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Cycloadditions of Allyl Cations, 22[1]

Allyl Alcohols as Precursors of Allyl Cations

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Allyl alcohols such as 3-ethoxy-2-methyl-3-buten-2-ol (**4**), the silylated alcohol **8** and also 2-methyl-3-pentyn-2-ol (**12**) have been converted into the corresponding trifluoroacetates (**5**, **9**, **13**), which in the presence of zinc halide/ethyldiisopropylamine react with conjugated dienes to form bridged seven-membered rings (**14**, **16**, **18**, **20** – **24**) in good to excellent yields. Thus, unlike all other oxyallyl precursors studied so far, **5** gives the bridged 1-ethoxy-1,4-cycloheptadiene (**14**, **16**, **18**, **20**) under the present conditions rather than the thermodynamically more stable 4-cyclohepten-1-one (**15**, **17**, **19**, **21**) which is formed from the initial enol ether by hydrolysis. It is concluded that structurally complex allyl cations can now be generated in very mild conditions, and owing to the presence of ethyldiisopropylamine, even in weakly alkaline solutions.

Cycloadditionen von Allyl-Kationen, 22[1]
Allylalkohole als Vorläufer für Allyl-Kationen

Allylalkohole wie 3-Ethoxy-2-methyl-3-buten-2-ol (**4**), der silylierte Alkohol **8** sowie 2-Methyl-3-pentin-2-ol (**12**) werden in die entsprechenden Trifluoressigsäureester (**5**, **9**, **13**) übergeführt und in Gegenwart von Zinkhalogenid/Ethyldiisopropylamin und eines konjugierten Diens in guten bis sehr guten Ausbeuten in verbrückte Siebenringe (**14**, **16**, **18**, **20** – **24**) umgewandelt. Demnach reagiert **5**, anders als alle bisher untersuchten Oxyallyl-Vorläufer, unter den beschriebenen Bedingungen zum verbrückten 1-Ethoxy-1,4-cycloheptadien (**14**, **16**, **18**, **20**) statt zum thermodynamisch stabileren 4-Cyclohepten-1-on (**15**, **17**, **19**, **21**), welches aus dem anfänglich gebildeten cyclischen Enolether durch Hydrolyse entsteht. Es wird geschlossen, daß jetzt strukturell komplexe Allyl-Kationen unter schonenden Bedingungen erzeugt werden können, dank der Gegenwart von Ethyldiisopropylamin sogar in schwach alkalischem Medium.

Allyl cations are useful reagents for a variety of cycloadditions and two methods for generating these reactive intermediates have generally been employed hitherto. 1. The silver ion (and Lewis acid) catalyzed heterolysis of preformed allyl halides[2,3] and 2. The dehalogenation of α,α'-dibromo ketones with reducing agents including zinc-copper couple[4] and variants thereof[5], with iron carbonyls[6] and also with iodide ion/copper[7]. Although these methods are useful, it is clear that many allyl alcohols are more readily accessible than allyl halides or the corresponding dibromo ketones, especially so when a structurally more complex allyl moiety needs to be considered. Indeed, in the course of a number of synthetic projects it became necessary to activate

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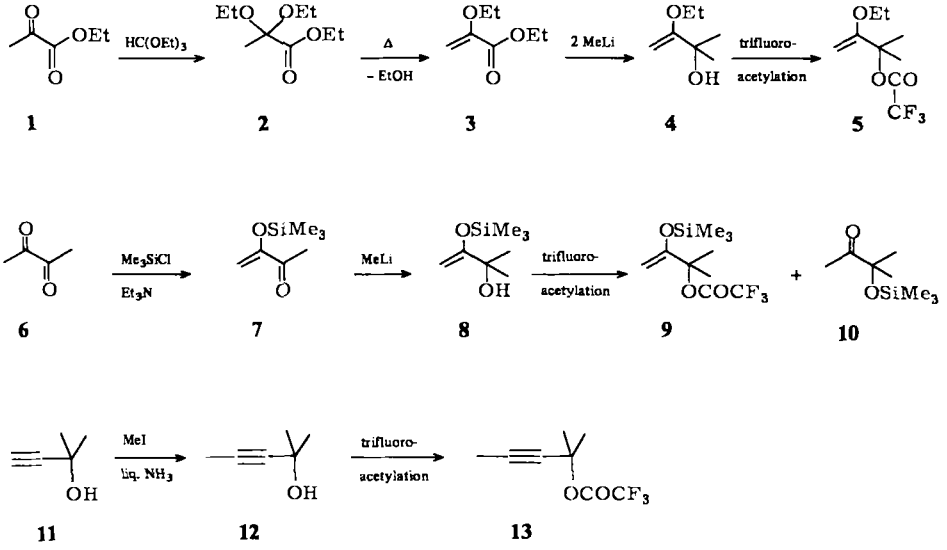
allyl alcohols toward formation of allyl cations which in turn had to be trapped by a variety of π systems. We now show that trifluoroacetylation of the allyl alcohol (cf. Scheme 1) followed by zinc halide induced heterolysis provides a simple and satisfactory experimental solution of this problem.

Scheme 1. Routes to Some Functionalized Allyl Alcohols and their Trifluoroacetic Esters



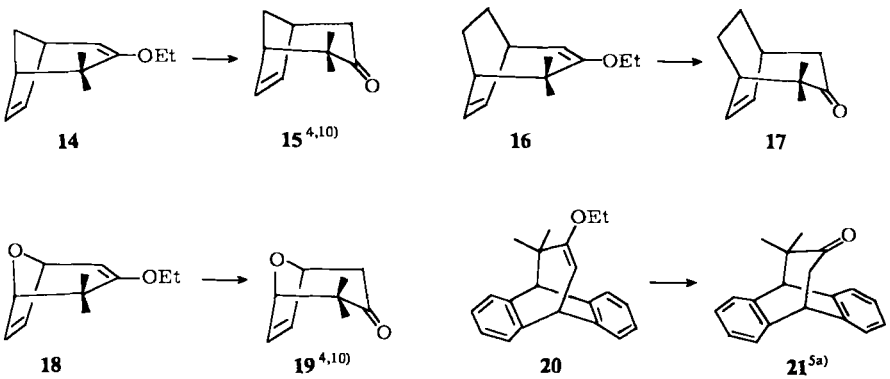
1. The Synthesis of Some Functionalized Allyl Alcohols and their Trifluoroacetic Esters

The allyl alcohols were prepared from common starting materials as outlined in Scheme 1. In searching for a suitable leaving group we tried first of all mesylation and tosylation with the corresponding sulfonyl chlorides and anhydrides. However, we confirmed that tertiary alcohols do not react fast enough with these reagents in the presence of pyridine[8]. In contrast, trifluoroacetic anhydride reacted smoothly and exothermically with **4** at $-40\,^{\circ}C$, giving **5** in 93% yield. Initial attempts at isolating the esters by aqueous work up led to substantial hydrolysis. An attempt to distil **5** directly from the crude mother liquor at $0\,^{\circ}C$ was not successful, either, the ester being decomposed. Therefore, the allylic esters were purified by filtration through a short column of alumina chilled to $-78\,^{\circ}C$ and eluting with pentane. Interestingly, once ester **5** had been purified in this fashion, it could also be distilled at $30-40\,^{\circ}C$. Trifluoroacetylation of **8** gave not only the desired **9**, but also **10**, presumably by intramolecular transfer of the trimethylsilyl group. The trifluoroacetic esters showed a characteristic carbonyl band in the IR at 1780 cm^{-1}, a clear ^1H NMR downfield shift of the geminal methyl protons compared to those of the parent allyl alcohols and a downfield shift of the vinylic protons.

2. Cycloadditions

2a. *Allylic Trifluoroacetate* **5**: In using an ester such as **5** as a cycloaddition reagent we had to generate the cation and also protect as far as possible the enol ether function of **5** from acids, or more generally, from reaction with electrophiles. Equimolar zinc chloride in acetonitrile was used as Lewis acid to promote S_N1-like heterolysis of the ester, whilst ethyldiisopropylamine served as acid trap. The progress of the reaction was monitored by ^1H NMR and GC. A successful cycloaddition was usually indicated visually by a colour change of the reaction mixture to yellow, orange-brown, or deep-red. Cycloadducts and yields are shown in Scheme 2 and Table 1, respectively. The cyclic enol ethers were further characterized by hydrolysis to the ketones (Scheme 2 and 3).

Scheme 2. Conversion of Cyclic Enol Ethers into Ketones



14 **15**[4,10] **16** **17**

18 **19**[4,10] **20** **21**[5a]

Table 1. Cycloadducts from Activated Allyl Alcohols and Conjugated Dienes (RT = Room Temperature)

Allyl Cation Precursor	Reaction Conditions	Conjugate Diene	Cycloadducts (Yields)
5	$ZnCl_2$, $EtN(iPr)_2$, CH_3CN solvent, RT	Cyclopentadiene	**14** (73%)
5	$ZnCl_2$, $EtN(iPr)_2$, CH_3CN solvent, RT	Cyclohexadiene	**16** (76%)
5	$ZnCl_2$, $EtN(iPr)_2$, CH_3CN solvent, RT	Furan	**18** (72%)
5	$ZnCl_2$, $EtN(iPr)_2$, CH_2Cl_2 solvent, reflux	Anthracene	**20** (96%)
9	$ZnCl_2$, $EtN(iPr)_2$, CH_2Cl_2 solvent, reflux	Anthracene	**21** + **22** (95%) (**21**:**22** = 3:7)
13	$ZnCl_2$, $EtN(iPr)_2$, CH_2Cl_2 solvent, RT	Cyclopentadiene	**24** (42%)
13	$ZnBr_2$, $EtN(iPr)_2$, CH_2Cl_2 solvent, RT	Cyclopentadiene	**25** (39%)

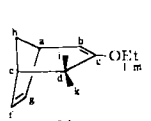
Several ^{1}H NMR features of the new bicyclo[3.2.1]octa-2,6-dienes deserve mention

1. The olefinic proton of the enol ether grouping appears as a well resolved doublet (J = 7 Hz in **14**, 4.6 Hz in **18**, 9 Hz in **16**, 9.3 Hz in **20** and **22**) upfield from the signals of the etheno protons 6- and 7-H.

2. The ^{1}H NMR singlet (and, by inference, the corresponding ^{13}C NMR quartet) due to the α or *endo* methyl group attached to C-4 appears at higher field than the singlet of the β or *exo* methyl group, because of the anisotropic effect of the C6 – C7 double bond.

3. Interestingly, in all the bicyclo[3.2.1]octa-2,6-dienes, which we have yet prepared, including 3-methylbicyclo[3.2.1]octa-2,6-diene (as well as 3-methylbicyclo[3.2.2]nona-2,6-diene[9]), the olefinic proton 7-H appears at *lower* field than 6-H. Similarly, in the ^{13}C NMR spectra C-7 appears at lower field than C-6. This fact is probably due to the inductive effect of the sp^2 hybridized C-2 carbon.

Table 2. ^{13}C NMR Spectra of Cycloadducts[a]



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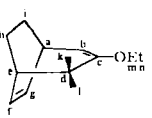

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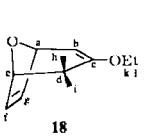

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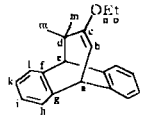


20

	14	**16**	**18**	**20**
C_a	28.1 d	30.4 d	76.4 d	44.0 d
C_b	97.8 d	98.9 d	97.8 d	99.1 d
C_c	159.3 s	161.7 s	158.9 s	158.5 s
C_d	38.4 s	42.4 s	38.9 s	40.3 s
C_e	38.0 d	43.8 d	87.3 d	58.8 d
C_f	129.9 d	130.9 d	126.4 d	140.0 s
C_g	141.6 d	137.3 d	140.5 d	146.8 s
C_h	40.7 t	(26.3) t	27.2 q	(123.5) d
C_i	22.3 q	(20.6) t	18.8 q	(125.0) d
C_k	13.9 q	24.1 q	61.6 t	(125.9) d
C_l	61.4 t	15.4 q	14.3 q	(128.5) d
C_m	14.4 q	61.7 t		26.5 q
C_n		14.6 q		61.4 t
C_o				14.3 q

[a] For assignments of signals see also ref.[5a] and *J. B. Stothers, J. R. Swenson,* and *C. T. Tan,* Can. J. Chem. **53**, 581 (1975).

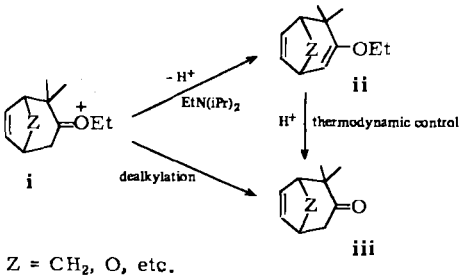
4. In the ^{1}H NMR spectrum of **14**, **16**, **18**, **20** and **22**, the "bisallylic" bridgehead protons attached to C-1 appear at lower field than the bridgehead protons attached to C-5. However, it appears that this pattern can be reversed by a different substitution pattern at C-2, C-3, and C-4.

5. The methylene protons of the *O*-ethyl group in adduct **16** are diastereotopic. Interestingly, although the two chiral bridgehead centres are remote, the methylene protons do not appear as a simple, but rather as a complex quartet. The *O*-methylene quartet in adducts **14**, **18**, and **20** is "clean".

The immediate precursor of products **14**, **16**, **18**, and **20** is considered to be oxonium ion **i**, which a priori could have been expected either to lose a proton, giving an enol ether of type **ii** or to suffer dealkylation with a suitable nucleophile, giving the thermodynamically more stable ketone **iii**.

In our earlier work with the 2-methoxyallyl cation[2,11] enol ethers **ii** were formed at best in traces and the dealkylation product, i. e. ketone of type **iii**, was isolated. In these reactions the medium had been buffered by suspended Na_2CO_3 and was still fairly acidic. Ethyldiisopropylamine could not be used as an acid trap in the earlier experiments because it forms a silver mirror with silver trifluoroacetate.

Scheme 3. Possible Reactions of Bicyclic Oxonium Ion **i**



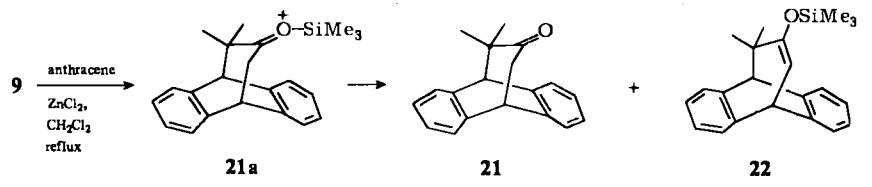
Z = CH_2, O, etc.

We were therefore pleased to find that the presence of hindered tertiary amine in homogeneous conditions changed the course of the reaction to give the product of kinetic control **ii**, proton loss being the fastest reaction. Although the strained bicyclic enol ethers, except for crystalline **20**, were sensitive to aqueous work up and also to oxygen, they could be isolated with little if any decomposition by extractive work up with pentane from the acetonitrile mother liquor and short path distillation. Alternatively, but less conveniently, the reaction of cyclopentadiene and **5** was run in dichloromethane. In this case, the product **14** was isolated by chromatography over alumina in anhydrous dichloromethane at −78°C; otherwise, the bicyclic ketone **15** was formed in almost quantitative yield. Finally, a one-pot reaction in which the allylic trifluoroacetate **5** was prepared in situ in the presence of cyclopentadiene and zinc halide was added afterwards, was also successful. However, in order to have more freedom in the choice of solvent and more control over the reaction we generally prefer isolating the intermediate ester. Following these experiments we carried out cycloadditions with cyclohexadiene and furan and obtained **16** and **18**, respectively. Because of its low solubility in most solvents, anthracene was more difficult to use. In this instance, reaction in boiling dichloromethane was convenient. As the separation of remaining anthracene from product was unsatisfactory by chromatography, we used *two* equivalents of trifluoroacetic ester **5**, thus forcing the conversion of anthracene into cycloadduct. Column filtration at −78°C gave crystalline enol ether **20** as the sole product.

2b. *Allylic Trifluoroacetate* **9**: Reaction of anthracene and **9** under the general conditions gave silyl enol ether **22** as well as ketone **21** in nearly quantitative yield. Apparently, ketone **21** is the product of kinetic control and not formed consecutively from silyl enol ether **22** and then desilylation. In other words, a trimethylsilyl group is a bet-

ter leaving group than an ethyl group under our conditions. This suggestion is supported by the trifluoroacetylation of silylated alcohol **8**, which in addition to the desired **9** gives some **10** by silicon shift (Scheme 1).

Scheme 4. Reaction Products from Anthracene and Silylated Oxyallyl Trifluoroacetate **9**

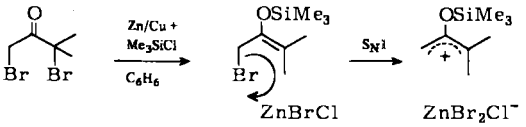


21a **21** **22**

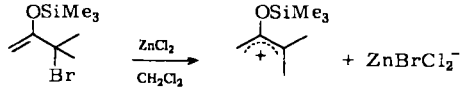
Shortly before the present work had been completed *Sakurai* et al.[3b] described the reaction of silylated 2-oxyallyl bromide **23** with conjugated dienes. Independently, the Japanese authors chose experimental conditions which have proven near optimum for our trifluoroacetates. As no base had been added in their work, cyclic enol ethers such as **22** did not arise, but rather cyclic ketones. Mechanistically, the work of *Sakurai, Shirahata,* and *Hosomi*[3b] is also related to the cycloadditions with dibromo ketones, zinc-copper couple and trimethylsilyl chloride, described by *Giguere* et al.[5a]. We have little doubt that the same electrophilic intermediate is involved in the crucial cycloaddition stage of all three reactions (Scheme 5).

Scheme 5. Convergence on a Single Cationic Intermediate in Three Oxyallyl Cycloadditions

1. According to *Giguere* et al.[5a]

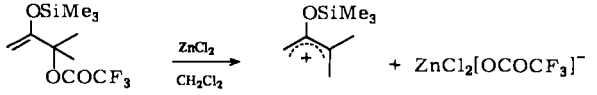


2. According to *Sakurai* et al.[3b]



23

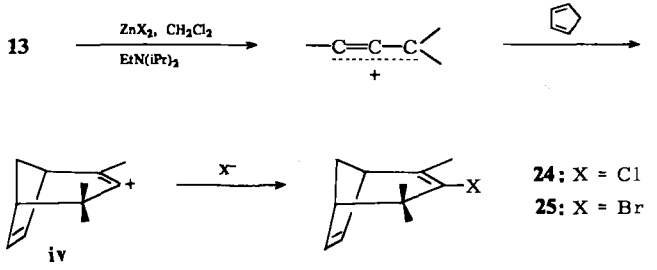
3. According to esterification-zinc halide method



9

2c. *Propargylic Trifluoroacetate* **13**: Recent work by *Mayr* and *Grubmüller*[12] suggested that the activation of dehydroallyl alcohol **12** might be feasible and serve as an

Scheme 6. Reaction of Cyclopentadiene with Dehydroallyl Trifluoroacetate **13**



experimental test of the esterification/Lewis acid induced heterolysis methodology. In any event, the silver salt route which was successfully used by these authors, is already known to be reliable and general[2]. When **13** was exposed to the usual conditions the bicyclic vinyl chloride **24** was the major product. Using $ZnBr_2$ instead of $ZnCl_2$ we obtained the corresponding vinyl bromide **25** in comparable yield. Bicyclic vinyl cation **iv** is a rational intermediate which for lack of any obvious intramolecular mode of stabilization is trapped intermolecularly by halide ion to give the observed bicyclic vinyl halides (Scheme 6).

3. Conclusions

The principle of activating allyl alcohols via esterification and Lewis acid induced heterolysis is flexible and general, leading to seven-membered rings in respectable yields. Thanks to the presence of hindered tertiary amine, the products are bicyclic enol ethers rather than bridged 4-cyclohepten-1-ones, which until now had been isolated exclusively in cycloadditions of oxyallyl cations to 1,3-dienes. Finally, our work augurs well for activating any structurally complex allyl alcohol bearing at least two alkyl groups at the allylic termini and we foresee many further preparative applications in the future.

Note added in proof (18.9.80): After submission of our paper *Schreiber* has shown that tertiary amines such as ethyldiisopropylamine are oxidized by trifluoroacetic anhydride at 0°C (*S. L. Schreiber,* Tetrahedron Lett. **21**, 1027 (1980)). As we have carried out our trifluoroacetylations at an initial temperature of −40°C and below, this potential side reaction is not important under our conditions. Further trifluoroacetylations of tertiary and related alcohols: *K. Okamoto, K. Takeuchi,* and *T. Inoue,* J. Chem. Soc., Perkin Trans. 2 **1980**, 842; *P. Sleevi, T. E. Glass,* and *H. C. Dorn,* Anal. Chem. **51**, 1931 (1979).

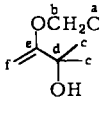
We thank Mr. *M. R. Ashcroft* and Dr. *O. R. Lalko* for model experiments, Dr. *L. Grotjahn* of the Gesellschaft für Biotechnologische Forschung m. b. H., Braunschweig-Stöckheim, for high resolution mass spectra, Drs. *R. Römer* and *H. U. Matthei* of the Medizinische Hochschule Hannover for 270 MHz ^1H NMR spectra, and the *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie* for financial support.

Experimental Part

^{1}H NMR spectra: Varian EM 360, Bruker HX 90 and WH 90. – ^{13}C NMR spectra: Bruker WH 90, internal reference tetramethylsilane. – Mass spectra: Varian MAT CH-5. – Microanalyses: Frau *Jirotka*, Institut für Organische Chemie der Universität Hannover. – Chromatography: Thick layer plates (ICN-Woelm). Silica gel, porous size 0.05 – 0.2 mm (Macherey-Nagel) and basic alumina, activity super I (ICN-Woelm).

Functionalized Allyl Alcohols

3-Ethoxy-2-methyl-3-buten-2-ol (**4**): Ethyl 2-ethoxyacrylate (**3**)[13] (5.76 g, 40 mmol) in ether (20 ml) were dropped into 100 ml of a 1 M solution of methyllithium (100 mmol) at –40 °C. The reaction mixture was stirred for 30 min at 0 °C, shaken with aqueous Na_2CO_3 to destroy the excess of methyllithium, washed with an aqueous solution of Na_2CO_3 saturated with NaCl and dried ($CaCO_3$, molecular sieves 4 Å). Distillation at 40 °C/8 Torr under exclusion of moisture gave 3.9 g (75%) of a colorless liquid, which crystallized at 14 °C in long needles. – IR (film): 3450 br (OH), 1660, 1620 cm^{-1} (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.35 (t, *J* = 7 Hz, 3H), 1.38 (s, 6H), 3.74 (q, *J* = 7 Hz, 2H), 3.90 (d, *J* = 2 Hz, 1H), 4.19 (d, *J* = 2 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 14.4 (q, C_a), 28.5 (q, C_c), 63.0 (t, C_b), 71.8 (s, C_d), 78.3 (t, C_f), 168.4 (s, C_e). – MS (70 eV, room temperature): *m/e* = 130 (6%, M^+), 115 (7), 87 (12), 85 (10), 69 (11), 59 (100). $C_7H_{14}O_2$ calcd. 130.0994, found 130.0991.



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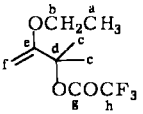

5

2-Methyl-3-(trimethylsiloxy)-3-buten-2-ol (**8**): 3-(Trimethylsiloxy)-3-buten-2-one (**7**)[14] (6.4 g, 40 mmol) in 80 ml pentane and 20 ml ether were mixed with 42 ml (42 mmol) of a 1 N solution of methyllithium in ether at –78 °C. After being stirred for 30 min at –78 °C the solution was worked up by adding pentane (100 ml), brief shaking with a buffer solution of $NaHCO_3$ and citric acid, drying over molecular sieves 4 Å, and distilling at 40 °C/30 Torr, giving 4.9 g (70%) of **8**. – ^{1}H NMR ($CDCl_3$): δ = 0.24 (s, 9H, $SiMe_3$), 1.32 (s, 6H), 4.03 (d, *J* = 2 Hz, 1H), 4.33 (d, *J* = 2 Hz, 1H); the signal of the OH proton is not discernible.

$C_8H_{18}O_2Si$ (174.3) Calcd. C 55.12 H 10.41 Found C 55.33 H 10.48

2-Methyl-3-pentyn-2-ol (**12**) was prepared by methylation of 2-methyl-3-butyn-2-ol (**11**) (purchased from EGA) with methyl iodide in liquid ammonia containing sodium amide and isolated by the usual work up. – 60 MHz ^{1}H NMR ($CDCl_3$): δ = 1.5 (s, 6H), 1.8 (s, 3H), 2.4 (br, OH).

Trifluoroacetic esters

2-Ethoxy-1,1-dimethyl-2-propenyl trifluoroacetate (**5**): The solution of alcohol **4** (3.25 g, 25 mmol) in CH_2Cl_2 (3 ml) was dropped into a solution of trifluoroacetic anhydride (3.5 ml, 25 mmol) and ethyldiisopropylamine (5 ml, 25 mmol) in CH_2Cl_2 (20 ml) at –40 °C under nitrogen. The reaction solution was stirred at room temperature for 30 min and the resulting ester was isolated by filtration through a short glass column (1.5 cm × 8 cm), filled with alumina using pentane as an eluent, and cooled externally with dry ice. The cooled mother liquor was treated with pentane (50 ml), passed down the column and eluted with 100 ml of pentane. After evaporation of the solvent at 0 °C/200 Torr ester **5** was distilled, b.p. 50 °C/3 Torr, yield 5.3 g (93%). – IR ($CHCl_3$): 1780 (C=O), 1660, 1620 cm^{-1} (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.27 (t, *J* = 7 Hz, 3H), 1.66 (s, 6H), 3.73 (q, *J* = 7 Hz, 2H), 4.04 (d, *J* = 3 Hz, 1H), 4.24 (d, *J* = 3 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (q, C_a), 25.7 (q, C_c), 63.5 (t, C_b), 81.3 (t, C_f), 85.6 (s, C_d), 114.7 (q, J_{CF}

= 286.8 Hz, C_h), 162.1 (s, C_e), 162.1 (s, C_g). – $C_9H_{13}F_3O_3$, calcd. 226.0817, found 226.0818 (MS).

1,1-Dimethyl-2-(trimethylsiloxy)-2-propenyl trifluoroacetate (**9**): Preparation as described for **5**. After evaporation of the solvent 6.0 g of a 2:1 mixture of **9** and **10** remained. Distillation at 55°C/10 Torr gave 3.5 g (52%) of **9**. – ^{1}H NMR: δ = 0.19 (s, 9H), 1.62 (s, 6H), 4.17 (d, *J* = 2.5 Hz, 1H), 4.36 (d, *J* = 2.5 Hz, 1H).

1,1-Dimethyl-2-butynyl trifluoroacetate (**13**): The solution of **12** (2.45 g, 25 mmol) in CH_2Cl_2 (5 ml) was dropped into a solution of trifluoroacetic anhydride (3.5 ml, 25 mmol) and ethyldiisopropylamine (5 ml, 25 mmol) in CH_2Cl_2 (20 ml) at –78°C. The reaction solution was stirred for 30 min at –40°C and worked up using a cooled column as described above. 2-Methyl-1-penten-3-yne was observed as the only byproduct and removed together with the solvent. Distillation of the mother liquor at 35°C/5 Torr gave 2.5 g (52%) of **13**. – IR ($CHCl_3$): 2250 (C≡C), 1780 cm^{-1} (C=O). – ^{1}H NMR ($CDCl_3$): δ = 1.40 (s, 6H), 1.60 (s, 3H). – $C_8H_9F_3O_2$ calcd. 194.0555, found 194.0555 (MS).

Cycloadditions

3-Ethoxy-4,4-dimethylbicyclo[3.2.1]octa-2,6-diene (**14**): To a solution of ethyldiisopropylamine (1.42 g, 11 mmol) in absol. acetonitrile (10 ml) under nitrogen at room temperature were added successively $ZnCl_2$ (2.72 g, 20 mmol), cyclopentadiene (2.0 g, 30 mmol), and **5** (2.26 g, 10 mmol), dissolved in absol. acetonitrile (2 ml). After 24 h the yellow-brown solution was extracted with pentane (200 ml altogether), which in turn was shaken with K_2CO_3 (5 g) and filtered. Even the crude product showed a well-structured ^{1}H NMR spectrum. Evaporation of pentane at room temperature/200 Torr gave 1.6 g of a brown oil, which on short path distillation at 76°C/2 Torr yielded 1.3 g (73%) of a light yellow liquid, containing a minor amount (<10%) of dicyclopentadiene which could not be separated. – IR ($CHCl_3$): 1625 cm^{-1} (C=C). – 90 MHz ^{1}H NMR ($CDCl_3$): δ = 0.93 (s, 3H, *endo*-CH_3), 1.20 (s, 3H, *exo*-CH_3), 1.21 (t, *J* = 7 Hz, CH_2CH_3), 1.60–1.65 (m, 1H) and 1.75–1.80 (m, 1H) (bridging CH_2), 2.30–2.45 (br, 1H, 5-H), 2.6–2.9 (br, 1H, 1-H), 3.54 (q, *J* = 7 Hz, OCH_2), 4.82 (d, *J* = 7 Hz, 1H, 2-H), 5.6–6.4, AA'XX' pattern with 6-H centered at 5.75, $J_{6,7}$ = 6, $J_{5,6}$ = 2.6 Hz, and 7-H centered at 6.30, $J_{6,7}$ = 6, $J_{1,7}$ = 2.6 Hz. – ^{13}C NMR (Table 2). – $C_{12}H_{18}O$ calcd. 178.1358, found 178.1353 (MS).

3-Ethoxy-4,4-dimethylbicyclo[3.2.2]nona-2,6-diene (**16**) was prepared from 1,3-cyclohexadiene and **5** using the procedure for preparing **14**. Even the crude product showed a well-structured ^{1}H NMR spectrum, the pattern of the signals of the olefinic 6-H, 7-H protons being very similar to that in 3-methylbicyclo[3.2.2]nona-2,6-diene[9] Distillation at 70°C/1 Torr gave 1.4 g (76%) of **16**. – IR ($CHCl_3$): 1640 cm^{-1} (C=C). – 90 MHz ^{1}H NMR ($CDCl_3$): δ = 1.05 (s, 3H, *endo*-CH_3), 1.18 (s, 3H, *exo*-CH_3), 1.22 (t, *J* = 7 Hz, CH_2CH_3), 1.4–2.8 (complex, 6H, CH_2CH_2 and bridgehead protons), 3.55 (q, *J* = 7 Hz, 2H, OCH_2), 4.80 (d, *J* = 9 Hz, 1H, C*H*=C(OEt)), 6.05 (t (br), *J* ≈ 8 Hz, dd, 1H, 6-H), 6.39 (t (br), *J* ≈ 8 Hz, dd, 1H, 7-H). – ^{13}C NMR (Table 2). – MS (70 eV, room temperature): *m/e* = 192 (100%, M^+), 177 (35), 164 (27), 163 (27), 149 (80), 131 (43), 121 (70), 119 (36), 117 (47), 91 (73). $C_{13}H_{20}O$, calcd. 192.1514, found 192.1509.

3-Ethoxy-4,4-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-diene (**18**) was prepared from furan and **5** analogously to the preparation of **14**. Even the crude product showed a well-structured ^{1}H NMR spectrum, which was also first-order. Distillation at 83°C/2 Torr yielded 1.3 g (72%) of a yellowish oil, which contained a minor amount (≈10%) of the thermodynamic product, i.e. the known[4,10] 2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**19**).

18: 90 MHz ^{1}H NMR ($CDCl_3$): δ = 0.83 (s, 3H, *endo*-CH_3), 1.23 (t, *J* = 7 Hz, 3H, CH_2CH_3), 1.33 (s, 3H, *exo*-CH_3), 3.59 (q, *J* = 7 Hz, 2H, OCH_2), 4.42 (d, *J* = 1.7 Hz, 1H, 5-H), 4.7–4.95, AB quartet with 1-H centered at 4.74 ppm, $J_{1,2}$ = 4.6, $J_{1,7}$ = 1.7 Hz, and 2-H centered at

4.87 ppm, $J_{1,2}$ = 4.6 Hz; 5.9–6.6 AB quartet, 6-H centered at 5.95 ppm, $J_{6,7}$ = 6, $J_{5,6}$ = 1.7 Hz, 7-H centered at 6.58 ppm, $J_{6,7}$ = 6, $J_{1,7}$ = 1.7 Hz. – ^{13}C NMR (Table 2). – $C_{11}H_{16}O_2$ calcd. 180.1150, found 180.1154 (MS).

12-Ethoxy-9,10-dihydro-13,13-dimethyl-9,10-([1]propeno)anthracene (**20**): The solution of anthracene (830 mg, 5.0 mmol) in CH_2Cl_2 (20 ml) was heated under reflux. After 10 min ethyldiisopropylamine (1.3 g, 10 mmol) and $ZnCl_2$ (1.36 g, 10 mmol) were added, and then **5** (2.26 g, 10 mmol) was dropped in over 3 h. After 4 h at room temperature the solution was filtered through a short column at –78 °C, as described above for the isolation of **5**. Removal of the solvent and recrystallization from hexane gave colorless crystals, 1.4 g (96%), m. p. 89 °C. – IR (KBr): 1635, 1475 (C=C, benzenoid C=C). – 90 MHz ^{1}H NMR ($CDCl_3$): δ = 1.10 [s, 6H, $(CH_3)_2$], 1.10 (t, J = 7 Hz, 3H, CH_2CH_3), 3.43 (q, J = 7 Hz, 2H, OCH_2), 3.60 (s, 1H, 10-H), 4.12 (d, J = 9.3 Hz, 1H, 9-H), 5.20 (d, J = 9.3 Hz, 1H, 11-H), 7.00–7.35 (m, 8H, aromatic protons). – ^{13}C NMR (Table 2). – $C_{21}H_{22}O$ (290.4) calcd. C 86.85 H 7.64, found C 86.72 H 7.60.

Conversion of Cyclic Enol Ethers into Ketones (Scheme 2). Typical procedure: 1.0 mmol (192 mg) of **16** was stirred with 10 ml of 1N aqueous hydrochloric acid and pentane (15 ml) at room temperature for 48 h. The pentane layer was separated, the aqueous phase shaken with further pentane, and the combined pentane layer neutralized with aqueous $NaHCO_3$ and dried ($MgSO_4$). After removal of the solvent *2,2-dimethylbicyclo[3.2.2]non-6-en-3-one* (**17**)[15] was obtained as a colorless oil, which decomposed on attempted chromatography with alumina (activity 1). – IR ($CHCl_3$): 1690 cm^{-1}. – 270 MHz ^{1}H NMR ($CDCl_3$): δ = 1.06 (s, 3H, *endo*-CH_3), 1.17 (s, 3H, *exo*-CH_3), 1.4–1.7 (complex, 4H, CH_2CH_2), 1.8–2.0 (m, 1H, CHCO), 2.1–2.3 (m, 1H, CHCO), 2.5–2.7 (m, 2H, 1, 5-H), 6.25–6.40 (m, 2H, 6, 7-H).

9,10-Dihydro-13,13-dimethyl-12-(trimethylsiloxy)-9,10-([1]propeno)anthracene (**22**) was prepared from anthracene and **9** as described for **20**. A 7:3 mixture of enol ether **22** and ketone **21** was isolated in ca. 95% combined yield. Attempted large scale chromatographic separation of **22** from the known[5a] ketone **21** was only partially successful owing to the easy conversion of **22** into **21**. – IR ($CHCl_3$): 1695, 1600, 1460 (C=C, benzenoid C=C). – 90 MHz ^{1}H NMR ($CDCl_3$): δ = 0.08 (s, 9H, $SiMe_3$), 1.05 [s, 6H, $(CH_3)_2$], 3.66 (s, 1H, 10-H), 4.08 (d, J = 9.3 Hz, 1H, 9-H), 5.43 (d, J = 9.3 Hz, 1H, 11-H), 7.0–7.4 (m, 8H, aromatic protons).

$C_{22}H_{26}OSi$ Calcd. C 78.98 H 7.83
Found C 78.05 H 7.71 Calcd. 334.1752 Found 334.1752 (MS)

3-Chloro-2,4,4-trimethylbicyclo[3.2.1]octa-2,6-diene (**24**): Ethyldiisopropylamine (3.5 g, 27.5 mmol) in CH_2Cl_2 (100 ml) containing $ZnCl_2$ (3.75 g, 27.5 mmol) at 0 °C was mixed with cyclopentadiene (3.3 g, 50 mmol) and **13** (4.85 g, 25 mmol). After 6 h at room temperature the resulting yellow solution was passed through a short column of alumina with pentane eluent. The crude product so obtained was purified by chromatography over silica gel giving **24** as a colorless oil, 1.9 g (42%). – ^{1}H NMR ($CDCl_3$): δ = 0.99 (s, 3H, *endo*-CH_3), 1.28 (s, 3H, *exo*-CH_3), 1.84 (s, 3H, olefinic CH_3), 1.85 (m, 2H, CH_2), 2.56 (m, 2H, bridgehead protons), 5.87 (dd, J = 6, J = 3 Hz, 1H), 6.36 (dd, J = 6, J = 3 Hz, 1H). – MS (70 eV, room temperature): *m/e* = 184 (22%, M^+), 182 (63), 169 (26), 167 (81), 147 (100), 132 (70), 131 (70), 117 (56), 105 (57), 91 (75). $C_{11}H_{15}{}^{35}Cl$ calcd. 182.0864, found 182.0871; $C_{11}H_{15}{}^{37}Cl$ calcd. 184.0833, found 184.0832.

3-Bromo-2,4,4-trimethylbicyclo[3.2.1]octa-2,6-diene (**25**) was prepared as described for **24**, $ZnBr_2$ being used instead of $ZnCl_2$. Colorless oil, 2.2 g (39%). – ^{1}H NMR ($CDCl_3$): δ = 1.00 (s, 3H, *endo*-CH_3), 1.27 (s, 3H, *exo*-CH_3), 1.98 (s, 3H, olefinic CH_3), 2.0 (m, 2H, CH_2), 2.74 (m, 2H, bridgehead protons), 6.00 (dd, J = 6.5, J = 3 Hz, 1H), 6.84 (dd, J = 6.5, J = 3 Hz, 1H).

MS (70 eV, room temperature): *m/e* = 228 (23%, M^+), 226 (26), 213 (14), 211 (15), 147 (100), 132 (51), 105 (62), 91 (41). $C_{11}H_{15}{}^{79}Br$ calcd. 226.0358, found 226.0363; $C_{11}H_{15}{}^{81}Br$ calcd 228.0338, found 228.0343.

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