Acid-Induced Stereoselective Formation of 3,5-Cycloheptadien-1-ones from Ketenes and Dienes☆

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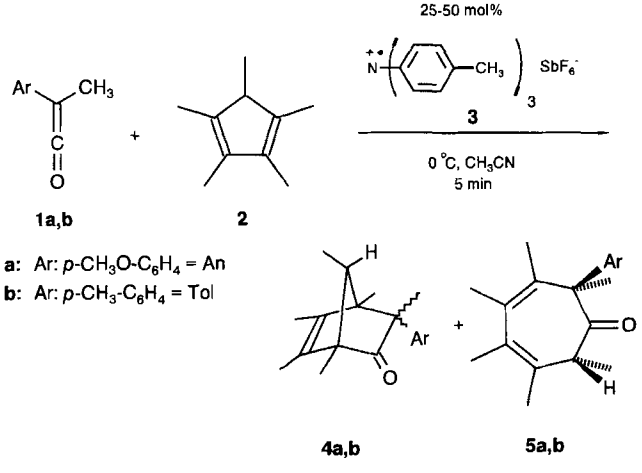
The reaction of ketenes **1a** or **1b** with diene **2** in the presence of trifluoromethanesulfonic acid providing the cycloheptadienones **5a** and **5b** constitutes the first example of an acid-induced ketene/diene "cycloaddition". The thermal [2 + 2] cycloadducts, bicyclo[3.2.0]hept-2-en-6-ones **9**, are not intermediates in the acid-catalyzed reaction since they rearrange under acidic conditions to the tetralinone derivatives **10**. The acid-catalyzed "cycloaddition" was mechanistically investigated and the scope of the reaction explored.

Almost a century after Staudinger's pioneering work[1] ketene chemistry is still of interest for theoretical[2], mechanistic[3], and synthetic investigations[4]. While most reports in the literature are concerned with the unique and synthetically important ability of ketenes to undergo [2+2] cycloadditions[5], we have developed a novel and "*peri*-selective" access to the [4+2] cycloaddition products by cation radical initiation[6]. In the presence of aminium salt **3** the electron rich alkylaryl-ketenes **1a,b** reacted with pentamethylcyclopentadiene (**2**) to yield Diels-Alder cycloaddition products, i.e. **4a,b**[6].



While mechanistic investigations indicated that the main products, the norbornenones **4a,b**, were formed on a cation radical-catalyzed route[6], formation of the 3,5-cycloheptadien-1-ones **5a,b** could be totally suppressed by the addition of 55 mol-% of 2,6-di-*tert*-butylpyridine (**8**). This observation pointed to an acid-induced process leading to **5a,b**, thus indicating a yet unprecedented mode for ketene/diene reactions, that is described in more detail in the present paper.

The structure assignment of **5a,b** to a 3,5-cycloheptadienone derivative was made on the basis of MS, ^{1}H-NMR, ^{13}C-NMR, and IR data. Especially the IR data [$\tilde{\nu}$(C=O) = 1698 cm^{-1}] exclude 2,4- or 2,5-cycloheptadien-1-one structures, as for those systems values of $\tilde{\nu}$(C=O) < 1670 cm^{-1} are expected[7]. Nevertheless, to further differentiate between the three possible, positional cycloheptadienone derivatives, **5a** was reduced with $LiAlH_4$ to alcohol **6a**. NMR-decoupling experiments with **6a** showed unambiguously the presence of a −CH(OH)−CHMe− fragment, thus supporting a 3,5-cycloheptadienone structure for **5a**. ^{1}H-NMR NOE experiments performed with **5a,b** provided additional support for the stereochemical structure assignment (see Figure 1).

Treatment of **1a** and **2** at 0°C with 25 mol-% of tris(1,10-phenanthroline)iron(III) hexafluorophosphate (**7**), a well-known outer-sphere one-electron oxidant[8], yielded as the sole non-polymeric compound the 3,5-cycloheptadienone **5a** in 25% yield.

Here too, as with aminium salt **3**, a control experiment showed that the formation of **5a** could be suppressed by the addition of a small excess of **8**. As it is well-known that in one-electron oxidation processes highly acidic cation radicals are formed[9], both the aminium and the iron(III) oxidation results are in accord with an acid-induced process with formation of **5**. Indeed, treatment of a 1:1 mixture of **1** and **2** with 150 mol-% of trifluoromethanesulfonic acid for 5 min at 0°C afforded 33% of **5a** or 59% of **5b**, respectively, besides mostly polymeric products[10]. Other acids proved to be much less effective (Table 1). In the presence of weaker acids, e.g. methanesulfonic acid or trifluoroacetic acid, formation of **5a** from **1a** and **2** was not observed. Rather a mixture of several pentamethyl-cyclopentadiene

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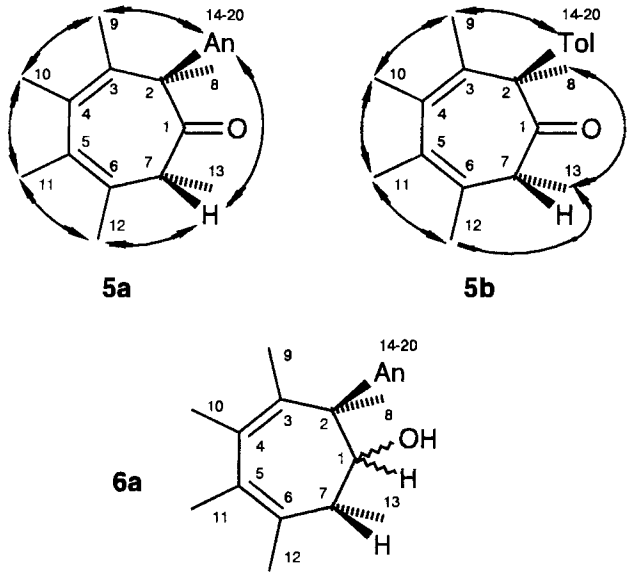
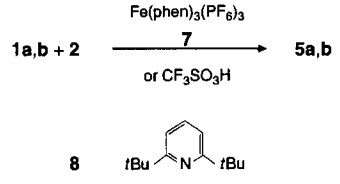


Figure 1. ^{1}H-NMR NOEs (indicated by double arrows) in the cycloheptadienones **5a, b** and structure of cycloheptadienol **6a**



homodimers (six dimers were identified by their mass spectra) and dehydro dimers (one identified dimer) in up to 99% was obtained besides up to 80% of unreacted **1a**.

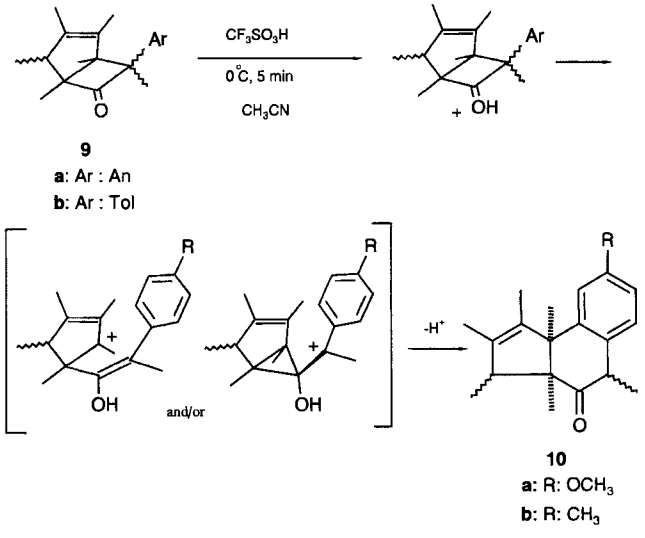
Table 1. Yields of products obtained by the acid-induced reaction of ketenes **1a, b** with diene **2** and by some related control experiments at 0°C (yields determined by ^{1}H-NMR analysis)[10]. Molar ratio **1**:**2** = 1:1 in all cases

Ketene	Acid or oxidant	mol-% of acid or oxidant	time [min]	yields[a] of **5**	other products
1a	**3**	25	5	11%	42% of **4a**
1a	**3**	50,55[b]	20	--	23% of **4a**
1a	**7**	25	5	25%	no **4a**
1a	**7**	25,28[b]	5	--	38% of acid[c], 55% dimers of **2**
1a	CF_3SO_3H	25	5	25%	< 5% dimers of **2**
1a	CF_3SO_3H	150	5	45%[d]	
1a	CF_3SO_3H	150	5	33%	no **4a**
1a	CH_3SO_3H	100	5	--	80% of acid[c], 55% dimers of **2**
1a	CH_3SO_3H	200	5	--	75% of acid[c], 99% dimers of **2**
1a	$SbCl_5$	200	5	9%	10% dimers of **2**
1b	**3**	50	5	6%	20% of **4b**
1b	CF_3SO_3H	150	5	59%	no **4b**
1b	CF_3SO_3H	150	95	30%[d]	

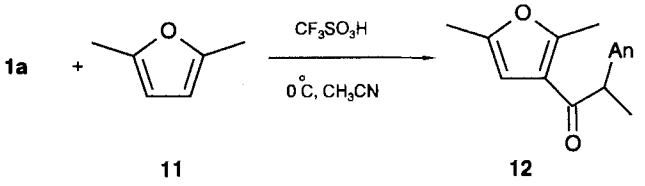
[a] mol-% compared to molar amount of **2**. – [b] The second number indicates the amount of added base **8**. – [c] Acid: 2-(4-methoxyphenyl)propionic acid formed by hydrolysis of **1a**. – [d] Isolated yield.

Reaction of **1a** with **2** in the presence of 150 mol-% of CF_3SO_3D (80% deuterated) yielded 30% of [D_1]-**5a** besides some [D_1]-**2**[11]. Interestingly, the reaction of **5a** with 150 mol-% of CF_3SO_3D showed no significant deuterium incorporation (<10%) even at room temperature within 20 min.

To test whether vinylcyclobutanone **9a**, the product of the thermal [2+2] cycloaddition of **1a** to **2**, is a potential intermediate in the above acid-catalyzed reaction, it was treated with CF_3SO_3H in acetonitrile. In 60% yield the new adduct **10a** was formed. Compound **10a** could be unequivocally identified by its spectral data to possess a tetralinone structure. The formation of **5a** was not detected. Analogously, reaction of **9b** with CF_3SO_3H under comparable conditions led to the tetralinone adduct **10b** in 35% yield. The formation of **10** is likely to proceed by the same mechanism as proposed by Lee-Ruff for the ring expansion of cyclobutanones to tetralinones[12].



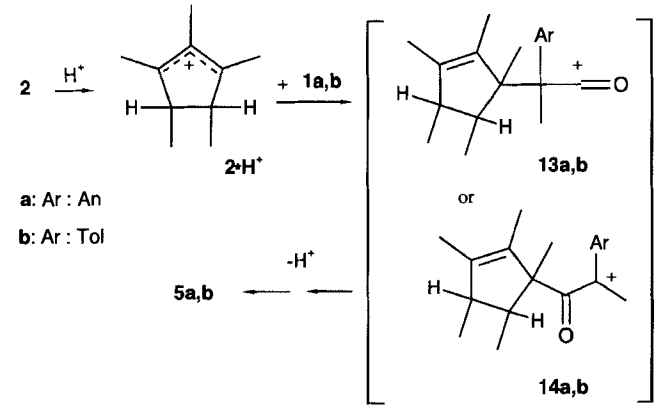
To investigate the scope of the acid-induced reaction of ketenes with dienes other model compounds were tested next. The reaction of **2** with diphenylketene in the presence of 170 mol-% of CF_3SO_3H provided a cross dimer in about 25% yield which could not be isolated. The MS fragmentation pattern argues against a cycloheptadienone structure. Analogous reactions of **1a** with 1,3-cyclohexadiene or cyclopentadiene did not show any sign of cross cycloadduct formation. In both cases only unchanged ketene was recovered besides polymeric products. The reaction of **1a** with the diene 2,5-dimethylfuran (**11**) in the presence of CF_3SO_3H afforded the cross adduct **12** in 80% yield as the only monomeric product. No cycloadduct could be detected.



Discussion

To the best of our knowledge the reaction of **1a,b** with **2** in the presence of CF_3SO_3H or one-electron oxidants constitutes the first example of an acid-induced "cycloaddition" of ketenes to dienes. While this reaction mode complements the thermal [2+2] and the aminium salt-initiated formal [4+2] cycloaddition, it does not seem to be of general scope. The mechanistic results obtained so far help to understand the limitations of the new reaction mode.

Although protonated ketenes[13] play an important role in acid-catalyzed hydration reactions, it is most obvious from the products formed that protonation of diene **2** and not of ketene **1a,b** initiates the cycloheptadienone formation[14].



The facile, basically quantitative formation of protonated $\mathbf{2}\cdot H^+$ has been demonstrated to occur even with weaker acids, as in neat CF_3CO_2H[15]. Similarly, deuterium incorporation under our reaction conditions into recovered **2** points to protonation of the diene even in dilute CF_3SO_3H. However, it is important to stress that in the presence of weaker acids, e.g. CH_3SO_3H (pK_a = 10.0)[16] and CF_3CO_2H (pK_a = 12.65)[16], in acetonitrile no cycloheptadienones but rather dimers of **2** were formed. Only CF_3SO_3H (pK_a = 2.60)[16] appears to be strong enough to achieve quantitative protonation of **2** which is necessary to push back acid-catalyzed homodimerization of **2** and $\mathbf{2}\cdot H^+$[17].

Regioselectivity: To answer the question whether the formation of the 3,5-cycloheptadien-1-ones **5** proceeds via the cationic intermediate **13** or **14** we refer to the plausible assumption that the attack of carbenium ion $\mathbf{2}\cdot H^+$ on **1** proceeds with the same regioselectivity as that of a proton.

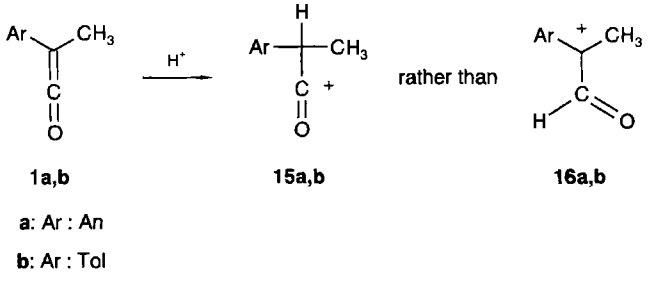
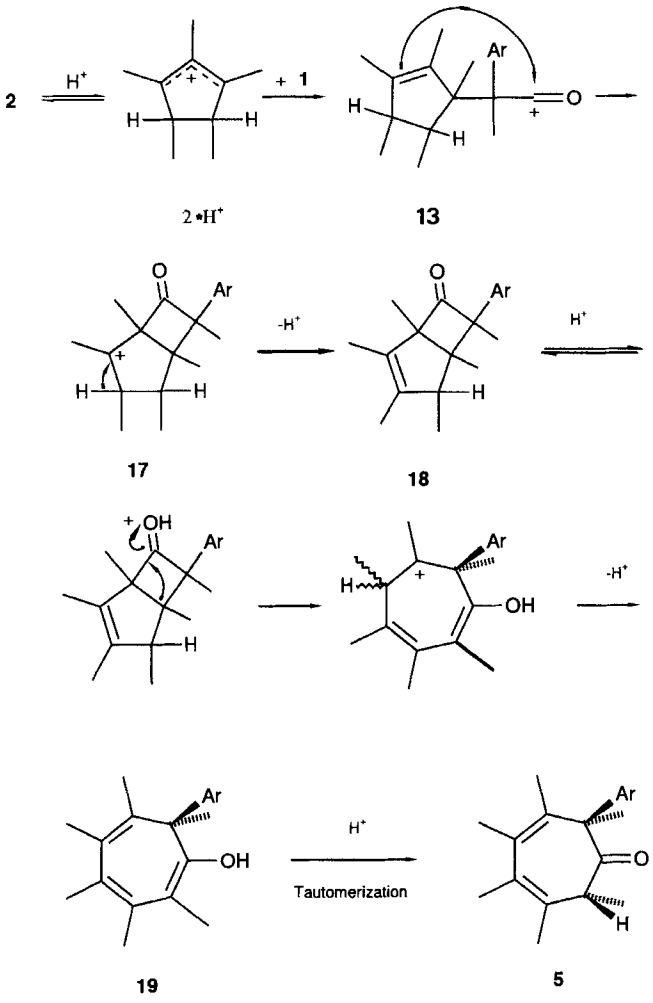


Figure 2. Protonation of ketenes **1a, b**

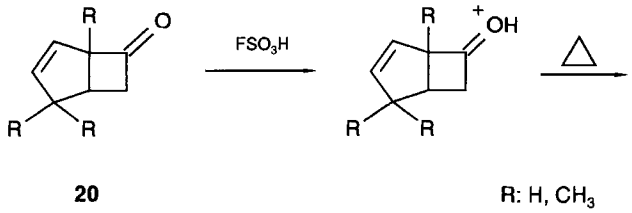


Protonation of **1** leads to the acylium ion **15** rather than to the benzyl cation **16**[18], as inferred from the formation of product **12** in the reaction of **1a** with **11** and from the higher stability of **15** in solution compared to **16**[19]. With this in mind the most plausible mechanism for the formation of cycloheptadienone **5** is that outlined in the scheme.

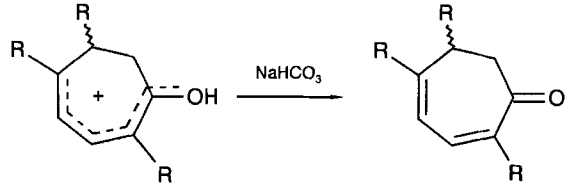
After initial protonation of **2** the reaction with **1** results in the formation of **13**, which closes to the protonated bicyclo[3.2.0]heptenone **17**, a process which is reminiscent of other [2+2] cycloadditions of allyl cations[20]. After deprotonation and reprotonation at the carbonyl group the cyclobutanone opens to the protonated cycloheptatrienol derivative. Deprotonation to **19** followed by acid-catalyzed tautomerization now affords the observed product **5**.

While the proposed mechanism can certainly be regarded as speculative the intermediate formation of **18** is strongly supported by the results of a study by Childs[21] who observed the acid-catalyzed rearrangement of bicyclo[3.2.0]-hept-2-en-7-one **20** to 2,4-cycloheptadien-1-one **21**.

Additional support for the proposed regioselectivity in the addition of $\mathbf{2}\cdot H^+$ to **1** and the intermediate formation of **18** may be derived from the fact that the regioisomeric bicyclo[3.2.0]hept-2-en-6-one derivative **9** could not be rearranged to a cycloheptadienone, but to the tetralinone **10**.

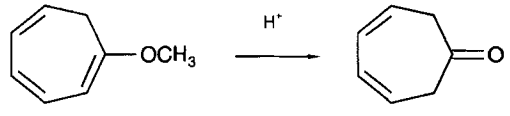


20 R: H, CH_3



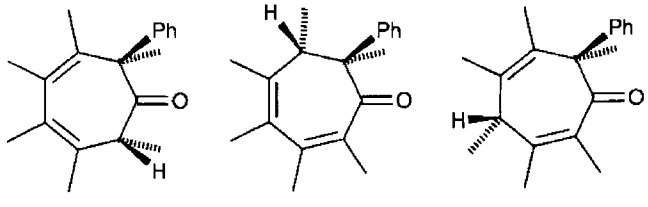
21

A critical point of the mechanism described above is to rationalize the selective formation of **5** as the sole isolable product. Most likely the protonation of **19** occurs under kinetic control since hardly any deuterium incorporation was found when **5a** was subjected to the acidic reaction conditions in a control experiment. In line with the observed regioselectivity the formation of **5a** by protonation at C-2 in trienol **19** is indeed supported by the exclusive protonation at C-2 in the acid-catalyzed hydrolysis of enol ether **22**[7a,22].



22

In addition, thermochemical data derived from AM1 calculations[23] on the various isomers of **5c**[24] indicate that 3,5-cyclohepta-dienone **5c** (with phenyl in a pseudo-axial position) is more stable than 2,4-cycloheptadienone **23** and 2,5-cycloheptadienone **24**.



5c **23** **24**

ΔH_f [kcal/mol] =

-1.8 1.4 -0.5

Figure 3. Positional isomers of cycloheptadienone **5c** and their AM1-calculated heats of formation

Another aspect of this reaction which deserves a brief comment is the exclusive formation of **5** as a *trans* isomer. Again, as outlined above, protonation under kinetic control aided by hydrogen bonding to the aryl group is thought to exert the necessary control. However, due to lack of further experimental evidence, this mechanistic conclusion mandates additional support.

To the best of our knowledge the present paper reports on the first example of an acid-catalyzed "cycloaddition" of ketenes with dienes to afford 3,5-cycloheptadien-1-ones. The scope of this reaction appears to be limited to electron-rich dienes like **2** and to few ketenes. From the mechanistic results it follows that quantitative protonation of the diene in the presence of the ketene is an important prerequisite for the reaction to occur.

Experimental

^{1}H- and ^{13}C-NMR: Bruker WM 250 and AM 400, respectively; TMS internal standard. The numbering follows the one given in Figure 1. Coupling constants 0.5 Hz < J < 1.3 Hz are listed as broadened signals. – MS: Finnigan MAT 44S. – IR: Perkin-Elmer 398. – Melting points: Büchi capillary melting point apparatus (Dr. Tottoli), uncorrected. – Elemental analyses: University of Freiburg Microanalysis Facility. – GC: Carlo Erba Vega 6000 or Perkin-Elmer Sigma 2b chromatographs equipped with capillary colums. – Preparative and analytical HPLC: Merck-Hitachi intelligent pump L-6200 with Merck-Hitachi L-4200 UV-VIS Detector. – AM1 calculations[23]: Micro VAX using MOPAC 6.00 (Quantum Chemistry Program Exchange No. 455) and ChemX (Chemical Design Ltd.). Fully optimized RHF energies were calculated from the MM3-optimized structures.

General Procedure for the Acid-Catalyzed Reactions: To a stirred acetonitrile solution (0.4 M in diene) of the ketene and diene in a test tube was added a solution of the acid or the one-electron oxidant at 0°C under Ar. The solution was stirred and finally the reaction quenched by addition of water. The products were extracted several times with dichloromethane. The combined organic layers were washed with a saturated aqueous NaCl solution and dried with Na_2SO_4. The yields given in Table 1 were determined by ^{1}H-NMR analysis after addition of *m*-nitroacetophenone as internal standard. The control experiments using CF_3SO_3D (80% deuterated) were conducted accordingly, the amount of incorporated deuterium being determined by ^{1}H-NMR and mass spectroscopy.

Cycloheptadienone **5a**: To a stirred solution of 160 mg (1.0 mmol) of **1a** and 136 mg (1.0 mmol) of **2** in 1.5 ml of acetonitrile under Ar was added within 1 min a solution of 225 mg (1.5 mmol) of CF_3SO_3H in 0.5 ml of acetonitrile at 0°C. During the addition the color changed to a dark yellow brownish hue. After stirring for 5 min, 0.5 ml of water was added. The product was extracted with several portions of dichloromethane. The combined organic layers were washed with a saturated NaCl solution and then dried with Na_2SO_4. Removal of the solvent afforded the crude product which was subsequently purified by chromatography on silica gel by using dichloromethane as eluent. Recrystallization from pentane at –30°C yielded 133 mg (45%) of **5a**, m.p. 152°C. – IR (CCl_4): $\tilde{\nu}$ = 1698 cm^{-1} (vs, C=O). – ^{1}H-NMR (250 MHz/$CDCl_3$): δ = 1.01 (br. s, 3H, 9-H), 1.05 (s, 3H, 8-H), 1.14 (d, J = 7.2 Hz, 3H, 13-H), 1.74 (br. s, 3H, 12-H), 1.82 (br. s, 3H, 10-H), 1.91 (br. s, 3H, 11-H), 3.35 (q, J = 7.2 Hz, 1H, 7-H), 3.74 (s, 3H, 20-H), 6.73 (d, J = 9.2 Hz, 2H, 16,18-H), 7.01 (d, J = 9.2 Hz, 2H, 15,19-H). – ^{13}C-NMR (100 MHz/$CDCl_3$): δ = 10.7 (C-12), 10.9 (C-11), 11.5 (C-10), 11.7 (C-9), 15.0 (C-13), 20.9 (C-8), 43.7 (C-7), 55.8 (C-20), 72.5 (C-2), 114.3 (C-16,18), 129.9 (C-15,19), 135.0 (C-14), 137.4 (C-

6), 137.6 (C-3), 141.5 (C-5), 141.6 (C-4), 211.0 (C-1). – MS (EI, 70 eV), *m/z* (%): 298 (83) [M^+], 162 (29) [**1a**$^+$], 136 (100) [**2**$^+$], 119 (56), 105 (95), 91 (56). – $C_{20}H_{26}O_2$ (298.4): calcd. C 80.48, H 8.80; found: C 80.24, H 8.71.

Cycloheptadienone **5b**: In analogy to the procedure described above 146 mg (1.0 mmol) of **1b** and 136 mg (1.0 mmol) of **2** were treated with 225 mg (1.5 mmol) of CF_3SO_3H. After 95 min 20 ml of H_2O was added. The product was purified by chromatography (silica gel, dichloromethane) to afford 85 mg (30%) of **5b** which decomposed within a few days at room temp. – IR (CCl_4): $\tilde{\nu}$ = 1698 cm^{-1} (vs, C=O). – ^{1}H-NMR (250 MHz/$CDCl_3$): δ = 1.03 (br. s, 3H, 9-H), 1.08 (s, 3H, 8-H), 1.18 (d, *J* = 7.2 Hz, 3H, 13-H), 1.77 (br. s, 3H, 12-H), 1.83 (br. s, 3H, 10-H), 1.93 (br. s, 3H, 11-H), 2.28 (s, 3H, 20-H), 3.40 (q, *J* = 7.2 Hz, 1H, 7-H), 7.13 (d, *J* = 9.0 Hz, 2H, 16,18-H), 7.22 (d, *J* = 9.0 Hz, 2H, 15,19-H). – ^{13}C-NMR (100 MHz/$CDCl_3$): δ = 10.6, 10.8, 11.4 (C-9 to C-12), 14.6 (C-13), 20.8 (C-6), 21.1 (C-8), 43.6 (C-7), 71.9 (C-20), 127.9 (C-15,19), 128.8 (C-16,18), 135.9 (C-17), 136.7 (C-6), 137.4 (C-3), 138.8 (C-14), 140.3 (C-5), 140.5 (C-4), 210.7 (C-1). – MS (EI, 70 eV), *m/z* (%): 282 (100) [M^+], 146 (100) [**1b**$^+$], 119 (100). – HRMS, $C_{20}H_{26}O$: calcd. 282.1977; found 282.1991.

Reaction of Diphenylketene with **2** *in the Presence of* CF_3SO_3H: To a stirred solution of 38 mg (0.20 mmol) of diphenylketene and 27 mg (0.20 mmol) of **2** in 0.4 ml of acetonitrile was added 51 mg (0.34 mmol) of CF_3SO_3H. The mixture was stirred for 5 min. Then water was added and the mixture extracted with dichloromethane. – ^{1}H-NMR (250 MHz/$CDCl_3$): the product contained 18% of diphenylacetic acid and 25% of an adduct of diphenylketene and **2** with the following signals: δ = 1.11 (s, 3H, CH_3), 1.31 (s, 6H, CH_3), 1.93 (s, 6H, CH_3), 4.66 (s, 1H, C*H*Ph_2), 7.1–7.4 (m, 10H, Ph). – GC-MS, EI (70 eV), *m/z* (%): 167 (100) [Ph_2CH^+], 136 (28) [**2**$^+$]. – CI (methane), *m/z* (%): 331 (11) [M + H], 195 (16) [protonated diphenylketene], 167 (100) [Ph_2CH^+], 136 (28) [**2**$^+$]. – Several attempts to purify the adduct failed.

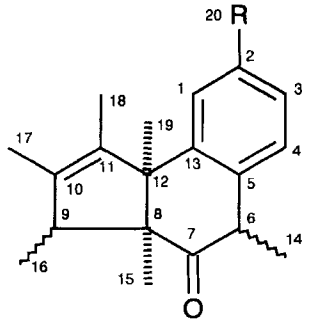
Reduction of **5a** *to Cycloheptadienol* **6a**: To a solution of 15 mg (0.05 mmol) of **5a** in 3 ml of benzene/ether (1:1) was added 10 mg (0.26 mmol) of $LiAlH_4$. The mixture was stirred for 1.5 h. After careful addition of 20 ml of 2 N NaOH the product was extracted several times with ether. The combined ether layers were washed with water and dried with Na_2SO_4. After removal of the solvent 15 mg (100%) of the unstable **6a** was obtained. After chromatography over silica gel (dichloromethane) **6a** could be isolated only with 95% purity. – IR (CCl_4): $\tilde{\nu}$ = 3560 cm^{-1} (m, OH). – ^{1}H-NMR (250 MHz/$CDCl_3$): δ = 1.03 (s, 3H, 8-H), 1.11 (d, *J* = 7.2 Hz, 3H, 13-H), 1.32 (br. s, 3H, 9-H), 1.66 (br. s, 3H, 12-H), 1.77 (br. s, 6H, 10,11-H), 2.45 (dq, J_1 = 7.2, J_2 = 4.0 Hz, 1H, 7-H), 3.70 (d, *J* = 4.0 Hz, 1H, 1-H), 3.76 (s, 3H, 20-H), 6.76 (d, *J* = 9.2 Hz, 2H, 16,18-H), 6.96 (d, *J* = 9.2 Hz, 2H, 15,19-H). – MS (EI, 70 eV), *m/z* (%): 300 (10) [M^+], 165 (10), 147 (5), 136 (100) [**2**$^+$], 121 (52). – HRMS, $C_{20}H_{28}O_2$: calcd. 300.2082, found 300.2100.

Tetralinone **10a**: *Acid-Catalyzed Rearrangement of* **9a**: Under Ar 26 mg (0.8 mmol) of CF_3SO_3H was added to a stirred solution of 35 mg (0.12 mmol) of **9a**[6b] in 1.0 ml of acetonitrile at 0°C within 15 s. The mixture was stirred for 5 min. Then 50 ml of dichloromethane was added. The organic phase was washed with a saturated NaCl solution. After drying of the organic layer with Na_2SO_4 the solvent was removed. The crude product (35 mg, 100%) was purified by reversed-phase HPLC (Merck RP 18/7, diameter = 25 mm, methanol/water, 95:5), affording 21 mg (60%) of **10a**. – IR (CCl_4): $\tilde{\nu}$ = 1706 cm^{-1} (vs, C=O). – ^{1}H-NMR (250 MHz/$CDCl_3$): δ = 1.05 (s, 3H, 19-H), 1.11 (d, *J* = 7.2 Hz, 3H, 16-H), 1.24 (q, *J* = 1.2 Hz, 3H, 18-H), 1.35 (d, *J* = 6.5 Hz, 3H, 14-H), 1.40 (s, 3H, 15-H), 1.61 (q, *J* = 1.2 Hz, 3H, 17-H), 2.39 (br. q, *J* = 7.2 Hz, 1H, 9-H), 3.78 (q, *J* = 6.5 Hz, 1H, 6-H), 3.80 (s, 3H, 20-H), 6.77 (dd, J_1 = 9.2, J_2 = 2.5 Hz, 1H, 3-H), 6.90 (d, *J* = 2.5 Hz, 1H, 1-H), 7.03 (d, *J* = 9.2 Hz, 1H, 4-H). – ^{13}C-NMR (100 MHz/$CDCl_3$): δ = 10.7, 11.4, 12.9, 14.1, 15.3, 23.0, 29.8, 43.2, 51.5, 55.3, 58.2, 111.0, 113.3, 124.9, 129.3, 135.0, 135.2, 142.2, 158.7, 215.4. – MS (EI, 70 eV), *m/z* (%): 298 (100) [M^+], 283 (46), 269 (49), 255 (52), 187 (51), 135 (29). – $C_{20}H_{26}O_2$ (298.4): calcd. C 80.48, H 8.80; found C 80.25, H 8.69.

10

a: R: OCH_3

b: R: CH_3



Tetralinone **10b**: *Aminium Salt-Initiated Rearrangement of* **9b**: According to the procedure described above for **10a**, 10.0 mg (36 μmol) of **9b**[6b] in 0.10 ml of acetonitrile was treated at 0°C with 14.5 mg (18 μmol) of tris(*p*-bromophenyl)aminium hexachloroantimonate in 0.15 ml of acetonitrile. The blue color of the mixture changed immediately to a light brownish hue. After 5 min the reaction was quenched using 2 N sodium methanolate in methanol. The crude product was purified by HPLC (see above) by using methanol/water/acetonitrile (8:1:1); yield of **10b**: 2.0 mg (20%). – IR (CCl_4): $\tilde{\nu}$ = 1709 cm^{-1} (s, C=O). – ^{1}H-NMR (250 MHz/$CDCl_3$): δ = 1.03 (s, 3H, 19-H), 1.10 (d, *J* = 7.2 Hz, 3H, 16-H), 1.23 (q, *J* = 1.2 Hz, 3H, 18-H), 1.35 (d, *J* = 6.5 Hz, 3H, 14-H), 1.42 (s, 3H, 15-H), 1.63 (q, *J* = 1.2 Hz, 3H, 17-H), 2.34 (s, 3H, 20-H), 2.49 (q, *J* = 7.2 Hz, 1H, 9-H), 3.83 (q, *J* = 6.5 Hz, 1H, 6-H), 7.03 (d, *J* = 9.0 Hz, 1H, 3-H), 7.06 (d, *J* = 9.0 Hz, 2H, 1,4-H). – MS (EI, 70 eV), *m/z* (%): 282 (2) [M^+], 187 (23), 173 (19), 161 (25). – MS (CI, NH_3), *m/z* (%): 300 (25) [M + NH_4^+], 297 (58), 287 (38), 234 (57), 194 (77), 177 (100), 136 (30) [**2**$^+$].

Acid-Catalyzed Rearrangement of **9b**: To a solution of **9b** (4.5 mg, 16 μmol) in 0.25 ml of acetonitrile was added at 0°C 3.6 mg (24 μmol) of CF_3SO_3H. After 5 min the reaction was quenched by the addition of water, and the crude mixture was analyzed. It contained 35% of **10b** (NMR-analysis).

3-[2-(4-Methoxyphenyl)propanoyl]-2,5-dimethylfuran (**12**): To a stirred solution of 40 mg (0.25 mmol) of **1a** and 72 mg (0.75 mmol) of **11** in 0.50 ml of acetonitrile was added 7.1 μl (0.079 mmol) of CF_3SO_3H at 0°C. During the addition the solution turned red. The mixture was stirred for 1.5 h, then 1 ml of water was added. The products were extracted several times with dichloromethane. The combined organic layers were washed with water and dried with Na_2SO_4. Product analysis showed 80% of **12** which was purified by chromatography on silica gel (dichloromethane). – IR (CCl_4): $\tilde{\nu}$ = 1667 cm^{-1} (s, C=O). – ^{1}H-NMR (250 MHz/$CDCl_3$): δ = 1.38 (d, *J* = 7.2 Hz, 3H, C*H*$_3$CH), 2.11 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 3.71 (s, 3H, CH_3O), 4.10 (q, *J* = 7.2 Hz, 1H, C*H*CH$_3$), 6.80 (d, *J* = 9.0 Hz, 2H, aryl-H), 7.14 (d, *J* = 9.0 Hz, 2H, aryl-H). – ^{13}C-NMR (100 MHz/$CDCl_3$): δ = 13.2, 14.4, 18.9, 49.5, 55.2, 105.9, 114.3, 121.1, 128.9, 133.6, 149.6, 158.1, 158.5, 197.1. – MS (EI, 70 eV), *m/z* (%): 258 (70) [M^+], 194 (26), 135 (100), 123 (100), 43 (43). – HRMS, $C_{16}H_{18}O_3$: calcd. 258.1251, found 258.1250.

☆ Dedicated to Prof. *C. Rüchardt* on the occasion of his 65th birthday.

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[402/93]