The Addition of 2-Oxido-2-cyclopenten-1-ylium to Some Olefins and Dienes in 2,2,2-Trifluoroethanol

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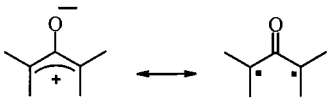
The title reaction has been studied with 2-methoxypropene, (*E*)-cyclooctene, ethoxyethene, 1,3-cyclopentadiene, 3-methylenecyclohexene, styrene and isoprene as the olefinic substrates. This sequence is one of decreasing reactivity of the substrates towards 2-oxido-2-cyclopenten-1-ylium (**1**) if [4 + 3] cycloaddition (the prevailing reaction in the case of cyclopentadiene and isoprene) is ignored. This reactivity encompasses: (a) the formation of intermediate 1,5-dipoles, which in the majority of cases give rise to a multitude of products including many of higher molecular mass, and (b) two types of ene reactions, dubbed "ene-type 1" and "ene-type 2". Type 1, in which the migrating hydrogen atom is abstracted from **1**, is ubiquitous (except with 2-methoxypropene) but is always a minor reaction; type 2, in which the migrating hydrogen atom is transferred to **1**, was encountered only in the cases of 3-methylenecyclohexene, in which it is a major reaction path, and isoprene. Both types were found to be slightly concerted. In this context, we observed an effect which we have dubbed "dipolar diversion of a concerted reaction". In general, those substrates incapable of forming [4 + 3] cycloadducts gave complicated mixtures, with the exception of two compounds, which were found to give one predominant product with **1**. The first of these is the *trans*-fixed 1,3-diene 3-methylenecyclohexene, which gave the ene-type 2 adduct **10d1**, while the second is the most nucleophilic substrate, 2-methoxypropene, which gave a mixture of four adducts (two pairs of epimers), all of which gave the diketone **17** on hydrolysis.

Introduction

"2-Oxyallyls" (Scheme 1) occur as unstable intermediates in several types of chemical reactions. Their reactivity has attracted considerable attention during the past three decades.[1−44] Their chemistry differs somewhat, depending on whether they are generated by the action of strong electrophiles (Nazarov cyclisation)[3−5] and so bear the electrophile covalently bound to their oxygen atom, by the action of carbonyliron compounds in nonpolar solvents ("Noyori conditions"),[6−11] thus presumably in complexation with iron, in the presence of other metals,[12−16] in a presumably free state in aprotic solvents − either by reversible thermal ring opening of cyclopropanones[17,18] or with the aid of photochemical reactions[19−27] − or by the action of bases in the highly polar and ionising solvents 2,2,2-trifluoroethanol and 2,2,3,3-tetrafluoro-1-propanol ("Föhlisch conditions"),[28−37] in which their oxygen atom is hydrogen-bonded to the solvent. Their outstanding bimolecular reaction behaviour throughout is [4 + 3] cycloaddition to *cisoid* 1,3-dienes, a reaction analogous to the Diels−Alder [4 + 2] cycloaddition, with the oxyallyl, a two-electron, three-carbon atom π component, assuming the role of the dienophile. According to high-level theoretical calculations,[38−42] the electronic ground states of "2-oxyallyls" are best described by the singlet diradical formula shown in Scheme 1, but in polar media and on approach by reactants they become polarised into the dipolar electron distribution also shown in Scheme 1.



Scheme 1

"2-Oxyallyls" are in equilibrium with cyclopropanones through rapid disrotatory electrocyclic ring closure/ring opening. This equilibrium normally remains completely on the side of the latter species. The exception are "2-oxyallyls" that form part of a C_5 ring: in other words, 2-oxido-2-cyclopenten-1-ylium compounds, which, according to high-level theoretical calculations[38−42] and experimental evidence[43,44] are energetically more stable than their cyclopropanone counterparts. Therefore, 2-oxido-2-cyclopenten-1-ylium compounds are more likely to exhibit clean oxyallyl chemistry uncontaminated by cyclopropanone chemistry (such as hemiacetal formation,[36] Favorskii rearrangement,[45] or cycloaddition to the carbonyl group[18]).[35]

When, some years ago, we allowed a photochemically generated condensed 2-oxido-2-cyclopenten-1-ylium to react with cyclopentadiene, we encountered a rather efficient addition,[46] analogous to the familiar "ene" reaction in the same sense that the [4 + 3] cycloaddition of "oxyallyls" is analogous to the Diels−Alder reaction. We were astonished to find only two precedents for this addition (Scheme 2),[35,47] both of them also happening to involve 2-oxido-2-cyclopenten-1-ylium and cyclopentadienes. *Formally*, a 1,3-diene is not required for this addition; a mono-ene would do. In the most recent investigation of the addition of mono-enes to a photochemically generated 2-oxido-2-cyclopenten-1-ylium, however, this type of addition (re-

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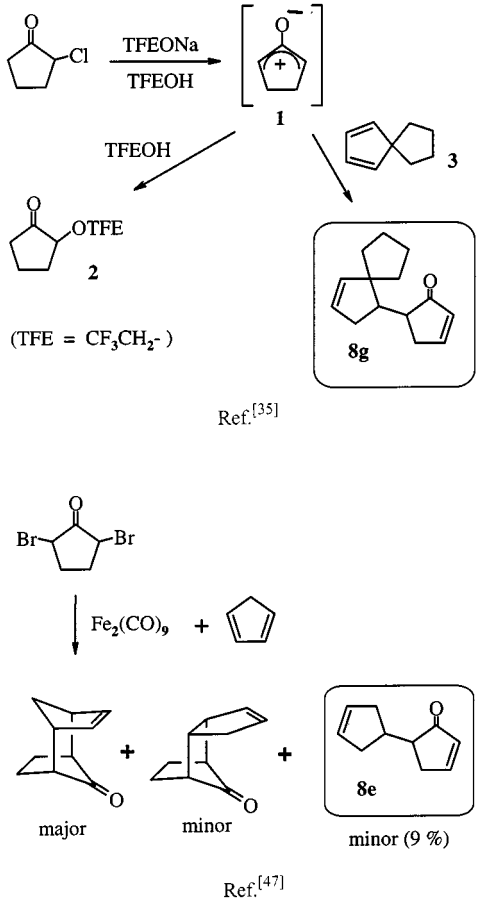
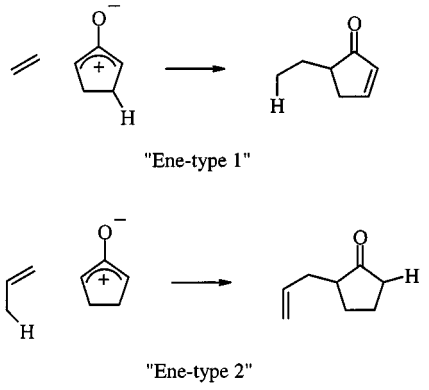


Scheme 2



Scheme 3

ferred to from now on as "ene-type 1" for simplicity; Scheme 3) did not show up; instead a different one with exchanged roles of both components ("ene-type 2" addition; Scheme 3) was found.[19] We felt that an investigation into the scope of these additions would be desirable. In order to study unsubstituted 2-oxido-2-cyclopenten-1-ylium in as free a state as possible, we chose Föhlisch conditions. To the best of our knowledge, no study of olefins that are not *cisoid* 1,3-dienes under Föhlisch conditions has yet been reported. Here we report the results of such a study with several olefins and dienes. Besides clarifying the scope of the ene-type additions, one main goal of the investigation was to survey and understand the chemistry of the investigated systems.

Results and Discussion

Scope

As shown by Föhlisch and Joachimi,[35] 2-oxido-2-cyclopenten-1-ylium (**1**), when generated in 2,2,2-trifluoroethanol (TFEOH) in the absence of a substrate, adds one molecule of solvent to give **2** (Scheme 2). When we generated **1** in TFEOH in the presence of the simple olefins 1-pentene, cyclopentene, or (*Z*)-cyclooctene, this result did not change. Obviously, these olefins are not reactive enough towards **1** to compete successfully for it with the solvent. An increase in the strain of the olefins should increase their reactivity. The strained olefins norbornene and norbornadiene did give small amounts of products (which were not investigated), but the main product was still **2**. A reaction successfully prevailing over formation of **2** was encountered only with the even more strained (*E*)-cyclooctene.

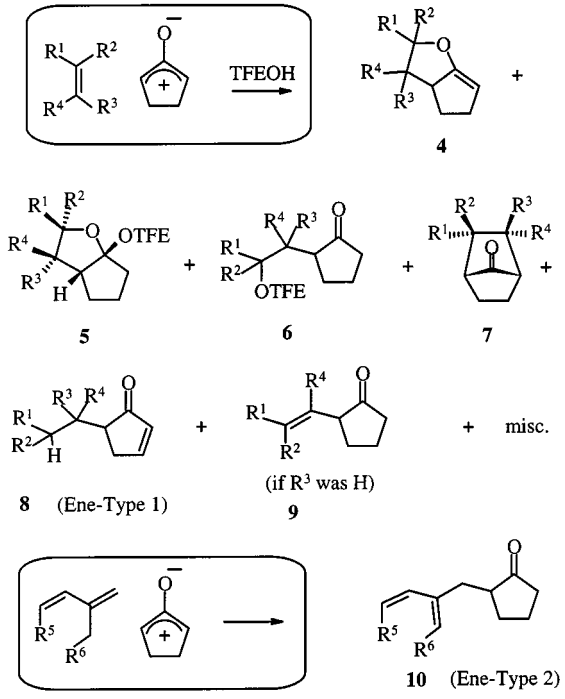
Conjugation was found much more efficient than strain in enhancing reactivity. Thus, 3-methylenecyclohexene, a 1,3-diene constrained in the *s-trans* form and thus incapable of giving the [4 + 3] cycloaddition, was nevertheless highly reactive towards **1**. As might then be expected, since phenyl is similar to vinyl in its conjugative power, styrene was also found to be reactive (the two 1′,2′-dimethylstyrenes, however, were much less reactive and **2** was the predominant product in those cases). Even more reactive than 3-methylenecyclohexene were the highly nucleophilic olefins 2-methoxypropene and ethoxyethene (ethyl vinyl ether), whereas the electrophilic olefin acrylonitrile was unreactive.

Here we present a more detailed investigation of the reaction in TFEOH between **1** and the substrates (*E*)-cyclooctene, 3-methylenecyclohexene, styrene, 2-methoxypropene and ethoxyethene. For the sake of comparison, we also included four *cisoid* 1,3-dienes already investigated by Föhlisch and Joachimi.[35] The molecular structures of all products reported here could be unambiguously deduced solely from NMR experiments (400 MHz ^{1}H NMR, including ^{1}H/^{1}H spin decoupling and ^{1}H/^{1}H NOE; ^{13}C BB and DEPT; C−H correlation). Our investigation proceeded in three steps. In the first step, the preparative part, we attempted to isolate and identify as many products as we could. In the second step, the analytic part, we obtained reaction mixtures from the individual substrates under defined conditions, and, using 500-MHz proton resonance spectroscopy and the proton resonance spectra previously obtained for the individual products, analysed the mixtures for the individual products qualitatively and quantitatively with the aid of signal integrals. The products were formed irreversibly and were suitably stable under the reaction and analysis conditions. Since the relative amount of **2** could be determined in all analysed reaction mixtures, we were able to obtain relative rates for formation of individual products referenced to **2** (that is, the relative rate for formation of **2** is ≡ 1 by definition) even from different reaction mixtures, on the assumption that the rate of formation of **2** would be the same in all cases. Finally, a few auxiliary experiments relevant to reaction mechanism were carried out and the

available evidence was combined to draw some general conclusions.

Preparative Experiments

Typically, the solution of base [15 mmol of triethylamine (TEA) or 10 mmol of sodium 2,2,2-trifluoroethoxide (TFEONa)] in 5 mL of TFEOH was added at 10 °C to a solution of 10 mmol of 2-chlorocyclopentanone and 20 or 40 mmol of substrate in 5 mL of TFEOH under Ar (this was done since in one experiment we had found by-products presumably arising from oxidation by air), at a rate sufficient to keep the temperature below 20 °C. Reaction was complete within 30 min. After standard workup (evaporation of TFEOH, partition between ether and water), the reaction mixture was chromatographed. Compound **2**, but not many other products, suffered partial decomposition during chromatography. Typical products are summarised in Scheme 4; products **5** arise from addition of TFEOH to products **4**. The yields given in this section refer to isolated material unless specified otherwise and are based on 2-chlorocyclopentanone.



(TFE = CF_3CH_2-)

a1: $R^1 + R^3 = (CH_2)_6$, $R^2 = R^4 = H$
a2: $R^2 + R^4 = (CH_2)_6$, $R^1 = R^3 = H$
b: $R^1 = Ph$, $R^2 = R^3 = R^4 = H$
c: $R^1 + R^2 = Me + C_2H_3$, $R^3 = R^4 = R^5 = R^6 = H$
d1: R^1----$R^2 = (CH_2)_3CH{=}CH$, $R^3 = R^4 = H$
$R^5 + R^6 = (CH_2)_2$
d2: R^2----$R^1 = (CH_2)_3CH{=}CH$, $R^3 = R^4 = H$
e: R^1----$R^4 = CH{=}CHCH_2$, $R^2 = R^3 = H$
f1: R^2----$R^3 = CH{=}CH[C(CH_2)_2]$, $R^1 = R^4 = H$
f2: R^1----$R^4 = CH{=}CH[C(CH_2)_2]$, $R^2 = R^3 = H$
g: R^1----$R^4 = CH{=}CH[C(CH_2)_4]$, $R^2 = R^3 = H$
h1: $R^1 = OEt$, $R^2 = R^3 = R^4 = H$
h2: $R^2 = OEt$, $R^1 = R^3 = R^4 = H$
i: $R^1 + R^2 = OMe + Me$, $R^3 = R^4 = H$

Scheme 4

Without Added Olefins

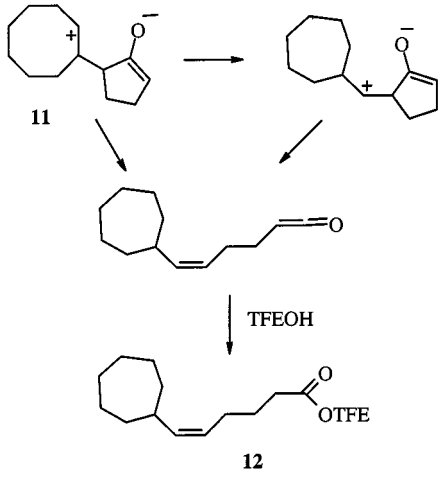
Treatment of 2-chlorocyclopentanone as above, but in the absence of substrate, gave **2** as reported.[35] By-products were cyclopent-2-en-1-one (1−10%) and material of higher molecular mass, with two broad ^{1}H NMR absorption envelopes in a ratio of ca. 5:1, between $\delta = 1.5$ and $\delta = 2.7$ and at $\delta \approx 4$ (6−14%). The yields of both by-products depended on reaction conditions (slight excess of either reactant, mode and rate of addition). We speculate that the higher molecular mass material derives from the enol of **2**, which should be an intermediate in the formation of **2** from **1**. This enol should be highly reactive towards addition to **1**, given the high reactivity of enol ethers towards **1** mentioned above; it might even be more reactive than enol ethers, since the enol hydrogen atom could cooperate in the addition reaction (cf. the highly efficient addition of an enol to an oxyallyl compound reported by us earlier[46]). The addition product may again be an enol and so might add a further molecule of **1**, and so on. Since the rate of conversion of the enols to the keto forms (such as **2),** and hence their quasi-stationary concentration during the reaction, should depend appreciably on the reaction conditions, the observed variation in the yield of the higher molecular mass material is understandable.

(*E*)-Cyclooctene

Isolated products were: **5a1** (7.4%), **5a2** (5.4%), **8a** (= **8a1** = **8a2**) (16.3%), and **12** (3.5%) (using 40 mmol of substrate; the yields were lower with 20 mmol). Compound **2** (1.7%) was observed in the 400-MHz ^{1}H NMR spectrum of the reaction mixture. In addition, numerous other chromatographic fractions were obtained; these were nonuniform and did not permit identification of any product in them solely from NMR-spectroscopic data. According to ^{1}H NMR, they contained only a few olefinic protons, some α-oxygen protons ascribable to TFEO protons, and − predominantly − saturated hydrocarbon protons. This NMR result could be translated into the overall presence of 14% TFEO units and 36% (cyclooctene + **1**) units in these unresolved fractions, in agreement with C,H,O,F analyses. This would account altogether for 70% of the 2-chlorocyclopentanone. The unresolved fractions could be separated by distillation into distillates and into not feasibly distillable residues in roughly comparable amounts. The latter probably have a proportion of **1** to cyclooctene units of two or more. They thus appear to have been produced analogously to the higher molecular mass material described in the preceding paragraph and for the same reasons as there, from the primary product of type **4**. The distillates were still not uniform according to NMR. The majority of their mass spectra, however, indicated a prevailing molecular mass corresponding to 1:1 adducts between cyclooctene and **1**. Such adducts might be of type **7**, given the lack of (or only small contributions from) olefinic proton signals in the NMR spectra.

Three stereoisomers of type **7** are possible, and more adducts with rearranged skeletons (compare next paragraph) may add to them, thus increasing the complexity of the mixtures. In the olefinic portion of the ^{1}H NMR spectra of unresolved fractions, 0.09% of a (*Z*)-$CCH_2CH{=}CHCHC_2$ unit was detected, and tentatively ascribed to the ene-type 2 adduct.

Product **12** presumably arises by way of the mechanism shown in Scheme 5. Formation of **12** must have involved a Wagner−Meerwein rearrangement, which points to the dipole **11** as the starting point. Compound **11** is also the presumed starting point[35] for the formation of **5a1**, **5a2**, and the adducts of type **7**. The exclusive (*Z*) configuration of the olefinic bond of **12** is remarkable; no (*E*) isomer could be detected in the isolated fractions. This may indicate that ketene formation from **11** may actually be concerted, rather than two-step.



Scheme 5

Styrene

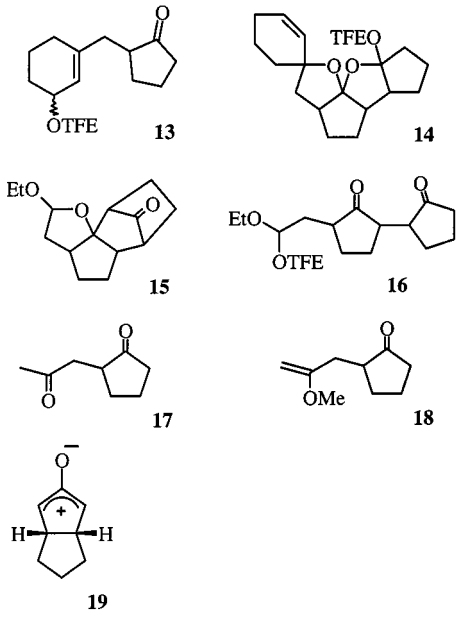
The only lower molecular mass products isolated were **2** (30−40%) and **8b** (6.5%). The residue was of higher molecular mass. The ^{1}H NMR spectrum of this residue analysed to give a ratio of styrene units to units of **1** of about 1:2.5; only a small amount of TFEO units was present. This material can again be assumed to have formed in analogous fashion to the higher molecular mass products in the preceding paragraphs; the much lower reactivity of styrene towards **1**, in comparison to the primary adduct of type **4**, may be responsible for strong predominance of formation of that material.

Isoprene

In agreement with Föhlisch and Joachimi,[35] the main isolated products (using 40 mmol of substrate) were [4 + 3] cycloadduct (56%), **2** (4.1%), and an adduct to which these authors had tentatively assigned structure **9c**, but which was actually the ene-type-2 adduct **10c** (3.6%). Further isolated products were **8c** (1.4%, 2 stereoisomers in a ratio of 1:1), **5c** (0.33%, 2 stereoisomers in a ratio of 4:3), and **7c** (0.16%, one isomer of unclarified stereochemistry); no further products could be detected in the reaction mixture by 400-MHz ^{1}H NMR, except for some higher molecular mass material containing no isoprene units.

3-Methylenecyclohexene

Isolated products (using 20 mmol of substrate) included the ene-type 2 adduct **10d1** (33.3%, 44% in the unseparated reaction mixture according to ^{1}H NMR), a 1:1 mixture of **5d1** and **5d2** (3.4%), a 4:1 mixture of **7d1** and **7d2** (3.9%), a 7:3 mixture of **8d1** and **8d2** (stereochemistry unclarified, 1.8%, 3.3% in the crude reaction mixture according to ^{1}H NMR), **13** (1.4%), and **2** (0.25%, 3.8% in the unseparated reaction mixture according to ^{1}H NMR). Numerous other chromatographic fractions were also obtained; these did not contain uniform products, however. The main material in two consecutive fractions was interpreted by ^{1}H NMR as **14** (3.4%) (Scheme 6). In view of the facile [4 + 3] addition of *cisoid* 1,3-dienes to **1**, it may be speculated that much of the originally formed **10d1**, containing a 1,3-cyclohexadiene moiety, had added to a second molecule of **1** in a secondary reaction**.** We did not succeed in isolating such adducts from the numerous chromatographic fractions, however.



Scheme 6

Cyclopenta-1,3-diene

As described by Föhlisch and Joachimi,[35] the predominant products were the two [4 + 3] cycloadducts. As a third product, we isolated **8e** (1.4%), albeit contaminated with the major [4 + 3] cycloadduct. According to ^{1}H NMR analysis, the unseparated reaction mixture (obtained with 20 mmol of substrate) contained *endo*-[4 + 3] cycloadduct (70.9%, structure as given in Scheme 2), *exo*-[4 + 3] cycloadduct (16.4%), **8e** (2.5%, cf. Scheme 2), **2** (0.44%), and an unidentified mixed material containing both olefinic and saturated CH protons (ca. 9.7%).

Spiro[2.4]hepta-4,6-diene (5,5-Ethylenecyclopenta-1,3-diene)

In agreement with Föhlisch and Joachimi,[35] when using 20 mmol of substrate, we isolated as principal products one single [4 + 3] cycloadduct (36%),[35] **9f2** (2.5%, 16.3% in the unseparated reaction mixture according to ^{1}H NMR), and **2** (6.5%, 16.8% in the unseparated reaction mixture). In addition, we isolated **5f2** (2%), **5f1** (0.8%), **7f2** (1.6%) and **7f1** (1.2%). Moreover, the characteristic low-field ^{1}H NMR signals revealed the presence of ca. 2.9% **8f** (= **8f1** = **8f2**) in the unseparated reaction mixture. Before chromatography, however, the complete reaction mixture obtained with either base was very complex according to ^{1}H NMR; this was also reflected in the numerous chromatographic fractions containing nonuniform material. It appears that the cyclopropane ring had given rise to cationic rearrangements, resulting in numerous products accounting for the residual 22.4%.

Spiro[4.4]nona-1,3-diene (3)

In agreement with Föhlisch and Joachimi,[35] using 20 mmol of substrate, we isolated as principal products **2** (31.8%, 48% in the unseparated reaction mixture according to ^{1}H NMR) and **8g** (7.7%, cf. Scheme 2; one single stereoisomer). In addition, we isolated **7g** (0.83%) and another chromatographic fraction of which $^1/_5$ could be interpreted, from the olefinic portion of its ^{1}H NMR spectrum, as **9g** (0.4%). The residue, according to the ^{1}H NMR spectrum of the unseparated mixture, appeared to be higher molecular mass material, in analogy to the experiments with styrene or (*E*)-cyclooctene. Remarkably, [4 + 3] cycloadducts were completely absent.

Ethoxyethene (Ethyl Vinyl Ether; EVE)

With TEA as the base, this substrate underwent extensive oligomerisation on prolonged standing under the reaction conditions, to give acetals with TFEOH. We isolated an (EVE/TFEOH = 2:1) oligomer (mixture of 2 stereoisomers) and an (EVE/TFEOH = 4:1; all head-to-tail) oligomer (mixture of stereoisomers). With TFEONa as the base, no oligomerisation was observed.

Using 20 mmol of substrate, isolated products included a 1:1 mixture of **6h1** and **6h2** (11.1%), **7h2** (21%), a 2:1 mixture of **7h1** (1.5%) and **15** (0.8%, stereochemistry not clarified), **16** (14.7%, stereochemistry not clarified), **8h** (= **8h1** = **8h2**, 4.9%) and **2** (2.9%, 7.4% before chromatography). There were several more minor products as mixtures in several fractions obtained by a combination of chromatography and distillation; these could not be identified.

2-Methoxypropene

In order to protect the acid-sensitive substrate, only TFEONa was used as the base and addition was inverse (2-chlorocyclopentanone was added to a solution of substrate and base in TFEOH). Products isolated after the usual aqueous workup were **6i** (7%, mixture of two stereoisomers), **7i** [1.3%, obtained as a 1:1 mixture with **2** (1.3%)], **17** (38%), and higher molecular mass material (ca. 25%). Since **17** had obviously arisen from primary products by hydrolysis during the aqueous workup or chromatography, further preparative experiments used distillative workup only. Such experiments typically gave **4i** (31.2%, 1:1 mixture of two stereoisomers) mixed with **7i** (2.7%, one stereoisomer of unclarified stereochemistry) as the lowest boiling fraction, followed by **6i** (41.8%, 1:1 mixture of two stereoisomers) mixed with various unknown isomeric products (ca. 6.7%). One attempt to redistill the impure **4i** resulted in its complete isomerisation to a mixture of **9i** and **18**. If the original reaction mixture was left standing before workup for 20 min, 80 min, or 19 h, and then analysed by ^{1}H NMR, the ratios of **4i** to **6i** were found to be 53:47, 38:62 and 0:100, respectively. Extrapolation to 0 min suggested an original **4i** to **6i** ratio of 3:2. Hence, in the presence of TFEOH, **4i** transforms slowly and irreversibly to **6i**, but much of the **6i** is *not* formed by way of **4i**. Both **4i** and **6i** are converted into **17** on standing in tetrahydrofuran/water in the presence of a catalytic amount of *p*-toluenesulfonic acid at room temperature.

Analytical Experiments

Rates of formation, relative to that for **2**, for adducts of olefinic substrates to **1** are presented in Table 1, grouped into types of adducts. Substrates are arranged in order of decreasing combined relative rates for "others"; "others" being the sum of all adducts that are certainly not formed in a concerted fashion (in other words, that are neither [4 + 3] nor ene-type) and hence are certainly formed by way of a 1,5-dipole such as **11** or the corresponding 1,4-diradical. Standard conditions (a) were preferred, except for **3**, for which conditions (b) had to be chosen for reasons of solubility of **3**; in order to provide for comparison, styrene was investigated under both sets of conditions. This comparison suggested that the relative rates for **3** are similar to those of styrene.

Reaction Mechanisms, Auxiliary Experiments

The molecular structures of all isolated adducts {except for the adducts of (*E*)-cyclooctene and for the [4 + 3] cycloadducts in which no regioisomerism is possible} reveal a strict regioselectivity of addition. Addition of **1** to an olefinic substrate is always such as would be expected if the primary adduct were the 1,5-dipole (such as **11**) with maximum stabilisation of its carbocation, or the corresponding 1,5-diradical with maximum stabilisation of its radical centres. This would suggest a two-step mechanism by way of 1,5-dipoles/diradicals for the formation both of those adducts classified as "others" in Table 1 and of the ene-type adducts. This mechanism would explain why simple unstrained nonconjugated olefins are so unreactive towards **1**. This mechanism is certainly true for "others", the concerted formation of which is symmetry-forbidden, but it also seems, to a first approximation, to be true for the ene-type adducts, the concerted formation of which is symmetry-allowed.[2,35] Generally speaking, if two reactants that are to form two new bonds between each other in a formally pericyclic reaction (as in ene-type additions) approach each

Table 1. Relative rates of formation of adducts of olefinic substrates to **1**, based on the rate of formation of **2**; conditions (a): olefinic substrate (20 mmol) was added to a solution of 2-chlorocyclopentanone (10 mmol) in TFEOH (5 mL) while stirring under Ar at 10 °C, this was followed by a solution of TFEONa in TFEOH (2 M, 5 mL) at such a rate as to maintain the temperature below 12 °C, overall reaction time 30 min; conditions (b): same as (a), but 2-chlorocyclopentanone (2.5 mmol) in TFEOH (5 mL), 25 °C, olefinic substrate (5 mmol) followed by triethylamine (3.75 mmol) in TFEOH (5 mL)

	[4 + 3]	Ene-type 1	Ene-type 2	others
(a) 	—	< 0.05	< 1	50 (major: **4i** + **6i**; minor: **7i** (1.5) + unknown)
	—	4.1	0.05	25 (**5a1+2, 12, 7a,** skeletally rearranged adducts)
	—	1.9	—	21.5 (**7h2** (10.3), **6h1** + **6h2** + **16** (7.1); **7hi** (1.0), **15** (0.4))
	290	3.7	<7.4[a]	17 (not identified)
	—	0.7	7.8	2.4 (**7d1** (0.6), **7d2** (0.15), **5d1** (0.5), **5d2**(0.5), **13** (0.65))
	—	0.5	—	1.2 (higher mol. wght.)
	5.9	0.14	0.4	0.05 (**5c, 7c**)
(b)  (3)	0	0.18	—	0.42 (**7g** (0.03), **9g** (0.015), others not identified)
	—	0.2	—	0.3 (higher mol. wght.)

[a] Compound not detected but may have been contained in "others".

other in a "closed" geometry that would allow simultaneous ("synchronous") formation of both new bonds, two extremes are conceivable. One extreme is synchronous formation; the other is a two-step reaction, in that the formation of the second bond starts only after completion of the formation of the first bond. Passing from the latter extreme (no concertedness of bond formation) to the former (fully concerted), it is possible to conceive of a continuous range of options, with increasing overlap in time between both bond-forming events, or put another way, increasing degree of concertedness. In the case of a small degree of concertedness, the transition state for the reaction may be close to the 1,5-dipole/diradical intermediate for the two-step reaction and thus may approach its degree of stabilisation. When applied to the ene-type additions of the present investigation, this means that their degree of concertedness is small at most. It is one goal of this work to find out whether there is some degree of concertedness at all.

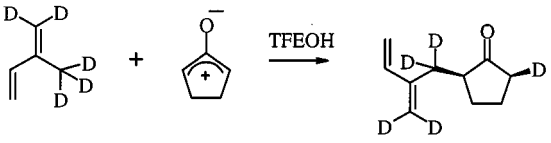
The unreactivity of acrylonitrile towards **1** (vide supra) deserves attention. Addition to position 3 of acrylonitrile would generate a significantly stabilised radical (by 5.3 kcal/mol[48]), whereas a highly unfavourable cation would result from addition to either position 2 or 3. The unreactivity of acrylonitrile thus suggests that two-step additions of **1** to olefins produce 1,5-dipoles rather than 1,5-diradicals in the primary addition step. The reactivity ranking of the unstrained substrates [thus disregarding the highly strained (*E*)-cyclooctene] for two-step additions ("others") as displayed in Table 1 bears this out: 2-methoxypropene, which of all substrates yields the most stable carbocation, ranks first, followed by ethyl vinyl ether. The preference of the 1,5-dipole over the 1,5-diradical also comes out of high-level quantum mechanical calculations for the addition of 1,3-dienes to **1**; these suggest a very high exothermicity (> 40 kcal/mol) for the formation of an open-chain intermediate (1,5-dipole or -diradical) from **1** and 1,3-diene.[49] From known heats of formation (e.g., ref.[40]) and group increments,[50] in contrast, one would estimate an approximate thermoneutrality for the formation of the intermediate 1,5-diradical from **1** and 1,3-diene. This not only demonstrates the preference for the 1,5-dipole over the 1,5-diradical, but also that the formation of the 1,5-dipole from **1** and 1,3-diene is irreversible. The following discussion is based on these two insights. The differences in reactivity among the individual 1,3-dienes as shown in Table 1 are readily explainable in terms of angle strain, steric hindrance, and lack of coplanarity, and shall not concern us here.

The enol ethers, 2-methoxypropene and ethyl vinyl ether, give adducts **6** rather than **5** whereas the other substrates give **5** rather than **6**; **5** originates from the 1,5-dipole by way of **4**, whereas **6** originates from the 1,5-dipole both by way of **4** and directly (vide supra). A possible explanation for this difference between enol ethers and other substrates originates from the higher stability of the carbocation in the 1,5-dipole derived from the enol ethers. The higher stability results in: (a) a slower ring closure to **4**, so that protonation of the enolate moiety by the solvent may instead occur, followed by eventual addition of one solvent molecule to the remaining carbocation to give **6**, and (b) reversibility of the ring closure to **4**.

The results obtained for 2-methoxypropene differ strikingly from those obtained for the other substrates, including the closely related ethyl vinyl ether, in that neither ene-type adduct could be detected and the bicyclic adducts **7i** are formed in only some 3% yield. Compounds **4i** and **6i** predominate, accompanied by some "trash" that is probably due to decomposition, since it increases with time. All ene-type 1 adducts **8** show characteristic olefinic ^{1}H NMR absorptions in a region that was entirely silent in the case of 2-methoxypropene.The absence of the ene-type 2 adduct **18** in the crude reaction mixtures could be verified because a mixture of **18** and **9i** obtained by (possibly catalysed) thermolysis of **4i** was available, so that the olefinic ^{1}H NMR absorptions of **18** were known exactly. The possibility that **18** and/or **9i** were initially formed but quickly converted into **6i** could be dismissed on the grounds that 2-methoxypropene, although converted into 2-methoxy-2-(2,2,2-trifluoroethoxy)propane within minutes at room temp. in pure

TFEOH, is converted only slowly (30% in 45 min) in TFEOH containing 1 M TFEONa. The striking absence of either ene-type adduct formation in the reaction between 2-methoxypropene and **1** has precedent in the reaction between 2-methoxypropene and photochemically generated **19**, which virtually exclusively produced adducts of type **4** and **7**, accompanied by only "a small amount" of ene-type 2 adduct.[19]

Matlin and co-workers,[19] in their investigation of additions of simple olefins to **19** in nonpolar aprotic solvents, concluded, using a circumstantial steric and electronic argument, that the ene-type 2 addition was concerted and that it proceeded by transfer of the hydrogen atom directly to the carbon − rather than the oxygen − atom of the oxyallyl moiety. Since we used the protic solvent TFEOH, we were in a position to address the latter point more directly. Deuterated isoprene [1,1-dideuterio-2-(trideuteriomethyl)buta-1,3-diene] with **1** in TFEOH gave the ene-type 2 adduct **10c**, with one of the α-carbonyl methylene hydrogen atoms fully deuterated (Scheme 7; isolation of this adduct required immediate workup since otherwise this deuterium atom would be lost by exchange with a hydrogen atom from the solvent). An intermediate 1,5-dipole would be expected to transfer the positively charged hydrogen to the negatively charged enolate oxygen atom (to form the enol) rather than to the carbon atom (to form the ketone), since the latter is only weakly negatively charged. Once bound to the enol oxygen atom, the deuterium atom would then have been quickly replaced by a hydrogen atom from the solvent before the enol could isomerise to the ketone.



Scheme 7

There is more evidence for the concertedness of the ene-type 2 addition: (*E*)-Cyclooctene undergoes no ene addition (this time in its original meaning) to benzyne (it undergoes only [2 + 2] cycloaddition) whereas (*Z*)-cyclooctene does so readily.[51,52] The reason for this is that, for a *concerted* ene addition to occur, the breaking C−H bond is poorly oriented in the case of (*E*)-cyclooctene but favourably oriented in the case of (*Z*)-cyclooctene; for a two-step reaction there would be no difference in product distribution between (*Z*) and (*E*) isomers because of conformational equilibration within the 1,4-dipole/diradical intermediate (this intermediate also being, for reasons of orbital symmetry, the origin of the [2 + 2] cycloaddition). Hence, the ene-addition of (*Z*)-cyclooctene to benzyne must be concerted. A comparison of the relative rates given in Table 1 for addition reactions of (*E*)-cyclooctene and 3-methylenecyclohexene to **1** allows a similar conclusion. The ratio of the rates for the ene-type 2 additions [(*E*)-cyclooctene over 3-methylenecyclohexene] is very low (0.05:7.8 = 0.0064) compared to the corresponding ratios for the ene-type 1 additions (5.8) and for "others" (10.4). This effect would not be understandable on the basis of the two-step mechanism for the ene-type 2 additions. It is, however, understandable, as in the case of the additions to benzyne, on the basis of concerted ene-type 2 additions; 3-methylenecyclohexene, unlike (*E*)-cyclooctene, does feature a favourable orientation of the breaking C−H bond. In conclusion, the highly efficient ene-type 2 addition observed with 3-methylenecyclohexene must be concerted.

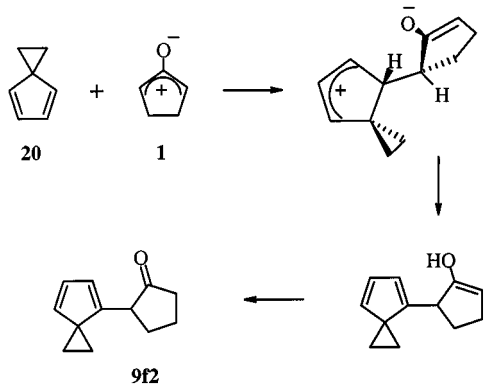
As mentioned, the rate of the ene-type 2 addition for 3-methylenecyclohexene is dramatically greater than that for simple nonconjugated olefins, which indicates the presence of some allylic stabilisation of the transition state in the former case and hence, that the ene-type 2 addition, although concerted (vide supra), is only weakly so and approximates an electrophilic addition of the olefinic substrate to **1**. One might therefore have expected an increase in the rate of the ene-type 2 addition on passing from 3-methylenecyclohexene to 2-methoxypropene, following the strong increase of the rate of electrophilic additions in the same direction (Table 1). Instead, we observe a strong *decrease* (Table 1). The explanation for this phenomenon is what we dub a "dipolar diversion of a concerted reaction". There may well be an *incipient* concerted ene-type 2 addition of 2-methoxypropene to **1** at a rate higher than observed for 3-methylenecyclohexene. However, if the carbocation in the 1,5-dipole intermediate of a *two-step* addition is particularly strongly stabilised (as with 2-methoxypropene), then this 1,5-dipole will firstly be a particularly deep energy trough on the potential energy hypersurface and hence will be a particularly strong attractor for trajectories, and, secondly, the degree of concertedness of the incipient ene-type 2 addition will be particularly small and so its trajectory will come particularly close to the 1,5-dipole even if the latter were not to act as an attractor. As a consequence of both effects combined, the incipient trajectory of a concerted ene-type 2 addition will be diverted away from its path to the ene-type 2 adduct and into the energy trough of the 1,5-dipole. The 1,5-dipole intermediate in the case of 2-methoxypropene does not produce ene-type 2 adducts to any significant extent, but rather **4i**, **6i** and **7i**.

Like the rate of the ene-type 2 addition, also the rates of the ene-type 1 addition and of the formation of **7** decrease on passing from ethyl vinyl ether to 2-methoxypropene (Table 1). Since the formation of **7** cannot be concerted, the explanation for the decrease that holds for the ene-type 2 addition cannot apply in this case. However, the rate decrease for formation of **7** (about 7.5) is much smaller than that for the ene-type 1 addition (> 38). In addition, in the related case of the addition of 2-methoxypropene to **19** in hexane, 47% of the type **7** adduct and 0% of the ene-type 1 adduct has been observed.[19] This rather sharp decrease in the case of the ene-type 1 adduct, but not in the case of adduct **7**, is best accounted for by a "dipolar diversion of a concerted reaction" which predicts a sharp switch in the trajectory path. Another fact that points to the concertedness of the ene-type 1 addition is the observed strict regiospecificity of the hydrogen transfer, which is particularly instructive in the case of unsubstituted 1,3-cyclopentadiene.

According to models, both ends of the allylic cation in an intermediate 1,5-dipole happen to be equally well disposed geometrically for abstracting the hydrogen atom and there would be no particular steric hindrance for either abstraction mode in the case of unsubstituted 1,3-cyclopentadiene. Thus, for a two-step reaction one would expect formation both of **8e** and of its double bond isomer with the unconjugated double bond shifted to the adjacent position, in contrast to what is observed. In a concerted reaction, on the other hand, the observed hydrogen abstraction mode producing **8e** is symmetry-allowed, while the unobserved alternative hydrogen abstraction mode is symmetry-forbidden.

To rule out the possibility that compounds **8** were formed not by ene-type 1 addition to **1** but rather by a Conia−LePerchec addition of cylopenta-1,4-dienol − a conceivable intermediate in the formation of the by-product cyclopent-2-enone − to olefin, we carried out the addition of (*E*)-cyclooctene to **1** in TFEOD instead of TFEOH. The **8a** isolated from this experiment had 50−80% of the three α-carbonyl hydrogen atoms deuterated, but zero deuterium in the cyclooctyl ring, thus ruling out this possibility.

The majority of the substrates studied in this work did not form adducts **9**; the intermediate 1,5-dipoles ring-closed to **4** and **7** rather than eliminate a proton to form a double bond. The notable exception is spiro[2,4]hepta-4,6-diene (**20**), for which **9f2** was even the second most important adduct after the [4 + 3] adduct,[35] as we were able to verify. The closely related diene **3** also appeared to form some **9g**. An aromaticity of the ring system of **20** (hyperconjugation of the cyclopropane ring with the diene system)[53] as the driving force for the preference of proton elimination over ring-closure, though conceivable, was found not to exist. From the experimentally determined heats of formation of **20** (56.8 kcal/mol[54]), 1,3-cyclopentadiene, cyclopropane, and also from group increments,[50] the aromatic stabilisation of **20** was calculated as −0.5 ± 1 kcal/mol. The cause was in fact found to be a steric effect specific to **3** and **20** out of all substrates studied in this work. One of the two diastereomeric 1,5-dipoles formed from **1** and **20** has a preferred conformation with a virtually orthogonal arrangement of the two five-membered rings (Scheme 8). Ring-closure from this conformation either to **4** or to **7**, or to the [4 + 3] adduct, would in any case require a relative rotation of the two five-membered rings that would entail the development of severe steric interactions between one cyclopropane-CH_2 and one cylopentene-CH_2. On the other hand, this conformation has the enolate oxygen atom optimally positioned for abstracting the proton from the other five-membered ring to give the enol of **9f2**.



Scheme 8

Conclusion

Only those olefins that are either highly strained [(*E*)-cyclooctene but not norbornene], highly nucleophilic (such as enol ethers) or conjugated − such as 1,3-dienes (which may well be *s-trans*-constrained like 3-methylenecyclohexene), or styrene − have been found to compete successfully with the solvent for 2-oxido-2-cyclopenten-1-ylium (**1**) in 2,2,2-trifluoroethanol (TFEOH). While many *cisoid* 1,3-dienes are well known to undergo efficient [4 + 3] cycloaddition to **1**, the addition reactions of most other olefins studied in this work are rather messy. Two exceptions to this general statement have been found. The first is the addition of 2-methoxypropene to **1**, which predominantly gives a mixture of **4i** and **6i**, both of which readily hydrolyse to the 1,4-diketone **17**. The second is the addition of 3-methylenecyclohexene to **1**, which gives the "ene-type 2" adduct **10d1** as the predominant adduct. The "ene-type 1" addition, the scope of which was one of the original goals of this investigation, is ubiquitous (except with the most strongly nucleophilic 2-methoxypropene) but is always a minor reaction. The addition of styrene to **1** in TFEOH, which gives ene-type 1 adduct **8b** accompanied by much material of higher molecular mass, contrasts with the reactions between styrenes and "2-oxyallyls" under Noyori conditions, which have been reported to give synthetically useful yields of the bicyclic compounds **7**.[11] Complexation of the oxyallyl oxygen atom by iron[11] probably forestalls addition to this oxygen atom and thus forces the two-step addition to go to **7**.

In spite of the complexity of the reactions (discounting [4 + 3] cycloadditions), it was possible to draw some conclusions about reaction mechanisms. Thus, in general the additions go by way of intermediate 1,5-dipoles, with a small but definite concertedness in the case of the two ene-type reactions.

Experimental Section

General Methods: Reagents and solvents: Fluka, used as received. Unless indicated otherwise, preparative reactions were carried out as follows. The substrate (20 or 40 mmol) was added in one portion to a solution of 2-chlorocyclopentanone (1.18 g, 10 mmol) in 2,2,2-trifluoroethanol (TFEOH, 5 mL), magnetically stirred under argon and maintained at ca. 10 °C. It was followed by a solution of either TFEONa (11 mmol) or triethylamine (TEA) (1.5 g, 15 mmol) in 5 mL of TFEOH, at a rate that maintained the temperature below 20 °C. The reaction mixture, initially colourless, turned yellow, then brown. After 30−120 min, TFEOH and volatile excess substrate

were evaporated under vacuum. The residue was partitioned between water and ether, the aqueous layer was extracted twice with more ether, and the combined ether layers were washed with dilute aqueous HCl followed by water and dried with sodium sulfate. The residue left after evaporation of the ether was chromatographed on 200−250 g of silica gel (0.04−0.063 mm; Kieselgel 60 "Merck") using *n*-pentane + 2% (initially; more later) ether as the eluent and an automatic fraction collector "Super Frac" (Pharmacia Biotech), TLC for monitoring, and 250-MHz ^{1}H NMR (Bruker ARX 250 instrument) for checking of uniformity. Unless indicated otherwise, products were stable under the reaction and workup conditions, and the purity of products was 95−98% according to their 400-MHz ^{1}H NMR spectra. None of the products was crystalline. In all cases, the degrees of purity permitted NMR-spectral analysis, since signals due to impurities and to known admixed compounds were readily separable. − In all cases, the NMR-spectroscopic data obtained allowed unambiguous identification of molecular structures by combined NMR techniques [^{1}H NMR including ^{1}H/^{1}H spin decoupling and NOE experiments where appropriate, ^{13}C NMR (BB and DEPT), ^{13}C,^{1}H correlation spectroscopy] in $CDCl_3$. Instrument: Bruker DRX 400 operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C. All δ values given below are relative to tetramethylsilane. Analytical experiments: Bruker DRX 500 instrument operating at 500 MHz for ^{1}H. The characteristic signal for one O−CH_2 proton of **2** at δ = 4.23 in $CDCl_3$ was free of overlap in all experiments and was used as a convenient quantitative reference.

(*E*)-Cyclooctene as the Substrate: Sequence of elution (pentane + 2% ether): Mixture of **5a1**, **5a2**, and **12** (first fraction), various mixtures, **8a**. Rechromatography of the first fraction (100% pentane): **12**, **5a2**, **5a1**.

2,2,2-Trifluoroethyl (5*Z*)-6-(Cycloheptyl)hex-5-enoate (12): ^{1}H NMR: δ = 1.40−1.52 (m, 6 H), 1.53−1.66 (m, 6 H), 1.69 (quint, *J* = 4 × 7.4 Hz, 2 H, 3-H), 2.07 (qd, *J* = 3 × 7.5, 1.6 Hz, 2 H, 4-H), 2.38 (m, 1 H, 6^1-H), 2.40 (t, *J* = 2 × 7.3 Hz, 2 H, 2-H), 4.44 (q, *J* = 3 × 8.5 Hz, 2 H, O−CH_2), 5.12 (dt, *J* = 10.8, 2 × 7.5 Hz, 1 H, 5-H), 5.34 (ddt, *J* = 10.8, 9.5, 2 × 1.6 Hz, 1 H, 6-H). − ^{13}C NMR: δ = 24.8 (C-3), 26.3 (2 × CH_2), 26.4 (C-4), 28.4 (2 × CH_2), 33.0 (C-2), 35.2 (2 × C-6^2), 37.8 (C-6^1), 60.1 (O−CH_2), 123.0 (CF_3), 124.6 (C-5), 138.4 (C-6), 172.0 (C-1).

(3aα,3bβ,9aα,10aα)-Dodecahydro-10a-(2,2,2-trifluoroethoxy)-1*H*-10-oxacycloocta[*a*]pentalene (5a2): ^{1}H NMR: δ = 1.30−1.70 (m, 10 H), 1.43 (dddm, *J* = 12.5, 2.7, 1.4, *x* Hz, 1 H, 3β-H), 1.53 (ddd, *J* = 12.1, 11.0, 7.5 Hz, 1 H, 1α-H), 1.55 (ddm, *J* = 9.0, 7.5, *x* Hz, 1 H, 3b-H), 1.56 (dm, *J* = 9.0, *x* Hz, 1 H, 9β-H), 1.64 and 1.81 (2 m, 2 H, 4-CH_2), 1.82 (dddd, *J* = 12.5, 11.0, 8.5, 6.0 Hz, 1 H, 3α-H), 1.89 (dddd, *J* = 12.1, 5.9, 2.3, 1.4 Hz, 1 H, 1β-H), 1.97 (dm, *J* = 4.1, *x* Hz, 1 H, 9α-H), 2.16 (ddd, *J* = 8.5, 7.5, 2.7 Hz, 1 H, 3a-H), 3.72 and 3.96 (two dq, each *J* = 11.7, 3 × 9.0 Hz, 2 H, O−CH_2), 3.87 (td, *J* = 2 × 9.0, 4.1 Hz, 1 H, 9a-H). − ^{1}H,^{1}H-NOE enhancements: (O−CH_2 proton signal at δ = 3.96; 3a-H), (O−CH_2; 1-CH_2), (9a-H; 3a-H), (3a-H, 1α-H). − ^{13}C NMR: δ = 23.5, 24.5, 25.9, 27.0, 28.2 (5 CH_2), 31.1 (C-3), 32.7 (C-4), 33.5 (C-9), 35.6 (C-1), 52.7 (C-3b), 58.2 (C-3a), 61.2 (O−CH_2), 84.7 (C-9a), 117.9 (C-10a), 124.3 (CF_3).

(3aα,3bα,9aβ,10aα)-Dodecahydro-10a-(2,2,2-trifluoroethoxy)-1*H*-10-oxacycloocta[*a*]pentalene (5a1): ^{1}H NMR: δ = 1.23−1.74 (m, 10 H), 1.35 and 1.74 (2 m, 2 H, 4-CH_2), 1.52 and 1.68 (2 m, 2 H, 3-CH_2),1.53 (dm, *J* = 10.0, *x* Hz, 1 H, 9β-H), 1.82 (ddd, *J* = 12.9, 9.0, 6.0 Hz, 1 H, 1β-H), 1.90 (ddd, *J* = 12.9, 7.6, 6.7 Hz, 1 H, 1α-H), 2.01 (dm, *J* = 4.2, *x* Hz, 1 H, 9α-H), 2.33 (ddd, *J* = 8.7, 7.1, 3.7 Hz, 1 H, 3b-H), 2.51 (ddd, *J* = 9.5, 8.9, 7.1 Hz, 1 H, 3a-H), 3.73 and 3.97 (2 dq, each *J* = 11.6, 3 × 9.0 Hz, 2 H, O−CH_2), 4.01 (ddd, *J* = 10.0, 8.7, 4.2 Hz, 1 H, 9a-H). − ^{1}H,^{1}H-NOE enhancements: (O−CH_2; 1α-H), (O−CH_2; 3a-H), (3b-H, 3a-H). − ^{13}C NMR: δ = 23.5, 23.9 (2 CH_2), 25.1 (C-3), 26.0, 27.3, 27.7 (3 CH_2), 29.6 (C-4), 34.4 (C-1), 36.7 (C-9), 44.7 (C-3b), 55.3 (C-3a), 61.3 (O−CH_2), 86.2 (C-9a), 117.7 (C-10a), 124.3 (CF_3).

5-(Cyclooctyl)cyclopent-2-enone (8a): ^{1}H NMR: δ = 1.2−1.7 (m, 14 H), 2.22 (ddq, *J* = 10.8, 8.7, 3 × 3.6 Hz, 1 H, 5^1-H), 2.29 (ddd, *J* = 6.55, 3.6, 2.7 Hz, 1 H, 5-H), 2.42 (dtd, *J* = 19.4, 2 × 2.7, 2.0 Hz, 1 H, 4α-H), 2.67 (dddd, *J* = 19.4, 6.5, 2.7, 2.0 Hz, 1 H, 4β-H), 6.17 (dt, *J* = 5.7, 2 × 2.0 Hz, 1 H, 2-H), 7.68 (dt, *J* = 5.7, 2 × 2.7 Hz, 1 H, 3-H). − ^{13}C NMR: δ = 25.3, 25.8, 26.3, 26.3, 26.5, 27.7 (6 CH_2), 31.9 (C-4), 32.7 (1 CH_2), 37.3 (C-5^1), 51.8 (C-5), 134.9 (C-2), 164.2 (C-3), 212.1 (C-1).

Styrene as the Substrate: Distillation of the crude product separated styrene (40 °C at 11 mbar), **2**[35] (60 °C at 10 mbar), and a fraction containing 60% **8b** (106 °C at 0.7 mbar) from an undistillable residue. Compound **8b** was purified by chromatography using pentane + 5% ether; this chromatography also gave a multitude of small, nonuniform fractions.

5-(2-Phenylethyl)cyclopent-2-enone (8b): ^{1}H NMR: δ = 1.62 (dddd, *J* = 13.9, 9.4, 8.6, 5.7 Hz, 1 H, 5^1-H), 2.13 (dddd, *J* = 13.9, 9.5, 7.0, 4.8 Hz, 1 H, 5^1-H), 2.28 (dddq, *J* = 9.4, 6.5, 4.8, 3 × 2.3 Hz, 1 H, 5-H), 2.35 (ddt, *J* = 19.0, 3.0, 2 × 2.3 Hz, 1 H, 4α-H), 2.66 (ddd, *J* = 13.8, 8.6, 7.0 Hz, 1 H, 5^2-H), 2.72 (ddd, *J* = 13.8, 9.5, 5.7 Hz; 1 H, 5^2-H), 2.83 (dddd, *J* = 19.0, 6.5, 3.0, 2.3 Hz, 1 H, 4β-H), 6.15 (dq, *J* = 5.72, 3 × 2.3 Hz, 1 H, 2-H), 7.17 (m, 3 H, Ph-H), 7.25 (m, 2 H, Ph-H), 7.63 (dtd, *J* = 5.72, 2 × 3.0, 2.3 Hz, 1 H, 3-H). − ^{13}C NMR: δ = 32.8 (C-5^1), 33.3 (C-5^2), 35.6 (C-4), 44.0 (C-5), 125.8 (2 Ph−C), 128.2 and 128.3 (3 Ph-C), 133.7 (C-2), 141.3 (*ipso*-Ph-C), 163.2 (C-3), 212.0 (C-1).

Isoprene as the Substrate: Sequence of elution: **5c** (2 unresolved stereoisomers, 4:3), **7c** (2 unresolved stereoisomers), **10c**, [4 + 3] adduct,[35] **2**,[35] **8c** (2 unresolved stereoisomers, 1:1), unknown mixture.

2-(2-Methylenebut-3-enyl)cyclopentanone (10c): ^{1}H NMR: δ = 1.47 (dtd, *J* = 12.4, 2 × 10.5, 6.5 Hz, 1 H, 3α-H), 1.73 (dtdd, *J* = 13.0, 10.5, 10.2, 8.5, 6.5 Hz; 1 H, 4β-H), 1.96 (ddddd, *J* = 13.0, 9.2, 6.5, 2.8, 1.9 Hz, 1 H, 4α-H), 1.97 (dd, *J* = 14.6, 10.2 Hz, 1 H, 1′-H), 2.11 (ddd, *J* = 18.4, 10.2, 9.2 Hz, 1 H, 5α-H), 2.15 (dddd, *J* = 12.4, 9.0, 6.5, 1.9 Hz, 1 H, 3β-H), 2.26 (ddddd, *J* = 10.5, 10.2, 9.0, 3.4, 1.4 Hz, 1 H, 2-H), 2.30 (dddt, *J* = 18.4, 8.5, 2.8, 2 × 1.4 Hz, 1 H, 5β-H), 2.83 (dd, *J* = 14.6, 3.4 Hz, 1 H, 1′-H), 4.97 and 5.02 (2 br. s, 2 H, 1′′-H), 5.05 (br. d, *J* = 10.9 Hz, 1 H, *E*-4′-H), 5.23 (br. d, *J* = 17.7, 1 H, *Z*-4′-H), 6.33 (dd, *J* = 17.7, 10.9 Hz, 3′-H). − ^{13}C NMR: δ = 20.5 (C-4), 29.9 (C-3), 31.8 (C-1′), 38.1 (C-5), 48.0 (C-2), 113.9 (C-4′), 116.9 (C-1′′), 138.2 (C-3′), 144.2 (C-2′), 220.6 (C-1).

(2α,5α)-5-Deuterio-2-[1,1-dideuterio-2-(dideuteriomethylene)but-3-enyl]cyclopentanone ([D$_5$]10c): Obtained from [D$_5$]isoprene [1,1-dideuterio-2-(trideuteriomethyl)buta-1,3-diene]. − ^{1}H NMR as for **10c** but resonances at δ = 5.02, 4.97, 2.83, 2.11, 1.97 and the corresponding couplings absent.

5-(2-Methylbut-3-enyl)cyclopent-2-enone (8c, 2 Stereoisomers, 1:1): ^{1}H NMR: δ = 1.00 and 1.01 (2 d, *J* = 6.7 Hz, 3 H, 1′′-H), 1.20 and 1.80 (2 m, 2 H, 1′-H), 2.19 (m, 1 H, 2′-H), 2.30 (m, 2 H, 4-H and 5-H), 2.81 (m, 1 H, 4-H), 4.92−4.98 (m, 2 H, 4′-H), 5.61 and 5.69 (2 m, 1 H, 3′-H), 6.13 (m, 1 H, 2-H), 7.62 (m, 1 H, 3-H). − ^{13}C NMR: δ = 19.8/21.2 (C-1′′), 36.0/36.6 (C-4), 36.7/37.0 (C-2′),

38.2/38.4 (C-1′), 43.3/43.4 (C-5), 113.1/114.0 (C-4′), 133.6/133.8 (C-2), 143.4/144.2 (C-3′), 163.1 (C-3), 212.5/212.6 (C-1).

3-Methylenecyclohexene as the Substrate: Sequence of elution: **5d1** + **5d2** (1:1 mixture followed by one pure isomer), mixtures, **7d1** + **7d2** (4:1), **10d1**, mixtures, **2**, mixtures containing **14**, **8d1** + **8d2** (7:3 or 3:7), mixtures, **13** (2 epimers, 1:1).

3′,3a′,4′,5′,6′,6a′-Hexahydro-6a′-(2,2,2-trifluoroethoxy)spiro-[cyclohex-2-ene-1,2′-[2*H*]cyclopenta[*b*]furan] (5d1 or 5d2, Pure Isomer): ^{1}H NMR: δ = 1.43 (m, 1 H, 4′-H), 1.46 (dd, *J* = 12.7, 7.8 Hz, 1 H, 3′-H), 1.55−2.0 (m, 8 H, 5′-, 6′-, 5-, 6-CH_2), 1.85 (m, 1 H, 4-H), 1.86 (m, 1 H, 4′-H), 2.02 (m, 1 H, 4-H), 2.23 (dd, *J* = 12.7, 9.1 Hz, 1 H, 3′-H), 2.77 (dddd, *J* = 9.1, 8.4, 7.8, 2.0 Hz, 1 H, 3a′-H), 3.75 and 4.01 (2 dq, each *J* = 11.5, 3 × 9.0 Hz, 2 H, O−CH_2), 5.51 (br. d, *J* = 10.0 Hz, 1 H, 2-H), 5.84 (dt, *J* = 10.0, 2 × 3.7 Hz, 1 H, 3-H). − ^{13}C NMR: δ = 20.1 (CH_2), 23.9 (CH_2), 24.9 (C-4), 31.9 (C-4′), 34.6 (CH_2), 36.3 (CH_2), 45.8 (C-3′), 48.9 (C-3a′), 61.7 (O−CH_2), 84.1 (C-1), 120.8 (C-6a′), 124.4 (CF_3), 131.3 (C-3), 131.5 (C-2). − **Second Isomer:** ^{1}H NMR: δ = 1.4−2.05 (m, 13 H), 2.23 (m, 1 H, 3′-H), 2.76 (m, 1 H, 3a′-H), 3.70 and 3.96 (2 dq, each *J* = 11.5, 3 × 9.0 Hz, 2 H, O−CH_2), 5.67 (dt, *J* = 10.0, 2 × 3.7 Hz, 1 H, 3-H), 5.84 (br. d, *J* = 10.0 Hz, 1 H, 2-H). − ^{13}C NMR: δ = 20.5, 23.9, 24.8, 31.9, 35.9, 36.1, 45.9 (7 CH_2), 48.7 (C-3a′), 61.3 (OCH_2), 84.1 (C-1), 120.6 (C-6a′), 124.3 (CF_3), 128.0 (C-3), 132.1 (C-2).

Spiro[bicyclo[2.2.1]heptane-2,1′-cyclohex[2]en]-7-one (7d1 + 7d2, 4:1). − Isomer 7d1: ^{1}H NMR: δ = 1.3−2.1 (m; 14 H), 5.40 (br. d, *J* = 10.0 Hz, 1 H, 2′-H), 5.53 (dt, *J* = 10, 2 × 3.5 Hz, 1 H, 3′-H). − ^{13}C NMR: δ = 17.1, 18.9, 23.8, 24.7, 32.3 (5 CH_2), 35.3 (C-2), 40.1 (C-4), 41.3 (C-3), 48.8 (C-1), 124.7 (C-3′), 134.7 (C-2′), 215.9 (C-7). − **Isomer 7d2:** ^{1}H NMR: δ = 1.3−2.1 (m, 14 H), 5.70 (br. d, *J* = 10.0 Hz, 1 H, 2′-H), 5.77 (dt, *J* = 10, 2 × 3.5 Hz, 1 H, 3′-H). − ^{13}C NMR: δ = 17.4, 19.4, 24.0, 24.8, (4 CH_2), 35.2 (C-2), 36.1 (CH_2), 39.9 (C-4), 42.3 (C-3), 49.2 (C-1), 128.9 (C-3′), 132.0 (C-2′), 216.5 (C-7).

2-[(Cyclohexa-1,5-dienyl)methyl]cyclopentanone (10d1): ^{1}H NMR: δ = 1.48 (dddm, *J* = 9.0, 8.5, 6.0 Hz, *x* 1 H, 3α-H), 1.71 (ddm, *J* = 8.0, 6.0, *x* Hz, 1 H, 4β-H), 1.87 (dd, *J* = 14.0, 9.6 Hz, 1 H, 2^1-H), 1.91 (ddm, *J* = 9.0, 3.2, *x* Hz, 1 H, 4α-H), 2.04 (m, 4 H, 2 3′-H and 2 4′-H), 2.05 (dm, *J* = 18.6 Hz, 1 H, 5α-H), 2.10 (m, 1 H, 3β-H), 2.12 (ddm, *J* = 8.5, 1.3, *x* Hz, 1 H, 2-H), 2.24 (dddd, *J* = 18.6, 8.0, 3.2, 1.3 Hz, 1 H, 5β-H), 2.47 [ddd, *J* = 14.0, 3.7, 1.3 (to signal at δ = 5.44) Hz, 1 H, 2^1-H], 5.44 (br. s, Σ*J* = 12 Hz, 1 H, 2′-H), 5.72 (br. d, *J* = 10.0 Hz, 1 H, 6′-H), 5.78 (dt, *J* = 10.0, 2 × 4.0 Hz, 1 H, 5′-H). − ^{1} H,^{1}H-NOE enhancements: (2′-H, either 2^1-H), (2′-H, either 3-H), (6′-H, either 2^1-H), (6′-H, either 3-H). − ^{13}C NMR: δ = 20.5 (C-4), 22.2 and 22.3 (C-3′, C-4′), 29.1 (C-3), 35.5 (C-2^1), 38.1 (C-5), 48.3 (C-2), 121.8 (C-2′), 126.7 (C-6′), 127.1 (C-5′), 133.6 (C-1′), 220.9 (C-1).

5-[(Cyclohex-2-enyl)methyl]cyclopent-2-enone (8d1 + 8d2): ^{1}H NMR: δ = 1.25 (m, 2 H, 1′-H and 6′′-H), 1.53 (m, 1 H, 5′′-H), 1.76 (m, 1 H, 5′′-H), 1.80 (m, 1 H, 6′′-H), 1.85 (m, 1 H, 1′-H), 1.96 (m, 2 H, 4′′-CH_2), 2.23 (m, 1 H, 1′′-H), 2.37 (m, 1 H, 4-H), 2.38 (m, 1 H, 5-H), 2.87 (m, 1 H, 4-H), 5.58/5.50 (m, 1 H, 2′′-H), 5.67 (m, 1 H, 3′′-H), 6.15 (m, 1 H, 2-H), 7.64 (m, 1 H, 3-H). − ^{13}C NMR: δ (major/minor isomer) = 21.28/21.16 (C-5′′), 25.28/25.28 (C-4′′), 29.74/28.45 (C-6′′), 33.63/33.63 (C-1′′), 36.55/36.40 (C-4), 38.03/38.11 (C-1′), 42.94/42.85 (C-5), 127.72/127.56 (C-3′′), 130.39/131.53 (C-2′′), 133.68/133.71 (C-2), 163.15/163.15 (C-3), 212.56/212.64 (C-1).

2-{[3-(2,2,2-Trifluoroethoxy)cyclohex-1-enyl]methyl}cyclopentanone (13; Two Epimers 1:1): ^{1}H NMR: δ = 1.50 (m, 1 H, 3-H), 1.5−1.9 (m, 6 H), 1.70 (m, 1 H, 4-H), 1.83 (m, 1 H, 1′-H), 1.95 (m, 1 H, 4-H), 2.10 (m, 1 H, 5α-H), 2.15 (m, 1 H, 3-H), 2.20 (m, 1 H, 2-H), 2.29 (dddd, *J* = 17.5, 7.5, 3.0, 1.5 Hz, 1 H, 5β-H), 2.49 (dd, *J* = 14.0, 3.0 Hz, 1 H, 1′-H), 3.80 (m, 2 H, OCH_2), 4.01 (br. s, Σ*J* = 20 Hz, 1 H, 3′′-H), 5.50 (br. s, Σ*J* = 12 Hz, 1 H, 2′′-H). − ^{13}C NMR: δ = 18.95/19.03 (C-5′′), 20.5 (C-4), 27.8/27.9, 28.3/28.4, 29.5 (C-3, C-4′′, C-6′′), 37.7/37.8 (C-5), 37.9 (C-1′), 47.26/47.31 (C-2), 65.50/65.54 (OCH_2), 75.1 (C-3′′), 121.9/122.1 (C-2′′), 124.0 (CF_3), 141.9/142.0 (C-1′′), 220.6 (C-1).

Cyclopenta-1,3-diene as the Substrate: Sequence of elution: minor [4 + 3] adduct,[35] major [4 + 3] adduct (Scheme 2),[35] major [4 + 3] adduct + **8e**[47] (7:9).

5-(Cyclopent-3-enyl)cyclopent-2-enone (8e): ^{1}H NMR: δ = 1.82 and 2.32, 2.21 and 2.57 (2 multiply split AB systems, each *J* = 16.8 Hz, 4 H, 2′-CH_2 and 5′-CH_2), 2.38 (dddd, *J* = 19.0, 2.8, 2.5, 2.0 Hz, 1 H, 4α-H), 2.46 (tdd, *J* = 2 × 6.3, 2.5, 1.2 Hz, 1 H, 5-H), 2.72 (tq, *J* = 2 ×9.0, 3× 6.4 Hz, 1 H, 1′-H), 2.72 (dddd, *J* = 19.0, 6.3, 2.8, 2.0 Hz, 1 H, 4β-H), 5.60 and 5.64 (multiply split AB system, *J* = 5.7 Hz, 2 H, 3′-H and 4′-H), 7.66 (dt, *J* = 5.7, 2 × 2.8 Hz, 1 H, 3-H), 6.15 (dtd, *J* = 5.7, 2 × 2.0, 1.2 Hz, 1 H, 2-H),. − ^{13}C NMR: δ = 32.7 (C-4), 34.7 and 37.2 (C-2′ and C-5′), 37.2 (C-1′), 48.6 (C-5), 129.8 and 130.1 (C-3′ and C-4′), 134.8 (C-2), 163.8 (C-3), 211.7 (C-1).

Spiro[2.4]hepta-4,6-diene as the Substrate: Sequence of elution: **5f1**, **5f2**, mixtures, **7f2**, **7f1**, **2**,[35] **9f2**,[35] mixtures, [4 + 3] adduct,[35] mixtures.

(3a′α,4a′α,7a′α,7b′α)-1′,2′,3′,3a′,4a′,7′,7a′,7b′-Octahydro-3a′-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,7′-dicyclopenta[*b*,*d*]-furan] (5f1): ^{1}H NMR: δ = 0.6−0.9 (m, 4 H, 2- and 3-CH_2), 1.72 (m, 1 H, 3′-H), 1.72 (m, 4 H, 1′- and 2′-CH_2), 1.99 (m, 1 H, 3′-H), 2.42 (td**,** *J* = 2 × 8.9, 8.4 Hz, 1 H, 7b′-H), 2.84 (dd**,** *J* = 8.4, 8.2 Hz, 1 H, 7a′-H), 3.75 and 3.98 (2 dq, each *J* = 11.7, 3 × 9.0 Hz, 2 H, O−CH_2), 5.32 (d**,** *J* = 5.4 Hz, 1 H, 6′-H), 5.40 (dd**,** *J* = 8.2, 1.7 Hz, 1 H, 4a′-H), 5.73 (dd**,** *J* = 5.4, 1.7 Hz, 1 H, 5′-H). − ^{1}H,^{1}H-NOE enhancements: (OCH_2, 4a′-H), (OCH_2, 3′-H), (4a′-H, 5′-H), (4a′-H, 7a′-H), (7a′-H, 7b′-H), (7a′-H, 2-CH_2). − ^{13}C−NMR: δ = 11.5 and 13.9 (C-2 and C-3), 23.7 (C-2′), 26.2 (C-1′), 30.0 (C-1), 33.1 (C-3′), 50.2 (C-7a′), 51.6 (C-7b′), 61.4 (OCH_2), 91.5 (C-4a′), 121.0 (C-3a′), 129.3 (C-5′), 141.5 (C-6′). The CF_3 signal was lost in the noise.

(3a′α,4a′β,7a′β,7b′α)-1′,2′,3′,3a′,4a′,7′,7a′,7b′-Octahydro-3a′-(2,2,2-trifluoroethoxy)spiro[cyclopropane-1,7′-dicyclopenta-[*b*,*d*]furan] (5f2): ^{1}H NMR: δ = 0.6−0.8 (m, 4 H, 2- and 3-CH_2), 1.34 (dq**,** *J* = 13.0, 3 × 4.8 Hz, 1 H, 1′β-H), 1.66 (m, 3 H, 3′-H and 2′-CH_2), 1.90 (m, 1 H, 1′α-H), 1.93 (m, 1 H, 3′-H), 2.24 (dd**,** *J* = 7.3, 3.2 Hz, 1 H, 7a′-H), 2.50 (ddd**,** *J* = 9.0, 4.8, 3.2 Hz, 1 H, 7b′-H), 3.72 and 3.88 (2 dq, each *J* = 11.7, 3 × 9.0 Hz, 2 H, OCH_2), 5.30 (dd**,** *J* = 5.7, 0.5 Hz, 1 H, 6′-H), 5.47 (ddd**,** *J* = 7.3, 1.9, 0.5 Hz, 1 H, 4a′-H), 5.69 (dd**,** *J* = 5.7, 1.9 Hz, 1 H, 5′-H). − ^{1}H,^{1}H-NOE enhancements: (OCH_2, 5′-H), (OCH_2, 7b′-H), (OCH_2, 3′-H), (4′-H, 7a′-H), (7a′-H, 1′β-H), (7a′-H, 2-H), (7b′-H, 2-H). − ^{13}C NMR: δ = 10.7 and 14.0 (C-2 and C-3), 24.1 (C-2′), 32.6 (C-1′), 33.7 (C-7′), 35.9 (C-3′), 54.7 (C-7b′), 55.7 (C-7a′), 61.6 (OCH_2), 92.0 (C-4a′), 121.5 (C-3a′), 124.3 (CF_3), 129.1 (C-5′), 141.0 (C-6′).

(1′*R,2′*R**,6′*S**,7′*S**)-Spiro[cyclopropane-1,5′-tricyclo[5.2.1.0^{2,6}]-dec[3]en]-10′-one (7f2):** ^{1}H NMR: δ = 0.55−0.9 (m, 4 H, 2- and 3-CH_2), 1.63 (m, 3 H), 1.74 (dd**,** *J* = 4.8, 4.4 Hz, 1 H, 7′-H), 2.0 (m, 1 H), 2.09 (dd**,** *J* = 5.0, 4.2 Hz, 1 H, 1′-H), 2.41 (dd**,** *J* = 10.2, 4.4 Hz, 1 H, 6′-H), 3.43 (dddd**,** *J* = 10.2, 5.0, 2.0, 1.6 Hz, 1 H, 2′-

H), 5.43 (dd, J = 5.5, 1.6 Hz, 1 H, 4′-H), 5.51 (dd, J = 5.5, 2.0 Hz, 1 H, 3′-H). − ^{13}C−NMR: δ = 11.9 and 15.0 (C-2 and -3), 17.8 and 19.2 (C-8′ and -9′), 29.6 (C-1), 42.6, 42.6, 42.8 (C-1′, -6′, and -7′), 45.5 (C-2′), 127.9 (C-3′), 141.8 (C-4′), 215.6 (C-10′).

(1′*R,2′*S**,6′*R**,7′*S**)-Spiro[cyclopropane-1,5′-tricyclo[5.2.1.0^{2,6}]-dec[3]en]-10′-one (7f1):** ^{1}H NMR: δ = 0.66 (m, 4 H, 2- and 3-CH_2), 1.48 (m, 1 H), 1.61 (m, 1 H), 1.70 (d, J = 3.8 Hz, 1 H, 7′-H), 1.86 (m, 1 H, 1′-H), 1.86 (m, 2 H), 2.20 (d, J = 8.8 Hz, 1 H, 6′-H), 3.16 (ddd, J = 8.8, 2.2, 1.5 Hz, 1 H, 2′-H), 5.18 (dd, J = 5.6, 1.5 Hz, 1 H, 4′-H), 5.46 (dd, J = 5.6, 2.2 Hz, 1 H, 3′-H). − ^{13}C NMR: δ = 11.0 and 15.1 (C-2 and -3), 22.4 and 22.7 (C-8′ and -9′), 34.0 (C-1), 42.8 (C-7′), 44.5 (C-1′), 47.6 (C-6′), 51.5 (C-2′), 128.4 (C-3′), 139.9 (C-4′). The C-10′ signal was lost in the noise.

Spiro[4.4]nona-1,3-diene (3) as the Substrate: Sequence of elution: **7g**, mixture containing **9g**, **2**,[35] **8g**.[35]

(1′*R,2′*R**,6′*S**,7′*S**)-Spiro[cyclopentane-1,5′-tricyclo[5.2.1.0^{2,6}]-dec[3]en]-10′-one (7g):** ^{1}H NMR: δ = 1.4−1.75 (m, 12 H, 6 CH_2), 1.90 (dd, J = 4.8, 4.0 Hz, 1 H, 7′-H), 2.09 (dd, J = 5.3, 4.2 Hz, 1 H, 1′-H), 2.27 (dd, J = 9.0, 4.0 Hz, 1 H, 6′-H), 3.22 (ddtd, J = 9.0, 5.3, 2 × 1.9, 1.7 Hz, 1 H, 2′-H), 5.52 (dd, J = 5.7, 1.9 Hz, 1 H, 3′-H), 5.82 (dd, J = 5.7, 1.9 Hz, 1 H, 4′-H). − ^{13}C NMR: δ = 18.1, 19.0, 24.1, 25.7, 33.9 (5 CH_2), 42.9 (C-7′), 43.0 (C-1′), 43.5 (CH_2), 43.9 (C-2′), 47.1 (C-6′), 56.7 (C-1), 127.1 (C-3′), 143.8 (C-4′), 215.5 (C-10′).

Ethoxyethene as the Substrate: Sequence of elution (starting with pentane + 5% ether, gradually raised to 20% ether): **15**, **15** + **7h1** (1:2), **2**, **6h1** + **6h2** (1:1), **7h2**, mixtures, **8h**, mixtures, **16** (two stereoisomers, 3:1). The overlapping fractions of **6h1** + **6h2** and **7h2** were separated by distillation: bp 69 °C/4 mbar (**7h2**), 93 °C/4.7 mbar (**6h1** + **6h2**).

4-Ethoxy-3-oxatetracyclo[8.2.1.0^{2,6}.0^{2,9}]tridecan-13-one (15): ^{1}H NMR: δ = 1.13 (m, 1 H), 1.17(t, J = 2 × 7.0 Hz, 3 H; CH_3), 1.61−2.19 (m, 9 H, 4.5 CH_2), 1.87 (m; 2 H, 2 CH), 2.08 (m, 1 H, CH), 2.17 (m, 1 H, CH), 3.41 and 3.75 (2 dq, each J = 9.6, 3 × 7.0 Hz, 2 H, O−CH_2), 5.10 (dd, J = 4.5, 1.1 Hz, 1 H, 4-H). − ^{13}C NMR: δ = 15.3 (CH_3), 16.2, 22.1, 30.8, 32.1, 37.7 (5 CH_2), 47.6, 47.8, 49.5, 53.5 (4 CH), 63.0 (O−CH_2), 95.0 (C-2), 105.5 (C-4), 215.4 (C-13).

***endo*-2-Ethoxybicyclo[2.2.1]heptan-7-one (7h1):** ^{1}H NMR: δ = 1.18 (t, J = 3 × 7.0 Hz, 3 H, CH_3), 1.39 (dd, J = 13.4, 3.5 Hz, 1 H, *endo*-3-H), 1.60 (m, 1 H), 1.65 (m, 1 H), 1.85 (m, 1 H), 1.95 (t, J = 2 × 4.5 Hz, 1 H, 4-H), 2.05 (m, 1 H), 2.22 (m, 1 H, 1-H), 2.25 (ddm, J = 13.4, 10.0, x Hz, 1 H, *exo*-3-H), 3.34 and 3.36 (m, 2 H, O−CH_2), 3.98 (dt, J = 10.0, 2 × 5.0 Hz, 1 H, 2-H). − ^{13}C NMR: δ = 14.5 (CH_2), 15.2 (CH_3), 24.0 (CH_2), 34.8 (C-3), 40.3 (C-4), 43.6 (C-1), 64.3 (O−CH_2), 71.9 (C-2), 214.2 (C-7).

2-[2-Ethoxy-2-(2,2,2-trifluoroethoxy)ethyl]cyclopentanone (6h1 + 6h2): ^{1}H NMR: δ = 1.17 (t, J = 2 × 7.1 Hz, 3 H, CH_3), 1.50 (m, 1 H, 1′-H), 1.5−2.3 (m, 3 CH_2), 2.10 (m, 2 H, 2-H and 1′-H), 3.49 (dq, each J = 9.5, 3 × 7.1 Hz, 1 H, *CH*CH_3), 3.66/3.64 (2 dq, each J = 9.5, 3 × 7.1 Hz, 1 H, *CH*CH_3), 3.837/3.840 (2 q, each J = 3 × 8.8 Hz, 2 H, CH_2CF_3), 4.793/4.780 (2 t, each J = 2 × 5.4 Hz, 1 H, 2′-H). − ^{13}C NMR: δ = 15.0 (CH_3), 20.8 (CH_2), 30.08/29.96 (CH_2), 32.98/32.95 (C-1′), 37.58/37.55 (CH_2), 45.39/45.26 (C-2), 61.68/61.65 (CH_2CH_3), 62.7/62.03 (CH_2CF_3), 101.63/101.59 (C-2′), 124.0 (CF_3), 220.1 (C-1).

***exo*-2-Ethoxybicyclo[2.2.1]heptan-7-one (7h2):** EI-MS: m/z = 154. − ^{1}H NMR: δ = 1.11 (t, J = 3 × 7.0 Hz, 3 H, CH_3), 1.39 (m, 2 H, *endo*-5-H and *endo*-6-H), 1.83 (m, 3 H, 3 *exo*-H), 1.91 (t, J = 2 × 4.1 Hz, 1 H, 4-H), 1.95 (dd, J = 13.3, 8.0 Hz, 1 H, *endo*-3-H), 2.03 (d, J = 4.8 Hz, 1 H, 1-H), 3.37 and 3.44 (2 dq, each J = 9.2, 3 × 7.0 Hz, 2 H, O−CH_2), 3.60 (dd, J = 8.0, 2.0 Hz, 1 H, 2-H). − ^{13}C NMR: δ = 15.2 (CH_3), 18.7 and 23.2 (C-5 and C−6), 35.5 (C-3), 37.7 (C-4), 42.6 (C-1), 63.9 (O−CH_2), 76.9 (C-2), 215.2 (C-7).

5-(2-Ethoxyethyl)cyclopent-2-enone (8h): ^{1}H NMR: δ = 1.13 (t, J = 2 × 7.0 Hz, 3 H, 2′′-H), 1.53 (ddt, J = 14.0, 9.0, 2 × 6.5 Hz, 1 H, 1′-H), 2.04 (dtd, J = 14.0, 2 × 6.5, 4.8 Hz, 1 H, 1′-H), 2.37 (dddd, J = 9.0, 6.5, 4.8, 2.6 Hz, 1 H, 5-H), 2.41 (dtd, J = 19.1, 2 × 2.6, 2.0 Hz, 1 H, 4α-H), 2.85 (dddd, J = 19.1, 6.5, 2.6, 2.0 Hz, 1 H, 4β-H), 3.41 and 3.42 (2 q, each J = 7 Hz, 2 H, 1′′-H), 3.49 (t, J = 2 × 6.5 Hz, 2 H, 2′-H), 6.12 (dt, J = 5.6, 2 × 2.0 Hz, 1 H, 2-H), 7.62 (dt, J = 5.6, 2 × 2.6 Hz, 1 H, 3-H). − ^{13}C NMR: δ = 15.1 (C-2′′), 31.1 (C-1′), 35.9 (C-4), 42.3 (C-5), 66.0 (C-1′′), 68.5 (C-2′), 133.6 (C-2), 163.3 (C-3), 212.1 (C-1).

5-[2-Ethoxy-2-(2,2,2-trifluoroethoxy)ethyl]-2,2′-bicyclopentanedione (16): ^{1}H NMR: δ = 4.78 (m, 1 H, 2^2-H), 3.84 (q, J = 3 × 8.7 Hz, 2 H, CH_2CF_3), 3.65 (m, 1 H, *CH*CH_3), 3.49 (m, 1 H, *CH*CH_3), 2.4−2.66 (m, 2 H), 2.2−2.38 (m, 2 H), 1.9−2.2 (m, 5 H), 1.4−1.83 (m, 6 H), 1.17 (t, J = 2 × 7.0 Hz, 3 H, CH_3). − ^{13}C NMR (main isomer): δ = 15.0 (CH_3), 20.8, 24.9, 26.8, 28.2, 33.2, 38.1 (6 CH_2), 45.8, 49.1, 49.6 (3 CH), 61.5 (*CH*$_2$CF$_3$), 62.4 (*CH*$_2$CH$_3$), 101.7 (CH), 124.0 (CF_3), 218.7 (C=O), 219.1 (C=O).

2-Methoxypropene as the Substrate. − (A) Workup according to the general method, sequence of chromatographic elution (pentane + 3% ether, gradually raised to 25% ether): **2** + **7i** (1:1), **6i** (mixture of two epimers, 1:1), **17**.[55−57]

2-Methoxy-2-methylbicyclo[2.2.1]heptan-7-one (7i): ^{1}H NMR: δ = 1.20 (s, 3 H, C−CH_3), 1.5−2.0 (m, 4 H, 5-H and 6-H), 1.55 (m, 1 H, 3-H), 1.88 (m, 1 H, 3-H), 1.97 (m, 1 H, 1-H), 2.02 (m, 1 H, 4-H), 3.15 (s, 3 H, O−CH_3). − ^{13}C−NMR: δ = 15.9 and 23.3 (C-5 and C−6), 23.6 (C-*CH*$_3$), 41.4 (C-4), 42.6 (C-3), 48.9 (C-1), 50.9 (O−CH_3), 75.3 (C-2), 214.0 (C-7).

2-[2-Methoxy-2-(2,2,2-trifluoroethoxy)propyl]cyclopentanone (6i, Two Epimers, 1:1): ^{1}H NMR: δ = 1.30/1.31 (2 s, 3 H, CCH_3), 1.4−2.3 (m, 8 H, 4 CH_2), 2.02 (m, 1 H, 2-H), 3.180/3.185 (2 s, 3 H, OCH_3), 3.75 (mc, 2 H, *CH*$_2$CF$_3$). − ^{13}C NMR: δ = 21.05/21.06 (C-4), 22.0/22.3 (C-3′), 32.0/32.1, 37.2/37.4, 37.5/37.6 (C-3, -5, and -1′), 46.1/46.3 (C-2), 48.9/49.2 (OCH_3), 58.9/59.0 (*CH*$_2$CF$_3$), 102.4/102.45 (C-2′), 124.25/124.3 (CF_3), 219.8 (C-1).

(B) The crude reaction product left behind after evaporation of excess substrate and TFEOH under vacuum was taken up with anhydrous ether, the resulting ethereal solution filtered from insoluble material and the ether evaporated. The residue was taken up in *n*-pentane, the resulting solution filtered from insoluble material and the pentane evaporated. The residue was separated by distillation into **4i** (two epimers 3:2) containing some **7i** (bp. 30 °C/0.033 mbar) and **6i** (two epimers; bp. 67 °C/0.008 mbar). An attempt to separate the former fraction into **4i** and **7i** by distillation resulted in complete rearrangement of **4i** into comparable amounts of **18** and **9i**, which were partially separated by distillation, **18** being the lower boiling (bp. 40 °C/0.007 mbar). All operations took place with precautions against moisture.

2-Methoxy-2-methyl-3,3a,4,5-tetrahydro-2*H*-cyclopenta[*b*]furan (4i, Two Epimers 3:2): ^{1}H NMR (major epimer/minor epimer): δ = 1.3−2.6 (m; 6 H, 3 CH_2), 1.49 /1.52 (s, 3 H, CCH_3), 3.12/3.33 (m, 1 H, 3a-H), 3.28/3.34 (s, 3 H, OCH_3), 4.40/4.41 (br. t, J = 2 × 6.0 Hz, 6-H),. − ^{13}C NMR (major epimer/minor epimer): δ = 22.3/

24.9 (CCH_3), 31.3/31.1, 33.0/33.5, 40.4/43.4 (C-3, -4, and −5), 45.2/45.4 (C-3a), 50.1/49.6 (OCH_3), 89.3/89.2 (C-6), 117.9/119.4 (C-2), 165.0/163.2 (C-6a).

2-(2′-Methoxyallyl)cyclopentanone (18): ^{1}H NMR: δ = 1.5 (m, 1 H), 2.0 (m, 5 H), 2.2 (m, 2 H, 2-H and 5-H), 2.50 (dd, J = 14.2, 4.2 Hz, 1 H, 1′-H), 3.43 (s, 3 H, OCH_3), 3.83 (br. s, 2 H, 3′-H). − ^{13}C NMR: δ = 20.4 (C-4), 28.9 (C-3), 34.8 (C-1′), 37.8 (C-5), 47.1 (C-2), 54 6 (O−CH_3), 81.8 (C-3′), 161.7 (C-2′), 220.2 (C-1).

2-(2-Methoxypropenyl)cyclopentanone (9i): ^{1}H NMR: δ = 1.73 (s, 3 H, 3′-H), 1.9−2.2 (m, 5 H), 2.25 (m, 1 H, 5-H), 2.74 (dt, J = 11.0, 2 × 8.3 Hz, 1 H, 2-H), 3.43 (s, 3 H, OCH_3), 4.14 (d, J = 8.3 Hz, 1 H, 1′-H). − ^{13}C NMR: δ = 16.7 (C-3′), 20.6 (C-4), 31.8 (C-3), 37.2 (C-5), 48.5 (C-2), 54.0 (OCH_3), 93.5 (C-1′), 156.7 (C-2′), 219.8 (C-1).

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