.3 (*s*, C(3′,5′)); 126.4 (*d*, C(4′)); 116.9 (*d*, C(2′,6′)); 28.7 (*t*, 2 MeCH$_2$); 15.2 (*q*, 2 *Me*CH$_2$).

Data of 2,6-Diisopropylphenyl Carbonochloridate (**14i**). Colorless oil, which solidified at –20°. ^{1}H-NMR ($CDCl_3$): 7.26–7.15 (*m*, H–C(3′,4′,5′)); 3.00 (*sept.*, 2 Me$_2$C*H*); 1.23 (*d*, 2 *Me*$_2$CH). ^{13}C-NMR ($CDCl_3$): 149.7 (*s*, C=O); 147.1 (*s*, C(1′)); 139.8 (*s*, C(2′,6′)); 127.8 (*d*, C(4′)); 124.5 (*d*, C(3′,5′)); 27.7 (*d*, 2 Me$_2$CH); 23.2 (*q*, 2 *Me*$_2$CH).

*Data of 2,4,6-Tri(*tert*-butyl)phenyl Carbonochloridate* (**14k**). Yellowish solid. M.p. 80–84°. ^{1}H-NMR ($CDCl_3$): 7.38 (*s*, H–C(3′,5′)); 1.39 (*s*, Me$_3$C–C(2′,6′)); 1.29 (*s*, Me$_3$C–C(4′)). ^{13}C-NMR ($CDCl_3$): 151.0 (C=O); 148.8 (*s*, C(1′)); 146.7 (*s*, C(4′)); 140.4 (*s*, C(2′,6′)); 123.8 (*d*, C(3′,5′)); 35.1 (*s*, Me$_3$*C*–C(2′,6′)); 34.5 (*s*, Me$_3$*C*–C(4′)); 31.2 (*q*, 3 *Me*$_3$C). EI-MS (GC/MS): 326/324 (10/30, $M^{+\bullet}$), 311/309 (30/100, $[M - Me]^+$), 265 (100, $[M - COCl]^+$).

Data of Naphthalen-2-yl Carbonochloridate (**14l**). Colorless crystals. M.p. 62–64° ([40]: 65–65.5°). ^{1}H-NMR ($CDCl_3$): 7.76–7.68 (*m*, 3 H); 7.57 (*d*-like, 1 H); 7.44–7.36 (*m*, 2 H); 7.22–7.18 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 149.6 (*s*, C=O); 149.1 (*s*, C(2′)); 133.4, 131.9 (2*s*, C(4′a,8′a)); 130.0, 127.8 (enhanced intensity), 127.1, 126.5, 119.2, 117.8 (7*d*, C(1′,3′,4′,5′,6′,7′,8′)). EI-MS (GC/MS): 208/206 (30/90, $M^{+\bullet}$), 162 (40), 143 (40, $[M - COCl]^+$), 127 (45), 115 (100).

1.2.3.2. *Sodium Prop-2-ynoate.* Distilled prop-2-ynoic acid (35 g, 0.5 mol) was neutralized under cooling by stirring with conc. aq. NaOH (20.02 g, 0.501 mol). The temp. was kept between 10–20°. The slight excess of NaOH was neutralized with dropwise addition of prop-2-ynoic acid to adjust pH 6.8–7.0. H_2O was then removed on a rotatory evaporator, and the residue was dried under high vacuum until the weight was constant (12–14 h). The solid salt was powdered in a mortar and dried again at 40°. Sodium prop-2-ynoate was thus obtained as an ivory-colored powder that was protected from light and stored at –20°.

1.2.3.3. *Formation of Prop-2-ynoates* **2**. *General Procedure:* The aryl carbonochloridate (0.1 mol) was dissolved in THF (100 ml), and sodium prop-2-ynoate (9.3 g, 0.1 mol) was added under stirring at r.t. In cases where the evolution of CO_2 did not start at r.t., the mixture was gently heated at 30°, 40°, or, for 2,6-disubstituted aryl compounds, at 40–65°. The progress of the reaction was followed by GC. Within 2–12 h, all reactions were complete. The product mixture was filtered over sea sand and silica gel. The solvent was distilled off, and the residue was dissolved in hexane or hexane/Et_2O, and filtered again over silica gel. The filtrate was cooled to 4 or –20° to induce crystallization, or the residue was purified by bulb-to-bulb distillation, when no crystallization occurred. For yields, see *Table 2*.

Data of Phenyl Prop-2-ynoate (**2a**): Colorless oil. ^{1}H-NMR ($CDCl_3$): 7.41–7.34 (*t*, with f.s., H–C(3′,5′)); 7.27–7.22 (*t*, with f.s., H–C(4′)); 7.15–7.10 (*d*, with f.s., H–C(2′,6′)); 3.05 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 151.0 (*s*, C=O); 149.8 (*s*, C(1′)); 129.6 (*d*, C(3′,5′)); 126.6 (*d*, C(4′)); 121.2 (*d*, C(2′,6′)); 76.7 (*d*, C(3)); 74.2 (C(2)); EI-MS (GC/MS): 146 (94, $M^{+\bullet}$), 145 (78), 118 (100, $[M - CO]^+$), 94 (78), 93 (39), 90 (100), 89 (87).

As by-product, diphenyl carbonate was obtained and spectroscopically identified.

Data of **2c**: See *1.2.2.2.*

Data of 2,3,4,5,6-Pentamethylphenyl Prop-2-ynoate (**2e**): Colorless crystals. M.p. 114–115°. ^{1}H-NMR ($CDCl_3$): 3.03 (*s*, H–C(3)); 2.20 (*s*, Me–C(3′,4′,5′)); 2.10 (*s*, Me–C(2′,6′)). ^{13}C-NMR ($CDCl_3$): 151.1 (*s*, C=O); 145.0 (*s*, C(1′)); 133.7 (*s*, C(3′,5′)); 133.4 (*s*, C(4′)); 125.0 (*s*, C(2′,6′)); 76.3 (*d*, C(3)); 74.3 (C(2)); 16.6/16.4 (2 q, Me–C(3′,4′,5)); 13.4 (q, Me–C(2′,6′)). EI-MS (GC/MS): 216 (65, $M^{+\bullet}$), 201 (100, $[M - Me]^+$), 164 (60).

Data of 2,3,5,6-Tetramethylphenyl Prop-2-ynoate (**2f**). Colorless crystals. M.p. 86–89°. ^{1}H-NMR ($CDCl_3$): 6.88 (*s*, C(4′)); 3.03 (*s*, H–C(3)); 2.22 (*s*, Me–C(3′,5′)); 2.04 (*s*, Me–C(2′,6′)). ^{13}C-NMR ($CDCl_3$): 151.8 (*s*, C=O); 148.1 (*s*, C(1′)); 135.92 (*s*, C(3′,5′)); 130.6 (*d*, C(4′)); 126.5 (*s*, C(2′,6′)); 77.37 (*d*, C(3)); 75.2 (*s*, C(2)); 20.6 (*q*, *Me*–C(3′,5′)); 13.5 (*q*, *Me*–C(2′,6′)).

Data of 3,4,5-Trimethylphenyl Prop-2-ynoate (**2g**). White solid. M.p. 54–56°. ^{1}H-NMR ($CDCl_3$): 6.77 (*s*, H–C(2′,6′)); 3.02 (*s*, H–C(3)); 2.27 (*s*, Me–C(3′,5′)); 2.13 (*s*, Me–C(4′)). ^{13}C-NMR ($CDCl_3$): 151.4 (*s*, C=O); 147.0 (*s*, C(1′)); 137.9 (*s*, C(3′,5′)); 133.5 (*s*, C(4′)); 119.8 (*d*, H–C(2′,6′)); 76.4 (*d*, C(3)); 74.5 (*s*, C(2)); 20.6 (*q*, *Me*–C(3′,5′)); 15.0 (*q*, Me–C(4′)).

As by-product, bis(3,4,5-trimethylphenyl) carbonate was obtained and spectroscopically identified.

Data of 3,5-Diethylphenyl Prop-2-ynoate (**2h**): Colorless oil. ^{1}H-NMR ($CDCl_3$): 6.96 (br. *s*, H–C(4′)); 6.79 (*s*, H–C(2′,6′)); 3.03 (*s*, H–C(3)); 2.62 (*q*, 2 MeC*H*$_2$); 1.22 (*t*, 2 *Me*CH$_2$). ^{13}C-NMR ($CDCl_3$): 150.2 (C=O); 149.0 (C(1′)); 145.0 (*s*, C(3′,5′)); 124.9 (*d*, C(4′)); 116.8 (*d*, C(2′,6′)); 75.5 (*d*, C(3)); 73.5 (*s*, C(2)); 27.7 (*t*, 2 Me*C*H$_2$); 14.3 (*q*, 2 *Me*CH$_2$).

As by-product, bis(3,5-diethylphenyl) carbonate was obtained and identified spectroscopically.

Data of 2,6-Diisopropylphenyl Prop-2-ynoate (**2i**). Colorless oil. ^{1}H-NMR ($CDCl_3$): 7.23 (*m*, J_o = 7.5, H–C(4′)); 7.17 (*m*, J_o = 7.5, H–C(3′,5′)); 3.05 (s, H–C(3)); 2.95 (*sept.*, 2 Me$_2$C*H*); 1.21 (*d*, 2 *Me*$_2$CH). ^{13}C-NMR ($CDCl_3$): 151.4 (*s*, C=O); 144.7 (*s*, C(1′)); 140.3 (*s*, C(2′,6′)); 127.2 (*d*, C(4′)); 124.2 (*d*, C(3′,5′)); 76.6 (*d*, C(3)); 74.2 (*s*, C(2)); 27.6 (*d*, 2 Me$_2$*C*H); 23.2 (*q*, 2 *Me*$_2$CH). EI-MS (GC/MS): 230 (73), 215 (17), 187 (95), 177 (100), 163 (82).

Data of Naphthalen-2-yl Prop-2-ynoate (**2l**): Colorless crystals. M.p. 73.5–75° ([29]: 74–75°). ^{1}H-NMR ($CDCl_3$): 8.00–7.90 (*m*, 3 H); 7.75 (*d*, *J* = 1.9, H–C(1′)); 7.65–7.55 (*m*, 2 H); 7.39 (*dd*, *J* = 8.9, 2.2, H–C(8′)); 3.21 (*s*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 151.0 (*s*, C=O); 147.4 (*s*, C(2′)); 133.6, 131.7 (2*s*, C(4′a,8′a)); 129.6, 127.7 (enhanced intensity), 126.8, 126.1, 120.3, 118.4 (7*d*, C(1′,3′,4′,5′,6′,7′,8′)).

As by-product, 40% of di(naphthalen-2-yl) carbonate was obtained and spectroscopically identified.

2. Cyclohepta[*b*]furan-2(2*H*)-ones 3 *via* Pyrolysis of Aryl Prop-2-ynoates 2. 2.1. *General Remarks.* The essential semi-micro apparatus for FVP for 650–670° had been already described in the theoretical part. A more detailed description is given in the work cited in *Footnote 1*. Some FVP experiments have been performed with a prep. FVP apparatus at *Givaudan-Roure* (Dübendorf/Zurich)[16]. The heated quartz tube (length 40 cm, diameter 2.5 cm; filled with quartz tubes 8 × 8 mm) was vertically amounted in this apparatus, which allowed the introduction of **2** in xylene soln. by dropping the soln. into the heated, vertical quartz tube. This apparatus allowed the pyrolysis of 10–20 g of **2e**. The yields of furanone **3e** were at the first attempts better, *i.e.*, at the upper end of the given yields in *Table 3*, than with the improvised semi-micro apparatus. All spectral data of the furanones **3** are compiled in *Tables 4–8*.

The following melting points were recorded (in parentheses: color of the crystals): **3a** (lemon), 73–74°; **3c** (yellow), 186–188°; **3e** (lemon); 169–172°; **3f** (greenish yellow) 180–183°; **3g** (yellow-orange) 144–146°.

3. Formation of Azulenes. *General Remarks. 1-(Cyclohex-1-enyl)pyrrolidine* (**19**) was prepared in the usual way from cyclohexanone and pyrrolidine. It was obtained after distillation as a colorless oil and in a purity of > 99% (GC analysis). Furanones **3** and a 3–5-fold amount of **19** were dissolved in toluene (*ca.* 5% soln. with respect to **3**), and the mixture was heated at 120–130° in a sealed *Pyrex* tube[17]. After heating, TLC analysis (hexane) showed in all cases an intense blue spot with R_f of *ca.* 0.8–0.9.

The solvent was removed by distillation, and the residue was dissolved again in hexane. H_2O and aq. H_3PO_4 (dropwise) were added to adjust the pH to 4–5. The greenish-blue hexane phase was washed with H_2O and dried (Na_2SO_4). The azulene was further purified by chromatography on Alox (basic, act. IV), and the solvent was distilled off. Residual hexane was removed in high vacuum.

3.1. *1,2,3,4-Tetrahydro-5,7,9-trimethylbenz[*a*]azulene* (**20c**). Reaction time 12–14 h, average yields 55–75%. ^{1}H- and ^{13}C-NMR: see *Table 9*. EI-MS (GC/MS): 224 (90, $M^{+\bullet}$), 209 (50, $[M - Me]^+$), 196 (100, $[M - CH_2{=}CH_2]^{+\bullet}$), 194 (< 6), 165 (27).

3.2. *1,2,3,4-Tetrahydro-5,6,7,8,9-pentamethylbenz[*a*]azulen*e (**20e**). Reaction time 8–12 h. The sensitivity of this compound to oxidative degradation by air did not allow complete purification by chromatography (Alox; basic, act. IV) under standard conditions. Hexane fractions of **20e** lost their intense blue color within hours on standing in air. ^{1}H- and ^{13}C-NMR: see *Table 9*. EI-MS (GC/MS): 252 (100, $M^{+\bullet}$), 237 (77, $[M - Me]^+$), 224 (7, $[M - CH_2{=}CH_2]^{+\bullet}$), 222 (21, $[M - 2\,Me]^+$), 209 (14, $[M - (Me + CH_2{=}CH_2)]^+$), 165 (14).

3.3. *1,2,3,4-Tetrahydro-5,6,8,9-tetramethylbenz[*a*]azulene* (**20f**). Reaction time 9–11. The azulene could not be purified completely by chromatography under standard conditions. Hexane fractions of **20f** lost their intense blue color on standing, but not as rapidly as those of **20e**. ^{1}H- and ^{13}C-NMR: see *Table 9*.

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16) We thank PD Dr. *G. Fráter* for allowing us to perform some FVP experiments with the *Givaudan* apparatus.

17) The azulene formation could also be performed by heating the reaction partners in boiling EtOH.

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