91. 2,2'-Bifurylidene-5,5'-diones, Coumarins, 3a,7a-Dihydro-1*H*-inden-1-ones, and 5*H*-Furo[3,2-*b*]pyran-5-ones from Propyne and Carbon Monoxide

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Dedicated to Dr. *G. Ohloff* on the occasion of his 65th birthday

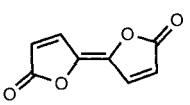
(25.I.89)

The $[Co_2(CO)_8]$-catalyzed reaction between propyne and CO in acetone at 110° and 170 bar was re-investigated. There are five major products: (*E*)-3,4'-dimethyl-2,2'-bifurylidene-5,5'-dione (**4**), 3,5,8-trimethylcoumarin (**8**), 3a,7a-dihydro-2,4,7,7a-tetramethyl-1*H*-inden-1-one (**9**), 2,6-dimethyl-5*H*-furo[3,2-*b*]-pyran-5-one (**11**), and 2,7-dimethyl-5*H*-furo[3,2-*b*]pyran-5-one (**12**); of these, only one, **4**, had previously been recognized. In parallel experiments were obtained 2,6-dipentyl-5*H*-furo[3,2-*b*]pyran-5-one (**13**), 2,7-dipentyl-5*H*-furo[3,2-*b*]pyran-5-one (**14**), 3a,7a-dihydro-2,4,7,7a-tetrapentyl-1*H*-inden-1-one (**15**), and 3a,7a-dihydro-2,4,6,7a-tetrapentyl-1*H*-inden-1-one (**16**) from hept-1-yne, and two further types of products from two atypical 1-alkynes: 3,6,9-tri(*tert*-butyl)-1-oxaspiro[4.4]nona-3,6,8-trien-2-one (**20**) from (*tert*-butyl)acetylene and the *exo*-dimer **21** of 2,5-bis(trimethylsilyl)cyclopenta-2,4-dien-1-one (**22**) from (trimethylsilyl)acetylene. Compounds **11**, **12**, and **20** were identified by X-ray analysis.

1. Introduction. – In 1959, two groups, at the *Dupont* company [1b-e] and at the Politecnico in Milan [1f-h], independently announced the discovery [1a] of a catalytic reaction between CO and certain simple alkynes (acetylene [1b] [1f] [1h] and 1-alkynes such as propyne [1b] [1g], hex-1-yne [1b], and some arylacetylenes [1b]) that produces 2,2'-bifurylidene-5,5'-diones[1]), *e.g.* the parent (*E*)- and (*Z*)-2,2'-bifurylidene-5,5'-diones **1** and **2**. Internal alkynes such as hex-3-yne also react, but the yield is much lower [1b] [2]. This reaction is a unique catalytic multistep process that does not fit into any normal category. Thus, simply consider the architecture of the products: *four CO* units are linked up in a contiguous chain O–C–O–C–C–O–C–O, and *two alkyne* units are attached to each C–O–C unit. The catalyst is $[Co_2(CO)_8]$, and the reaction has been run at temperatures around 100° and CO pressures of 100–300 and up to 1000 bar. Polar aprotic solvents such as MeCN [1b], $MeNO_2$ [1b], acetone [1b] [1f] [1g], *N,N,N',N'*-tetramethylurea [1b], esters [1b], and ethers [1b] appear to be most suitable, but apolar solvents, namely benzene [1h], halogenated hydrocarbons [1b], and even hydrocarbons [1b] have also been used. The yields in acetone as the solvent can be improved by adding phosphines or phosphites [3].

[1]) Previous nomenclature: bifurandiones [1b-e], octatrienediolides [1f-h]; systematic nomenclature: 5-(oxofuran-2(5*H*)-ylidene)furan-2(5*H*)-ones.

In 1965, a group at *BASF* reported that coumarin (**3**) is formed besides **1** and **2** [1i]. This is intriguing, because **3** cannot be built up from acetylene and CO units: it contains an extra C-atom *(2 CO + 3 acetylene + C)*. Patents were filed by all three groups, but there have been no reported industrial applications.



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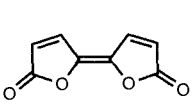

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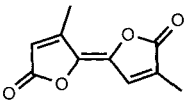

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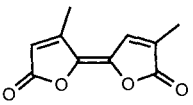

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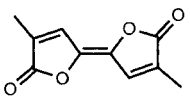

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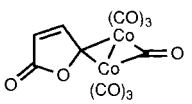

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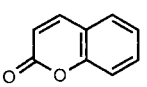

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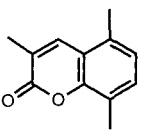

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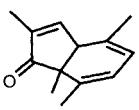

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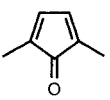

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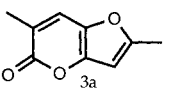

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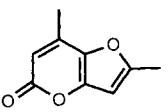

12

The structures of **1**, **2**, (*E*)-3,4'-dimethyl-2,2'-bifurylidene-5,5'-dione (**4**), and the corresponding (*Z*)-isomer **5** were established chemically – no mean feat, *inter alia* by conversion into octanedioic acid [1b] [1c] [1f] and the 2,6-dimethyloctanedioic acids [1g] – and those of **1**, **2**, and (*E*)-4,4'-dimethyl-2,2'-bifurylidene-5,5'-dione (**6**) also by X-ray diffraction [4]. The geometries of **4** and **5** were assigned on the basis of their dipole moments [1g].

In 1959, it was again independently discovered that the corresponding stoichiometric reaction between alkynes, $[Co_2(CO)_8]$, and CO under pressure leads to Co complexes that contain 5-oxofur-2(5*H*)-ylidene groups as bridging carbene ligands [5], the structure of the parent complex **7** again being determined by X-ray analysis [6]. The complexes are formed regioselectively [7]: thus, the 5-oxofur-2(5*H*)-ylidene ligands derived from 1-alkynes have the alkyl group exclusively $\alpha$to the C=O group [2] [7b]. In 1975, it was shown that these complexes are intermediates in the catalytic reaction that leads to the bifurylidenediones [2] [7c], as expected. This does not proceed by dimerization of the carbene units; instead, CO and the alkyne are grafted onto the complex.

Under the conditions of the bifurylidenedione-forming reaction, but in the presence of H_2O, succinic acid is generated from acetylene and CO [8].

2. Results. – In the course of a study of a *Pauson-Khand* reaction [9], we have re-investigated[2]) the products that are formed from propyne under the conditions of the bifurylidenedione-forming reaction by present-day GC techniques. In the early Italian work, the bifurylidenediones **4–6** were isolated by fractional crystallization [1g], and the yields and proportions of these three products were not determined. The group that proved that complexes such as **7** are intermediates in the catalytic cycle repeated the Italian work and found only trace amounts of **5** and **6**, with **6** the least abundant [2], but no other products[3]).

We now report that there are in fact five major products: the bifurylidenedione **4** [1g], 3,5,8-trimethylcoumarin (**8**), which corresponds to *Reppe*'s parent coumarin (**3**) [1i], 3a,7a-dihydro-2,4,7,7a-tetramethyl-1*H*-inden-1-one (**9**), which is derived from 2,5-dimethylcyclopenta-2,4-dien-1-one (**10**), and two entirely new products, 2,6-dimethyl-5*H*-furo[3,2-*b*]pyran-5-one (**11**) and 2,7-dimethyl-5*H*-furo[3,2-*b*]pyran-5-one (**12**). In our hands, distillation and recrystallization furnished only **4** and traces of **5**, which explains why **8**, **9**, **11**, and **12** were previously overlooked.

The furopyranones **11** and **12** contain *three CO* units instead of four in **4**, in a contiguous chain O–C–O–C–C–O, again with *two alkyne* units attached to it. Mechanistically, the formation of the furopyranones and coumarins is clearly linked, and that link makes it obvious that the extra C-atoms in the coumarins come from the CO, and also how the O-atoms are lost.

2.1. *Details.* We repeated *Albanesi*'s procedure [1g] several times and injected the crude concentrates obtained after evaporation of the solvent acetone directly into a capillary GC. The chromatograms show five major components, numbered *I* to *V* in the order in which they are eluted, against an uninterrupted background of innumerable minor and trace components (some 200 resolved peaks), and indicate that these main components make up *ca.* 6, 13, 12, 12, and 10%, respectively, a total of *ca.* 50%, of the volatiles in the crude mixture. Rough bulb-to-bulb fractionation which also removed non-volatiles followed by recrystallization from toluene enriched *IV*, as monitored by GC. Four recrystallizations from toluene[4]) gave nearly pure *IV* (m.p. 179–181° after the third and fourth recrystallization, pale yellow needles, *ca.* 95% pure by GC). Two further recrystallizations from AcOEt raised the m.p. to 181–182° without improving the purity as determined by GC. That *IV* is **4** was established by comparison of the IR spectrum with the published spectrum [1g]; the published structure assignment had been based on chemical transformations and the dipole moment, reinforced by the crystal structures of the bifurylidenediones **1**, **2**, and **6** (see above). Our m.p. is lower than the published one (188–189°, yellow needles [1g]). The ^{1}H- and ^{13}C-NMR spectra and the MS, which had not been recorded before, are consistent with structure **4** without proving it; as in the case of **11** and **12** (see below), the spectra do not contain enough information to permit an independent structure assignment or confirmation.

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[2]) Under milder conditions, at 65°/1 bar, acetylene and CO (1:1 mixture) react in benzene or 1,2-dimethoxyethane in the presence of $[Co_2(CO)_8]$ to give, in low yield, bicyclo[3.3.0]octa-3,7-diene-2,6-dione, benzoquinone, and four compounds derived from cyclopenta-2,4-dien-1-one, but **1** and **2** are not formed [10].

[3]) Analogous experiments with pent-1-yne and hex-1-yne have also been carried out, and (*E*)-/(*Z*)-bifurylidenedione (*cf.* **4/5**) ratios of 9:1 were determined; only traces of the symmetrical isomers (*cf.* **6**) were detected and no other products described [3].

[4]) We recrystallized from toluene instead of benzene [1g].

GC indicates that our samples contain another component (one small peak just before that of **4** integrating for *ca.* 5% of the main peak), and GC/MS shows that the major and minor component have identical MS. We, therefore, assume that the minor component is the (*Z*)-isomer **5**. The shape of the minor peak suggests that this **5** may be formed in part by isomerization of **4** on the column (column at 150°, injector at 280°). Directly by GC/MS of the unseparated fraction, we also identify **4** and what we assume is **5**, the ratio of the two being likewise *ca.* 95:5, but we did not find the third isomer **6**; the Italian group had isolated **4**, **5** (m.p. 182–183°, white needles), and **6** (m.p. 261–262°, white needles) by fractional crystallization [1g] (see above).

Because of the low solubility of **4** (main component *IV*), the first mother liquors contained almost no **4**, but still most of the components *II*, *III*, and *V* originally present in the fraction that had been crystallized. These three could be conveniently isolated from the mother liquors by prep. GC: direct separation of **8** (*IV*) and *V* by GC would have been difficult.

From the ^{1}H- and ^{13}C-NMR spectra and the MS, we conclude that *II* (m.p. 85–86°, yellow needles, pure by GC) and *III* (m.p. 109–111°, pale yellow needles, pure by GC) have the same composition *(3 CO + 2 propyne)* and probably the same basic structure: thus, they probably differ only in that one or both Me groups are in different positions. However, the spectra do not contain enough information to permit an assignment of the basic structure. For example, the ^{1}H-NMR spectra consist only of two Me *singlets* and two low-field 1-H *singlets*. The correct structures were conceived at one point and then excluded, despite the fact that the UV and ^{1}H-NMR spectra of *III* fit those of the single 5*H*-furo[3,2-*b*]pyran-5-one in the literature [11], because the ^{13}C-NMR spectra exhibit two signals that are typical for ester C=O groups, at 156 and 163 ppm in the case of *II*, and at 157 and 163 ppm in the case of *III*; in the spectra of the dipentyl analogs **13** and **14** (see below), these signals are even closer together, at 160 and 163 ppm for **13**, and at 161 and 163 ppm for **14**. Since the compounds contain only three O-atoms, the two signals suggested that they were anhydrides. Saponification was tried to no avail. Slow evaporation under Ar of EtOH solutions of *II* and *III* isolated by prep. GC provided crystals suitable for X-ray analyses which establish that *II* is **11** and *III* is **12**. We assign the ^{13}C-NMR signals at *ca.* 160 ppm to the C(3a)-atoms of the furopyranones.

We know from the MS that *V* (m.p. 95–96°, white needles, pure by GC) has a mol. wt. of 188 and from the ^{13}C-NMR spectrum that it contains 12 C-atoms, which defines the composition *(2 CO + 3 propyne + C)*. The extra C-atom reminded us of *Reppe*'s coumarin **3** [1i]. These clues, combined with the ^{1}H-NMR spectrum and the mechanism of the formation of the furopyranones (see *Chapt. 3*), convinced us that *V* is **8**, which was confirmed by an independent synthesis of **8** *via Reimer-Tiemann* formylation of 2,5-dimethylphenol [12] followed by *Perkin* synthesis [13].

Component *I* could be isolated by prep. GC from the first fraction of the bulb-to-bulb distillation. The structure of the tetrapentyl analog, 3a,7a-dihydro-2,4,7,7a-tetrapentyl-1*H*-inden-1-one (**15**), was solved first (see *Chapt. 2.2*). That *I* is the tetramethyl analog **9**, was established by correlation of the ^{1}H- and ^{13}C-NMR spectra and the MS. The analog **15** was independently synthesized *via Diels-Alder* dimerization of 2,5-dipentylcyclopenta-2,4-dien-1-one (**17**) [14] and decarbonylation of the dimer [14]. The indenones **9** and **15** undoubtedly also arise in this fashion under the conditions of the bifurylidenedione-forming

reaction (see *Chapt. 3*). Accordingly, the Co-catalyzed process furnishes free 2,5-dimethylcyclopenta-2,4-dien-1-one (**10**) and the free dipentyl analog **17** (see below), which are then transformed into **9** and **15**, respectively, by purely thermal reactions, dimerization, and decarbonylation, the latter re-liberating one of two CO molecules introduced in the Co-catalyzed process. The mol. wt. of **9** is 188 and its composition is *1 CO + 4 propyne*, which we first thought was also that of **8**.

By GC/MS of a fraction of the bulb-to-bulb fractionation, which contained the entire mixture of the volatile products but had the non-volatiles removed, we were able to record a total of 24 MS: those of the five major components and of 19 minor ones. Of the latter, seven are partially or tentatively identified: two further trimethylindenones (**a** and **b**) and three further trimethylcoumarins (**c**,**d**, and **e**) with unknown substitution patterns, the compound we assume is **5**, and a compound **f** with a mol. wt. of 176, probably with the composition *2CO + 3 propyne*, which could be 3,6,9-trimethyl-1-oxaspiro[4.4]nona-3,6,8-trien-2-one (*cf.* **20**, see *Chapt. 2.2*). In another coupling, we detected another minor component **g** with a mol. wt. of 204 corresponding to the composition *3 CO + 3 propyne*, which is probably a hydroxytrimethylcoumarin formed by rearrangement of the corresponding oxepin or perhaps that oxepin (see *Chapt. 3*).

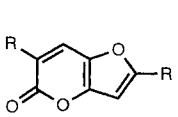
From the GC analyses and the weights of the three fractions in the bulb-to-bulb distillation, we estimate that the yields of the main products formed from 100 mmol propyne are *approximately* as follows: 6.0% of **9**, 4.6% of **11**, 4.4% of **12**, 4.0% of **4**, and 6.6% of **8**; thus, a total of *ca.* 25% of the propyne is converted into these five compounds which make up *ca.* 50% of the volatile products detected by GC (see above); we did not check whether the propyne was completely consumed.

We did not carry out a systematic study, but we have found that the product distribution is strongly affected by the CO pressure and the propyne concentration.

2.2. *Background.* The starting point of the present investigation was a *Pauson-Khand* reaction [9] involving hept-1-yne, hept-1-ene, and CO under pressure. Since hept-1-ene is unreactive in the *Khand* reaction, we saw reactions that did not involve it, and to learn what these are, we ended up leaving it out altogether. We report here that four major products are formed from hept-1-yne and CO under *Albanesi*'s reaction conditions [1g]: the furopyranones corresponding to **11** and **12**, *i.e.* 2,6-dipentyl-5*H*-furo[3,2-*b*]pyran-5-one (**13**) and 2,7-dipentyl-5*H*-furo[3,2-*b*]pyran-5-one (**14**), and in addition two dihydroindenones, *i.e.* 3a,7a-dihydro-2,4,7,7a-tetrapentyl-1*H*-inden-1-one (**15**), which corresponds to **9** (see *Chapt. 2.1*), and 3a,7a-dihydro-2,4,6,7a-tetrapentyl-1*H*-inden-1-one (**16**). We did *not* find the bifurylidenediones that we expected (see *Chapt. 1*); they are certainly not major products.

Compounds **13** and **14** are oils and their spectra correspond to and, thus, are as uninformative as those of **11** and **12**. Their structures were only assigned by correlation of the spectra, once the crystal structures of **11** and **12** were on hand. But we did not head straight for **11** and **12**, because they are the products of a reaction that had been reported to lead to **4**–**6**, and *not* to **11** and **12**.

On the other hand, **15** and **16** could be identified by their spectra, and **15** was independently synthesized *via* the generation of its precursor, 2,5-dipentylcyclopenta-2,4-dien-1-one (**17**; see *Chapt. 2.1* and *3*). The spectra of **15** and **16** can be correlated so that the identification of **16** is also secure. Compound **16** is formed *via* a regioselective *Diels-Alder*



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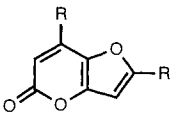

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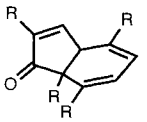

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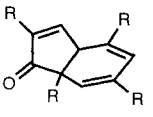

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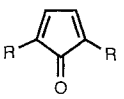
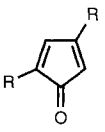


17, 22



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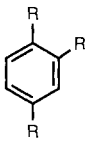

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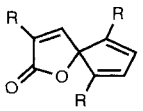

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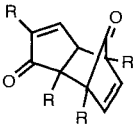


21

13 – 19 : R = Pentyl
20 : R = *t*-Bu
21, 22 : R = Me_3Si

reaction between **17** as the ene and 2,4-dipentylcyclopenta-2,4-dien-1-one (**18**) as the diene. This *Diels-Alder* reaction was not re-enacted, because it requires side-by-side generation of **17** and **18**.

As in the case of propyne, the product distribution (**13–16**) depends on the CO pressure and the concentration of the alkyne. In addition, a fifth major product, 1,2,4-tripentylbenzene (**19**), was seen, when the reaction was run at a higher concentration of hept-1-yne, in toluene. The critical factor here is probably the concentration of hept-1-yne. Whether there is also a solvent dependence is still under investigation. Alkyne trimerization [15] can, thus, also compete; this was not studied in the reactions involving propyne.

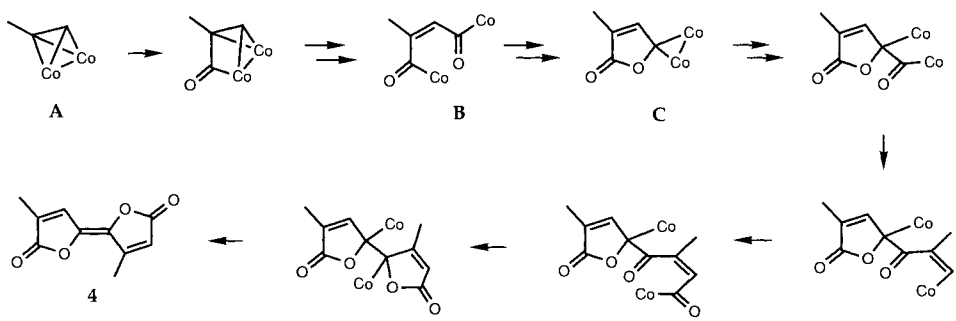
Chronologically, we did not head straight for **11** and **12** (see above), but instead ran analogous experiments with (*tert*-butyl)acetylene and (trimethylsilyl)acetylene, hoping to prepare crystalline analogs of **13** and **14**. In neither case did we find the analogs. From (*tert*-butyl)acetylene, we obtained, *inter alia*, the crystalline 3,6,9-tri(*tert*-butyl)-1-oxaspiro-[4.4]nona-3,6,8-trien-2-one (**20**) with the composition *2 CO + 3 (*tert*-butyl)acetylene* instead of *3 CO + 2 alkyne*, whose structure could again only be solved by X-ray analysis. This reaction is new[4a]). (Trimethylsilyl)acetylene reacted to give, *inter alia*, the *exo*-dimer **21** of 2,5-bis(trimethylsilyl)cyclopenta-2,4-dien-1-one (**22**) [16].

We did not study the new reaction (→**20**) further, because it involves an atypical alkyne. The bifurylidenedione-, furopyranone-, and coumarin-forming reactions may be more general, and the cyclopentadienone-forming reaction is probably the most general. Instead, we decided to re-investigate the analogous experiment involving propyne, if only to have in hand the spectra of the bifurylidenediones **4**, **5**, and **6**, in order to be able to compare them with those of **13** and **14**: at one time, we thought that **13** and **14** might be bifurylidenediones after all, despite strong evidence to the contrary.

[4a]) **Added in proof** (31.V.89): it is not! The same synthesis of **20** and its identification by X-ray analysis has just been reported [27].

3. Mechanisms. – *Schemes 1–3* sketch out one published and two new mechanisms (the CO ligands on the Co-atoms are left out for clarity). *Scheme 1* is *Heck*'s mechanism for the formation of bifurylidenediones [17] starting from the complex $[Co_2(CO)_6(propyne)]$ (**A**) [18]. The key steps are the generation of the maleoyl-bis(cobalt) derivative **B** *via* cleavage of the Co–Co bond in its precursor, and the intramolecular addition in **B**, of one acyl-Co group to the other leading to the furanone ring and eventually to the (5-oxofur-2(5*H*)-ylidene)dicobalt derivative **C** corresponding to **7**. The second ring is created *via* a second, similar intramolecular addition. Only the main pathway to **4** is shown. The overall reaction is selective for **4**. This means that both the first intramolecular addition and the propyne insertion are regioselective as shown, and also that the (*E*)-isomer **4** is favored over the (*Z*)-isomer **5**. The first two reactions are certainly under kinetic and the third probably under thermodynamic control [2]. The selectivity in the intramolecular addition is such that the first propyne unit ends up in an orientation opposite to that of the second propyne insertion; this was one of the early arguments against a carbene-dimerization mechanism [2].

Scheme 1

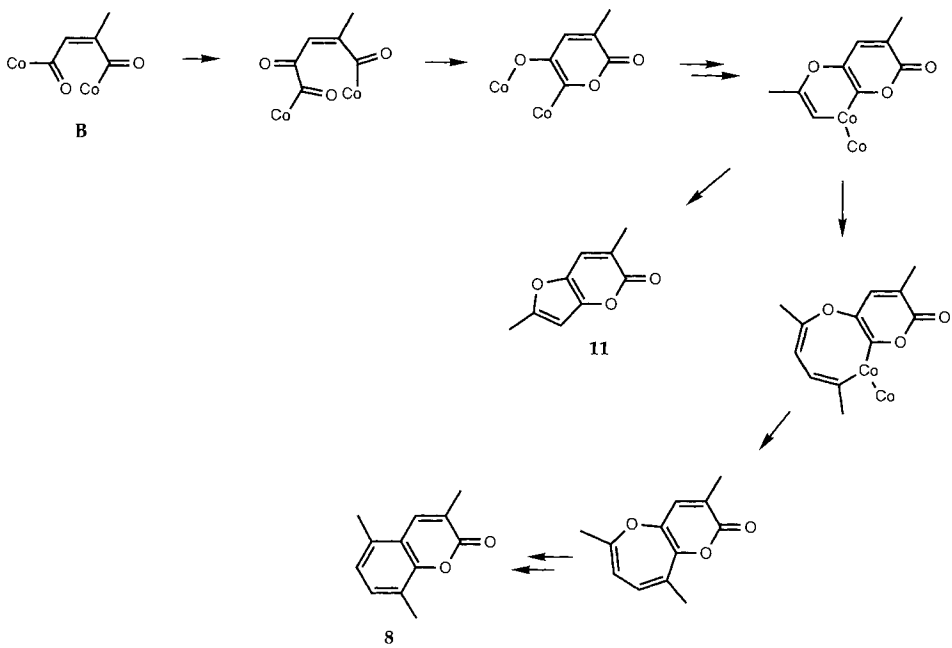


Scheme 2 suggests how **8**, **11**, and **12** are assembled. Insertion of CO into either of the acyl–Co bonds of **B** (there is now no regioselectivity, but only the insertion that leads to **11** and **8** is shown) and then intramolecular addition of the oxoacyl-Co group to the acyl-Co group generates the α-pyranone ring. Regioselective insertion of one propyne then leads to **11** and of two propynes to an oxepin-benzene oxide [19] which is then somehow deoxygenated to **8**.

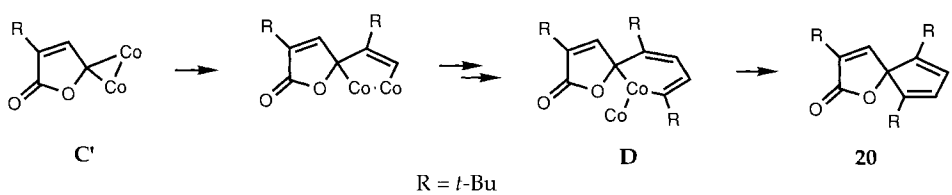
Scheme 3 illustrates how **20** arises *via* regioselective, two-fold insertion of (*tert*-butyl)acetylene starting from **C'** (*cf. Scheme 1*). Remarkably, four complexes which correspond to **D**, except for the head-to-tail orientation of the alkyne units, have previously been isolated, and the structures of two of these are known from X-ray analyses [20].

In *Chapt. 2.1* and *2.2*, it was stated that the free cyclopentadienones **10**, **17**, and **18** are the precursors of the dihydroindenones **9**, **15**, and **16**, respectively. This mechanistic information was introduced early on for clarity, since it explains the origin and provides the basis of the proof of structures **9**, **15**, and **16**. The statement is based on the known chemistry of cyclopentadienones [14] and on the actual isolation of the *Diels-Alder* dimer **21** (see *Chapt. 2.1* and *2.2*) . It is known that this particular dimerization is reversible [16], while normally decarbonylation ensues at higher temperatures [14]. There is also precedent for the

Scheme 2



Scheme 3



R = *t*-Bu

proposed catalytic reactions in that the stoichiometric, thermal reaction between complexes $[Co_2(CO)_6$((*tert*-butyl)acetylene)] or $[Co_2(CO)_6$((trimethylsilyl)acetylene)] and excess alkyne that produces complexes $[Co_2(CO)_4$(cyclopentadienone)$_2]$ [21], and the photochemical synthesis of complexes [CoCp(cyclopentadienone)] from (trimethylsilyl)acetylene and $[CoCp(CO)_2]$ [16] [21b] [21c] are well established. Ours is a catalytic version of the former process. There is even direct precedent for the entire reaction sequence in that four products derived from cyclopenta-2,4-dien-1-one, among these the *Diels-Alder* dimer (*cf.* **21**) and indan-1-one, have been obtained in low yield from acetylene and CO at atmospheric pressure at 65° in the presence of $[Co_2(CO)_8]$ [10].

Experimental Part

1. *General.* FC = flash chromatography. GC: *Hewlett-Packard* 5790, 12.5-m *Hewlett-Packard* methylsilicone cross-linked fused-silica capillary column, split-mode injection, He as carrier gas. Prep. GC: *Carlo-Erba GT*, glass columns packed with *Carbowax 20 M 15*, He as carrier gas. M.p.: *Büchi* apparatus, precision thermometers. VIS/UV: *Uvikon 820*, in EtOH, λ_{max} in nm (ε). IR: *Perkin Elmer* 597 and *Polaris-Mattson FT*; KBr in cm^{-1}. NMR: *Bruker AM 360*, 360.13 and 90.53 MHz, $CDCl_3$, δ values in ppm relative to TMS. GC/MS: *Finnigan 1020* and *4021*, 30- and 60-m *Supelco SPB1* fused-silica capillary columns; He as carrier gas.

2. *(E)-3-Methyl-5-(3-methyl-5-oxofur-2(5H)-ylidene)furan-2(5H)-one* (**4**), *3,5,8-Trimethyl-2H-[1]benzopyran-2-one* (**8**), *2,4,7,7a-Tetramethyl-3a,7a-dihydro-1H-inden-1-one* (**9**), *2,6-Dimethyl-5H-furo-[3,2-b]pyran-5-one* (**11**), *and 2,7-Dimethyl-5H-furo[3,2-b]pyran-5-one* (**12**) [1g]. Under Ar, a soln. of $[Co_2(CO)_8]$ (750 mg, 2.19 mmol) and Ac_2O (1.25 ml) in acetone (35 ml) was cooled to *ca.* –50°, and *ca.* 6.0 ml of liq. cold (–50°) propyne (d = 0.706 at –50°; *ca.* 4.2 g, 100 mmol) were added. The cold, dark-brown mixture was rapidly transferred in air into a cooled (–50°) 100-ml stainless-steel autoclave and rinsed with another 5 ml of acetone. The autoclave was purged with N_2, sealed, warmed to r.t., pressurized with 170 bar CO, and heated to 110° (pressure rise to 200 bar) for 2.5 h while stirring with a magnetically coupled mechanical high-speed stirrer. The autoclave was cooled to r.t., degassed, and its contents concentrated in a rotary evaporator. The crude concentrate was injected into a cap. GC and then subjected to bulb-to-bulb distillation at 0.002–0.005 Torr: *Fr. 1* (oven temp. 120–130°, 0.679 g, dark-brown oil), *Fr. 2* (oven temp. 130–150°, 2.397 g, some dark-brown oil and a mass of orange crystals), *Fr. 3* (oven temp. 150–220°, 1.019 g, dark-brown oil and some orange crystals), residue (2.02 g, black oil). *Fr. 2* was fractionated again: *Fr. 2.1* (oven temp.120–130°, 1.738 g, yellow crystals), *Fr. 2.2* (oven temp. 130–150°, 0.465 g, orange crystals), residue (0.192 g, dark brown oil). GC showed that, with respect to the volatiles, the composition of *Fr. 2.1* corresponded well to that of the crude concentrate, and *Fr. 2.1* was analyzed by GC/MS. *Fr. 2.2* was recrystallized 4 × from toluene, which gave 53 mg of **4**: pale-yellow needles, *ca.* 95% pure by GC.

Data of **4**. M.p. 179–181°. UV: 340 (32500). IR: 1760*s*, 1595*w*, 1380*w*, 1350*w*, 1315*w*, 1285*w*, 1220*m*, 1190*s*, 1170*w*, 1090*s*, 1045*m*, 980*m*, 905*m*, 890*m*, 860*w*[5]), 850*m*, 800*m*, 750*m*. ^{1}H-NMR: 2.14 (*d*, *J* = 1, 3 H); 2.46 (*d*, *J* = 1, 3 H); 6.11 (*s*, 1 H); 7.60 (*d*, *J* = 1, 1 H). ^{13}C-NMR: 11.25 (*q*); 14.26 (*q*); 118.68 (*d*); 131.77 (*s*); 134.39 (*d*); 136.35 (*s*); 137.35 (*s*); 153.87 (*s*); 167.82 (*s*); 169.41 (*s*). MS: 192 (56, $M^{+\cdot}$), 164 (31), 136 (27), 135 (20), 108 (14), 96 (53), 80 (11), 69 (11), 68 (100), 40 (84), 39 (74).

Anal. samples of **8**, **11**, and **12** were isolated by prep. GC from the mother liquors of **4** from two different, analogous runs, and of **9** from a fraction corresponding to *Fr. 1* above, but again in a different, analogous run. The samples were pure by GC.

Data of **8**. White needles. M.p. 95–96°. ^{1}H-NMR: 2.23 (*s*, 3 H); 2.40 (*s*, 3 H); 2.47 (*s*, 3 H); 6.96 (*d*, *J* = 3, 1 H); 7.18 (*d*, *J* = 3, 1 H); 7.69 (*s*, 1 H). ^{13}C-NMR: 15.33 (*q*); 17.39 (*q*); 18.13 (*q*); 118.05 (*s*); 123.59 (*s*); 124.65 (*s*); 125.06 (*d*); 131.49 (*d*); 132.44 (*s*); 136.59 (*d*); 152.10 (*s*); 162.28 (*s*). MS: 189 (13), 188 (97, $M^{+\cdot}$), 160 (80), 159 (96), 145 (100), 129 (15), 128 (12), 117 (14), 116 (18), 115 (48), 91 (38), 89 (10), 79 (12), 77 (19), 65 (19), 64 (12), 63 (16), 51 (19), 39 (11).

Data of **9**. Yellow oil. ^{1}H-NMR: 1.21 (*s*, 3 H); 1.79 (*s*, 3 H); 1.82 (*s*, 3 H); 1.91 (*s*, 3 H); 2.93 (br. *s*, 1 H); 5.57 (*d*, *J* = 6, 1 H); 5.64 (*d*, *J* = 6, 1 H); 7.07 (br. *s*, 1 H). ^{13}C-NMR: 10.58 (*q*); 18.04 (*q*); 21.22 (*q*); 22.65 (*q*); 52.89 (*s*); 53.90 (*d*); 119.15 (*d*); 119.53 (*d*); 130.69 (*s*); 132.17 (*s*); 140.49 (*s*); 153.62 (*d*); 210.06 (*s*). MS: 188 (36, $M^{+\cdot}$), 174 (12), 173 (100), 145 (52), 130 (19), 129 (12), 128 (12), 120 (11), 117 (10), 115 (11), 105 (43), 91 (13), 77 (13), 39 (11).

Data of **11**. Yellow needles[6]). M.p. 85–86°. UV: 342 (12800), 235 (3800), 205 (8100). ^{1}H-NMR: 2.15 (*s*, 3 H); 2.40 (*s*, 3 H); 6.20 (*s*, 1 H); 7.44 (*s*, 1 H). ^{13}C-NMR: 14.52 (*q*); 17.74 (*q*); 99.65 (*d*); 117.21 (*s*); 128.67 (*d*); 135.85 (*s*); 147.91 (*s*); 156.04 (*s*); 163.39 (*s*). MS: 164 (65, $M^{+\cdot}$), 136 (33), 135 (100), 68 (32), 40 (20), 39 (33).

Data of **12**. Pale-yellow needles[6]). M.p. 109–111°. UV: 340 (12800), 230 (sh, 2900), 205 (11700). ^{1}H-NMR: 2.32 (*s*, 3 H); 2.42 (*s*, 3 H); 5.81 (*s*, 1 H); 6.21 (*s*, 1 H). ^{13}C-NMR: 14.58 (*q*); 15.47 (*q*); 99.91 (*d*); 105.74 (*d*); 136.75 (*s*); 144.60 (*s*); 148.85 (*s*); 157.24 (*s*); 162.57 (*s*). MS: 164 (100, $M^{+\cdot}$), 136 (65), 135 (51), 121 (12), 107 (10), 96 (12), 68 (57), 67 (10), 40 (36), 39 (51).

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[5]) The band at 860 cm^{-1} is *weak* in our spectrum and *medium* in [1g]; all other bands are in agreement with those reported in [1g].

[6]) In air, the yellow needles of **11** were quickly coated by an orange-brown oil, presumably through surface reaction with O_2. The light-yellow needles of **12** appeared to be more stable in air.

GC/MS of Fr. 2.1. The spectra of the dihydroindenones **a** and **b** were identical to those of **9**, and the spectra of the coumarins **c**, **d**, and **e** identical to those of **8**; compound **f** was tentatively identified as 3,6,9-trimethyl-1-oxaspiro[4.4]nona-3,6,8-trien-2-one. MS: 176 (65, $M^{+\cdot}$), 161 (19), 148 (26), 138 (97), 133 (26), 123 (10), 120 (10), 108 (10), 105 (89), 96 (70), 95 (32), 91 (17), 82 (11), 79 (22), 77 (27), 70 (18), 68 (62), 67 (42), 65 (10), 55 (12), 53 (17), 51 (17), 42 (29), 41 (59), 40 (29), 39 (100). Compound **g** was tentatively identified as a (hydroxy)(trimethyl)coumarin. MS: 204 (58, $M^{+\cdot}$), 176 (10), 175 (14), 161 (49), 159 (10), 148 (14), 147 (17), 136 (12), 133 (56), 121 (10), 120 (28), 108 (35), 107 (12), 105 (46), 103 (14), 96 (89), 91 (12), 80 (44), 79 (100), 77 (89), 68 (96), 67 (17), 65 (29), 53 (14), 51 (15), 44 (52), 43 (19), 40 (58), 39 (59).

3. *Independent Synthesis of* **8.** 3.1. *2-Hydroxy-3,6-dimethylbenzaldehyde* (**23**). Within *ca.* 20 min, $CHCl_3$ (29 ml, 43 g, 0.36 mol) was added dropwise to a refluxing soln. of 2,5-dimethylphenol (22.6 g, 185 mmol) in 1 l aq. NaOH soln. (40.0 g, 1.0 mol). Reflux was continued for 1.5 h, another 29 ml of $CHCl_3$ were added within 20 min, and reflux continued for another 6 h. Acidification and standard workup furnished 24.5 g of crude material. GC: 60% of 2,5-dimethylphenol, 9% of **23**, 23% of *4-hydroxy-2,5-dimethylbenzaldehyde* (**24**), and 3 unidentified compounds (2, 2, and 4%) among the volatiles. On FC (SiO_2, Et_2O/hexane 1:9), **23** (990 mg, 6.60 mmol, 3.6%) was eluted first.

Data of **23**. Pale-yellow needles, pure by GC. M.p. 60–61°, after one crystallization from hexane ([12b]: m.p. 62–63°). ^{1}H-NMR: 2.21 (*s*, 3 H); 2.57 (*s*, 3 H); 6.61 (*d*, *J* = 3, 1 H); 7.24 (*d*, *J* = 3, 1 H); 10.29 (*s*, 1 H); 12.16 (*s*, 1 H). MS: 150 (93, $M^{+\cdot}$), 149 (100), 132 (10), 121 (18), 107 (10), 104 (21), 103 (14), 91 (28), 78 (18), 77 (33), 65 (12), 51 (10).

The method described in [22] led to **24** only. White needles. M.p. 131–132°, after one crystallization from hexane/Et_2O ([12a]: m.p. 129–130°). ^{1}H-NMR: 2.19 (*s*, 3 H); 2.53 (*s*, 3 H); 4.91 (br. *s*, 1 H); 6.63 (*s*, 1 H); 7.53 (*s*, 1 H); 9.96 (*s*, 1 H). MS: 150 (68, $M^{+\cdot}$), 149 (100), 121 (47), 91 (31), 77 (37), 65 (12), 51 (11).

3.2. *Coumarin* **8**. A mixture of **23** (300 mg, 2.00 mmol), sodium propionate (304 mg, 3.17 mmol), two drops of piperidine [13b], and propionic anhydride (1.0 ml, 1.01 g, 7.78 mmol) was heated to 160° for 3 h. Standard workup, bulb-to-bulb distillation (oven temp. 190°, *ca.* 0.05 Torr), and one crystallization from hexane furnished **8** (121 mg, 0.64 mmol, 32%). White needles, pure by GC. M.p. 95–96°.

Data of **8**: see *Exper. 2.*

4. *2,6-Dipentyl-5*H*-furo[3,2-*b*]pyran-5-one* (**13**), *2,7-Dipentyl-5*H*-furo[3,2-*b*]pyran-5-one* (**14**), *3a,7a-Dihydro-2,4,7,7a-tetrapentyl-1*H*-inden-1-one* (**15**), *and 3a,7a-Dihydro-2,4,6,7a-tetrapentyl-1*H*-inden-1-one* (**16**). The method of *Albanesi* (*Exper. 2*) was modified by substituting hept-1-yne (13.1 ml, 9.6 g, 100 mmol) for the cold propyne (6.0 ml) and omitting the cooling cycle. The crude concentrate was injected into a cap. GC. The chromatogram showed 4 volatile main components: *ca.* 9% of **13**, 9% of **14**, 16% of **15**, and 15% of **16**. Anal. samples were isolated by FC, bulb-to-bulb distillation, and prep. GC in this and several parallel runs. **13** and **14**: nearly pure or pure by GC. **15** and **16** could not be separated; spectra of a pure (GC) *ca.* 1:1 mixture and of 86% pure **15** synthesized independently (see *Exper. 5.4*) were recorded.

Data of **13**. Pale-yellow oil. ^{1}H-NMR: 0.81–0.97 (*m*, 6 H); 1.23–1.43 (*m*, 8 H); 1.52–1.75 (*m*, 4 H); 2.48 (*t*, *J* = 7, 2 H); 2.68 (*t*, *J* = 7, 2 H); 6.18 (*s*, 1 H); 7.41 (*s*, 1 H). ^{13}C-NMR: 13.92 (*q*); 14.02 (*q*); 22.32 (*t*); 22.49 (*t*); 27.30 (*t*); 27.84 (*t*); 28.79 (*t*); 31.22 (*t*); 31.35 (*t*); 31.41 (*t*); 98.81 (*d*); 121.31 (*s*); 127.94 (*d*); 135.83 (*s*); 147.60 (*s*); 160.46 (*s*); 163.08 (*s*). MS: 276 (12, $M^{+\cdot}$), 220 (24), 219 (100), 205 (10), 192 (19), 191 (55), 178 (13), 163 (21), 149 (13), 135 (13), 134 (18), 81 (15), 68 (11), 67 (91), 55 (18), 53 (18), 41 (20), 39 (27).

Data of **14**. Pale-yellow oil. ^{1}H-NMR: 0.91 (*t*, *J* = 7, 6 H); 1.27–1.43 (*m*, 8 H); 1.63–1.76 (*m*, 4 H); 2.64 (*t*, *J* = 7, 2 H); 2.70 (*t*, *J* = 7, 2H); 5.80 (*s*, 1 H); 6.20 (*s*, 1 H). ^{13}C-NMR: 13.90 (*q*); 22.31 (*t*); 27.27 (*t*); 27.40 (*t*); 27.84 (*t*); 28.85 (*t*); 29.90 (*t*); 31.23 (*t*); 31.35 (*t*); 99.05 (*d*); 104.68 (*d*); 136.25 (*s*); 148.85 (*s*); 149.05 (*s*); 161.44 (*s*); 162.95 (*s*). MS: 276 (9, $M^{+\cdot}$), 233 (18), 221 (13), 220 (100), 205 (20), 177 (17), 164 (13), 163 (94), 149 (10), 135 (24), 96 (12), 95 (15), 81 (37), 68 (16), 67 (78), 54 (19), 53 (29), 43 (11), 41 (19), 39 (28).

Data of **15**. Pale-yellow oil. ^{1}H-NMR: 0.80–1.00 (*m*, 12 H); 1.00–1.70 (series of *m*, 26 H); 1.90–2.30 (3 series of *m*, 6 H); 3.03 (br. *s*, 1 H); 5,69 (*d*, *J* = 6, 1 H); 5.72 (*d*, *J* = 6, 1 H); 6.93 (br. *s*, 1 H). ^{13}C-NMR: 14.03 (*q*); 22.45 (*t*); 22.51 (*t*); 22.67 (*t*); 24.10 (*t*); 25.18 (*t*); 27.10 (*t*); 27.37 (*t*); 28.79 (*t*); 29.03 (*t*); 31.59 (*t*); 31.72 (*t*); 31.88 (*t*); 32.36 (*t*); 34.78 (*t*); 36.11 (*t*); 50.23 (*d*); 58.41 (*s*); 118.81 (*d*); 119.59 (*d*); 134.93 (*s*); 135.07 (*s*); 145.25 (*s*); 152.66 (*d*); 210.10 (*s*). MS: 412 (25, $M^{+\cdot}$), 342 (13), 341 (100), 285 (8), 215 (7), 43 (19).

Data of **16**. Pale-yellow oil. ^{1}H-NMR: high-field signals very similar to those of **15** except that the 26-H series of *m* reach down to *ca.* 1.77; 3.07 (br. *s*, 1 H); 4.82 (br. *s*, 1 H); 5.56 (br. *s*, 1 H); 7.05 (br. *s*, 1 H). MS: 412 (23, $M^{+\cdot}$), 342 (23), 341 (100), 285 (6), 215 (8), 43 (21), 41 (8).

5. *Independent Synthesis of* **15**. 5.1. *2-Oxo-3-pentylcyclopent-3-ene-1-carbaldehyde* (**25**). Within *ca.* 1.5 h, a mixture of ethyl formate (18.25 g, 0.25 mol) and 2-pentylcyclopent-2-en-1-one (38.00 g, 0.25 mol) was added

dropwise to a stirred suspension of NaH (60% dispersion in mineral oil; 6.0 g, 0.25 mol) in cyclohexane (125 ml), the addition rate being adjusted to maintain gentle reflux. Stirring was continued overnight at r.t. Standard workup and distillation (short *Vigreux* column, b.p. 92°/*ca.* 0.05 Torr) gave 28.70 g (0.16 mol, 64%) of **25**, 99% pure by GC. ^{1}H-NMR ($CDCl_3$): complex, because several isomers are present. GC and GC/MS: 1 sharp peak. MS: 180(28, M^+), 152 (11), 151 (24), 137 (13), 125 (19), 124 (53), 123 (78), 110 (11), 109 (18), 105 (12), 96 (33), 95 (100), 94 (10), 91 (12), 82 (13), 81 (37), 79 (22), 77 (26), 67 (51), 66 (14), 65 (20), 55 (39), 53 (21), 51 (11), 43 (11), 41 (44), 39 (31).

5.2. *2-Oxo-1,3-dipentylcyclopent-3-ene-1-carbaldehyde* (**26**). Within *ca.* 30 min, **25** (14.40 g, 80.0 mmol) was added dropwise to a stirred, cooled (ice bath) suspension of NaH (60% dispersion in mineral oil; 1.92 g, 80.0 mmol) and Bu_4NI (1.29 g, 3.50 mmol) in toluene (40 ml), the resulting white paste being successively diluted with a total of 20 ml of toluene. At once, 1-iodopentane (17.3 ml, 26.17 g, 132 mmol) was added and the mixture stirred and heated to 110° for 22 h. Standard workup and distillation (short *Vigreux* column, b.p. 142°/*ca.* 0.05 Torr) furnished 8.60 g of a mixture containing 3 main components (GC): 21% of **26**, 11% of *2,5-dipentylcyclopent-2-en-1-one* (**27**), and 57% of *2-pentyl-5-(pentyloxymethylidene)cyclopent-2-en-1-one* (**28**; one isomer with unknown geometry). Anal. samples of **26**–**28** were isolated by prep. GC. **26** readily decomposed (in part to **27**), and the purity test by GC, the ^{1}H-NMR, and GC/MS showed impurities. **27** and **28**: nearly pure by GC.

Data of **26**. ^{1}H-NMR: 0.78–0.94 (*m*, 6 H); 1.10–1.70 (series of *m*, 12 H); 1.75–1.86 (*m*, 1 H); 1.92–2.04 (*m*, 1 H); 2.13 (br. *t*, *J* = 7, 2 H); 2.33 (*dd*, *J* = 19, 2, 1 H); 3.18 (*dd*, *J* = 19, 2, 1 H); 7.35 (br. *s*, 1 H); 9.44 (*s*, 1 H). MS: 250 (1, M^+), 222 (11), 221 (24), 181 (10), 180 (58), 166 (32), 165 (100), 152 (17), 151 (22), 147 (10), 138 (17), 137 (13), 125 (28), 124 (78), 123 (52), 110 (13), 109 (67), 107 (20), 105 (12), 96 (28), 95 (47), 93 (12), 91 (23), 82 (10), 81 (37), 79 (34), 77 (25), 71 (12), 69 (21), 67 (30), 65 (13), 57 (10), 55 (58), 53 (21), 43 (32), 41 (55), 39 (20).

Data of **27**. See *Exper. 5.3*.

Data of **28**. ^{1}H-NMR: 0.80–0.95 (*m*, 6 H); 1.15–1.40 (*m*, 8 H); 1.41–1.57 (*m*, 2 H); 1.62–1.76 (*m*, 2 H); 2.22 (br. *t*, *J* = 7, 2 H); 3.08 (br. *s*, 2 H); 4.02 (*t*, *J* = 7, 2 H); 7.00 (br. *s*, 1 H); 7.25 (br. *s*, 1 H). MS: 250 (30, M^+), 194 (20), 165 (10), 151 (22), 138 (12), 137 (28), 125 (23), 124 (69), 123 (100), 110 (11), 109 (11), 107 (10), 105 (10), 96 (10), 95 (31), 90 (11), 81 (16), 79 (14), 77 (17), 67 (13), 65 (10), 55 (33), 53 (10), 43 (68), 41 (40), 38 (17).

5.3. *2,5-Dipentylcyclopent-2-en-1-one* (**27**). 12.51 g of the mixture prepared in *Exper. 5.2* (containing **26** (*ca.* 2.63 g, 10.50 mmol) and **27** (1.38 g, 6.20 mmol)) and NaOH (4.17 g, 104 mmol) in 30 ml of MeOH/H_2O 1:1 were stirred for 75 min. Acidification, standard workup, FC (SiO_2, hexane/Et_2O 9:1), and bulb-to-bulb distillation (oven temp. 200°, *ca.* 0.05 Torr) gave **27** (2.79 g, 11.90 mmol, 71%), 95% pure by GC (trace impurities). ^{1}H-NMR: 0.88 (br. *t*, *J* = 7, 6 H); 1.20–1.40 (*m*, 11 H); 1.40–1.53 (*m*, 2 H); 1.74–1.84 (*m*, 1 H); 2.10–2.27 (*m*, 3 H); 2.27–2.36 (*m*, 1 H); 2.67–2.78 (*m*, 1 H); 7.23 (br. *s*, 1 H). ^{13}C-NMR: 14.02 (*q*); 22.45 (*t*); 22.55 (*t*); 24.87 (*t*); 26.95 (*t*); 27.44 (*t*); 31.59 (*t*); 31.86 (*t*); 33.54 (*t*); 45.58 (*d*); 145.96 (*s*); 155.70 (*d*); 212.00 (*s*). MS: 222 (5, M^+), 165 (22), 153 (10), 152 (79), 109 (25), 97 (11), 96 (100), 95 (87), 82 (12), 81 (16), 79 (16), 67 (19), 55 (25), 53 (12), 43 (10), 41 (24).

5.4. *Indenone* **15** [14]. A suspension of *N*-bromosuccinimide (874 mg, 4.91 mmol) in a soln. of the batch of **27** prepared in *Exper. 5.3* (1.013 g, 4.33 mmol) and α,α'-azoisobutyronitrile (3 mg) in CCl_4 (8 ml) was stirred at reflux for 75 min. The succinimide formed was filtered off after cooling and the filtrate concentrated (rotary evaporator). This bromination presumably produces mainly cis- *and* trans-*4-bromo-2,5-dipentylcyclopent-2-en-1-one* [23], which were not characterized. Instead, the crude product was taken up in THF (12 ml) and treated at once with 1,5-diazabicyclo[4.3.0]non-5-ene (623 mg, 5.02 mmol). A white precipitate appeared immediately. The mixture was stirred at r.t. for 45 min. Standard workup and bulb-to-bulb distillation (oven temp. 200°, *ca.* 0.05 Torr) gave 682 mg of a mixture containing **15** as the main component. GC: *ca.* 60% of **15**, *i.e. ca.* 400 mg (0.97 mmol; 45% based on **24**); *ca.* 11 minor and some trace components, all of which were not identified. Purification by FC (SiO_2, hexane/Et_2O 9:1) and re-distillation gave 48 mg of **15**, 86% pure by GC: 2 minor (5 and 2%) and trace impurities.

Data of **15**. See *Exper. 4*.

6. *3,6,9-Tri*(tert-*butyl)-1-oxaspiro[4.4]nona-3,6,8-trien-2-one* (**20**). A 40-ml stainless-steel autoclave was charged with $[Co_2(CO)_8]$ (685 mg, 2.00 mmol), MeCN (0.25ml, 195 mg, 4.80 mmol), and (*tert*-butyl)acetylene (4.26 ml, 2.87 g, 35.0 mmol) in toluene (5 ml), sealed, pressurized with 60 bar CO at r.t., and heated to 120° (pressure rise to 80 bar) for 4.5 h with magnetic stirring. Chromatography on neutral Al_2O_3 (hexane/Et_2O 9:1) gave as a major fraction 938 mg (*ca.* 3.10 mmol, 25%) of **20**, nearly pure by GC. Recrystallization from MeOH led to pure **20**. A number of other compounds were also formed (not identified), but no furopyranones and bifurylidenediones were found.

Data of **20**. White needles, pure by GC. M.p. 114–115°. ^{1}H-NMR: 1.08 (*s*, 18 H); 1.30 (*s*, 9 H); 6.08 (*s*, 2 H); 6.79 (*s*, 1 H). ^{13}C-NMR: 27.50 (*q*); 30.51 (*q*); 31.86 (*s*); 34.03 (*s*); 97.31 (*s*); 126.91 (*d*); 140.92 (*s*); 149.87 (*d*);

153.24 (*s*); 172.85 (*s*). MS: 302 (5, $M^{+\cdot}$), 246 (25), 232 (15), 231 (100), 175 (11), 105 (11), 94 (23), 91 (20), 79 (10), 77 (11), 67 (11), 57 (89), 55 (13), 43 (12), 41 (38).

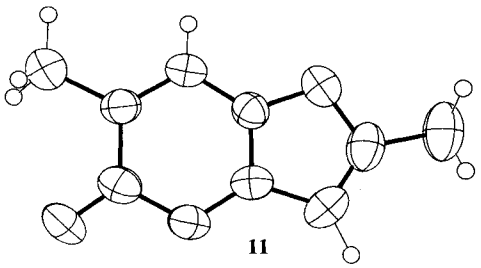
7. exo-*Dimer* **21** *of 2,5-Bis(trimethylsilyl)cyclopenta-2,4-dien-1-one* (**22**). Same procedure as in *Exper.* 6: **21** was a major product (yield not established). A number of other compounds were also formed (not identified); no furopyranones and bifurylidenediones were found.

8. *Crystallographic Data.* Crystals were placed in glass capillaries and sealed under Ar. Cell parameters and reflection intensities were measured at r.t. on *Philips-PW-1100* (**12** and **20**) and *Nonius-CAD-4* (**11**) diffractometers with graphite monochromated Mo$K\alpha$ radiation. The structures were solved by direct methods (MULTAN 84 [24]) and refined by full-matrix least-square analysis (XRAY 76 [25] for **20** and XTAL [26] for **11** and **12**). Crystal data, intensity measurements, and structure refinements are given in the *Table.* Crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre*, University Chemical Lab., Cambridge CB2 1EW, England. The *Figure* shows perspective views of **11**, **12**, and **20**.

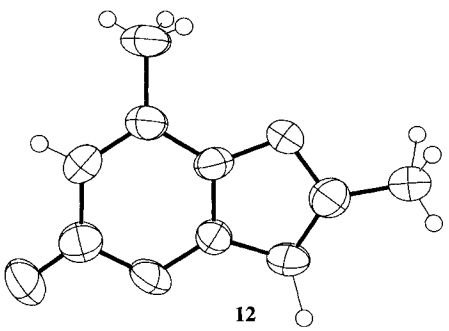
Table. *Crystal Data, Intensity Measurement, and Structure Refinement for* **11**, **12**, *and* **20**

	11	**12**	**20**
Formula	$C_9H_8O_3$	$C_9H_8O_3$	$C_{20}H_{30}O_2$
Molecular weight	164.2	164.2	302.5
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$
a [Å]	13.204(3)	7.0972(9)	15.378(3)
b [Å]	6.1547(6)	17.086(4)	9.8568(17)
c [Å]	20.133(1)	7.3454(9)	12.8153(15)
β [°]	99.75(1)	115.77(1)	99.85(1)
Z	8	4	4
D_c [g · cm^{-3}]	1.35	1.36	1.050
F_{000}	688	344	664
μ [mm^{-1}]	0.095	0.096	0.061
Unit-Cell Determination[a])			
No. of reflections	27	23	20
2θ range	20–29	18–36	19–26
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.550	0.572	0.481
No. of measured reflections	1268	1413	2026
No. of observed reflections	655	656	1191
R_{int} for equiv. reflections	0.013	0.022	0.011
Criterion for observed reflections	$\|F_0\| > 4\,\sigma(F_0)$	$\|F_0\| > 4\,\sigma(F_0)$	$\|F_0\| > 4\,\sigma(F_0)$
Refinement (on F)	full matrix	full matrix	full matrix
No. of parameters	133	133	199
Weighting scheme	$\omega = 1/\sigma^2(F_0)$	$\omega = 1/\sigma^2(F_0)$	1
H-atoms	observed and refined	observed and refined	calculated
Max. and average Δ/σ	0.806, 0.105[b])	0.140, 0.015[b])	0.023, 0.002
Max. and min. $\Delta\rho$ [e·Å^{-3}]	0.38, –0.33	0.45, –0.59	0.40, –0.50
S	2.22	3.61	8.41
R, ωR [%]	6.6, 3.0	8.7, 5.3	0.095

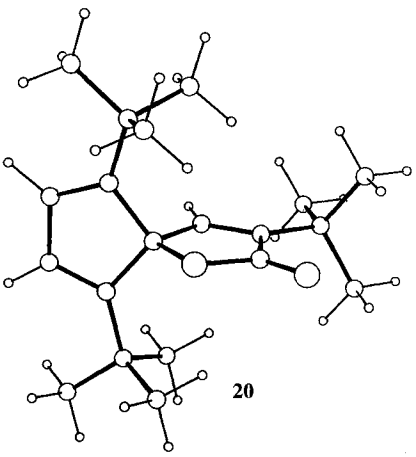
[a]) Unit cell determined by least-squares fit.
[b]) For H-atoms.



11



12



20

Figure. *Perspective views of* **11**, **12**, *and* **20**

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