120. Stereoselective Ring Opening of Electronically Excited Cyclohexa-2,4-dienones: Cause and Effect[1][2]

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Dedicated to *Edgar Heilbronner* on the occasion of his 76th birthday

(10. III. 97)

The two conformers of a cyclohexa-2,4-dienone with different substituents at C(6) on irradiation are believed to undergo ring opening stereospecifically affording a mixture of two configurationally isomeric diene-ketenes (and descendents thereof). Exceptions are generally found for those dienones with one C and one O substituent or even with two C substituents, if one of them carries a polar group at a site able to interact through space with the ring C=O group. In these cases, only one of the two anticipated diene-ketenes (and descendents thereof) is produced. A thorough investigation of the photochemistry of a series of structurally different cyclohexa-2,4-dienones on analytical as well as on preparative scale extends our mechanistic knowledge of the various routes from diene-ketenes into a variety of compound classes. Novel compound classes accessible to diene-ketenes are seven-membered carbocycles (by intramolecular aldolization of the zwitterion of appropriately substituted, transiently formed diene-(*N,O*)-ketene acetals) and β-lactams (by *Staudinger* reaction).

1. Photochemistry of Cyclohexa-2,4-dienones Bearing Two C Substituents at C(6). – The photochemical reaction courses, and their associated transient species and products, of 6,6-dimethylcyclohexa-2,4-dienone (**A**) [18] and androsta-2,4-dienone (**B**) [19] have been studied in detail from room temperature to liquid N_2 temperature, with the aid of UV, IR, NMR, and flash spectroscopy, by means of kinetic studies, and the determination of quantum yields. This publication continues those studies, beginning with results found for 6-methyl-6-phenylcyclohexa-2,4-dienone, which have substantially enhanced our understanding of the photochemistry of linear-conjugated cyclohexadienones.

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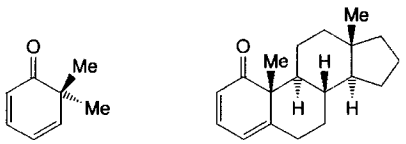
[1]) From the doctoral dissertations or diploma theses of *S. Sch.* [1], *D.R.* [2], *H.-P.N.* [3], *H.W.* [4], *A.E.* [5], *K.U.* [6], *K.W.* [7], *K.-P.M.* [8], *G.W.* [9], *G.P.* [10], *B.B.* [11], *B.-J.F.* [12], *I.W.* [13], *D.L.* [14], *P.B.* [15], *T.C.* [16], *D.H.* [17].

[2]) Abbreviations used in this paper: 9-BBN: 9-borabicyclo[3.3.1]nonane; DABCO: 1,4-diazabicyclo[2.2.2]-octane; ED: extinction differences; EDQ: quotients of extinction differences; EPA: Et_2O/isopentane/EtOH 5:5:2; HMPT: hexamethylphosphorictriamide, MCI: methylcyclohexane/isopentane 1:4; MTB: *t*-butyl methyl ether; NMI: *N*-methylimidazole; NOE: nuclear *Overhauser* enhancement; PPTS: pyridinum *p*-toluenesulfonate; PTS: *p*-toluenesulfonic acid; TFE: 2,2,2-trifluoroethanol; THP: tetrahydropyran-2-yl; TMEDA: *N,N,N,N*-tetramethylethylenediamine.



A **B**

1.1. *(R)-, (S)-, or (RS)-6-Methyl-6-phenylcyclohexa-2,4-dienone* (**1**, *ent*-**1**, or *rac*-**1**) exhibit a more complex reaction behavior[3]) than **A** or **B**. Light-induced ring-opening leads to two configurationally isomeric diene-ketenes **C** and **D** (see *Scheme 1*), and then, in the presence of protic nucleophiles, to product components of types **2** and **3**[4]) or, in the presence of suitable imines, to the two β-lactams of types **4** and **5** (see *Sect. 4*).

The ratios of compounds of types **2** and **3** depend on the wavelength of the irradiating light. Preparative-scale irradiation of *rac*-**1** at room temperature using light of wavelength > 340 nm affords **2a** and **3a** (in cyclohexylamine-containing Et_2O), or **2b** and **3b** (in EtOH) in ratios of 1:1.9 or 1:1.8, respectively[5]). Careful examination of the **2b**/**3b** product-component ratio (*Exper. 1.3.1.2.3*) shows that it is constant when 365-nm light is used, but liable to change (up to 1:10) with 313-nm light. This arouses suspicion that the light-induced rearrangement of cyclohexa-2,4-dienones of type **1** is being swamped by photoisomerization of compounds of type **2** into compounds of type **3**. This *product-analysis*-based conclusion is confirmed by complementary *reaction analysis*. These observations, moreover, permit definitive conclusions to be drawn about the involvement of diverse transients, structural interpretation of which seamlessly delineates the pathway from dienone to carboxylic-acid derivative.

If a solution of *rac*-**1** in MCI, containing sufficient cyclohexylamine[6]), is irradiated with 365-nm light at room temperature, then, with the aid of *Mauser*'s UV-spectroscopically determined formal analysis of reaction kinetics[7]), a homogeneous photoreaction (linear ED diagram; see *Fig. 1*), with only the educt and the product being detectable, is found. With 313-nm light (*Fig. 2*), however, a heterogenous reaction (nonlinear ED diagram) takes place, in which two spectroscopically indiscernible steps (linear EDQ diagram) can be identified. Photoisomerization of **2a** (→ **3a**) with 313-nm light, suggested above, can be shown spectroscopically to be a homogenous step (*Fig. 3*).

Similar behavior is observed upon irradiating *rac*-**1** in EtOH at room temperature with 365-nm or 313-nm light. If irradiation is initially carried out using 365-nm light,

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[3]) Certain aspects of the photochemical behavior of *rac*-**1** have been mentioned in communications [20] or review articles [21].

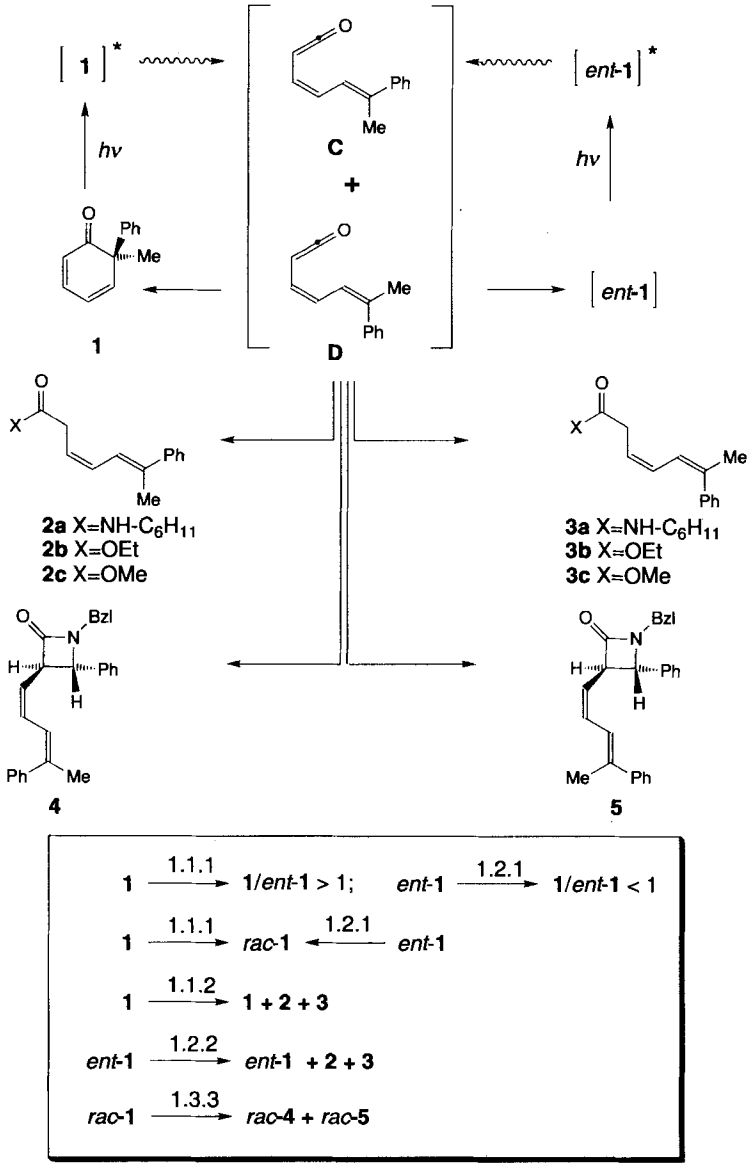
[4]) As the four *N*-cyclohexyl-amides showing the constitution of a 6-phenylhepta-3,5-dienoic acid, but differing in configuration, have been prepared in a transparent way [22], the configurations of **2a** and **3a** are known without any doubt.

[5]) Overirradiation causes secondary isomerization affording a product which, in addition to **2b** and **3b**, contains **65** and **66** (see *Exper. 1.3.1.2.1*).

[6]) It may be assumed, as soon as the quantum yield of the photochemical disappearance of starting material levels off as the concentration of added protic nucleophile increases, that the initially generated diene-ketene is being wholly trapped by the nucleophile.

[7]) See [23] regarding formal kinetic examination, interpretation and characterization of light-induced reactions; see [21a] for application to cyclohexa-2,4-dienones.

Scheme 1



followed by 313-nm light, then two mutually independent photochemical steps, each spectroscopically homogenous, can be seen straightaway (*Fig. 4*).

On comparing the two linear ED diagrams obtained for irradiation of *rac*-**1** in the presence of varying concentrations of cyclohexylamine (*Fig. 5*) or in EtOH (*Fig. 6*) at 25° in Et_2O/isopentane 1:1, it is possible in the former case, but not in the latter, to ascertain that the straight-line gradient is independent of the protic nucleophile concentration.

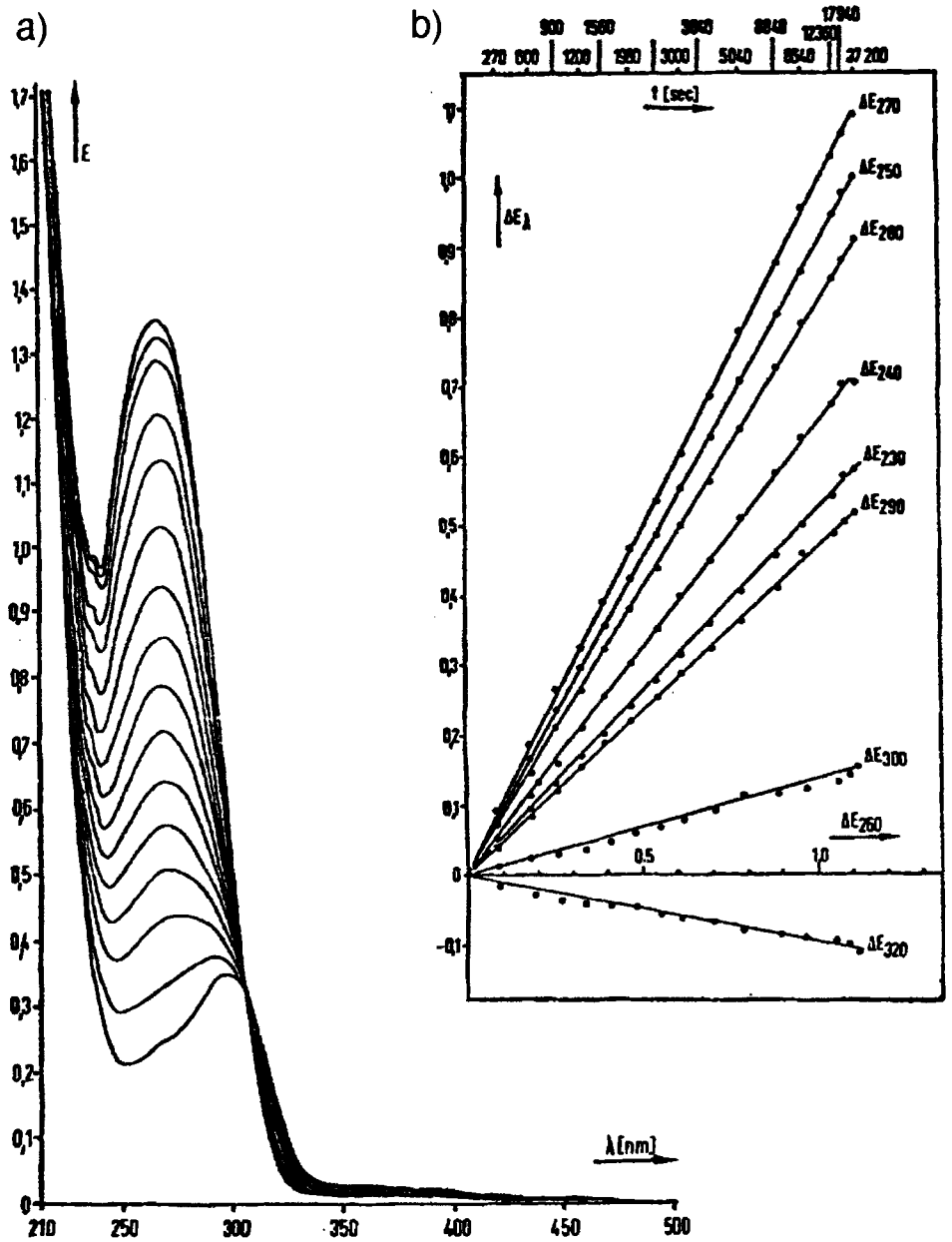


Fig. 1. *Analytical irradiation of a MCI solution of* rac-**1** *and cyclohexylamine at r.t. with 365-nm light* (see *Exper. 1.3.1.1.2.1*). *a*) Electronic absorption spectra with isosbestic point; *b*) linear ED diagram.

This difference reflects the greater nucleophilicity of the amine relative to the alcohol, but also reveals that, besides educt and product, a transient is involved, whose *retro*-reaction to the starting material might compete against the addition of a relatively weak protic nucleophile. This transient is made up of the diene-ketenes **C** and **D** (*Scheme 1*),

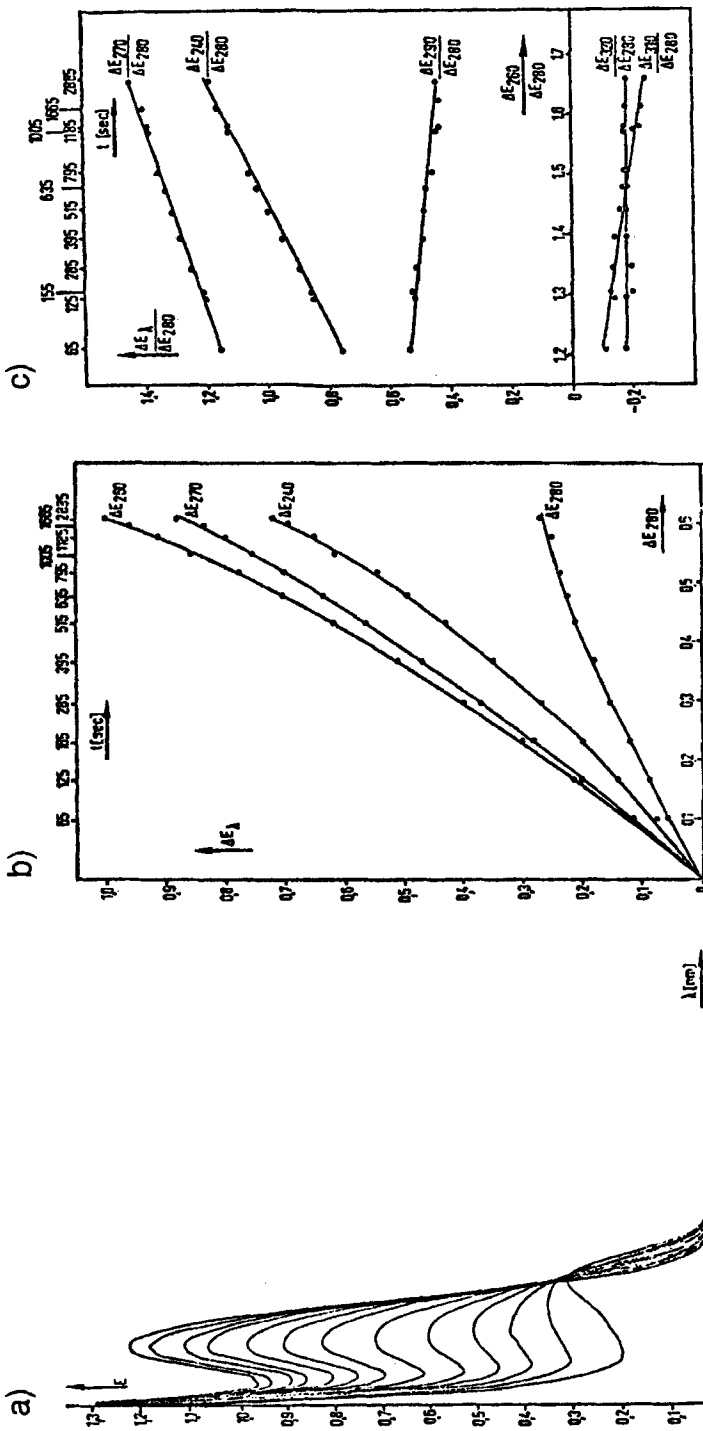


Fig. 2. *Analytical irradiation of a MC/1 solution of* rac-**1** *and cyclohexylamine at r.t. with 515-nm light* (see *Exper. 1.5.1.1.2.2*). *a*) Electronic absorption spectra without an isosbestic point; *b*) nonlinear ED diagram; *c*) linear EDQ diagram.

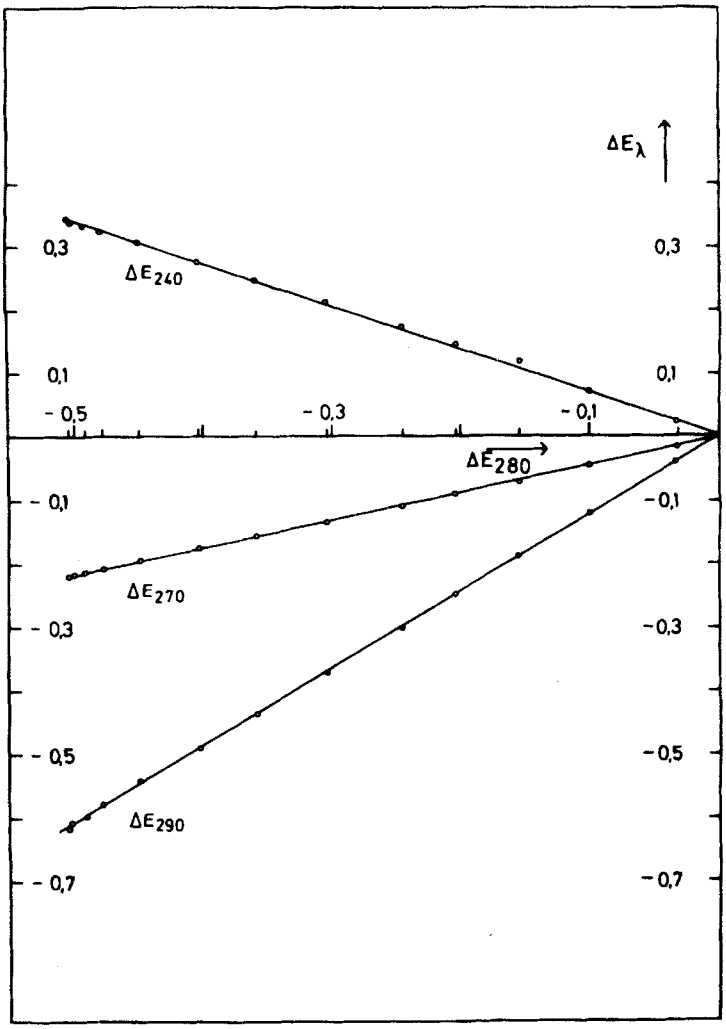


Fig. 3. *Linear ED diagram for the irradiation of an EtOH solution of* **2a** *and cyclohexylamine at 25° with 313-nm light* (see *Exper. 1.3.1.1.2.4*)

seco-isomers of the dienones of type **1**. Conventional spectroscopy at low temperature and flash spectroscopy at or around room temperature both confirm this.

Hence, IR spectroscopy at *ca.* −190° (*Fig. 7*) reveals the intermediacy of a ketene transient, which, according to IR and UV observations (λ_{max} 305 (25000) in MCI at −185°; *Exper. 1.3.2.2.1*; *vide infra*: *Fig. 9*), reverts thermally to *rac*-**1**.

^{1}H-NMR Spectra (*Exper. 1.3.2.3.4*) at −50° in C_6D_6 (at −60° in $CDCl_3$), furthermore, show that this ketene transient consists of two components: an unsurprising finding in view of the two product components of type **2** and **3**. The linear ED diagram in *Fig. 8* reveals that the binary ketene transient is generated in a spectroscopically homogenous photoreaction at −60° in CH_2Cl_2.

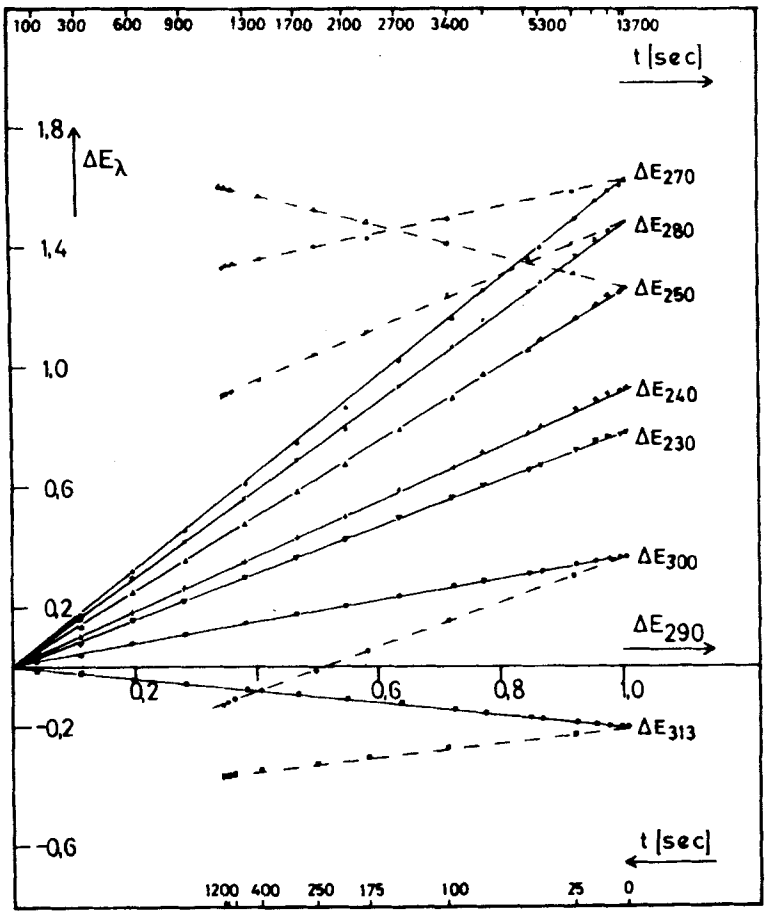


Fig. 4. *Linear ED diagram for the irradiation of* rac-**1** *in EtOH at 25°* (see *Exper. 1.3.1.2.2.3*) *at first with 365-nm light* (–) *and then with 313-nm light* (– – –)

Watching the irradiation of *rac*-**1** with 365-nm light in EPA at low temperature UV spectroscopically (*Fig. 9*) takes one by surprise. At −185° the ketene transient with an absorption maximum at 309 nm is smoothly formed. At −163°, a slow dark reaction takes place which, *via* another transient with an absorption maximum at 350 nm, leads to the ester product with an absorption maximum at 278 nm.

The new transient, which must be filed between the ketenes (**C** + **D**) and the esters of types **2** and **3**, fits the structural gap which can be filled by kinetically favored ester-enols of type (**G** + **H**) (*Scheme 2*).

In flash-spectroscopy examination of *rac*-**1** in cyclohexane (*Exper. 1.3.1.2.5.1*), it was only possible to detect educt and the binary ketene transient (**C** + **D**), whose activation parameters of recyclization could be determined. In MeOH, however, the ester-enol transient (**G** + **H**) could also be discerned (*Fig. 10*).

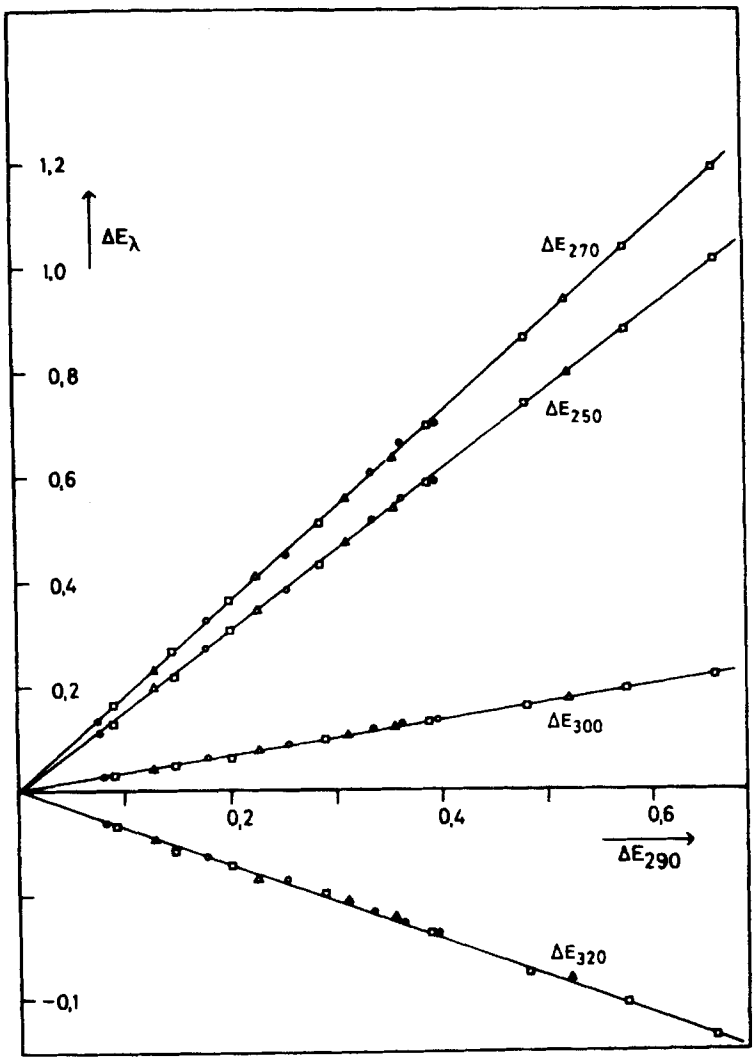


Fig. 5. *Linear ED diagram for the irradiation of* rac-**1** *and various concentrations of cyclohexylamine in* Et_2O*/isopentane 1:1 at 25° with 365-nm light*: The gradients of the lines are independent of the chosen concentrations of cyclohexylamine (see *Exper. 1.3.1.1.2.3*).

It is only logical that the sequence of different structures formed in the course of the addition of a protic nucleophile to a diene-ketene must, after all, commence with a zwitterion transient: the pair (**E** + **F**) in this instance (see *Scheme 2*). In the case of addition of DABCO in MCI to the diene-ketene transient, the enol transient is out of question, only the zwitterion transient warrants consideration. Because of the aprotic conditions, the latter is unable to rearrange into the former. At −150°, it is possible to observe an absorption with its maximum at 364 nm (*Fig. 11*).

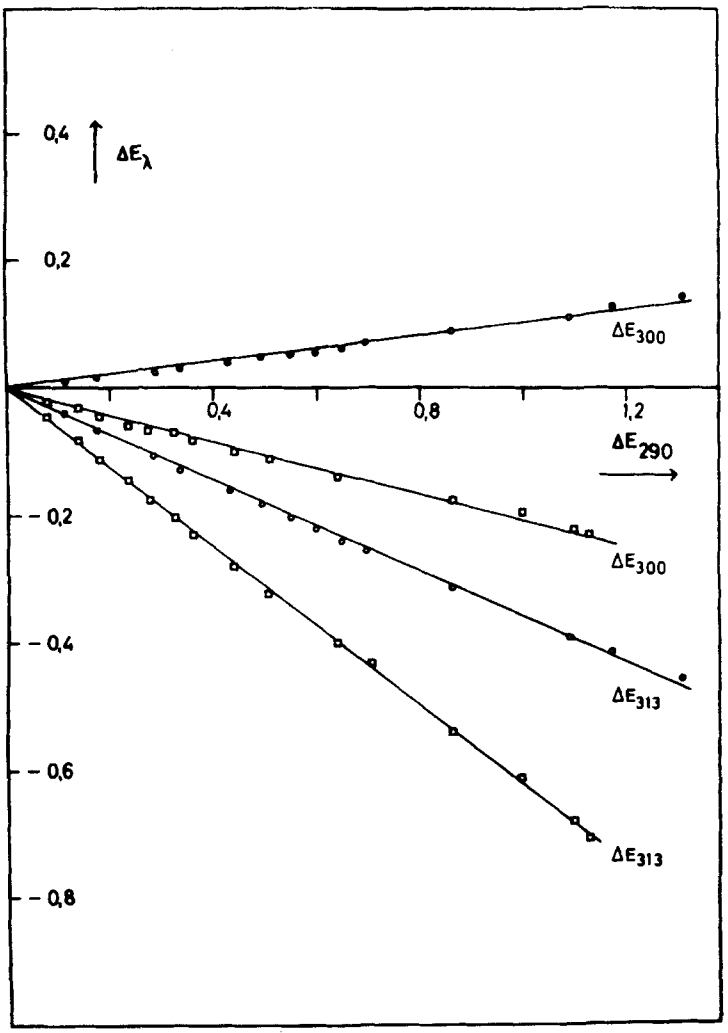


Fig. 6. *Linear ED diagram for the irradiation of* rac-**1** *and various concentrations of EtOH in* Et_2O*/isopentane 1:2 at 25° with 365-nm light*: The gradients of the lines depend on the used wavelength and the concentration of EtOH (see *Exper. 1.3.1.2.2.4*)

Point-for-point measurement of the changes in optical density following flash photolysis of *rac*-**1** in the presence of DABCO at −80° gives a transient spectrum with its maximum at 370 nm (*Fig. 12*), in close agreement with the above absorption spectrum.

Substitution of the aprotic nucleophile DABCO by cyclohexylamine results in an absorption spectrum with maxima at 464 and 484 nm at −185°, and a transient spectrum with a maximum at 465 nm at −140° (*Fig. 13*). This long-wavelength absorption region is ascribed to the enol transient.

The information contained in *Figs. 11* and *12*, on one hand, and in *Fig. 13* on the other, can certainly be pieced together, in mosaic-fashion, to give a complete picture.

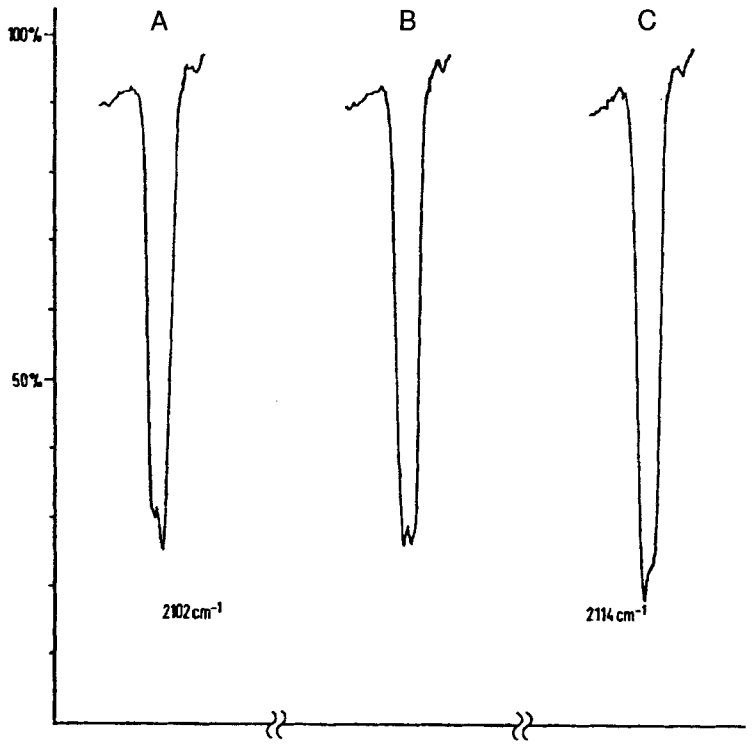


Fig. 7. *Part of IR spectra taken from a sample of* rac-**1** (film), *which had been irradiated for 3 min* (A), *10 min* (B), or *45 min* (*C*) *at* $-190°$ *with 365-nm light* (see *Exper. 1.3.2.3.3*)

However, information relating exclusively to the one particular case of the flash photolysis of *rac*-**1** in the presence of cyclohexylamine is best obtained from individual features from the oscillograms of *Fig. 14*.

These features support the detailed assumptions of *Scheme 2* (*Exper. 1.3.1.1.4*): At room temperature, the lifetime of the ketene transient, measured in MCI, decreases dramatically after cyclohexylamine has been added (compare *Fig. 14,a*, with *Fig. 14,b*). Decomposition of the ketene transient is first-order, *i.e.*, the reaction with excess cyclohexylamine, giving the zwitterion transient, is pseudo-monomolecular. From low-temperature measurements, it follows that the lifetime of the ketene transient decreases with decreasing temperature (compare *Fig. 14,c*, with *Fig. 14,d*). This means that the formation of the zwitterion transient is reversible, and the *retro*-reaction has a higher free activation enthalpy than the forward reaction[8]).

The zwitterion transient can be detected directly at $-150°$ (*Exper. 1.3.2.2.2*). It disappears in a first-order reaction with the same rate with which the enol transient appears (see *Fig. 27*). The growth of the signal at 460 nm correlates satisfactorily with the decline of the signal at 380 nm. Since the form of the decay curve is highly dependent on

[8]) See [24] regarding complex reactions involving equilibrium steps.

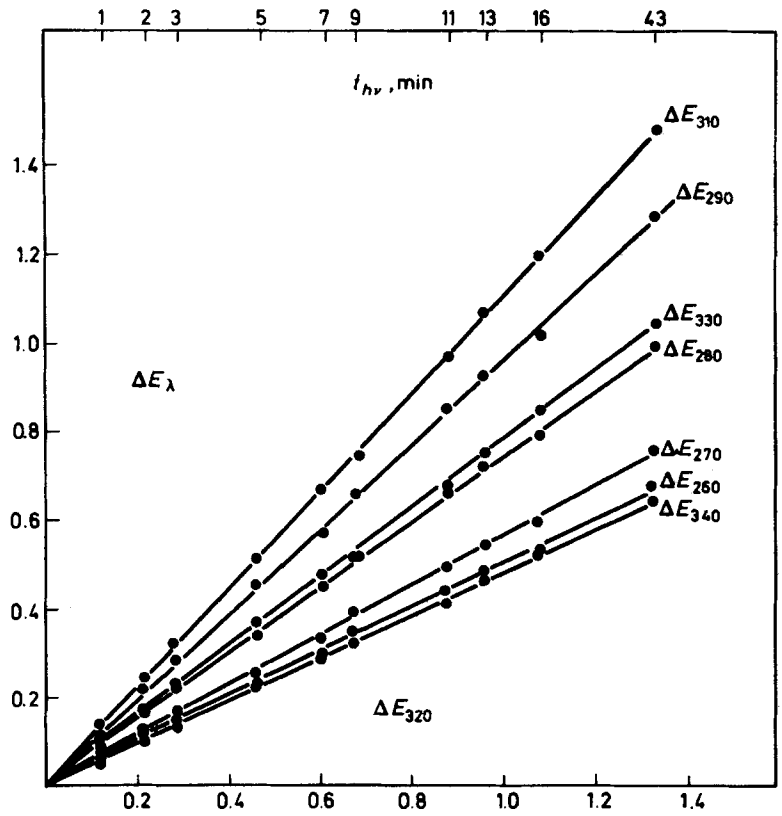


Fig. 8. *Linear ED diagram for the irradiation of* rac-**1** *in* CH_2Cl_2 *at* $-60°$ *with 365-nm light* (see *Exper. 1.3.2.3.2*)

the wavelength used to measure it, it follows that the absorption spectra of the enol and the zwitterion transients must overlap considerably. The enol transient's absorption spectrum may easily be obtained by point-for-point measurement at $-140°$ (see *Fig. 13*), as that of the zwitterion transient can no longer be deteced at this temperature (see *Fig. 11,B*). Decay of the enol transient is first-order, too. In this case, however, the reaction becomes slower with decreasing temperature.

Hence, the acyclic transients of *Scheme 2* have all been detected directly. To justify this publication's title, structural selectivity in the ring opening of electronically excited cyclohexa-2,4-dienones must still be discussed in depth. First, however, attention should be given to the question already posed [21b], whether a 'biradical' should be assumed between the electronically exited dienone and its diene-ketene *seco*-isomer.

A physical answer[9]) was expected from the enantiomers **1** and *ent*-**1** (see *Exper. 2.2* and *2.3* for their preparation and identification). As the quantum yields for the disappearance of *rac*-**1** in the presence of cyclohexylamine (*Exper. 1.3.1.1.3*) guarantee that, given a 500-fold excess of cyclohexylamine, every diene-ketene molecule (**C** + **D** in

[9]) For a chemical answer, *vide infra*.

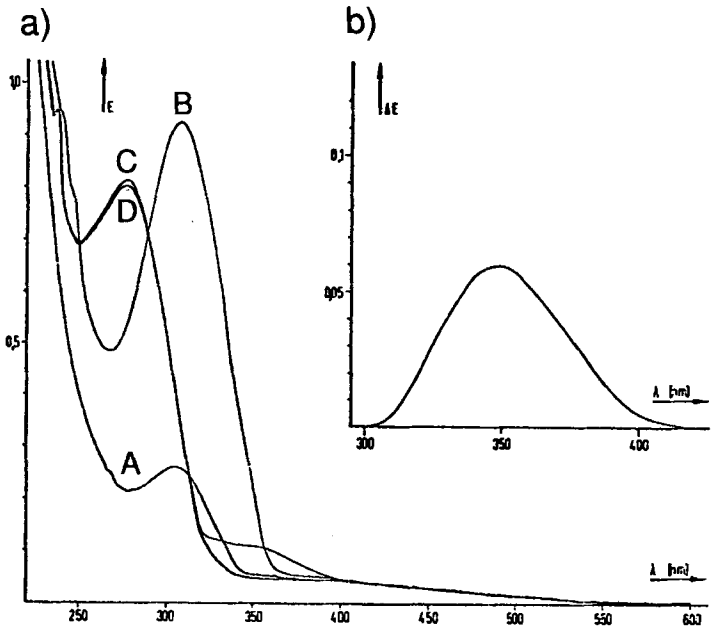


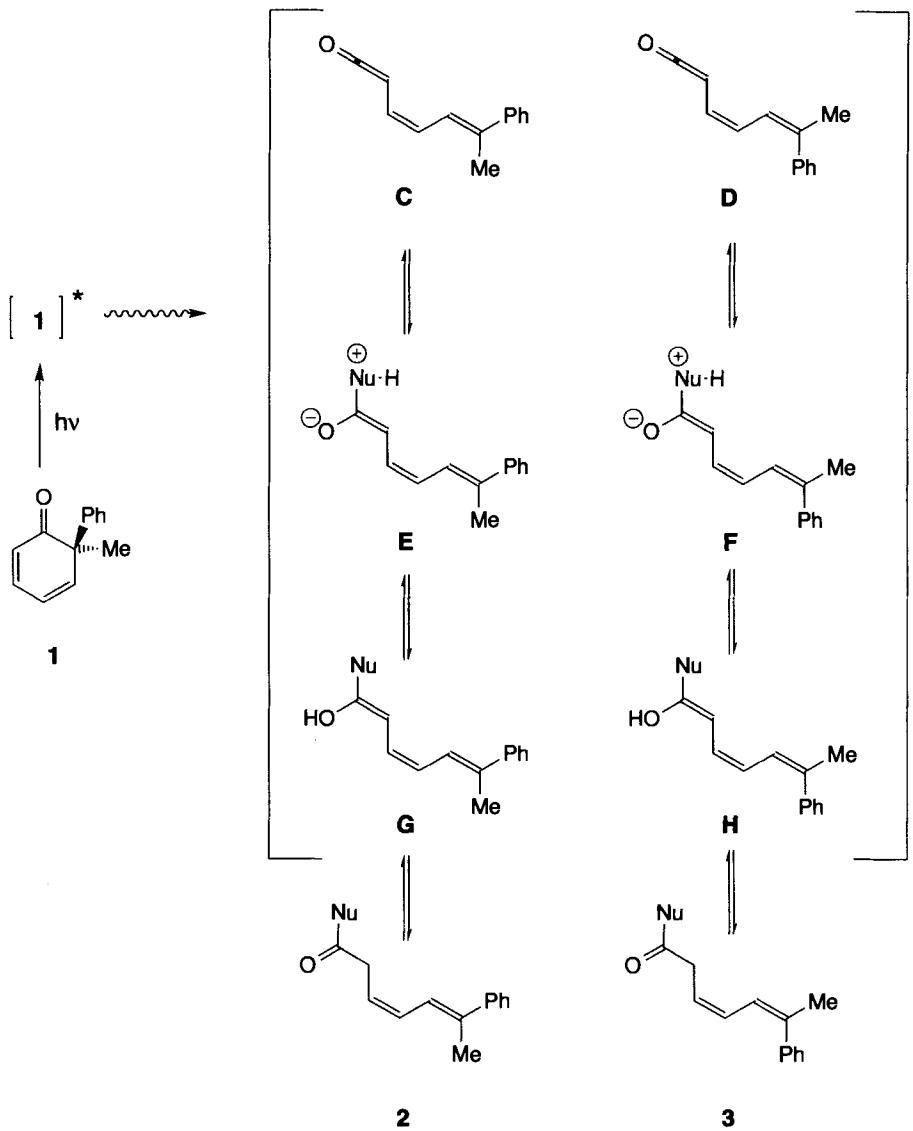
Fig. 9. *Electronic absorption spectra of* rac-**1** *in EPA before and after irradiation at low temperature with 365-nm light. a*) Before irradiation at −185° (*A*); after irradiation at −185° for 150 min (*B*) after warming up to −163° during 210 min in the dark (*C*); after warming up to r.t. and cooling down to −163° (*D*); *b*) difference spectrum by subtraction of *D* from *C* (see *Exper. 1.3.2.1.2*).

Scheme 1) will react to **2a** or **3a** and not recyclize to the original starting material, incomplete photolysis of both **1** and *ent*-**1** was carried out in anhydrous Et_2O, in the presence of 500 equiv. of cyclohexylamine, using light of wavelength > 340 nm. The specific optical rotation of each re-isolated dienone was identical with that of the original starting material within experimental error (± 1%; *Exper. 1.1.2* and *1.2.2*). This was not the case, when **1** or *ent*-**1** was irradiated in the absence of a protic nucleophile (*Exper. 1.1.1* and *1.2.1*). From these observations, it can be concluded that any biradical of lifetime sufficient for an alteration of configuration at C(6) may be discounted.

Of the compounds in *Scheme 2*, all have been commented upon, except for the electronically excited dienone [**1**]*. Depending on the wavelength of irradiating light, it is possible, at 365 nm, to obtain the (π^*,n)- and even, at 313 nm, the (π^*,π)-electron isomer[10]). As the quantum yield for disappearance of dienone, in the presence of a particular nucleophile above the limiting concentration specific to that nucleophile, is independent of the wavelength of exciting light (*Exper. 1.3.1.2.4*), it may be assumed that the chemical part of the total photochemical process proceeds from only one electron isomer, the (π^*,n) one in this case. As the quantum yield, in the presence of the triplett quencher (*Z*)-penta-1,3-diene, is not diminished (*Exper. 1.3.1.1.3*), photochemist's experience excludes the triplet spin isomer[10]).

[10]) See [25], Sect. 3.1, for the meanings of the terms *electronic isomer* and *spin isomer*.

Scheme 2



1.2. *(RS)-6-Methyl-6-(3'-oxopropyl)cyclohexa-2,4-dien-1-one* (*rac*-**6**). This compound represents a cyclohexa-2,4-dienone with a C=O group in the side chain at C(6). Irradiation of it with light of wavelength > 340 nm, both in cyclohexylamine-containing Et_2O solution and in MeOH results in the binary photoproducts (**7a**/**8a** 72:28; 70%) or (**7b**/**8b** 65:35; 95%) (*Scheme 3*).

The configurations of the separated product components with matching UV spectra were determined by NOE. Since both isomers were available, it was possible to identify

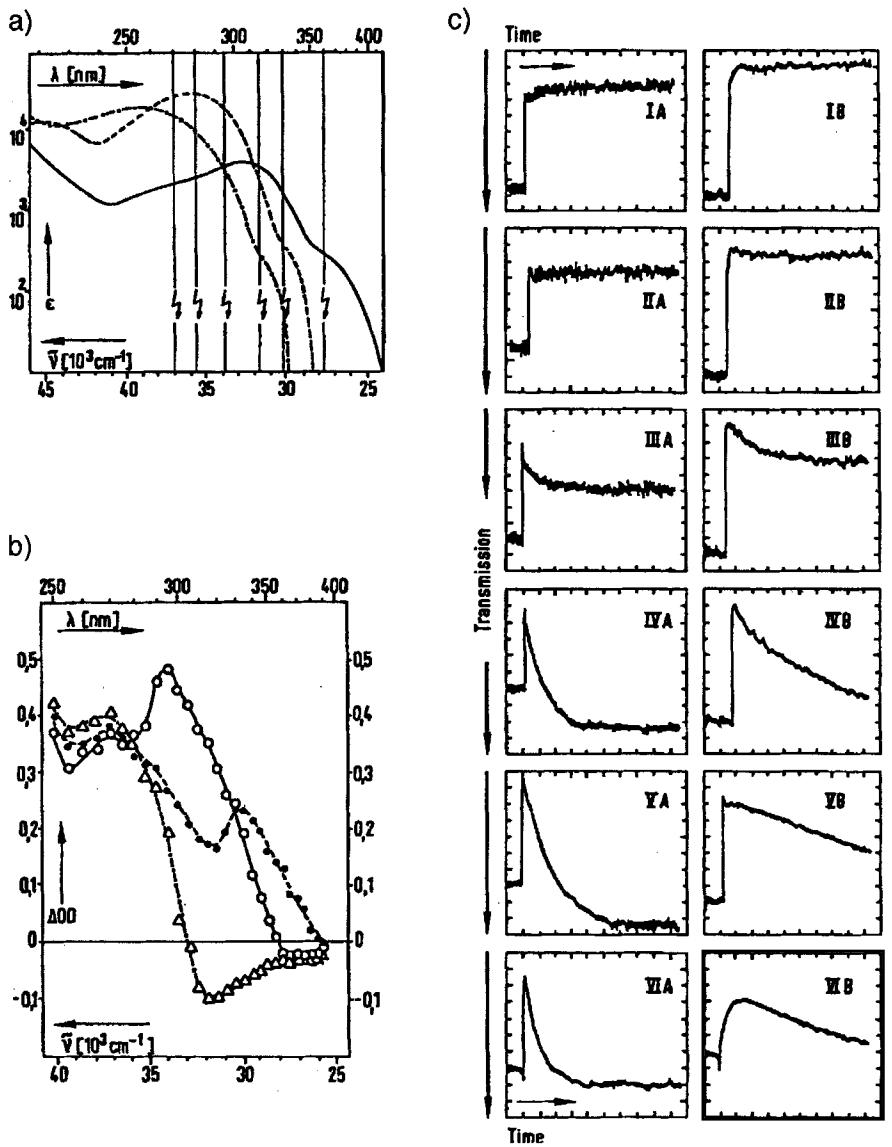


Fig. 10. a) *Electronic absorption spectra in MeOH at r.t. of* rac-**1** (——), **2c** (– – – –), *and* **3c** (–·–·–) (see *Exper. 1.3.1.2.5.2.1*). b) *Difference spectra during flash photolysis of* rac-**1**: *0* (o-o-o), *1* (•···•···•), *and 45 ms* (Δ-Δ-Δ) *after the flash.* c) *Transmission/time plot* (see *Exper. 1.3.1.2.5.2.2*) *at different wavelengths* (rows 1 through VI) *and various time resolutions* (columns *A* and *B*)

compounds of type **7**, thanks to their relatively large NOE effects between H–C(5) and H–C(7), and distinguish them, by grace of the interaction between Me–C(6) and H–C(4), from compounds of type **8**, with their interaction between Me–C(6) and H–C(5). A C=O group at C(3) has no effect on the composition of the relevant photoproduct. This changes when it advances one position closer to the dienone ring.

1.3. *(RS)-4-(Hydroxymethyl)-2,6-dimethyl-6-(2'-oxopropyl)cyclohexa-2,4-dien-1-one* (*rac*-**9**). Irradiation of *rac*-**9** with light of wavelength > 340 nm in cyclohexylamine-containing CH_2Cl_2 or in MeOH solution results in a solitary photoproduct, with (5*E*)-configuration in either case (**10a** (86%) or **10b** (79%); *Scheme 4*). The reasons for this stereoselection will be gone into in *Sect. 5*.

The irradiation products of *rac*-**9**, *rac*-**10a** and *rac*-**10b**, both show two regions of UV absorption. The relatively strong (π^*,π) absorption of the diene chromophore is hypsochromically and hypochromically shifted relative to the standard (photoproduct of (*RS*)-6-acetoxy-6-methylcyclohexa-2,4-dien-1-one (**M**); see *Table 1*). This makes it possible to identify the separate, relatively weak, (π^*,n) absorption of the C=O chromophore. The cause lies in twisting of the diene chromophore, arising from the relief of *Newman* strain[11]).

2. Photochemistry of *o*-Quinolacetates[12]). – If one of the two C substituents at C(6) in cyclohexa-2,4-dienones of the type previously discussed is replaced with an O substituent, the result is a compound class in which *o*-quinolacetates – not least because of their easy accessibility by *Wessely* acetoxylation [27] – form a prominent subclass. This subclass is worth forming because, in the photolytic ring opening of *o*-quinolacetates (like *rac*-**9**; *vide supra*), only one of the two anticipated diene-ketenes – that of (5*E*)-configuration – is produced, and so only half of the normally expected subsequent reaction products are formed. The special behavior of *o*-quinolacetates was brought to light after in-depth studies published in detail earlier[13]). Additional results obtained since for further *o*-quinolacetates are presented below.

2.1. *(RS)-6-Acetoxy-6-cyclopropylcyclohexa-2,4-dien-1-one* (*rac*-**11**). A chemical answer[14]) to the biradical question was expected of the cyclohexadienone *rac*-**11**. The cyclopropylcarbinyl-radical is known to rearrange into the allylcarbinyl radical[15]). This ought to react to give a product in which the cyclopropyl group would no longer be present. Irradiation of *rac*-**11** in cyclohexylamine-containing Et_2O with light of wavelength > 340 nm affords the amide **12** in 57% chemical yield (*Scheme 5*). In the absence of a protic nucleophile, *rac*-**11** reacts photochemically to give the phenols **13** and **14**. This finding rules out a biradical of medium lifetime ($> 10^{-8}$ s), although it is less rigorous than the physical answer already given.

Results obtained from the irradiation of the bicyclic *o*-quinolacetates *rac*-**15**, *rac*-**18**, *rac*-**20**, and *rac*-**22** are described next. These were of interest in the fields of macrolide synthesis and/or photochemically modifiable cation carriers.

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[11]) See [26] for the definition of the term *Newman* strain.

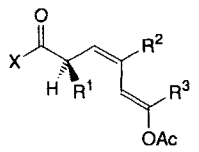
[12]) To match the enumerations of the *o*-quinolacetates with those of the corresponding adducts formed by addition of protic nucleophiles to the diene-ketenes involved, we name *rac*-**11** *(6RS)-6-acetoxy-6-cyclopropyl-cyclohexa-2,4-dien-1-one* instead of *(1RS)-6-oxocyclohexa-2,4-dien-1-yl acetate* (IUPAC nomenclature) and **12** *(3Z,5E)*-N-*cyclohexyl-6-acetoxy-6-cyclopropylhexadienamide* instead of *(1E,3Z)-6-(cyclohexylamino)-1-cyclopropyl-6-oxohexa-1,3-dien-1-yl acetate* (IUPAC nomenclature). Other *o*-quinolacetates and their photoproducts are treated similarly.

[13]) Detailed reports about diene-ketenes derived from six *o*-quinolacetates have been presented in [28].

[14]) For the physical answer *vide supra*.

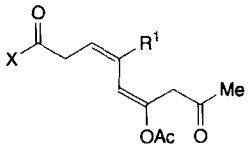
[15]) For pursuits of proving biradicals as transients by rearrangement of cyclopropylcarbinyl to allylcarbinyl radicals, see [29a]. For a recent paper on *clocking tertiary cyclopropylcarbinyl radical rearrangements*, see [29b].

Table 1. *Characteristic UV Data for Acyclic Product Components Obtained from Various Cyclohexa-2,4-dienones*



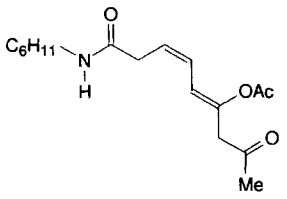
I

a R^1=R^2=H; R^3=Me; X=NH-C_6H_{11}
b R^1=R^2=R^3=Me; X=NH-C_6H_{11}
c R^1=R^3=^{t}Bu; R^2=H; X=NH-C_6H_{11}
d R^1=R^3=^{t}Bu; R^2=Me; X=NH-C_6H_{11}

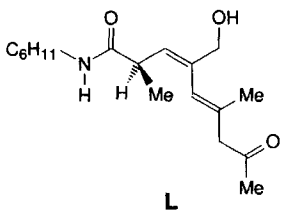


J

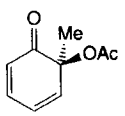
a R^1=H; X=NH-C_6H_{11}
b R^1=Ph; X=NH-Bzl
c R^1=^{i}Pr; X=NH-Bzl
d R^1=^{t}Bu; X=NH-Bzl



K



L



M

Code	Compound	λ_{max}	ε	Reference
Ia	[24]: **48**	237	24100	[24]
Ib	[24]: *rac*-**33**	222	6685	[24]
Ic	*rac*-**25a**	242	24020	*Scheme 8*
Id	*rac*-**28**	219	4725	*Scheme 9*
Ja	**34b**	242	23190	*Scheme 10*
Jb	**41c**	252	14610	*Scheme 14*
Jc	**35b**	230, 285	4380, 318	*Scheme 12*
Jd	**37a**	230, 290	3540, 375	*Scheme 13*
K	**34c**	242	24190	*Scheme 10*
L	*rac*-**10a**	220, 281	6160, 140	*Scheme 4*

2.2. *(RS)-1-Acetoxybicyclo[9.3.1]pentadeca-11,13-dien-15-one* (*rac*-**15**). Analytical-scale irradiation of *rac*-**15** at room temperature in MeOH results in a spectroscopically homogenous photoreaction, determined by UV-spectroscopically substantiated formal kinetics[7]), with both 365-nm and 313-nm light (*Exper. 1.7.1.1.2*). Preparative-scale irradiation of *rac*-**15** at room temperature in MeOH with light of wavelength > 340 nm gives *rac*-**16a** in 84% chemical yield (*Scheme 6*).

X-Ray crystal-structure analysis of *rac*-**16a** reveals its *constitution* (1,3-diene), *relative configuration* ((1*E*,3*Z*)), and trapezoidal (5333) *conformation*, with C(5), C(8), C(11), and C(14) occupying the corner positions (*Fig. 15*).

At −159°, the C(1)–C(2)–C(3)–C(4) torsion angle diverges appreciably from its ideals value of 180°. The torsion angles at the C(8) and C(11) apical atoms are 68.3° and 71.2°, respectively, their deviation from the ideal value (60°) arising from short, transannular H,H contacts (d(H–C(9),H–C(6)) = 2.14(6) Å; d(H–C(9),

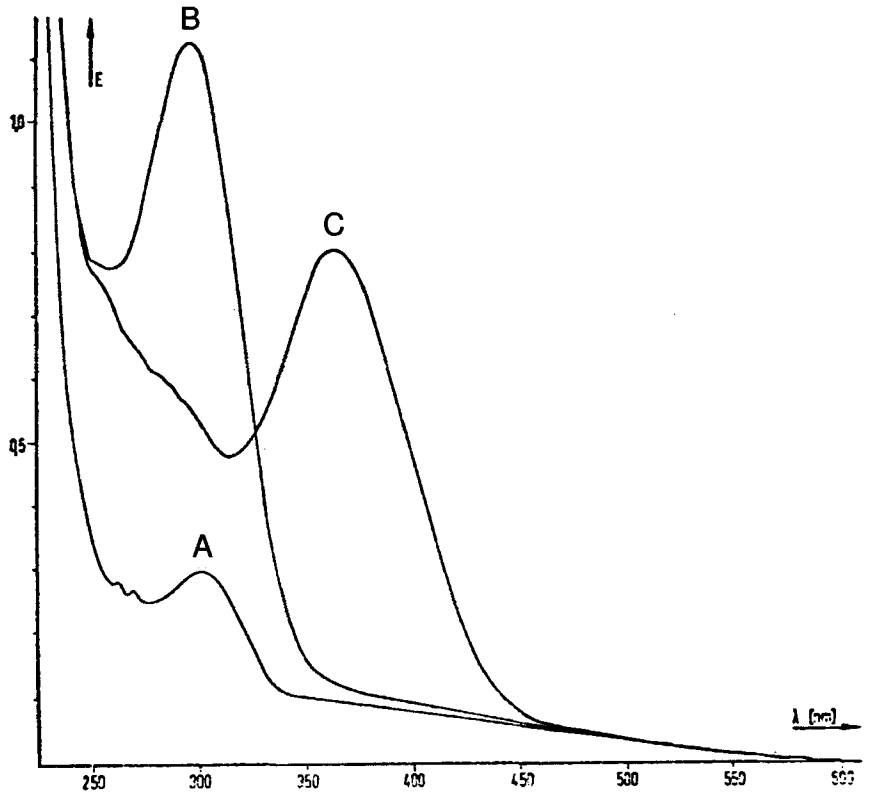


Fig. 11. *Electronic absorption spectra of* rac-**1** *and related transients in MCI. A*: *rac*-**1** at −185°; *B*: ketene transient obtained after irradiation with 365 nm-light at −152°; *C*: zwitterion transient formed after addition of DABCO at −150° (see *Exper. 1.3.2.2.1*).

H–C(12)) = 2.13(6) Å; *d*(H–C(10),H–C(7)) = 2.14(6) Å; *d*(H–C(10),H–C(13)) = 2.21(7) Å). The crystal structure reveals no intermolecular *van der Waals* contacts, but does display one electrostatic O,H contact with a separation of 2.49(5) Å.

If *t*-BuOH is used instead of MeOH, in addition to the 1,2-adduct *rac*-**16b** (59%), the 1,6-adduct *rac*-**17** (7%) is isolated as well[16]).

At low temperature in paraffin oil, a thermally recyclizable (to *rac*-**15**) transient can be detected by IR spectroscopy, thanks to its characteristic ketene bands (*Exper. 1.7.2.1*): UV-spectroscopically determined formal kinetics[7]) for the irradiation of *rac*-**15** in MCI at −185° with 365-nm light (*Exper. 1.7.2.2*) suggests that this transient appears as two different conformers (λ_{max} at 247 and 281 nm), which revert almost entirely to starting material on warming to room temperature.

2.3. *(RS)-1-Acetoxybicyclo[10.3.1]hexadeca-12,14-dien-1-one* (*rac*-**18**). Irradiation of *rac*-**18** with light of wavelength > 340 nm gives the methyl esters of *rac*-**19** in 85% chemical yield (*Scheme 6*). The crystal structure (*Fig. 16*) contains four independent molecules.

[16]) See [19] and [28], Sect. 3.4.3, on the formation of 1,6-adducts.

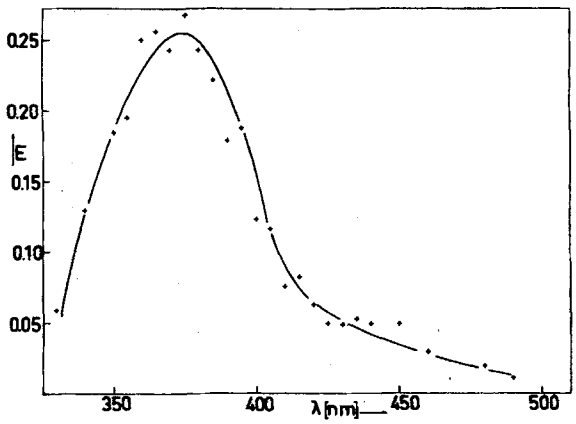


Fig. 12. *Transient spectrum* (λ_{max} 370 nm) *obtained after point-for-point measurement after flashing a solution of* rac-**1** *in DABCO-containing MCI at* $-80°$ (see *Exper. 1.3.2.2.1.2*)

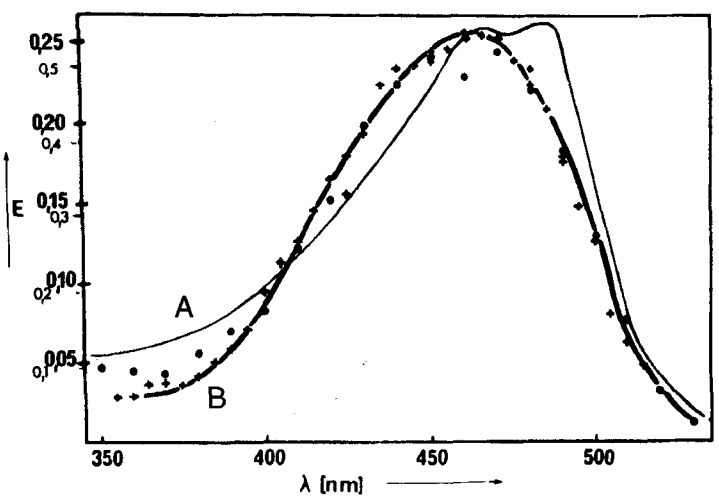


Fig. 13. *Low-temperature spectra of an enol transient obtained from a solution of* rac-**1** *and cyclohexylamine in MCI. A*: electronic absorption spectrum at $-189°$ (see *Exper. 1.3.2.2.2.1*); *B*: spectrum of absorption differences after flashing at $-140°$ (see *Exper. 1.3.2.2.2.2*).

Those of types 1 and 3 are conformationally identical, that of type 2 has a different conformation, while the type 4 molecule is disordered and can adopt two different conformations; either that of molecule type 1 (and hence 3) or that of molecule type 2. *Grosso modo*, therefore, there are only two different conformations present in the crystal structure. All molecules adopt a trapezoidal shape, molecules of types 1 and 3 having a (5334) conformation in which atoms C(5), C(8), C(11), and C(15) occupy the apexes of the trapezium. Molecule type 2 is of (5433) conformation, with atoms C(5), C(9), C(12), and C(15) at the apexes of the trapezium.

The diene system has a (1*E*,3*Z*)-configuration and is appreciably strained: the torsion angle C(1)–C(2)–C(3)–C(4) around the single bond of the diene system, for molecules 1, 2, 3, and 4, is $-157.8(5)°$, $-159.0(5)°$, $-155.7(5)°$ and $-159.3(6)°$, respectively, and so deviates notably from the ideal value (180°) of a planar system. In contrast, the C=C bonds are nearly planar, with average values for the C(15)–C(1)–C(2)–C(3) and C(2)–C(3)–C(4)–C(5) torsion angles of 6.4° and 4.1°, respectively. The crystal packing shows no intermolecular *van der Waals* contacts. Intermolecular interactions are based on weak electrostatic contacts between O- and H-atoms.

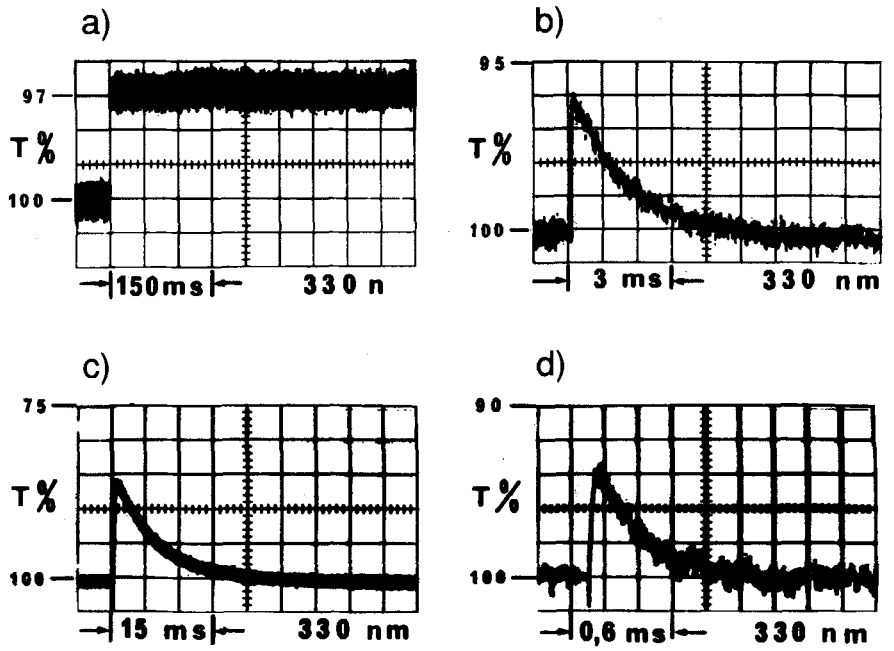
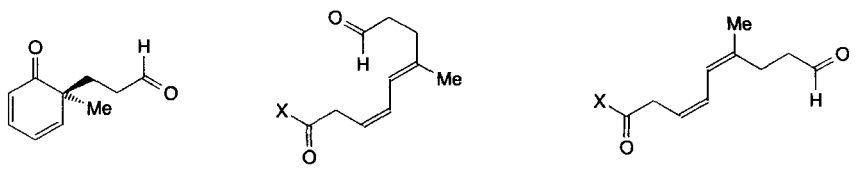
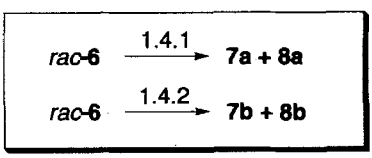


Fig. 14. *Oscillograms at 330 nm of flash spectroscopy of a solution of* rac-**1** *in MCI. a*) Before and *b*) after addition of cyclohexylamine, *c*) at r.t., *d*) at −50°. For details, see *Exper. 1.3.1.1.4.*

Scheme 3



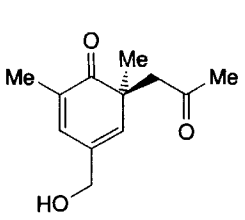
6 **7a** X=NH-C_6H_{11}; **b** X=OMe **8a** X=NH-C_6H_{11}; **b** X=OMe



2.4. *(RS)-1-Acetoxy-3,6,9,12-tetraoxabicyclo[12.3.1]octadeca-14,16-dien-18-one* (*rac*-**20**). To obtain the best possible chemical yield of *rac*-**21** from irradiation of *rac*-**20** in MeOH at room temperature (*Scheme 7*), it was found appropriate to add 10 equiv. of LiSCN to the reaction medium. Under these conditions, the yield rises from 46 (without additive) to 60%.

2.5. *(RS)-1-Acetoxy-3,6,9,12,15-pentaoxabicyclo[15.3.1]heneicosa-17,19-dien-21-one* (*rac*-**22**). As in the previous case, the chemical yield of *rac*-**23** is increased from 33 to 51%

Scheme 4



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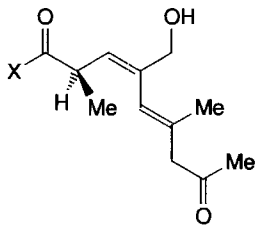
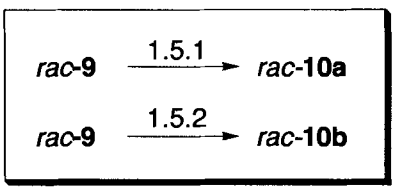
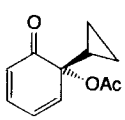


10a X=NH-C_6H_{11};
b X=OMe



Scheme 5



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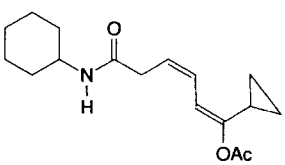

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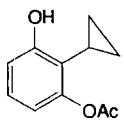

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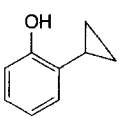
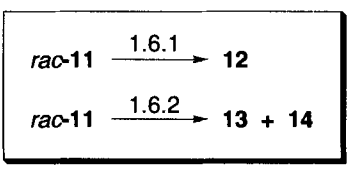


14



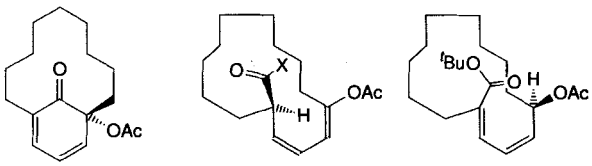
if *rac*-**22** is irradiated at room temperature in MeOH and in the presence – in this instance – of KSCN with light of wavelength > 340 nm (*Scheme 7*).

The two *o*-quinolacetates with *t*-Bu groups at C(2) and C(6), *rac*-**24a** and *rac*-**24b**, both gave complex photoproducts.

2.6. *(*RS*)-6-Acetoxy-2,6-di(*tert*-butyl)cyclohexa-2,4-dien-1-one* (*rac*-**24a**). Irradiation of *rac*-**24a** in cyclohexylamine-containing Et_2O solution (or in MeOH) led to *rac*-**25a** (or *rac*-**25b**) in 62% (86%) chemical yield. The corresponding esters, here *rac*-**25c**, appear – besides phenol **27** (15%) – with 19% yield in TFE as well, provided that 10 equiv. of NMI[17]) were added to the irradiated solution. In pure TFE, a trace of *rac*-**25c**, the phenol **27** (30%), and a mixture **26a**/**26b** (41%) was produced (*Scheme 8*).

[17]) For the effect additives such as NMI (or DABCO) may exert on the chemical yield of 1,2-adducts formed by addition of protic nucleophiles to diene-ketenes, see [30a].

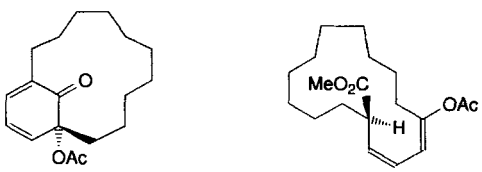
Scheme 6



15 **16a** X=OMe; **b** X=O^{t}Bu **17**

rac-**15** $\xrightarrow{1.7.1.1.1}$ *rac*-**16a**

rac-**15** $\xrightarrow{1.7.1.2}$ *rac*-**16b** + *rac*-**17**



18 **19**

rac-**18** $\xrightarrow{1.8}$ *rac*-**19**

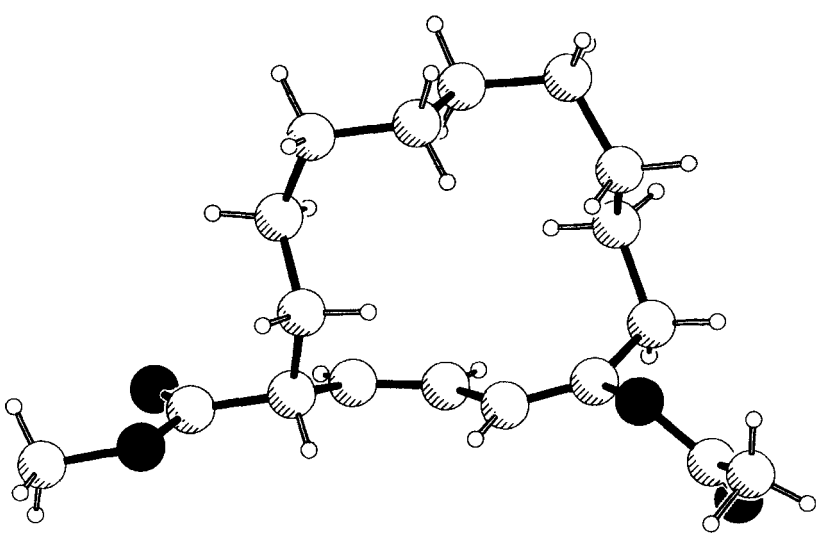


Fig. 15. *Representation of single-crystal X-ray structure of* rac-**16a**

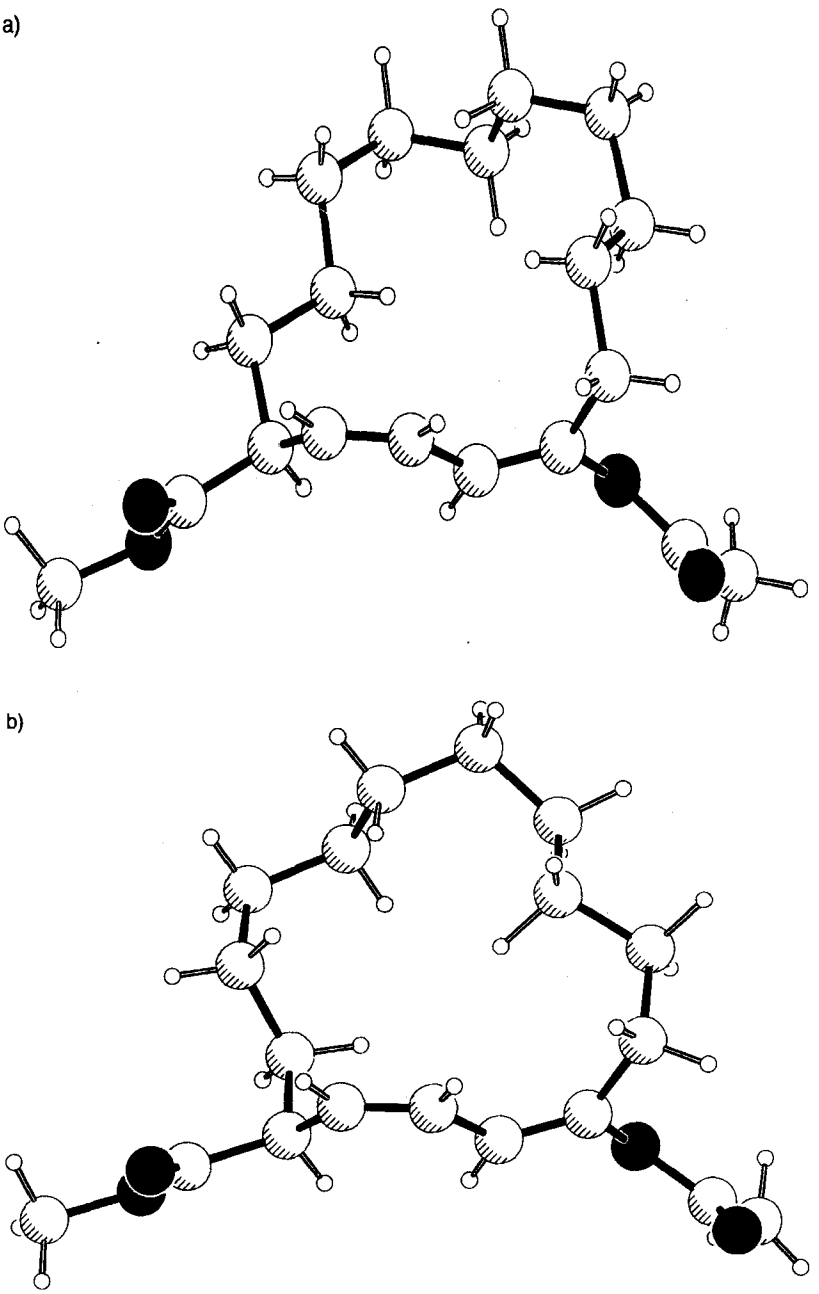
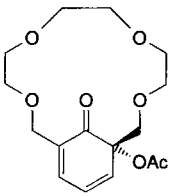


Fig. 16. *Representations of single-crystal structures of two independent types of molecules of* rac-**19** *with (5334)* (a) *or (5433)* (b) *conformation*

Scheme 7



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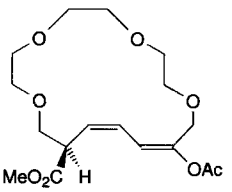
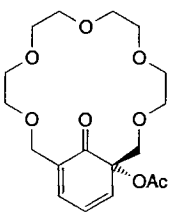
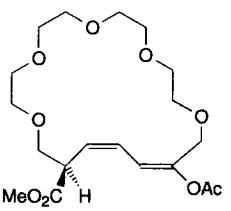


21

rac-**20** $\xrightarrow{1.9}$ *rac*-**21**



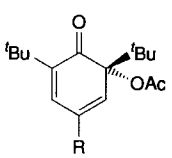
22



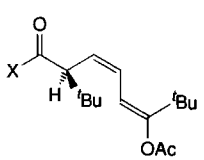
23

rac-**22** $\xrightarrow{1.10}$ *rac*-**23**

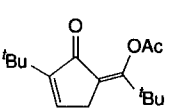
Scheme 8



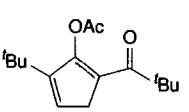
24a R=H
24b R=Me



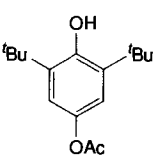
25a X=NH-C_6H_{11}
b X=OMe
c X=OCH_2CF_3



26a



26b



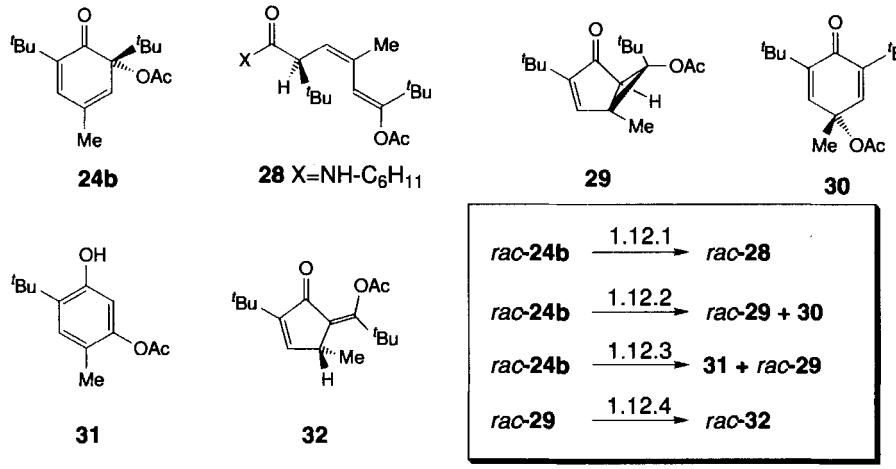
27

rac-**24a** $\xrightarrow{1.11.1}$ *rac*-**25a**; *rac*-**24a** $\xrightarrow{1.11.2}$ *rac*-**25b**

rac-**24a** $\xrightarrow{1.11.3.1}$ *rac*-**25c** + **27**; *rac*-**24a** $\xrightarrow{1.11.3.2}$ *rac*-**25c** + **27** + (**26a** $\rightleftharpoons$ **26b**)

2.7. *(RS)-6-Acetoxy-2,6-di(*tert*-butyl)-4-methylcyclohexa-2,4-dien-1-one* (*rac*-**24b**). Compound *rac*-**28** was isolated in 81% chemical yield following irradiation of *rac*-**24b** in cyclohexylamine-containing Et_2O solution with light of wavelength > 340 nm (*Scheme 9*).

Scheme 9



Information about constitution (3,5-diene), relative configuration ((3*Z*,5*E*)), and conformation was obtained from X-ray crystal-structure analysis (*Fig. 17*). Including the bridging H-atom between the NH group of the amide moiety and the C=O group of the acetate rest, an eleven-membered ring with minimum *Newman* strain[11]) is observed.

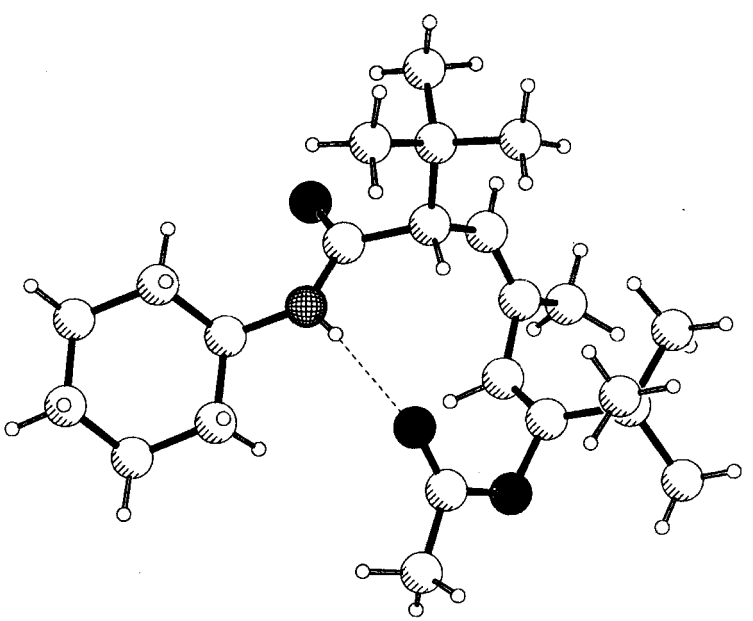


Fig. 17. *Representation of single-crystal X-ray structure of* rac-**28**

The two C=C bonds are oriented virtually perpendicular to one another: the C(3)=C(4)–C(5)=C(6) torsion angle is 98°. The amide group shows a local (*z*)-conformation: C(18)–N–C(1)–O(1) torsion angle is 2°. At 44°, the C(1)–N–C(18)–H torsion angle lies in the region of the U-shaped arrangement of O(1) and H–C(18). No steric hindrance exists between the Me and the *t*-Bu groups.

Comparison of the UV absorption of *rac*-**28** with that of *rac*-**25a** permits conclusions to be drawn about the unperturbed (the latter) and the twisted (the former) diene chromophore (see *Table 1*).

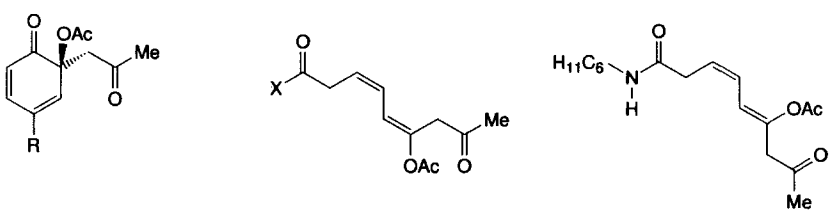
Irradiation of *rac*-**24b** in DABCO-containing MeOH gave rise to a mixture of the bicyclic ketones *rac*-**29** (34%) and their photochemical descendents (see [28], Sect. 3.4.2), the cross-conjugated dienone **30** (*Scheme 9*). In TFE, the bicyclic ketones *rac*-**29** (22%) and phenol **31** were formed. The latter can be ruled out as a secondary photoproduct of *rac*-**29**, as this role is assumed as a terminal of the $^3(\pi^*,\pi)$ route by *rac*-**32**. It can rather be understood, however, as a secondary photoproduct of **30**.

3. Photochemistry of *o*-Quinolacetates[12]) with Side Chains Containing a 2-Oxo Group. – 3.1. *(RS)-6-Acetoxy-6-(2'-oxopropyl)cyclohexa-2,4-dien-1-one* (*rac*-**33a**). *o*-Quinolacetates belonging to this category behave like *rac*-**9** (*Sect. 1.3*), *i.e.*, they provide a singular photoproduct only[18]). Thus, *rac*-**33a** affords the ester **34b** in 81% chemical yield on irradiation in MeOH at room temperature with light of wavelength > 340 nm (*Scheme 10*). An apparent contradiction in the photochemical reaction in cyclohexylamine-containing Et_2O, which gives rise to the binary mixture **34a**/**34c**, is resolved by invoking a base-induced isomerization of **34a** to **34c**.

A new type of diene-ketene secondary product, in the form of a seven-membered carbocycle, is encountered with derivatives of *rac*-**33a** bearing an i-Pr, *t*-Bu, or Ph substituent at C(4) instead of H. *Table 2* gives a summary of the respective product components isolated.

In the *acyclic* product components, increasing demand on space by the C(4) substituent results in increasing deviation from the planar conformation. *Table 1* (*vide supra*)

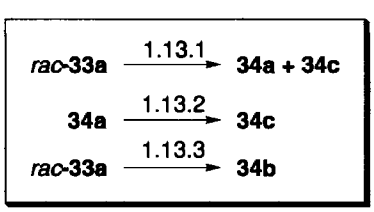
Scheme 10



33a R=H; **b** R=^{i}Pr; **c** R=^{t}Bu; **d** R=Ph

34a X=NH-C_6H_{11}; **b** X=OMe

34c



[18]) For the first two examples of this type, see [31].

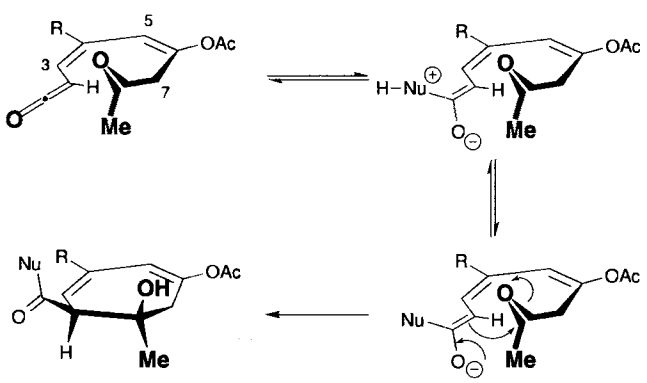
Table 2. *Influences the Nature of R in Cyclohexa-2,4-dienones of Type* rac-**33** *Exerts on the Composition of the Related Photoproducts*

R	Nu	Dienone	Cyclic product component	Acyclic product component	*Scheme*
H	NHC_6H_{11}	*rac*-**33a**	–	**34a**/**34c** (66%)	*10*
	MeO		–	**34b** (81%)	
^{i}Pr	NH_2	*rac*-**33b**	*rac*-**36a** (17%)	**35a** (33%)	*12*
	NHBzl		*rac*-**36b** (36%)	**35b** (25%)	
^{t}Bu	NH_2	*rac*-**33c**	*rac*-**38a** (45%)	–	
	NHC_6H_{11}		*rac*-**38b** (53%)	–	*13*
	NHBzl		*rac*-**38c** (51%)	–	
	MeO		*rac*-**38d**[a]) (9%)	**37b** (67%)	
Ph	NH_2	*rac*-**33d**	*rac*-**42a** (11%)	**41a** (20%)	
	NHC_6H_{11}		*rac*-**42b** (21%)	**41b** (21%)	*14*
	NHBzl		*rac*-**42c** (21%)	**41c** (27%)	
	MeO			**41d** (86%)	

[a]) Stereoisomer *rac*-**40** was also formed.

gives wavelengths and molar extinction coefficients of UV maxima for representative cases. The *cyclic* product components are *intramolecular aldol adducts*, originating from transiently formed zwitterions of diene-(*N*,*O*)-ketene acetals (see *Scheme 2*) of (2*e*,4*z*)-conformation type[19]) with an electrophilic C=O group in the sterically optimal situated 2′-position of a (5*Z*)-configured side chain (*Scheme 11*). The nonideal (2*e*,4*z*)-conformation type, with helical topology, becomes favored for avoiding unnecessary *Newman* strain[11]) from the bulky substituents at C(4).

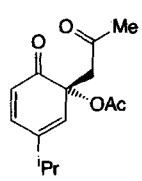
Scheme 11



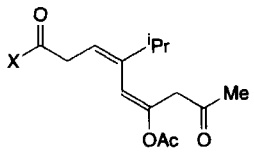
[19]) See [28], Scheme 11, regarding the four different, idealized conformation types. To distinguish between them in a topologically unambiguous manner, upper case letters ((*E*) or (*Z*)) refer to the configuration at a C=C bond, lower case ((*e*) or (*z*)) to the orientation of substituents about a C–C bond.

3.2. *(RS)-6-Acetoxy-4-isopropyl-6-(2'-oxopropyl)cyclohexa-2,4-dien-1-one* (*rac*-**33b**). Irradiation of *rac*-**33b** in an ammoniacal ($PhCH_2NH_2$-containing) Et_2O solution affords the amide **35a** in 33% yield (the benzylamide **35b** in 25% yield) and also the seven-membered ring compound *rac*-**36a** in 17% yield (*rac*-**36b** in 36% yield; *Scheme 12*).

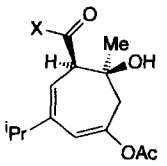
Scheme 12



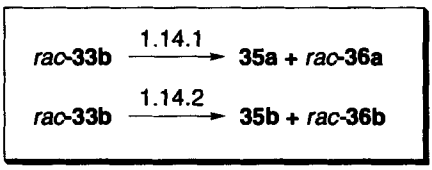
33b



35a X=NH_2; **b** X=NH-Bzl



36a X=NH_2; **b** X=NH-Bzl



The cyclohepta-1,3-diene constitution, with substituents at C(1), C(3), C(5), and C(6), the *cis*-configuration and a *staggered* orientation of the adjacent carbamoyl and OH groups, and also the twisted diene chromophore (C(1)–C(2)–C(3)–C(4) torsion angle −38°) can be seen in the X-ray crystal-structure analysis of *rac*-**36b** (*Fig. 18*).

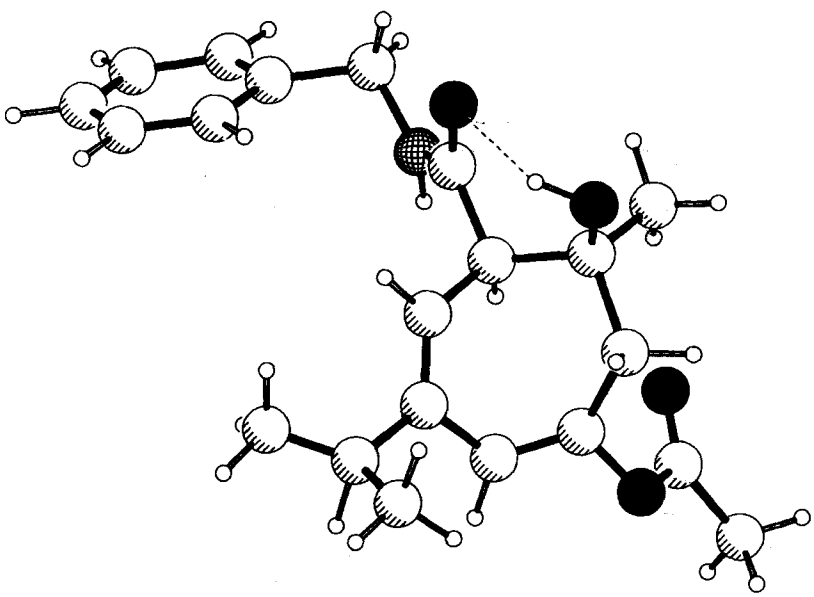
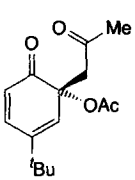


Fig. 18. *Representation of single-crystal X-ray structure of* rac-**36b**

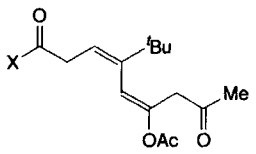
The arrangement of molecules in the crystal permits the amide group to participate in an intermolecular N–H ··· O bond, so that chains of H-bridged molecules are formed along a screw axis coinciding with the crystallographic *b*-projection.

3.3. *(RS)-6-Acetoxy-4-(*tert*-butyl)-6-(2'-oxopropyl)cyclohexa-2,4-dien-1-one* (*rac*-**33c**). Photochemical reaction of *rac*-**33c** in ammoniacal (cyclohexylamine-containing) Et_2O leads to *rac*-**38a** (*rac*-**38b**) in 45% (53%) chemical yield (*Scheme 13*).

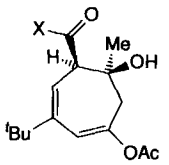
Scheme 13



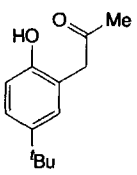
33c



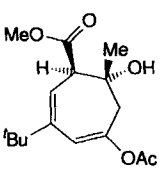
37a X=NH-Bzl
b X=OMe



38a X=NH_2
b X=NH-C_6H_{11}
c X=NH-Bzl
d X=OMe



39



40

rac-**33c**	1.15.1.1 →	*rac*-**38a**
rac-**33c**	1.15.1.2 →	*rac*-**38b**
rac-**33c**	1.15.2.1 →	**37a**
rac-**33c**	1.15.2.2 →	**37a** + *rac*-**38c** + **39**
rac-**33c**	1.15.3 →	**37b** + *rac*-**38d** + **40**

In the presence of $PhCH_2NH_2$, the acyclic amide **37a** (38%) is formed when hexane is the solvent (*Exper. 1.15.2.1*). In Et_2O, the cyclic amide *rac*-**38c** (51%) is formed at relatively low $PhCH_2NH_2$ concentrations, a mixture of **37a** (30%), *rac*-**38c** (3%), and phenol **39** (19%) being obtained at relatively high $PhCH_2NH_2$ concentrations. After irradiation of *rac*-**33c** in MeOH, both the acyclic ester **37b** (67%) and the configurationally isomeric esters (*rac*-**38d** + *rac*-**40**) (9% in total) were isolated. A single-crystal X-ray structure analysis is available for *rac*-**38a** (see *Fig. 19*).

The unit cell contains two molecules of different geometry, which do not differ significantly from one another. The most important structural detail is the *cis*-arrangement of OH and amide group, which share in an intramolecular H-bond. The diene system is nonplanar: the torsion angle amounts to *ca.* 42°. The crystal packing clearly indicates intermolecular H-bonding between the amide NH group, C=O groups, and OH groups.

3.4. *(RS)-6-Acetoxy-6-(2'-oxopropyl)-4-phenylcyclohexa-2,4-dien-1-one* (*rac*-**33d**). Like *rac*-**33b** and *rac*-**33c**, *rac*-**33d** affords both acyclic and seven-membered carbocyclic-acid derivatives when irradiated with light of wavelength > 340 nm in the presence of protic nucleophiles (*Scheme 14*). The photoproduct components **41a** (29%) and *rac*-**42a** (11%) were obtained from ammoniacal Et_2O, **41b** (21%) and *rac*-**42b** (37%) from cyclohexylamine-containing Et_2O, and **41c** (27%) and *rac*-**42c** (21%) from $PhCH_2NH_2$-

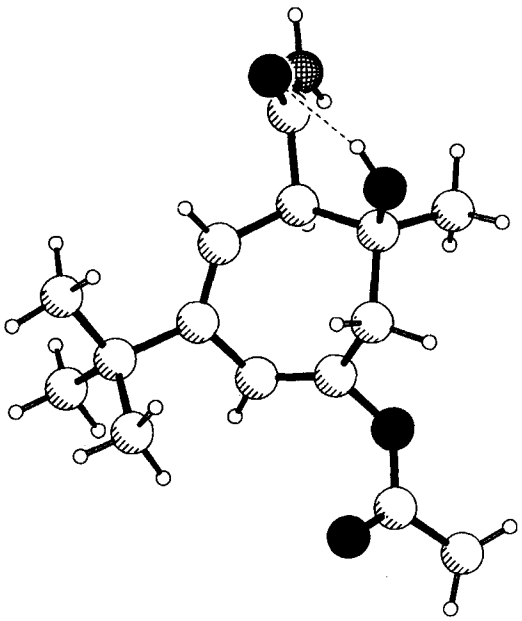
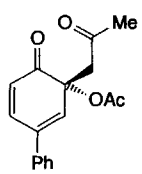


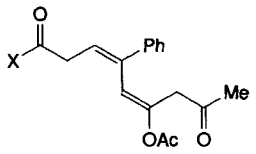
Fig. 19. *Representation of single-crystal X-ray structure of* rac-**38a**

containing Et_2O. On irradiation in MeOH, **41d** was obtained in 86% chemical yield. The relative configurations of both the cyclic and also the acyclic iradiation products were established by analysis of NOE spectra.

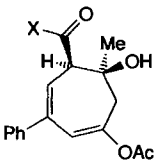
Scheme 14



33d



41a X=NH_2
b X=NH-C_6H_{11}
c X=NH-Bzl
d X=OMe

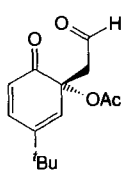


42a X=NH_2
b X=NH-C_6H_{11}
c X=NH-Bzl

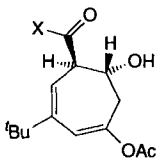
rac-**33d**	1.16.1 →	**41a** + *rac*-**42a**
rac-**33d**	1.16.2 →	**41b** + *rac*-**42b**
rac-**33d**	1.16.3 →	**41c** + *rac*-**42c**
rac-**33d**	1.16.4 →	**41d**

3.5. *(RS)-6-Acetoxy-4-(*tert*-butyl)-6-(2'-oxoethyl)cyclohexa-2,4-dien-1-one* (*rac*-**43**). After irradiation of *rac*-**43** in ammoniacal ($PhCH_2NH_2$-containing) Et_2O solution with light of wavelength > 340 nm, the seven-membered cyclic compounds *rac*-**44a** (*rac*-**44b**/*rac*-**45** 1:1.4) were isolated in 47% (59%) chemical yield (*Scheme 15*). In this case, it was found necessary to add the $PhCH_2NH_2$ dropwise to the reaction medium, as the starting compound was significantly degraded by $PhCH_2NH_2$ even in the absence of light.

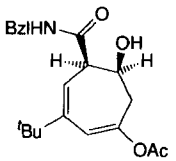
Scheme 15



43



44a X=NH_2
b X=NH-Bzl



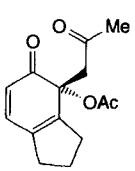
45

rac-**43** —1.17.1→ *rac*-**44a**

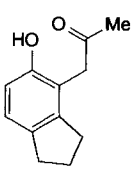
rac-**43** —1.17.2→ *rac*-**44b** + *rac*-**45**

3.6. *(RS)-4-Acetoxy-4,5-dihydro-4-(2'-oxopropyl)indan-5-one* (*rac*-**46**). From the crude product of irradiation of *rac*-**46** in MeOH, it was possible to isolate phenol **47** (9%) and the 1,2-adduct **48** (5%) formed by reaction of the solvent with the photochemically generated diene-ketene (*Scheme 16*). The (3*Z*)-configuration in **48** was supported by NOE: interaction of H–C(3) with the spatially close allylic protons at C(5) (3%), as well as interaction between protons at C(2) and C(10) (2.9%). On irradiation of *rac*-**46** in $PhCH_2NH_2$-containing Et_2O, indanol **47** (21%) appeared once more, together with the seven-membered ring compound *rac*-**49** (14%). Analysis of NOE, difference spectra indicates the *cis*-configuration of carbamoyl and OH groups.

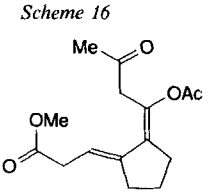
Scheme 16



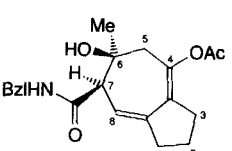
46



47



48



49

rac-**46** —1.18.1→ **47** + **48**

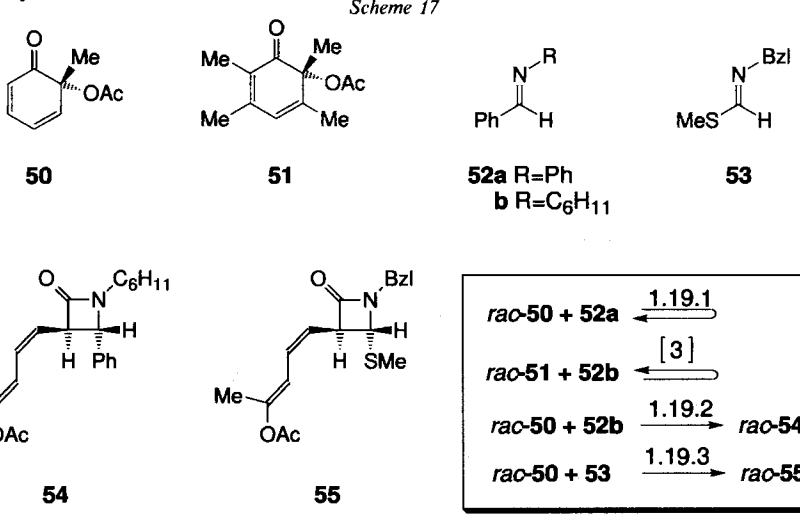
rac-**46** —1.18.2→ **47** + *rac*-**49**

The results of these investigations into the photochemistry of cyclohexa-2,4-dienones in general (*Sect. 1*) and *o*-quinolacetates in particular (*Sect. 2*) have once more demonstrated the three known (see [28]: Sect. 3.4) reaction pathways opened up by the *seco*-isomer phototransients of diene-ketene constitution: namely recyclization to the original starting compound or a configurational isomer, bicyclization to bicyclo[3.1.0]hex-3-en-2-ones, and addition of protic nucleophiles, either intermolecularly to give derivatives of substituted hexadienoic acids, or intramolecularly to give substituted diene-lactones [30a] or diene-lactams [30b]. As the type of photoproduct had been found to be modified by changing solvent in the case of cyclohexa-2,4-dienones [32], and changing solvent was known to alter wavelength of absorption, *wavelength-dependent photochemistry* could only be an educated guess. It was instrumental, nevertheless, in leading to a *theory of photochemical reactions* [33]. Flash spectroscopy, in particular, revealed, however, that what had been attributed to wavelength-dependent photochemistry of cyclohexa-2,4-dienones was actually due to *medium-dependent thermochemistry* of their related diene-ketenes [28] [34].

A new pathway, peculiar to the *seco*-isomers of *o*-quinolacetates bearing a 2'-oxo-containing substituent at C(6), has been found now (*Sect. 3*), leading to *intramolecular aldol adducts*. The following section addresses the question of whether imines merit consideration as nucleophiles for diene-ketenes, resulting in the formation of β-lactams.

4. β-Lactams by Cycloaddition of Imines with Diene-ketenes. – Cycloadditions of imines and ketenes produce β-lactams. This reaction was documented even in the most ancient monograph about '*Die Ketene*' [35] and is still exciting considerable interest in the newest book about '*Ketenes*' [36]. β-Lactams only stand a chance of being formed from diene-ketenes and imines if the desired cycloaddition occurs before the diene-ketene recyclizes. It is, furthermore, an advantage if the imines do not absorb in the same wavelength region of the cyclohexa-2,4-dienones, the cyclic precursors of diene-ketenes. It is, therefore, not surprising that no reaction is observed either upon irradiating *rac*-**50** (= **M** of *Table 1*) in the presence of **52a**, or on irradiating *rac*-**51** in the presence of **52b** (*Scheme 17*). However, *rac*-**50** does react with **52b**, exclusively affording *rac*-**54** in a chemical yield of 98%.

Scheme 17



50 **51** **52a** R=Ph **b** R=C_6H_{11} **53**

54 **55**

As the X-ray crystal-structure analysis shows (*Fig. 20*), the *trans*-configured β-lactam is produced with extremely high diastereoselectivity.

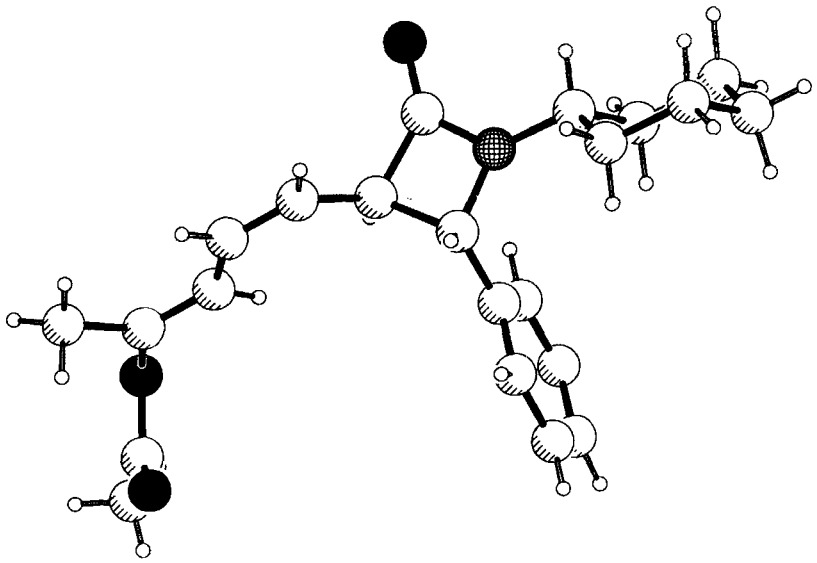


Fig. 20. *Representation of single-crystal X-ray structure of* rac-**54**

Reaction of **53** with the diene-ketene, photochemically generated from *rac*-**50** (*Scheme 17*), also results exclusively in the *trans*-configured product *rac*-**55**, as shown by X-ray crystal-structure analysis (*Fig. 21*).

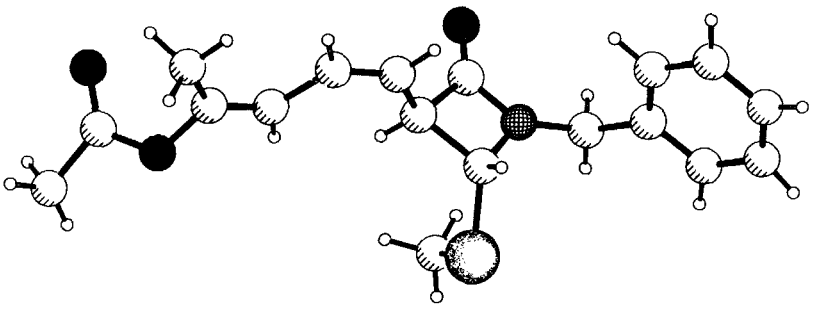
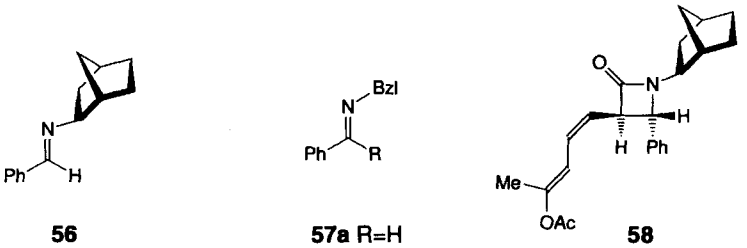


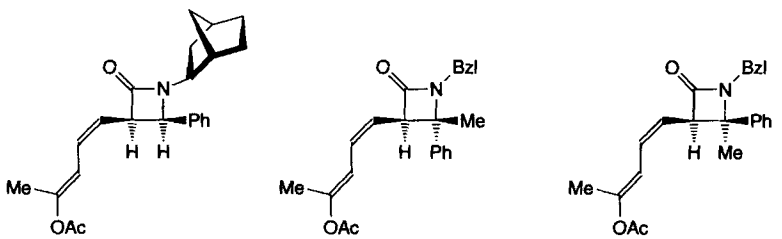
Fig. 21. *Representation of single-crystal X-ray structure of* rac-**55**

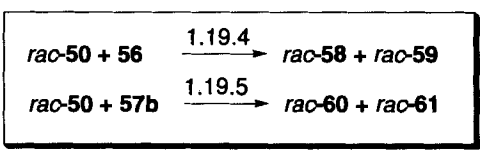
The diene-ketene transient (**C** + **D**) originating from *rac*-**1** reacts with imine **57a** to give a binary product consisting of *rac*-**4** and *rac*-**5** (*Scheme 1*). The β-lactam ring has the *trans*-configuration in both product components. The configuration of the diene system in the C(3)-substituents differs between the two diastereoisomers: (2′*Z*,4′*Z*)-geometry in *rac*-**4** and (2′*Z*,4′*E*) in *rac*-**5**.

Irradiation of *rac*-**50** in the presence of imines **56** or **57b** also leads to a binary product in either case. Here, however, the two sets of product components, *rac*-**58** + *rac*-**59**, and *rac*-**60** + *rac*-**61** (*Scheme 18*), differ in their configurations at the β-lactam ring.

Scheme 18





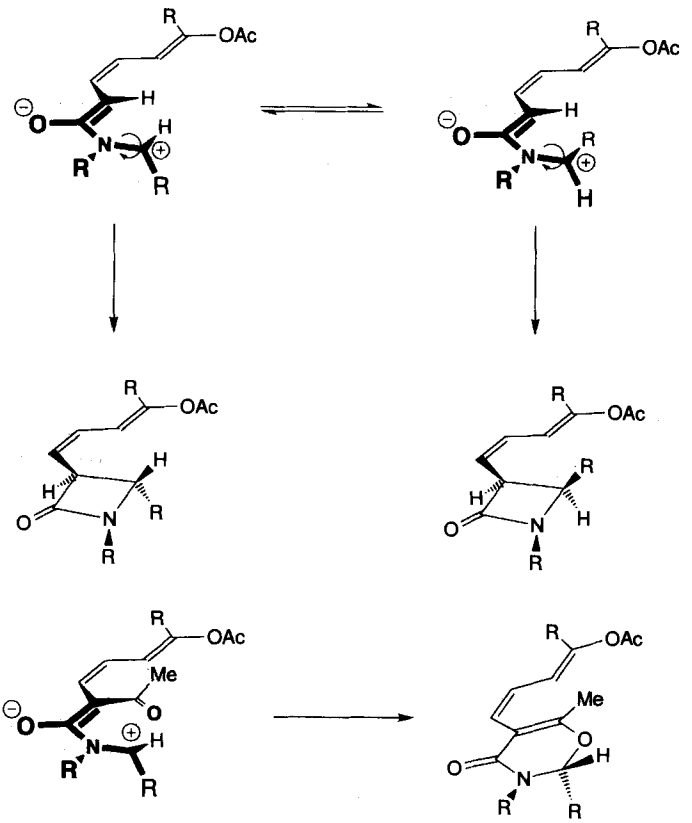


The examples given here for the preparation of β-lactams from ketenes and imines (*Staudinger* reaction) fit the assumption [37] of a non-concerted, stepwise course for this [2 + 2] cycloaddition: nucleophilic addition of the imine to the electrophilic C-atom of the ketene's C=O group results in the formation of a zwitterion transient, whose configurational stability dictates the complexity and stereostructure of the product components (*Scheme 19*), arising from a conrotatory cyclization. This assumption of a zwitterionic transient also serves to explain the reaction between *rac*-**62** and **52b**, giving *rac*-**63** (*Scheme 20*).

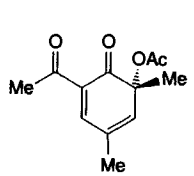
The oxazinone derivative *rac*-**63**, whose identity has been unequivocally established by X-ray crystal-structure analysis (*Fig. 22*), is produced under mild reaction conditions. It is easily hydrolyzed, transforming into *rac*-**64** (*Scheme 20*), which can also be obtained on irradiating *rac*-**62** in the presence of cyclohexylamine.

5. Interaction of Orbitals or Groups through Bond or through Space in the Conformational Equilibria of Cyclohexa-2,4-dienones. – These endeavors to construct a detailed, complete picture of the photochemistry of cyclohexa-2,4-dienones have highlighted the role played by the diene-ketene phototransients (see [28]: Sect. 3) arising from the (π^*,n)-excited *cyclo*-isomeric dienones. Here, the *Franck-Condon* principle applies, but not the *Curtin-Hammett* principle, so that the conformational make-up of the photo-

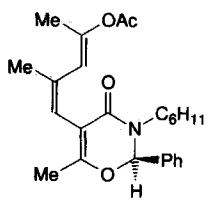
Scheme 19



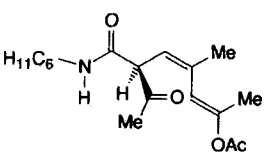
Scheme 20



62



63



64

rac-**62**	1.20.1 →	*rac*-**63**
rac-**62**	1.20.2 →	*rac*-**64**
rac-**63**	1.20.3 →	*rac*-**64**

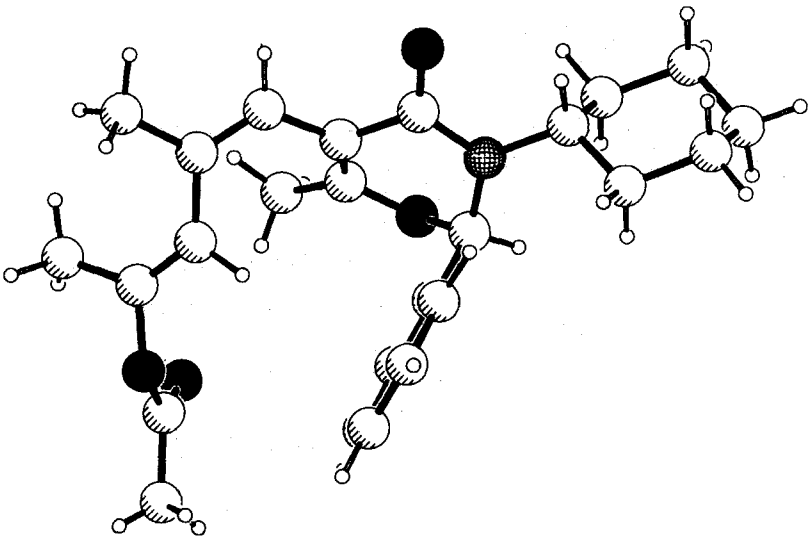


Fig. 22. *Representation of single-crystal X-ray structure of* rac-**63**

educt determines the configurational composition of the phototransient and – in the absence of any perturbations – of the photoproduct[20]). This is the case if equilibration between the dienone conformers in the electronic ground state comes about more slowly than ring-opening of the electronically excited dienone conformers, and if this ring opening proceeds stereospecifically, in accordance with the *least-motion principle*[21]).

The achiral photoeducts **A** and **O**, bearing identical substituents at C(6), represent special cases in *Scheme 21*, as here two diastereomorphically degenerate conformations coalesce into a single one with an idealized planar ring system. The C(5)=C(6) bond in the respective phototransients or photoproducts, moreover, is non-stereogenic. Constitutionally distinct substituents at C(6) result in nonplanar topology, and hence the existence of two diastereomorphic dienone conformers. Therefore, *rac*-**6** affords a binary phototransient, and consequently a binary photoproduct (see *Scheme 3*), as one would expect. However, this is not the case with *rac*-**9** (*Scheme 4*), *rac*-**N** (*Scheme 22*), *rac*-**50** (*Scheme 17* and [28]: Scheme 11), and *rac*-**33a** (*Scheme 10*) of the above series. It remains to be explained why, unlike with *rac*-**6**, only solitary phototransients or photoproducts appear in these instances, or, put in another way, why the dienone-conformer equilibrium lies entirely on one side for these compounds.

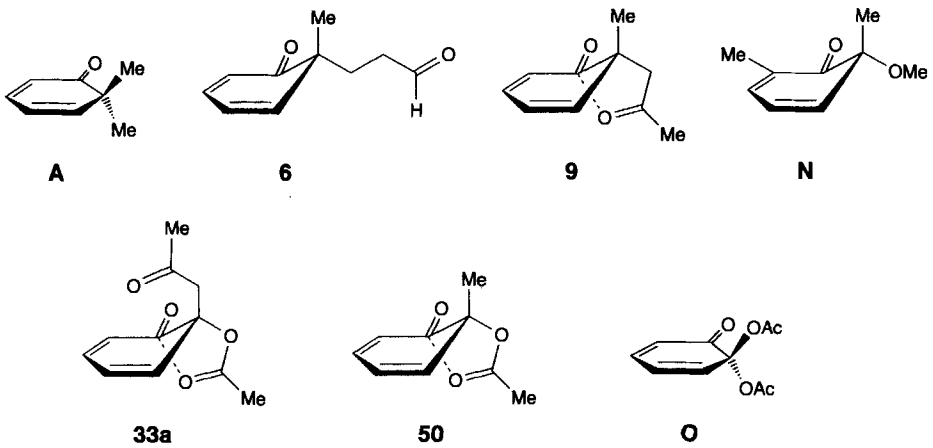
The *o*-quinolacetates of *rac*-**50**, reacting to give only phototransients of (5*E*)-configuration, has already been interpreted by invoking stabilizing interactions between the σ orbital of the C(6)–C(7) bond and the π^* orbital of the ring C=O group[22]), or

[20]) See discussion in [28]: Sect. 3.3.

[21]) Most authors commenting on the stereoselectivity of the ring opening of cyclohexa-2,4-dienones [38] have applied the *least-motion principle* to atomic nuclei instead to electrons. For the necessity for differentiating in this sence, see [39].

[22]) Separation between the antibonding π^* orbital and the bonding σ orbital filled with the electrons of the C(6)–C(7) bond is smaller (and their interaction stronger) than that between the former and the bonding σ orbital filled with the electrons of the C(6)–O bond.

Scheme 21



otherwise expressed, *stereoelectronic* promotion of that dienone conformation with a pseudoaxial Me group. Exclusive formation of that photoproduct of (5*E*)-configuration, however, cannot be explained in this manner in the case of *rac*-**9**. Thermodynamic promotion of that dienone conformation of pseudo-equatorial orientation of the 2-oxopropyl substituent at C(6), resulting from *through-space interaction* between the two polar C=O groups, certainly is the cause here. In a forthcoming publication we are going to discuss the detailed geometry of quite a few cyclohexa-2,4-dienones each obtained by single-crystal X-ray structure analysis.

Our photochemical investigations have substantially been backed up throughout the years by *Deutsche Forschungsgemeinschaft*, *Fonds der Chemischen Industrie*, and *Hoechst AG*. *M. Christof*, *U. May*, *E. Müller*, *A. K. Neumann*, and *G. Stracke* did the numerous analytical investigations. *J. Wermuth* executed many of the complex illustrations. *A. Dlabal*, as usual, has coped splendidly with the many successive versions of the manuscript. We are grateful to the mentioned persons for their assistance and to the indicated institutions for their generous support.

Experimental Part[23])

General. M.p. (uncorrected): *Kofler* hot-plate microscope. UV: *Cary 15*/*Zeiss PMQ II*/*Perkin-Elmer 552*. IR: *Beckman 4230*/*Perkin-Elmer 1600*; in cm^{-1}; band positions standardized with a calibration film on polystyrene. *NMR*: *Varian T60* (^{1}H-NMR)/*Bruker HX90* with *Nicolet 1080* computer/*Bruker WH 270* with *BNC 28* and *Aspect 2000* computer/*Nicolet NT 300 WB* with *NIC 1280* data processor/*Bruker AM 300* with *Aspect 3000* computer (^{1}H- and ^{13}C-NMR); δ values in ppm relative to TMS as internal standard (= 0.00 ppm); *J* in Hz; usual abbreviations apply for signal fine structure; a ψ prefix denotes pseudomultiplicity; f.s.: fine structure. Probes for NOE measurements were degassed in high vacuum and sealed; positions of ^{13}C-NMR signals were taken from the broad-band decoupled spectra, fine structure (*s*, *d*, *t*, *q*) from the 'off-resonance' spectra. If not mentioned otherwise, $CDCl_3$ was used as solvent in NMR measurements. *Optical rotations*: *Perkin-Elmer 241*; *c* in g/100 ml. MS: *Varian CH 7*/*Varian MAT SM 1 B*. TLC: glass plates 20 × 20 cm; silica gel *P*/*UV 254* + *366*, *Riedel de Haen*/preprepared silica gel *60F*/*UV 254*, *Merck* or *Woelm*; layer thickness 0.25 mm. Chromatograms were made visible using *Fluotest* (*Quarz-Lampengesellschaft*, Hanau), an oxidizing reagent based on cerium(IV) sulfate or I_2. Column chromatography (CC): silica gel (63–200 μ), *Macherey & Nagel*, *Merck*, or *Woelm*. *Flash*

[23]) In the first section of the *Exper. Part*, phototransients and photoproducts are described. The second section informs the reader how to prepare the related photoeducts.

chromatography (*FC*): silica gel (40–63 μm), *Merck. High-Pressure Liquid Chromatography* (HPLC) (stationary phase: *MN Nucleosil 50-10*). *Anal. HPLC*: *Waters 244 M 6 KA Cabinet System* with *BBC Metrawatt Servogor 220* two-channel potentiometer recorder. *Semi-Prep. HPLC*: *Waters 590* with *BBC Metrawatt Servogor 220* two-channel potentiometer. *Prep. HPLC*: *Waters Prep. LC System 500*; bracketed information gives, in order, mobile phase, pump throughput, detector wavelength, and/or volume injected if appropriate. Anal. GC: *Hewlett-Packard 5750/F & M Scientific Corporation Type 810*; 2.20 m × 2.5 mm; *Silicon Gum Rubber*, 10% UCCW 982, or 5% (or 3%) *XE 60* on *Chromosorb W-AW-DMCS* (80–100 mesh) or *Diataport W* (60–80 mesh); the injection block was heated to 250 or 270°, resp., the flame ionization detector to 245 or 300°, resp. N_2 as carrier gas; temp. given relate to the oven chamber. Prep. GC: *Hewlett-Packard* type *776*. *Elemental analyses* were performed by the own laboratory or the *Analytical Laboratory Malissa & Reuter*, Engelskirchen. Ozonolysis: Ozone generator *LO-50-1*, *Gebr. Herrmann*, Köln, Prep. and some anal. irradiations were performed in a *Southern New England Ultraviolet Co. Rayonet* reactor fitted with 3500-Å lamps. A four-wall, cylindrical *Pyrex* reaction vessel was used. The outermost compartment contained distilled water. The middle compartment (∅ = 1 cm) was filled with a filter soln. (0.01% aq. soln. of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene to cut off light of wavelengths < 340 nm), and the innermost one with the soln. to be irradiated which a gentle stream of dry N_2 was passed through *via* a capillary before and during the reaction, taking care that no evaporation did occur. The *workup procedures* for all the reactions leading to or away from cyclohexa-2,4-dienones were conducted under red light. The remainder of the *anal. irradiations* were performed on an optical bench in a quartz cuvette (pathlength 2, 10, or 20 mm, the latter equipped with a magnetic stirring bar, surrounded by a thermostatically controlled copper mantle and closed by a *Hostaflon* stopper); light-source: *HBO 200* (*Osram*); IR filter (H_2O); grating monochromator *Bausch & Lomb*, 1200 lines/mm (slit with 5/5 mm if not indicated otherwise); a parabolic mirror was mounted behind the cuvette at a distance matching its focal length; photoelement for wave-length calibration. *Low-temp. UV spectra* before and after irradiation were taken using a special cell (width: 1.275 cm; see [40]: Fig. 7) and a special setup (see [21b]: Fig. 5, and [40]: Fig. 8). *UV-Spectroscopically Determined Formal Analysis of Reaction Kinetics*: Irradiation in a special device (see [21b]: Fig. 5a and 5b, and [40]: Fig. 8) in a special cuvette (see [40]: Fig. 7), placed in the cuvette bay (see [40]: Fig. 9) of the *Cary 15*, was carried out using a *HBO 200* high-pressure lamp (*Osram*) in combination with a *Model 5* grating monochromator (*Bausch & Lomb*; split width: 10/10 mm). *Low-temp. IR spectra* before and after irradiation were obtained using a special cell (see [21b]: Fig. 6, and [18]: Figs. 3 and 4) in an appropriate device (see [19]: Fig. 18). *Quantum yields*: The experimental setup and its calibration have been described earlier (see [18]: Exper. 5.1.3.1–5.1.3.3, and [19]: Exper. 6.4.1.2.4.1 and 6.4.1.2.4.2). *Flash Spectroscopy*: a) *Experimental Setup and Calculation*: [19]: Fig. 20. Discharge of the condenser through the two flash lamps was initiated by a brief, low-energy, high-tension impulse from the spark generator; the photolysis flash had an electrical energy of 600 J and a full width at half maximum of *ca.* 10 μs. Disappearance of the diene-ketene and or formation of educt, transient or product was monitored by absorption spectroscopy at discrete wavelengths by measurement of transmission as a function of time. The U_0 signal, representing the transmitted light intensity of the soln. before photolysis, was determined using a digital voltmeter. For measurement times of up to 10 s, the measured signal U_1 was recorded digitally (transient recorder in pretrigger mode; triggering by optical cable and photodiode). It was then displayed directly onto an oscilloscope and either traced by recorder or puched onto paper-tape and entered into a computer for evaluation. For measurement times in excess of 10 s, the signal was passed directly to a recorder with constant feed. In this case, the measuring light was periodically interrupted by a shutter to keep its effect on the course of the reaction as slight as possible. Measurement were made on a cylindrical cuvette (*Suprasil*; internal diameter $d = 14$ mm, pathlength $l = 10$ cm; see [41]) or a cuvette of rectangular cross-section (*Suprasil*, internal dimensions 4 × 10 mm, pathlength $l = 10$ cm; see [42]). Thermostating of the cuvettes was performed by a Cu block in a horizontal fitted *Dewar* flask (*Suprasil*) to ± 0.2°. The flash-light was filtered using a cut-off filter (3 mm; *Schott*). b) *Interpretation*: The change in optical density (Δ(OD)) at wavelength λ and time t for i absorbing components is

$$\Delta(\mathrm{OD})_{\lambda,\,t} = d_i \cdot \varepsilon_{\lambda,i} \cdot c_{i,t} = \lg[U_0/(U_0 - U_t)]$$

assuming that the measured signals are proportional to light intensity. For measurement of transient spectra, the wavelength of the monitoring light was altered stepwise by 5 nm at r.t. The data given for transient spectra are, in order, the concentration of the dienone, the filter used, and the range of measurement. If several transients were observed, or if transmission did not re-attain the value of prior to the flash, then the Δ(OD) value was calculated for many reaction times. The maximum (minimum) of a Δ(OD) curve hence corresponds to the absorption maximum of the respective transient or product (transformed starting material), as long as no absorption of any further transient or product (the diene-ketene or the end-product) overlaps it. The intersection with the reference

line corresponds to the isosbestic point observed in spectroscopically homogenous reactions. Kinetic determinations made use of the measurements described in the preceding section (unless otherwise stated).

For simple processes, change in optical density over time followed first-order or pseudo-first-order kinetics. Data listed for the determination of activation parameters denotes, in order, the concentration of the dienone, the filter used, and the monitoring light wavelength. Activation energies E_a and frequency factors lg A were calculated by the method of *Arrhenius*, activation enthalpies ΔH, activation entropies ΔS, and free activation energies ΔG_{25} by that of *Eyring*, straight-line gradients lg k *vs.* $1/T$ or lg (k/T) *vs.* $1/T$ were determined with the aid of a linear regression program: Maximum error in the rate constants is ± 10%, in E_a ΔH and ΔG values ± 0.5 kcal/mol, and for ΔS values ± 3 cal/(mol · K).

In the case of competing first-order or pseudo-first-order reactions, the concentration of all participating components varies with the sum of the rate constants for all processes (for interpretation, see [12]: Sect. 5.2.1.2.2.2, and [43]: Chapt. 1.II.1; for interpretation of secondary reactions, see [12]: Sect. 5.2.1.2.2.3). For calculation of percentage involvement in recyclization and product formation at a particular temp., the relevant transmission/time curves of the Δ(OD) values of dienone and product at the beginning and end of measurement were taken. Inhouse-developed programs were used to calculate rate constants and *Arrhenius* and *Eyring* parameters, using the university's *DEC-1091* (mainframe) computer.

Solvents were distilled before use: Et_2O, THF (Na-benzophenone), toluene (Na), MeCN (CaH_2), MeOH (Mg), or filtered: CH_2Cl_2 and DMF (alumina *B*, Act. I; *ICN*). $Pb(OAc)_4$ was crystallized from glacial AcOH, dried *in vacuo*, and stored under Ar at −15° for *Wessely* acetoxylations. All reactions were carried out under N_2, unless otherwise stated. For reactions in CH_2Cl_2 or $(CH_2Cl)_2$, CH_2Cl_2, for reactions in Et_2O, THF or i-BuOH, Et_2O was used for distribution of the particular product between that org. solvent and sat. aq. $NaHCO_3$ soln. (*basic workup*), aq. HCl soln. (*acidic workup*), or sat. aq. NH_4Cl soln. (*usual workup*). The org. layer was washed with brine, dried ($MgSO_4$), filtered (silica gel), and evaporated. Single-crystal structure determination at r.t. (−160° for *rac*-**19**) with *Enraf Nonius CAD4* diffractometer (CuK_α) by direct methods. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/55. Copies of the data can be obtained, free of charge, on application to the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-(0)1223-336033 or e-mail: teched@chemcrys.cam.ac.uk).

1. Irradiation of Individual Cyclohexa-2,4-dienones. – 1.1. *Irradiation of* **1** (see *Scheme 1*). 1.1.1. *In Anh.* Et_2O. A soln. of **1** (121 mg; for preparation, see *Exper. 2.2*) in anh. Et_2O (200 ml) was irradiated for 12 min using the prep. reaction vessel. The solvent was removed with a rotary evaporator to yield a yellow oil, which was filtered through silica gel (10 g; hexane/Et_2O 1:1), and after evaporation to give **1**/*ent*-**1** > 1. $[\alpha]_{589}$ = + 49.5 (c = 0.847, CH_2Cl_2); $[\alpha]_{578}$ = + 50.9; $[\alpha]_{546}$ = + 56.4; $[\alpha]_{436}$ = − 28.9. Spectroscopic data identical with those of **1** (*Exper. 2.2*). A soln. of **1** (100 mg) in anh. Et_2O (150 ml) was irradiated for 1 h to afford optically inactive *rac*-**1**, following the same workup as above.

1.1.2. *In the Presence of Excess Cyclohexylamine.* A soln. of **1** (166 mg; 0.90 mmol) and freshly distilled cyclohexylamine (51.5 ml; 430 mmol) in anh. Et_2O (248.5 ml) was irradiated for 12 min (62% conversion) according to HPLC (hexane/MeOAc 100:3 + 25% CH_2Cl_2; 0.5 ml/min; refract.). After acidic workup, the residue was purified by prep. HPLC (hexane/AcOEt 30:13; 5 ml/min; refract.) and separated by semi-prep. HPLC (hexane/AcOEt 5:1; 2 ml/min; refract. and 254 nm) to give **1** (52 mg; 32%; $[\alpha]_{589}$ = + 109.7 (c = 0.746, CH_2Cl_2); $[\alpha]_{578}$ = + 114.4; $[\alpha]_{546}$ = + 126.1; $[\alpha]_{436}$ = − 74.5) and a mixture **2a**/**3a** which was separated by semi-prep. HPLC (hexane/i-PrOAc 3:2; 10 ml/min; refract.) to afford 93 mg (48% rel. to conversion) of **2a** and 40 mg (21% rel. to conversion) of **3a**.

(3Z,5Z)-N-Cyclohexyl-6-phenylhepta-3,5-dienamide (**2a**): M.p. 101° (CH_2Cl_2/pentane). TLC (hexane/AcOEt 1:1): R_f 0.54. UV (MeOH): λ_{max} 253.6 (17303). IR (KBr): 3247*s* (N–H); 3076*m*, 3051*w* (unsat. C–H); 2936*s*, 2851*m* (sat. C–H); 1659*s*, 1570*s* (C=C); 1636*s* (amide); 1449*w*, 1345*w*, 1349*w*, 1255*w*, 1187*w*, 1026*w*, 770*m*, 721*m*, 700*s*. ^{1}H-NMR: 1.04–1.92 (*m*, 10 H, 2 H–C(2′) through 2 H–C(6′)); 2.16 (*s*, 3 H–C(7)); 3.16 (*d*, *J*(H–C(2),H–C(3)) = 7.8, 2 H–C(2)); 3.71–3.85 (*m*, H–C(1′)); 5.43 (*dd*, *J*(H–C(3),H–C(2)) = 8.0, *J*(H–C(3),H–C(4)) = 17.1, H–C(3)); 5.56 (br. *s*, N–H); 6.20–6.35 (*m*, H–C(4), H–C(5)); 7.18–7.39 (*m*, 5 arom. H). Anal. calc. for $C_{19}H_{25}NO$ (283.41): C 80.52, H 8.89, N 4.94; found: C 80.28, H 9.05, N 4.88.

(3Z,5E)-N-Cyclohexyl-6-phenylhepta-3,5-dienamide (**3a**): M.p. 120–121° (CH_2Cl_2/pentane). TLC (hexane/AcOEt 1:1): R_f 0.54. UV (MeOH): λ_{max} 281.5 (23937). IR (KBr): 3290*s* (N–H); 3075*w*, 3051*w*, 3030*w* (unsat. C–H); 2931*m*, 2851*w* (sat. C–H); 1636*s* (amide); 1550*s* (C=C); 1446*m*, 1408*m*, 1351*w*, 1246*m*, 756*m*, 698*m*. ^{1}H-NMR: 1.02–1.90 (*m*, 10 H, 2 H–C(2′) through 2 H–C(6′)); 2.20 (*s*, 3 H–C(7)); 3.21 (*d*, *J*(H–C(2),H–C(3)) = 7.8, 2 H–C(2)); 3.70–3.84 (*m*, H–C(1′)); 5.54 (br. *s*, N–H); 5.64–5.76 (*m*, H–C(3));

6.56–6.68 (*m*, H–C(4), H–C(5)); 7.23–7.46 (*m*, 5 arom. H). Anal. calc. for $C_{19}H_{25}NO$ (283.41): C 80.52, H 8.89, N 4.94; found: C 80.22, H 8.94, N 4.91.

1.2. *Irradiation of* ent-**1** (see *Scheme 1*). 1.2.1. *In Anh. Et_2O.* A soln. of *ent*-**1** (78 mg; for preparation, see *Exper. 2.3*) in anh. Et_2O (150 ml) was irradiated for 12 min following the procedure of *Exper. 1.1.1* to give **1**/*ent*-**1** < 1 (76 mg): $[\alpha]_{589} = -50.1$ ($c = 0.650$ in CH_2Cl_2); $[\alpha]_{578} = -51.3$; $[\alpha]_{546} = -56.8$; $[\alpha]_{436} = +29.5$. Spectroscopic data identical with those of **1** (*Exper. 2.2*). A soln. of *ent*-**1** (100 mg) in anh. Et_2O was irradiated for 1 h to afford optically inactive *rac*-**1**, following the same workup as above.

1.2.2. *In the Presence of Excess Cyclohexylamine.* A soln. of *ent*-**1** (166 mg; 0.90 mmol) and freshly distilled cyclohexylamine (51.5 ml; 430 mmol) in anh. Et_2O (248.5 ml) was irradiated according to *Exper. 1.1.2*. After 13.5 min (62% conversion), the reaction was stopped to give *ent*-**1** (50 mg; 31%; $[\alpha]_{589} = -109.0$ ($c = 0.578$ in CH_2Cl_2); $[\alpha]_{578} = -113.8$; $[\alpha]_{546} = -126.8$; $[\alpha]_{436} = +76.4$), **2a** (96 mg; 50%), and **3a** (46 mg; 24%). Spectroscopic data of **2a** and **3a** were identical with those from *Exper. 1.1.2*.

1.3. *Irradiation of* rac-**1**. 1.3.1. *At r.t.* 1.3.1.1. *In the Presence of Cyclohexylamine.* 1.3.1.1.1. *Preparative.* To a soln. of *rac*-**1** (1.25 g; 6.78 mmol; for preparation, see *Exper. 2.1*) in Et_2O (300 ml) freshly distilled cyclohexylamine (1.35 ml; 13.6 mmol; 2 equiv.) was added and the mixture irradiated for 4.5 h. Anal. GC followed disappearance of *rac*-**1** and formation of (**2a** + **3a**) side by side (ratio 1:1.85). After acidic workup, a solid material remained which was recrystallized from Et_2O to afford 1.77 g (92%) of (**2a** + **3a**). Separation of the amides by prep. HPLC gave **2a** (0.56 g, 29%) and **3a** (1.04 g, 54%), with data identical with those under *Exper. 1.1.2*.

1.3.1.1.2. *Formal Analysis of Reaction Kinetics.* 1.3.1.1.2.1. *With 365-nm Light*: A soln. of *rac*-**1** ($6.36 \cdot 10^{-5}$ M) and cyclohexylamine ($97.7 \cdot 10^{-5}$ M) in MCI was irradiated for 620 min. The absorption spectra taken after 0, 270, 600, 900, 1200, 1560, 1980, 2460, 3000, 5040, 6840, 8640, 12360, 17940, and 37200 s at 25° intersect at an isosbestic point (λ 306 (3540); *Fig. 1,a*) and undergo a hypsochromic shift (λ_{max} 266 (16270)). The corresponding ED diagram (*Fig. 1,b*) is linear.

1.3.1.1.2.2. *With 313-nm Light*: A soln. of *rac*-**1** ($5.67 \cdot 10^{-5}$ M) and cyclohexylamine ($87.2 \cdot 10^{-5}$ M) in MCI was irradiated for 2885 s at 25° as in *Exper. 1.3.1.1.2.1.* The absorption spectra taken after 0, 65, 125, 185, 285, 395, 515, 635, 795, 1005, 1185, 1665, and 2885 s do not intersect at an isosbestic point (*Fig. 2,a*). In contrast to the EDQ diagram (*Fig. 2,c*), the corresponding ED diagram (*Fig. 2,b*) is nonlinear.

1.3.1.1.2.3. *At Various Concentrations of Cyclohexylamine* (see *Fig. 5*). A soln. of *rac*-**1** ($1.511 \cdot 10^{-4}$ M) and cyclohexylamine ($7.30 \cdot 10^{-2}$ M (ΔΔΔ); $1.35 \cdot 10^{-1}$ M (□□□), and $1.73 \cdot 10^{-1}$ M (○○○)) in Et_2O/isopentane 1:1 were irradiated with 365-nm light. The gradient of the straight-lines in the corresponding linear ED diagram were independent of the nucleophile concentration.

1.3.1.1.2.4. *Analytical Isomerization of* **2a** *at 25°*. A soln. of **2a** ($5.01 \cdot 10^{-5}$ M) was irradiated for 45 min with 313-nm light leading to a linear ED diagram (*Fig. 3*). Using the molar absorption coefficients at 313 nm for **2a** ($\varepsilon = 4980$) and **3a** ($\varepsilon = 540$), according to the *Beer-Lambert* law at photostationary state, **3a** predominates by 92 ± 3%. For the reverse isomerization, 94 ± 3% of **3a** were found.

1.3.1.1.3. *Quantum Yields at 25° in Et_2O/Isopentane.* The quantum yield for the disappearance of *rac*-**1** ($1.511 \cdot 10^{-4}$ M) in the presence of cyclohexylamine ($1.726 \cdot 10^{-1}$ M) amounted to 0.559 ± 0.010 (0.548 ± 0.007) in the absence (presence) of (*Z*)-penta-1,3-diene.

1.3.1.1.4. *Flash Spectroscopy.* 1.3.1.1.4.1. *At r.t. in the Absence of a Protic Nucleophile* (see *Fig. 14,a*). A soln. of *rac*-**1** ($5 \cdot 10^{-4}$ M) in MCI was flashed: filter *WG 295*; 330 through 650 nm. The lifetime of the transient detectable at 330 nm lies in the min range and could, therefore, not be determined quantitatively.

1.3.1.1.4.2. *At r.t. in the Presence of Cyclohexylamine* (see *Fig. 14,b*). A soln. of *rac*-**1** ($5 \cdot 10^{-4}$ M) and cyclohexylamine ($5 \cdot 10^{-4}$; $1.25 \cdot 10^{-3}$; $2.5 \cdot 10^{-3}$; $3.75 \cdot 10^{-3}$, $5 \cdot 10^{-3}$; $1 \cdot 10^{-2}$ M) in MCI at r.t. was flashed. The decay of the transient detectable at 330 nm is of first-order with rate constants $k[s^{-1}]$ (40; 200; 680; 1300; 2000; 4800).

1.3.1.1.4.3. *At Various Temp. in the Presence of Cyclohexylamine.* A soln. of *rac*-**1** ($5 \cdot 10^{-4}$ M) and cyclohexylamine ($5 \cdot 10^{-3}$ M) in MCI was flashed at r.t. (*Fig. 14,c*) and at −50° (*Fig. 14,d*). The two oscillograms demonstrate an increase of the decay rate with decreasing temp. For quantitative data, see *Table 3*.

1.3.1.2. *In the Presence of an Alcohol.* 1.3.1.2.1. *Preparative.* A soln. of *rac*-**1** (3.5 g; 19 mmol) and EtOH (20 ml) in anh. Et_2O (200 ml) was irradiated for 20 h. Reaction progress was monitored by anal. GC. After 3.5 h, *rac*-**1** had disappeared, and **2b** and **3b** formed. Further irradiation caused isomerization of **2b** and **3b** leading to a quartett of product-components **66**/**3b**/**2b**/**65** 4:3:1:2. After removal of solvent, under reduced pressure, the isolated product was purified by bulb-to-bulb distillation (90–120°/0.01 Torr) to give a colorless oil (3.87 g; 88.5%), which was fractionated by prep. GC, accentuating pure compounds rather than optimal yields. The fractions were each purified by bulb-to-bulb distillation to yield **2b** (560 mg; b.p. 100–120°/0.01 Torr), **3b** (310 mg; b.p. 170–180°/0.03 Torr), **65** (710 mg; b.p. 125–130°/0.02 Torr), and **66** (480 mg; b.p. 120–130°/0.01 Torr), and identified by comparing their spectroscopic data with those of the corresponding *N*-cyclohexyl amides [22].

Table 3. *Data at Various Temperatures after Flashing* rac-**1** *in the Presence of Cyclohexylamine*

Temp. [°]	$1000/_T$	k(a)	log k(a)	k(b)	log k(b)
+20	3.413	69	1.840	168	2.256
0	3.663	268	2.429	520	2.716
−10	3.802	391	2.592	805	2.906
−20	3.953	595	2.755	1224	3.088
−30	4.115	1030	3.013	1825	3.260
−40	4.292	1460	3.164	2825	3.450
−50	4.484	2227	3.348	4250	3.630
−60	4.695	4080	3.611	6890	3.840

Ethyl (3Z,5Z)-6-Phenylhepta-3,5-dienoate (**3b**): UV (Et_2O): λ_{max} 254 (19800). IR (film): 1740*s* (ester). ^{1}H-NMR: 1.27 (*t*, *J*(*Me*CH_2O, MeCH_2O) = 7, *Me*CH_2O); 2.13 (*s*, 3 H–C(7)); 3.25 (*d*, *J*(H–C(2),H–C(3)) = 6, 2 H–C(2)); 4.17 (*q*, *J*(MeCH_2,*Me*CH_2O) = 7, MeCH_2O); 5.20–6.50 (*m*, H–C(3), H–C(4), H–C(5)); 7.26 (m_c, 5 arom. H). Anal. calc for $C_{15}H_{18}O_2$ (230.29): C 78.23, H 7.88, O 13.89; found: C 78.15, H 7.90, O 14.00.

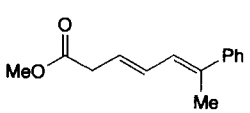
Ethyl (3Z,5E)-6-Phenylhepta-3,5-dienoate (**2b**): UV (Et_2O): λ_{max} 278 (24200). IR (film): 1740 (ester). ^{1}H-NMR: 1.23 (*t*, *J*(*Me*CH_2O, MeCH_2O) = 7, *Me*CH_2O); 2.13 (*s*, 3 H–C(7)); 3.28 (*d*, *J*(H–C(2),H–C(3)) = 6.2, H–C(2)); 4.16 (*q*, *J*(MeCH_2O, *Me*CH_2O) = 7, MeCH_2O); 5.50–6.70 (*m*, H–C(3), H–C(4), H–C(5)); 7.20–7.50 (*m*, 5 arom. H). Anal. cal. for $C_{15}H_{18}O_2$ (230.29): C 78.23, H 7.88, O 13.89; found: C 78.00, H 7.81, O 14.14.

Ethyl (3E,5Z)-6-Phenylhepta-3,5-dienoate (**66**): UV (Et_2O): λ_{max} 251 (17800). IR (film): 1740 (ester), 965 ((*E*)–CH=CH). ^{1}H-NMR: 1.20 (*t*, *J*(*Me*CH_2O, MeCH_2O) = 7, *Me*CH_2O); 2.10 (*s*, 3 H–C(7)); 3.02 (*d*, *J*(H–C(2),H–C(3)) = 6, 2 H–C(2)); 4.13 (*q*, *J*(MeCH_2O, *Me*CH_2O) = 7, MeCH_2O); 5.40–6.40 (*m*, H–C(3), H–C(4), H–C(5)); 7.30 (m_c, 5 arom. H). Anal. calc for $C_{15}H_{18}O_2$ (230.29): C 78.23, H 7.88, O 13.89; found: C 77.71, H 8.07, O 14.08.

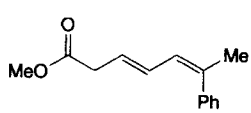
Ethyl (3E,5E)-6-Phenylhepta-3,5-dienoate (**65**): UV (Et_2O): λ_{max} 278 (29400). IR (film): 1740 (ester), 960 ((*E*)–CH=CH). ^{1}H-NMR: 123 (*t*, *J*(MeCH_2O, *Me*CH_2O) = 7, MeCH_2O); 2.11 (*s*, 3 H–C(7)); 3.18 (*d*, *J*(H–C(2),H–C(3)) = 6, 2 H–C(2)); 4.16 (*q*, *J*(MeCH_2O, *Me*CH_2O) = 7, MeCH_2O); 5.60–6.70 (*m*, H–C(3), H–C(4), H–C(5)); 7.20–7.50 (*m*, 5 arom. H). Anal. calc for $C_{15}H_{18}O_2$ (230.29): C 78.23, H 7.88, O 13.89; found: C 77.79, H 7.81, O 14.20.

1.3.1.2.2. *Formal Analysis of Reaction Kinetics.* 1.3.1.2.2.1. *With 365-nm Light.* A soln. of *rac*-**1** ($4.34 \cdot 10^{-5}$ M) in EtOH was irradiated for 1770 s at 25° according to *Exper. 1.3.1.1.2.* The absorption spectra taken after 0, 30, 105, 240, 450, 750, 1170, and 1770 s intersect at an isosbestic point (λ 306 (3770); see [21b]: Fig. 16A) and undergo a hypsochromic shift (λ_{max} 268 (16690)). The corresponding diagram of extinction differences (see [21b]: Fig. 16B) is linear. HPLC Analysis (hexane/AcOEt 50:1; 2 ml/min; 313 nm) of the various samples show a constant ratio of **2b**/**3b** 1.2:1.

1.3.1.2.2.2. *With 313-nm Light.* A soln. of *rac*-**1** ($5.34 \cdot 10^{-5}$ M) in EtOH was irradiated for 750 min at 25° as in *Exper. 1.3.1.1.2.1.* The absorption spectra taken after 0, 30, 75, 135, 210, 330, and 570, 5280, 6470, and 45000 s did not intersect at an isosbestic point (see [21b]: Fig. 17A). In contrast to the EDQ diagram (see [21b]: Fig. 17B), the corresponding ED diagram (see [21b]: Fig. 17C) was nonlinear. HPLC Analysis (*vide supra*) of the various samples showed a change in the ratio of **2b**/**3b** finally leading to 1:10.



65



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1.3.1.2.2.3. *With 365- and Then with 313-nm Light* (see *Fig. 4*). A soln. of *rac*-**1** ($1.995 \cdot 10^{-4}$ M) in EtOH was irradiated at 25° with 365-nm light: the straight lines (——) of the corresponding linear ED diagram intersected at the origin of the coordinate system. When the reaction had been completed, 313-nm light was used: the straight-lines obtained (– – – –) each started at the end of the straight-lines due to 365-nm light.

1.3.1.2.2.4. *At Various Concentrations of EtOH* (see *Fig. 6*). A soln. of *rac*-**1** ($1.511 \cdot 10^{-4}$ M) and EtOH ($8.05 \cdot 10^{-2}$ M (□□□); $1.71 \cdot 10^{-1}$ M (○○○)) in Et_2O/isopentane 1:1 was irradiated at 25° with 365-nm light. The corresponding linear ED diagram contained straight-lines the gradients of which were dependent on nucleophile concentration.

1.3.1.2.3. *Ratio of Product Components.* A soln. of *rac*-**1** in EtOH, provided with Ph_2O ($4.367 \cdot 10^{-3}$ M as reference compound for HPLC: hexane/AcOEt 50:1; 2 ml/min; 313 nm for educt, 280 nm for product), was irradiated on an optical bench.

1.3.1.2.3.1. *With 365-nm Light* (conc. of *rac*-**1**; photovoltage at the sample; decay of educt; irradiation time; conc. of **2b**; conc. of **3b**; ratio of **2b**/**3b**; chemical yield): $1.874 \cdot 10^{-3}$ M; 265 μA; 99.5%; 50 min; $7.817 \cdot 10^{-4}$ M; $9.319 \cdot 10^{-4}$ M; 1:1.2; 91.5%.

1.3.1.2.3.2. *With 313-nm Light:* $1.874 \cdot 10^{-3}$ M; 56 μA; 99.4%; 195 min; $1.524 \cdot 10^{-4}$ M; $1.551 \cdot 10^{-3}$ M; 1:10; 91%.

1.3.1.2.3.3. *With 365-nm Light* (conc. of *rac*-**1**; photovoltage at the sample; decay of educt; irradiation time): $1.834 \cdot 10^{-3}$ M; 210 μA; 99.7%; 70 min; HPLC analysis after 15, 20, 25., 30, 35, 40, 50, 60, and 70 min showed a constant ratio of **2b**/**3b** 1:1.2.

1.3.1.2.3.4. *With 313-nm Light*: $1.834 \cdot 10^{-3}$ M; 44 mA; 99.6%; 210 min. HPLC Analysis after 107, 120, 135, 150, 165, 180, 190, and 210 min showed a steady shift of the ratio of **2b**/**3b** in favor of **3b** finally up to 1:10.

1.3.1.2.4. *Quantum Yields.* 1.3.1.2.4.1. *With 365-nm Light in Isopentane:* 1. Run: $4.60 \cdot 10^{-3}$ M; $13.73 \cdot 10^{-3}$ M; (3.0); 1.335; 362 min (4.2%); $4.468 \cdot 10^{13}$ quanta/s; 0.255 ± 0.012. 2. Run: $4.50 \cdot 10^{-3}$ M; $20.6 \cdot 10^{-3}$ M (4.6); 1.324; 345 min (6.6%); $4.486 \cdot 10^{13}$ quanta/s; 0.391 ± 0.01. 3. Run: $4.66 \cdot 10^{-3}$ M; $27.46 \cdot 10^{-3}$ M (5.9); 1.338; 367 min (8.9%); $4.468 \cdot 10^{13}$ quanta/s; 0.391 ± 0.009. 4. Run: $4.60 \cdot 10^{-3}$ M; $35.7 \cdot 10^{-3}$ M (7.76); 1.380; 280 min (7.4%); $4.468 \cdot 10^{13}$ quanta/s; 0.526 ± 0.006. 5. Run: $4.40 \cdot 10^{-3}$ M; $41.2 \cdot 10^{-3}$ M (9.4); 1.312; 413 min (11.6%); $4.468 \cdot 10^{13}$ quanta/s; 0.550 ± 0.006. 6. Run: $4.44 \cdot 10^{-3}$ M; $44.62 \cdot 10^{-3}$ M (10); 1.359; 353 min (10.6%); $4.468 \cdot 10^{13}$ quanta/s; 0.574 ± 0.007. 7. Run: $4.50 \cdot 10^{-3}$ M; $85.8 \cdot 10^{-3}$ M (19); 1.400; 360 min (10.4%); $4.468 \cdot 10^{13}$ quanta/s; 0.580 ± 0.012. 8. Run: $4.60 \cdot 10^{-3}$ M; $172 \cdot 10^{-3}$ M (37.4); 1.386; 353 min (10.5%); $4.468 \cdot 10^{13}$ quanta/s; 0.588 ± 0.015. 9. Run: $4.10 \cdot 10^{-3}$ M; $172 \cdot 10^{-3}$ M (42); 1.224; 300 min (9.5%); $4.468 \cdot 10^{13}$ quanta/s; 0.580 ± 0.015.

1.3.1.2.4.2. *With 365-nm Light in EtOH.* 1. Run: $3.96 \cdot 10^{-3}$ M; –; (–); 2.133; 406 min (12.5%); $3.947 \cdot 10^{13}$ quanta/s. 2. Run: $3.7 \cdot 10^{-3}$ M; –; (–); 2.037; 360 min (11.5%); $3.947 \cdot 10^{13}$ quanta/s.; mean value for runs 1 and 2 of $\phi = 0.579 \pm 0.01$.

1.3.1.2.5. *Flash Spectroscopy.* 1.3.1.2.5.1. *At or Near r.t. in Cyclohexane.* 1.3.1.2.5.1.1. *Transient Spectrum* ($c = 1.2 \cdot 10^{-5}$ M soln. of *rac*-**1**, *WG 295*; 260 through 360 nm; see *Fig. 23,a*): λ_{max} at *ca.* 300 nm.

1.3.1.2.5.1.2. *Difference Spectra during Flash Photolysis of* rac-**1**: By extrapolation to $t = 0$ ms the ketene transient ($\lambda_{max} \approx 290$ nm) becomes visible; see *Fig. 23,b*.

1.3.1.2.5.1.3. *Kinetics*: At 10°; 300 nm; 4.62 V; 1 scale unit to 100 s (see *Fig. 23,c*); at 55°; 300 nm; 5.34 V; 1 scale unit to 1 s (see *Fig. 23,d*); with rates of decay (k_d) of the ketene transient (see *Fig. 23,e* and *f*).

Activation parameters were extracted from the *Arrhenius* diagram (*Fig. 24*).

The values for k_d [s^{-1}] and τ [s] at various temp. (between 10 and 55°): 10°: 0.005; 200. 15°: 0.008; 125. 20°: 0.012; 83. 25°: 0.013; 77. 30°: 0.021; 48. 35°: 0.32; 31. 40°: 0.043; 23. 45°: 0.058; 17. 50°: 0.082; 12. 55°: 0.101; 10.

1.3.1.2.5.2. *In MeOH*: 1.3.1.2.5.2.1. *Electronic Absorption Spectra of* rac-**1** (——), **2c** (– – – –), *and* **3c** (–·–·–) (*Fig. 10,a*); *Transient Spectra* ($c = 5.61 \cdot 10^{-5}$ M of *rac*-**1** in MeOH; *WG 295*; 250 through 390 nm; see *Fig. 10,b*). By extrapolation to $t = 0$ ms, the ketenes **C** and **D** (maximum at 295 nm) become visible. According to Δ(OD) curve obtained after 1 ms, they are followed by enol-esters (maximum at *ca.* 330 nm which has disappeared after 45 ms). At that time, the Δ(OD) curve shows a maximum at *ca.* 270 nm (**2c** and **3c**), a minimum at 315 nm (*rac*-**1**, reacted), and a crossing of the 0 line at 305 nm.

1.3.1.2.5.2.2. *Kinetics* (see *Fig. 10,c*; column *A*: 1 scale unit to 5 ms; column *B*: 1 scale unit to 0.5 ms). *IA* and *IB* (270 nm; 0.70 V) as well as *IIA* and *IIB* (280 nm; 0.70 V): the ketenes, enol-esters, and esters absorb similarly here and much stronger than *rac*-**1**. *IIIA* and *IIIB* (295 nm; 0.70V): decay of ketenes to esters without resolution in separate steps. *IVA* and *IVB* (315 nm; 0.75 V) as well as *VA* and *VB* (330 nm; 0.75 V): The enol-esters cause an initial deviation from a steady decrease of extinction. *VIA* and *VIB* (360 nm; 1.00 V): rise and fall of enol-esters.

1.3.2. *At Low Temp.* 1.3.2.1. *In the Presence of EtOH.* 1.3.2.1.1. *Formal Analysis of Reaction Kinetics.* Solns. of *rac*-**1** in EPA were irradiated at –185° (conc. of *rac*-**1**; slit widths of monochromator; irradiation time).

1.3.2.1.1.1. *At 365-nm Light:* $2.75 \cdot 10^{-5}$ M; 10/10; 14700 s. The absorption curves (*Fig. 25,a*) taken after 0, 180, 420, 660, 900, 1200, 1620, 2160, 2940, 3960, 5280, 7500, and 14700 s intersected in an isosbestic point (221 nm (6450)) and were shifted bathochromically (308 nm (24640)). The corresponding ED diagram (*Fig. 25,b*) was linear.

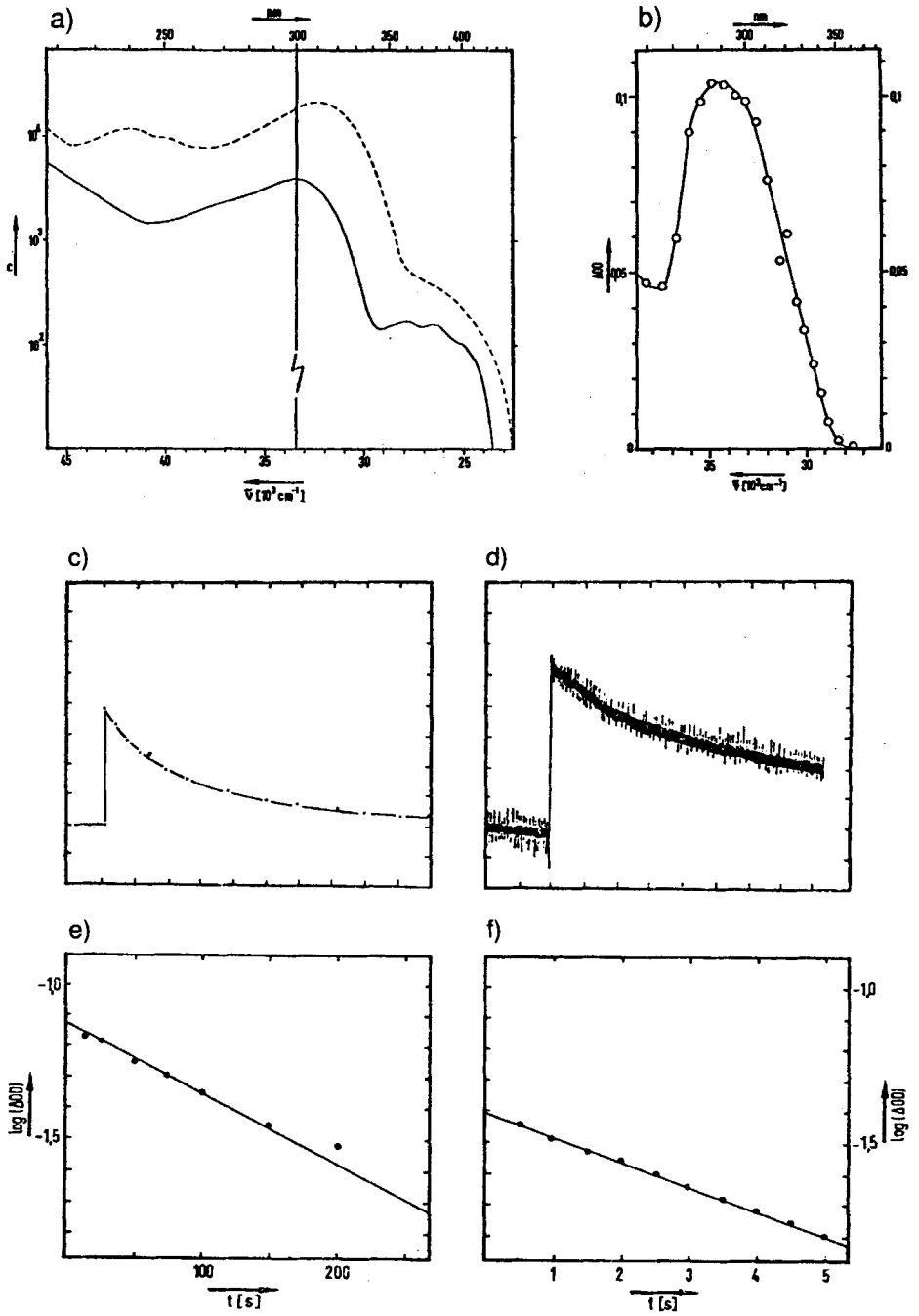


Fig. 23. a) *Electronic absorption spectra at r.t. of* rac-**1** (——) *and the related ketene transient* (**C** + **D**)(– – – –) *in cyclohexane*; b) *difference spectrum for flash photolysis of* rac-**1** *in cyclohexane; transmission/time plots* (*c* and *d*) *and their kinetic representation* (*e* and *f*) *at 10°* (*c* and *e*) *or 55°* (*d* and *f*)

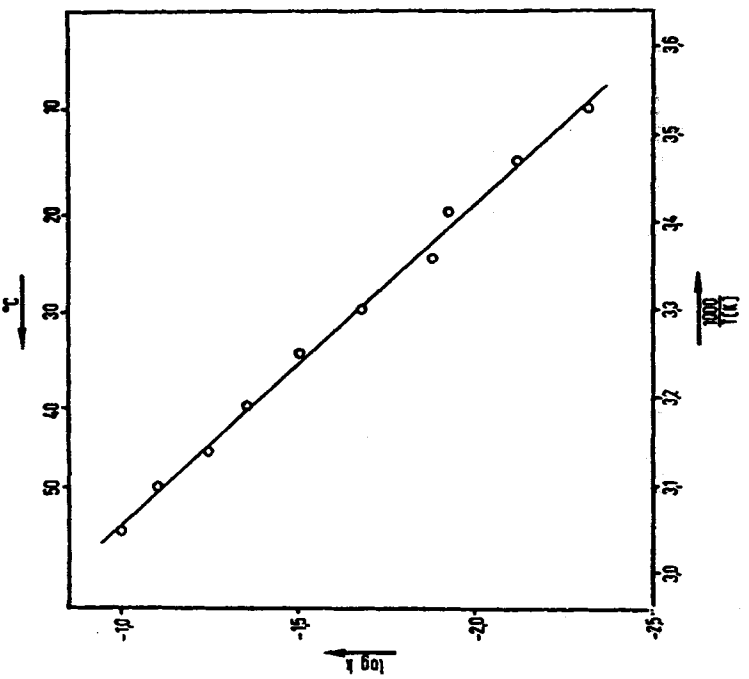


Fig. 24. Arrhenius *diagram for the decay of the ketene transient due to* rac-**1**

1.3.2.1.1.2. *At 313-nm Light.* $2.76 \cdot 10^{-5}$ M; 10/10; 9550 s. The absorption curves (*Fig. 26,a*) taken after 0, 40, 102, 162, 222, 302, 433, 603, 813, 1150, 1750, 2950, 5050, and 9550 s intersected in an isosbestic point (221 nm (7800)) and were shifted bathochromically (309 nm (24500)). The corresponding ED diagram (*Fig. 26,b*) was linear.

1.3.2.1.2. *UV-Spectroscopical Proof in EPA of a Phototransient that Thermally Reacts Producing* **2b** *and* **3b** (see *Fig. 9*). A soln. of *rac*-**1** ($3.634 \cdot 10^{-5}$ M) in EPA was irradiated at $-185°$ with 365-nm light for 150 min using the cell and setup of *Exper. 1.3.2.1.1.* The hyperchromically shifted absorption (λ_{max} 309 nm) of the irradiated sample disappeared at warming to $-163°$ for 210 min leaving a spectrum that was composed of the absorption of **2b** and **3b** (λ_{max} 278 nm) as well as of another transient absorbing at 350 nm. The spectrum of the latter was easily obtained by difference spectra at $-163°$ before and after warming temporarily at r.t.

1.3.2.1.3. *Quantum Yields at* $-185°$ *in EPA.* 1.3.2.1.3.1. *For* $c = 5.531 \cdot 10^{-5}$ M. The numbers given are due to irradiation time [s], $1 - c_E/c_0$, ϕ_E: 0, 0, 0; 360, 0.112, 0.469, 480, 0.146, 0.476; 600, 0.175, 0.478; 720, 0.200, 0.472; 840, 0.225, 0.474; 960, 0.250, 0.477; 1260, 0.301, 0.478; 1600, 0.350, 0.479; 2300, 0.432, 0.487. Mean value for $\phi_E = 0.476 \pm 0.006$.

1.3.2.1.3.2. *For* $c = 5.52 \cdot 10^{-5}$ M: 600, 0.202, 0.468; 800, 0.252, 0.469; 1000, 0.300, 0.479; 1200, 0.331, 0.467; 1400, 0.370, 0.476; 1700, 0.414, 0.477; 2000, 0.454, 0.480; 2300, 0.486, 0.475. Mean value for $\phi_E = 0.475 \pm 0.006$.

1.3.2.2. *In the Presence of Amines.* 1.3.2.2.1. *With DABCO.* 1.3.2.2.1.1. *Electronic Absorption Spectra in MCI* (see *Fig. 11*). The reactions were performed under stirring in a quartz cell (1 cm × 1 cm) placed in a Cu mantle [44]. The temp. was determined at a central position in the medium using a calibrated thermoelement and controlled by letting a specific amount of liquid N_2 pass through the mantle. A soln. of *rac*-**1** ($3.691 \cdot 10^{-5}$ M) in MCI was irradiated for 120 min at $-152°$ with 365-nm light. Then the build-up of the ketene transient had been completed. A cooled soln. of DABCO ($5.583 \cdot 10^{-4}$ M) in MCI was added from an automatic syringe with such a rate that the temp. did not rise above $-152°$. 20 min after the amine had been added, the UV-spectroscopically observable change (from 297 to 364 nm) came to a standstill.

1.3.2.2.1.2. *Flash Spectroscopy at* $-80°$ (see *Fig. 12*). A soln. of *rac*-**1** ($2 \cdot 10^{-5}$ M) and DABCO ($3 \cdot 10^{-3}$ M) in MCI was flashed (*WG 295*; 330 through 550 nm). Point-for-point measurement revealed a transient spectrum with a maximum at 370 nm.

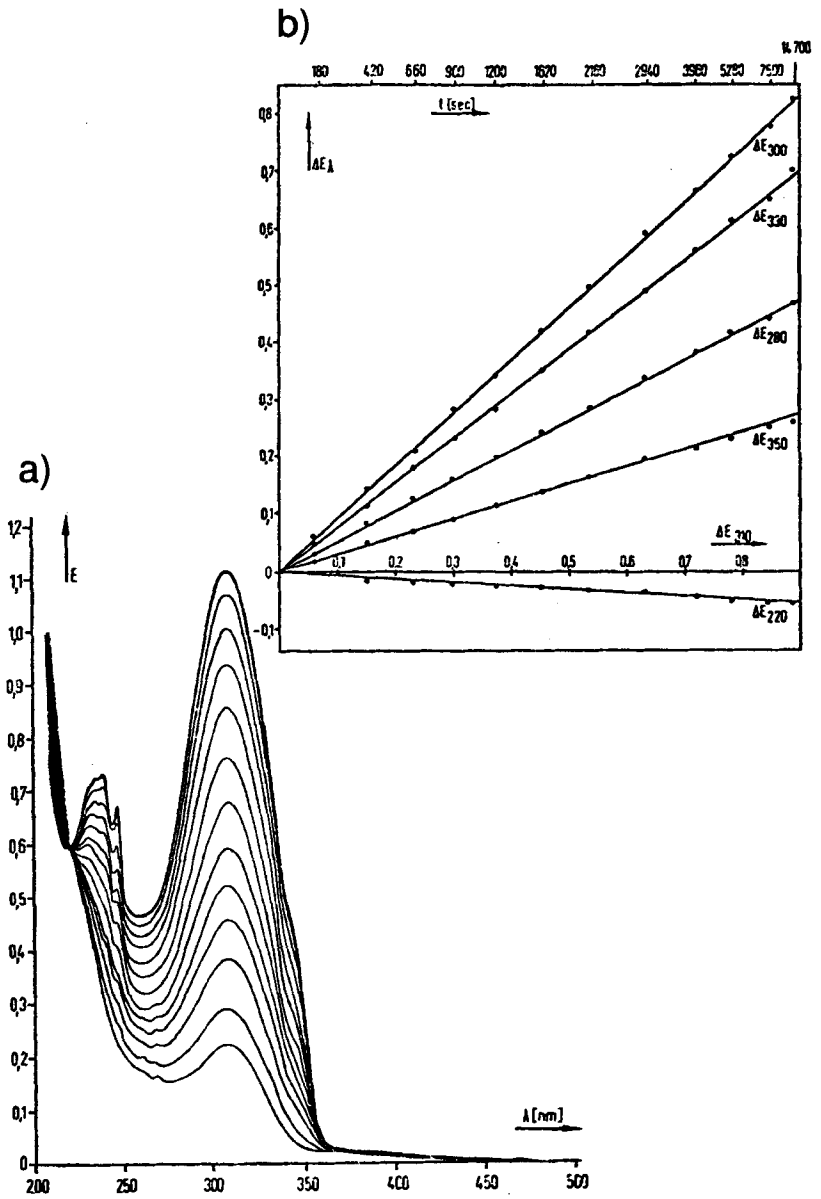


Fig. 25. *Analytical irradiation of a solution of* rac-**1** *at* $-185°$ *in EPA with 365-nm light. a*) Electronic absorption spectra with isosbestic point; *b*) linear ED diagram.

1.3.2.2.2. *With Cyclohexylamine.* 1.3.2.2.2.1. *Electronic Absorption Spectrum in MCI at* $-189°$ (see *Fig. 13,A*). A soln. of *rac*-**1** (0.185 mg) and freshly distilled cyclohexylamine (2.5 µl) in MCI (25 ml) was irradiated with 365-nm light at $-189°$, until all dienone had disappeared. A transient spectrum was measured with maxima at 464 and 484 nm. After warming up to $-70°$, the spectrum was rapidly substituted by that one of a mixture of **2a** and **3a**.

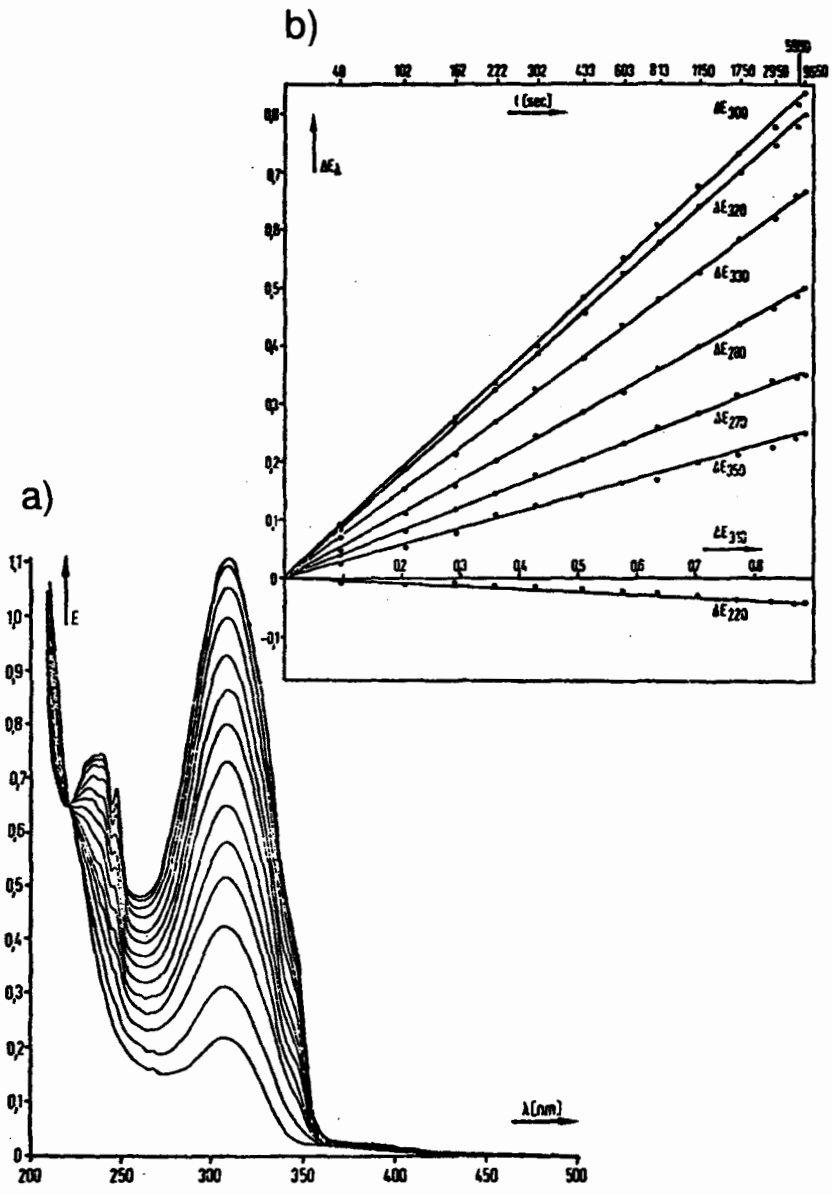
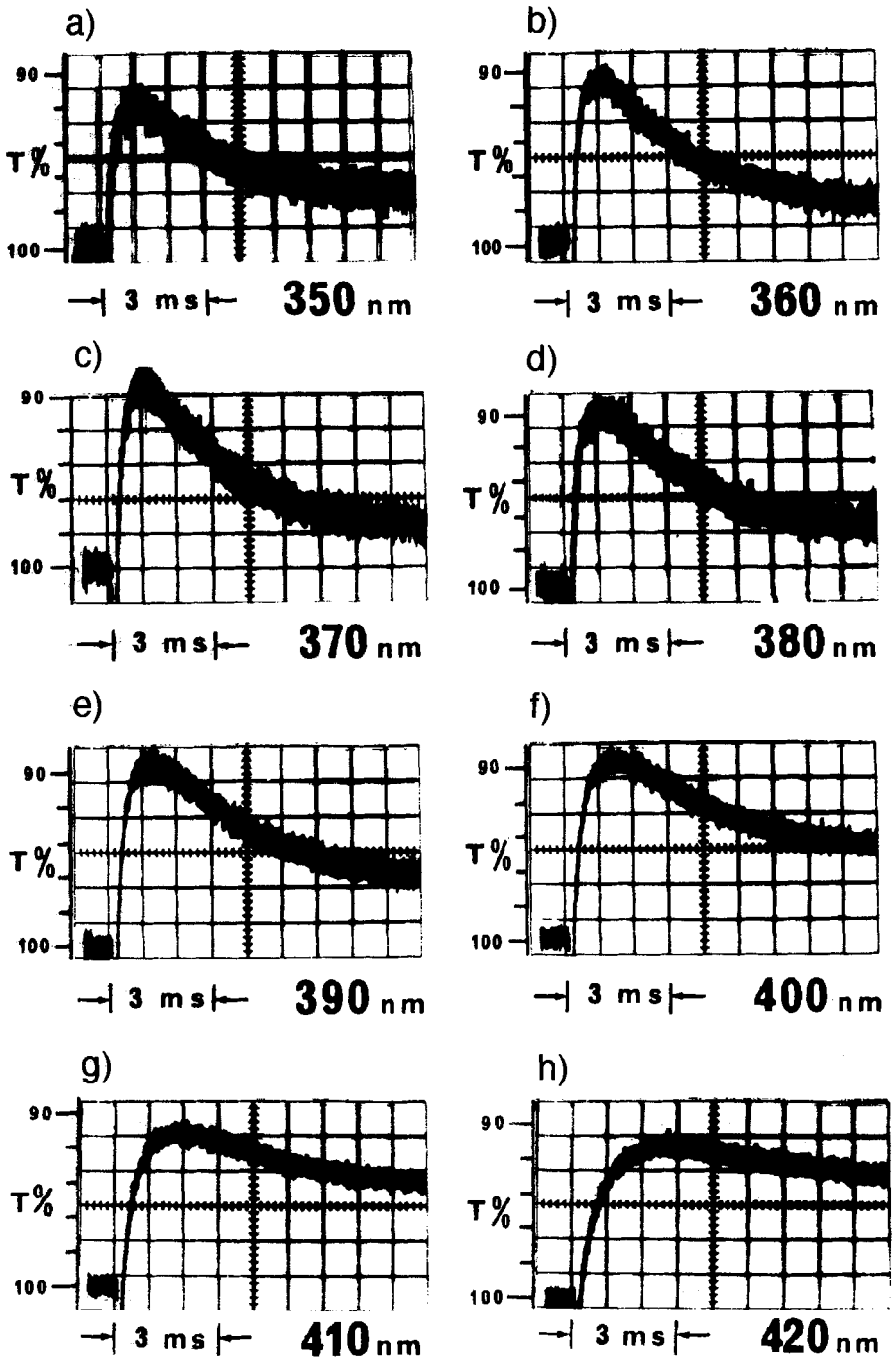


Fig. 26. *Analytical irradiation of a solution of* rac-**1** *at* $-185°$ *in EPA with 313-nm light. a*) Electronic absorption spectra with isosbestic point; *b*) linear ED diagram.

1.3.2.2.2.2. *Flash Spectroscopy.* A soln. of *rac*-**1** ($2 \cdot 10^{-4}$ M) and cyclohexylamine ($1 \cdot 10^{-3}$ M) in MCI was flashed at $-150°$. The rise of the signal at 460 nm (for the enol transient) correlates satisfactorily with the decay of the signal at 380 nm (for the zwitterion transient). As the shape of the decay curves depend on the used wavelength, there is overlap of the absorption spectra of (**E** + **F**) and (**G** + **H**) in some wavelength areas of *Fig. 27*. The absorption spectrum of (**G** + **H**) may easily be obtained by point-for-point measurement at $-140°$ (see *Fig.13, B*), where (**E** + **F**) are absent.


a)
90
T%
100
3 ms
350 nm
b)
90
T%
100
3 ms
360 nm
c)
90
T%
100
3 ms
370 nm
d)
90
T%
100
3 ms
380 nm
e)
90
T%
100
3 ms
390 nm
f)
90
T%
100
3 ms
400 nm
g)
90
T%
100
3 ms
410 nm
h)
90
T%
100
3 ms
420 nm

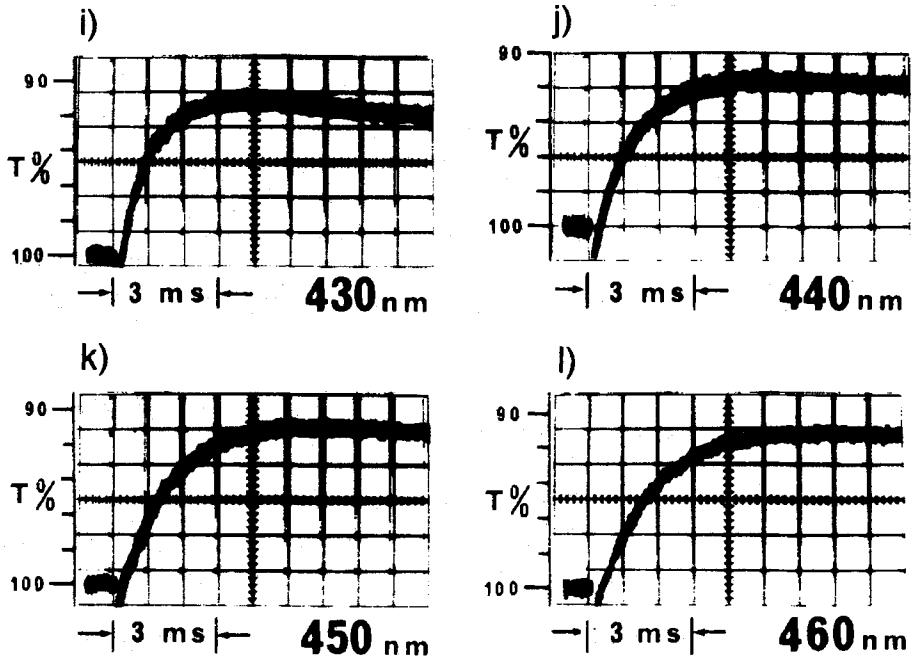


Fig. 27. *Oscillograms of flash spectroscopy of a solution of* rac-**1** *and cyclohexylamine at −150° monitored between 350 and 460 nm* (*a–l*: time resolution 1 ms/cm; see *Exper. 1.3.2.2.2.2*)

The rate constant for the decay of (**E** + **F**) are within the limit of accuracy independent on the used wavelength and agree well with the rate constant for the rise of (**G** + **H**): $k = 488\ s^{-1}$.

1.3.2.3. *In the Absence of a Protic Nucleophile.* 1.3.2.3.1. *UV-Spectroscopical Proof in MCI of a Phototransient That Thermally Reforms rac-***1**: see [21b]: Figs. 13 and 14, as well as [21a]: Figs. 21 and 22. The absorption of *rac*-**1** shifted bathochromically on cooling (from λ_{max} 296 nm (3900) to λ_{max} 305 nm (4200)); λ_{max} of phototransient at −185°: 305 nm (25000).

1.3.2.3.2. *Formal Analysis of Reaction Kinetics in CH_2Cl_2 at −60° with 365-nm Light.* A soln. of *rac*-**1** ($4.13 \cdot 10^{-5}$ M) was irradiated for 43 min. The absorption spectra taken after 1, 2, 3, 4, 7, 9, 13, 16, and 43 min were used to construct a linear ED diagram (see *Fig. 8*).

1.3.2.3.3. *IR-Spectroscopical Proof of a Transient Ketene* (see *Fig. 7*). *rac*-**1** (*ca.* 1 mg) spread as a thin liquid film between two rock-salt plates in a special cell plate holder was irradiated at −190° with 365-nm light for 0.75 s (*ca.* 6% conversion). The IR spectra obtained after 3 (*Fig. 7,A*), 10 (*Fig. 7,B*), and 45 min (*Fig. 7,C*) showed two ketene bands the relative intensities of which changed gradually from 2102 to 2114 cm^{-1}. Warming up to r.t. and cooling down to −190° showed only IR bands belonging to *rac*-**1**.

1.3.2.3.4. *^{1}H-NMR-Spectroscopical Proof of the Binary Nature of the Ketene Transient* (see [21a]: Fig. 24, and [21b]: Fig. 19). NMR Tubes, containing soln. of *rac*-**1** ($5.428 \cdot 10^{-1}$ M) in $CDCl_3$ (or C_6D_6), were sealed using vacuum-line techniques and irradiated at −60° (−50°). Every 30 min a ^{1}H-NMR spectrum was recorded. The following data are the mean values of ratios of areas under the resonance signals at $\delta = 1.92$ and 2.05 (Me groups) after distinct irradiation periods. 30 min: 1.3 (1.4); 60 min: 1.26 (1.27); 90 min: 1.28 (1.20): 120 min: 1.27 (1.23); 150 min: 1.28 (1.28); 180 min: 1.29 (1.32); 210 min: 1.27 (1.24): 255 min: 1.26 (1.28). Overall arithmetic mean: 1.27 ± 0.02 (1.27 ± 0.06).

1.3.3. *In the Presence of* N-*(Phenylmethylidene)benzylamine* (see *Scheme 1*). A soln. of *rac*-**1** (1.5 g; 24 mmol) and **57a** [45] [46] (4.8 g; 24.6 mmol; see *Scheme 18*) in anh. CH_2Cl_2 was irradiated for 6 h until *rac*-**1** had disappeared (UV and TLC control). After concentration under reduced pressure, a residue was obtained, which was purified by FC (100 g of silica gel; hexane/AcOEt 4:1) to give an oily product (2.2 g; 71%), an anal. sample

of which was fractionated by prep. HPLC (hexane/AcOEt 10:1 + 30% CH_2Cl_2) to yield *(3RS,4RS)-1-benzyl-3-[(1Z,3Z)-4-phenylpenta-1,3-dienyl]-4-phenylazetidin-2-one* (*rac*-**4**): TLC (hexane/AcOEt 2:1): R_f 0.39. UV (MeOH): λ_{max} 261.5 (21046). IR (film): 3030*m* (unsat. C–H); 2911*m* (sat. C–H); 1755*s* (lactam); 1455*m*; 1388*m*. ^{1}H-NMR: 2.02 (*s*, Me); 3.80 (*d*, *J*(H–C(1'),H'–C(1')) = 15.0, H–C(1')); 4.17 (*d*, *J*(H–C(3),H–C(1'')) = 8.4, H–C(3)); 4.17 (*d*, *J*(H–C(4),H–C(3)) = 2.1, H–C(4)); 4.85 (*d*, *J*(H'–C(1'),H–C((1')) = 15.0, H'–C(1')); 5.42 (ψt, *J*(H–C(1''),H–C(2'')) = *J*(H–C(1''),H–C(3)) = 9.4, H–C(1'')); 6.08–6.25 (*m*, H–C(2''),H–C(3'')); 7.11–7.45 (*m*, 15 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 4.85/3.80; 5.42/4.17, 6.08–6.25. ^{13}C-NMR: 25.60 (Me); 44.59 (C(1')); 59.88 (C(3)); 61.89 (C(4)); 121.69 (C(1'')); 122.14 (C(2'')); 126.43, 126.64, 127.14, 127.69, 128.04, 128.24, 128.43, 128.57, 128.74, 129.00 (Ph); 135.51, 137.31, 141.03 (C_{ipso}); 141.49 (C(4'')); 168.57 (C(2)). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks between 25.60/2.02; 44.59/3.80 and 4.85; 59.88/4.17; 61.89/4.17; 121.69/5.42; 122.14/6.08–6.25; 126.43/7.11–7.45; 126.64/7.11–7.45; 127.14/7.11–7.45; 127.69/7.11–7.45; 128.04/7.11–7.45; 128.24/7.11–7.45; 128.43/7.11–7.45; 128.57/7.11–7.45; 128.74/7.11–7.45. NOEs from difference spectra (irradiated signal/NOE): H–C(3)/H–C(1') (2.3%); H–C(3)/H–C(3') (9.6%); H–C(1')/H–C(2') (10.4%); H–C(3')/H–C(3) (8.8%); H–C(3')/Me (5.8%); H–C(2')/H–C(1') (9.7%). Anal. calc. for $C_{27}H_{25}NO$ (379.50): C 85.45, H 6.64, N 3.69; found: C 85.20, H 6.68, N 3.61 and 0.67 g.

(3RS,4RS)-1-Benzyl-3-[(1Z,3E)-4-phenylpenta-1,3-dienyl]-4-phenylazetidin-2-one (*rac*-**5**): TLC (hexane/AcOEt 4:1): R_f 0.39. UV (MeOH): λ_{max} 288.5 (23795). IR (KBr): 3024*w* (unsat. C–H); 2910*w* (sat. C–H); 1769*s* (lactam); 1618*w*, 1360*m*. ^{1}H-NMR: 2.13 (*d*, *J*(Me, H–C(3'')) = 0.9, Me); 3.80 (*d*, *J*(H–C(1'),H'–C(1')) = 15.0, H–C(1')); 4.13 (ψd, *J*(H–C(3),H–C(1'')) = 8.3, H–C(3)); 4.18 (*d*, *J*(H–C(4),H–C(3)) = 2.2, H–C(4)); 4.84 (*d*, *J*(H'–C(1'),H–C(1')) = 15.0, H'–C(1')); 5.70 (*dd*, *J*(H–C(1''),H–C(3)) = 8.3, *J*(H–C(1''),H–C(2'')) = 11.5, H–C(1'')); 6.35 (*dt*, *J*(H–C(3''),H–C(2'')) = 11.5, *J*(H–C(3''),H–C(1'')) = *J*(H–C(3''), Me) = 1.2, H–C(3'')); 6.58 (*dt*, *J*(H–C(2''),H–C(3'')) = *J*(H–C(2''),H–C(1'')) = 11.5, *J*(H–C(2''),H–C(3)) = 1.7, H–C(2'')); 7.11–7.38 (*m*, 15 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 3.80/4.84; 4.13/5.70; 6.58/6.35, and 5.70. ^{13}C-NMR: 15.90 (Me); 44.63 (C(1')); 59.86 (C(3)); 62.05 (C(4)); 122.05 (C(3'')); 123.31 (C(1'')); 125.74, 126.71, 127.27, 127.69, 128.16, 128.46, 128.58, 128.75, 129.09 (Ph); 129.49 (C(2'')); 135.49, 137.11, 138.50 (C_{ipso}); 142.70 (C(4'')); 168.49 (C(2)). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. NOEs from difference spectra (irradiated signal/NOE): H–C(1')/H–C(3) (3.9%); H–C(1')/H–C(2') (7.1%); H–C(2')/H–C(2') (8.1%); H–C(2')/CH_3–C(4') (7.4%); H–C(3')/H–C(3) (9.6%); H–C(3')/CH_3–C(4') (2.3%). Anal. calc. for $C_{27}H_{25}NO$ (379.50): C 85.45, H 6.64, N 3.69; found: C 85.22, H 6.90, N 3.82.

1.4. *Irradiation of* rac-**6** (see *Scheme 3*). 1.4.1. *In the Presence of Cyclohexylamine.* A soln. of *rac*-**6** (392 mg; 2.39 mmol; for preparation, see *Exper. 2.4*) and freshly distilled cyclohexylamine (820 µl; 7.16 mmol) in anh. Et_2O (250 ml) were irradiated. After 2 h, *rac*-**6** could not be longer detected UV-spectroscopically. Acidic workup left a residue which was chromatographed (40 g of silica gel; CH_2Cl_2/AcOEt 5:1) to give a colorless solid (439 mg; 70%) containing **7a**/**8a** in a ratio of 72:28 (according to HPLC; hexane/AcOEt 1:1 + 20% CH_2Cl_2, 2 ml/min, 254 nm and refract.). 210 mg of the mixture were separated by semi-prep. HPLC to afford 24 mg of **7a**/**8a**, 109 mg of (36%) **7a**, and 53.3 mg of (18%) **8a**.

(3Z,5E)-N-*Cyclohexyl-6-methyl-9-methyl-9-oxonona-3,5-dienamide* (**7a**): M.p. 45° (pentane/Et_2O). TLC (CH_2Cl_2/AcOEt 5:1): R_f 0.20. UV (hexane): λ_{max} 244 (21220). IR (KBr): 3285*m*, 3080*w* (N–H); 2720*w* (C–H); 1715*s* (aldehyde); 1640*s* (amide I); 1555*m* (amide II). ^{1}H-NMR: 1.02–1.90 (*m*, 2 H–C(2') to 2 H–C(6')); 1.78 (*d*, *J*(Me, H–C(5)) = 0.9, Me); 2.40–2.46 (*m*, 2 H–C(7)); 2.55–2.61 (*m*, 2 H–C(8)); 3.08 (*dd*, *J*(H–C(2), H–C(3)) = 7.8, *J*(H–C(4),H–C(2)) = 1.3, 2 H–C(2)); 3.68–3.82 (*m*, H–C(1')); 5.52 (*dt*, *J*(H–C(3),H–C(4)) = 11.1, *J*(H–C(3),H–C(2)) = 7.8, H–C(3), underneath br. *d*, N–H); 6.02 (ψdq, *J*(H–C(5),H–C(4)) = 11.3, *J*(H–C(5),H–C(3)) = *J*(H–C(5), Me) = 1.3, H–C(5)); 6.40 (ψtt, *J*(H–C(4),H–C(5)) = *J*(H–C(4),H–C(3)) = 11.1, *J*(H–C(4),H–C(2)) = 1.4, H–C(4)); 9.77 (*t*, *J*(H–C(9),H–C(8)) = 1.7, H–C(9)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (3.3%); H–C(2)/H5) (3.6%); H–C(3)/H–C(2) (2.5%); H–C(3)/H–C(4) (3.3%); H–C(4)/H–C(3) (3.5%); H–C(4)/Me–C(6) (3.9%); H–C(5)/H–C(2) (5.8%); H–C(7)/H–C(5) (1.4%); H–C(7)/H–C(8) (8.4); H–C(8)/H–C(7) (8.5%); H–C(8)/H–C(9) (1.3%). Anal. calc. for $C_{16}H_{25}NO_2$ (263.38): C 72.97, H 9.57, N 5.32; found: C 72.71, H 9.73, N 5.45.

(3Z,5Z)-N-*Cyclohexyl-6-methyl-9-oxonona-3,5-dienamide* (**84**): M.p. 91° (Et_2O). TLC (CH_2Cl_2/AcOEt 5:1): R_f 0.28. UV (hexane): λ_{max} 244 (22480). IR (KBr): 3280*s*, 3070*w* (N–H); 2730*w* (C–H); 1715*s* (aldehyde); 1640*s* (amide I); 1550*s* (amide II); 1225*m* (C–O). ^{1}H-NMR: 1.02–1.90 (*m*, 2 H–C(2') to 2 H–C(6')); 1.82 (*s*, Me); 2.46–2.58 (*m*, 2 H–C(7), 2 H–C(8)); 3.09 (*dd*, *J*(H–C(2),H–C(3)) = 7.8, *J*(H–C(2),H–C(4)) = 1.1, 2 H–C(2)); 3.68–3.83 (*m*, H–C(1')); 5.51 (*dt*, *J*(H–C(3),H–C(4)) = 10.8, *J*(H–C(3),H–C(2)) = 7.8, H–C(3), underneath br. *d*, N–H); 6.05 (*d*, *J*(H–C(5),H–C(4)) = 11.5, H–C(5)); 6.42 (ψt, *J*(H–C(4),H–C(5)) = *J*(H–C(4),H–C(3)) = 11, H–C(4)); 9.79 (*t*, *J*(H–C(9),H–C(8)) = 1.4, H–C(9)). NOEs from difference spectra

(irradiated signal/NOE): H–C(2)/H–C(3) (1.8%); H–C(2)/H–C(5) (2.6%); H–C(3)/H–C(3) (4.0%); H–C(4)/H–C(7) (5.8%); H–C(5)/H–C(2) (4.9%); H–C(5)/H–C(4) (1.5%); H–C(5)/Me–C(6) (4.2%); H–C(7)/H–C(4) (1.9%); H–C(8)/H–C(4) (0.8%). Anal. calc. for $C_{16}H_{25}NO_2$ (263.38): C 72.97, H 9.57, N 5.32; found: C 72.74, H 9.46, N 5.61.

1.4.2. *In MeOH.* A soln. of *rac*-**6** (678 mg; 4.13 mmol) in MeOH (400 ml) was irradiated. After 2 h, *rac*-**6** could not be longer detected UV-spectroscopically. The solvent was removed with a rotary evaporator and the residue chromatographed (80 g of silica gel; hexane/AcOEt 4:1 to 2:1) to afford **7b** and **8b** (772 mg; 95%; according to HPLC, in a ratio of 65:35; hexane/i-PrOAc 10:3, 2 ml/min, 254 nm and refract.). By semi-prep. HPLC, 340 mg of the mixture were separated to give 52 mg of **7b**/**8b**, 143 mg of **7b** (40%), and 108 mg of **8b** (30%).

Methyl (3Z,5E)-6-Methyl-9-oxonona-3,5-dienoate (**7b**): TLC (hexane/AcOEt 2:1): R_f 0.43. UV (MeOH): λ_{max} 240 (24650). UV (hexane): λ_{max} 241 (24330). IR (film): 2840*w*, 2725*w* (C–H); 1740*s* (C=O); 1650*w* (C=C); 1175*m* (C–O). ^{1}H-NMR: 1.76 (ψs, Me–C(6)); 2.39–2.45 (*m*, 2 H–C(7)); 2.54–2.61 (*m*, 2 H–C(8)); 3.20 (*dd*, *J*(H–C(2),H–C(3)) = 7.4, *J*(H–C(2),H–C(4)) = 17.2, H–C(2)); 3.68 (*s*, MeO); 5.54 (*dt* with f.s., *J*(H–C(3),H–C(4)) = 11.1, *J*(H–C(3),H–C(2)) = 7.4, H–C(3)); 6.02 (*d* with f.s., *J*(H–C(5),H–C(4)) = 11.3, H–C(5)); 6.32 (ψtt, *J*(H–C(4),H–C(5)) = *J*(H–C(4),H–C(3)) = 11.1, *J*(H–C(4),H–C(2)) = 1.7,H–C(4)); 9.77 (*t*, *J*(H–C(9),H–C(8)) = 1.6, H–C(9)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (3.4%), H–C(2)/H–C(5) (2.4%); H–C(3)/H–C(2) (3.4%); H–C(3)/H–C(4) (3.5%); H–C(3)/OCH_3 (2.2%); H–C(4)/H–C(3) (3.4%); H–C(4)/Me–C(6) (3.4%); H–C(5)/H–C(2) (4.8%); H–C(5)/H–C(4) (2.6%); H–C(5)/H–C(5) (3.3%); Me–C(6)/H–C(4) (1.7%); Me–C(6)/H–C(7) (1.0%); H–C(7)/H–C(5) (1.8%); H–C(7)/Me–C(6) (1.3%). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.42, H 8.21.

Methyl (3Z,5Z)-6-Methyl-9-oxonona-3,5-dienoate (**8b**). TLC (hexane/AcOEt 2:1): R_f 0.43. UV (MeOH): λ_{max} 240 (24570). UV (hexane): λ_{max} 240 (23900). IR (film): 2845*w*, 2730*w* (C–H); 1735*s* (C=O); 1650*w* (C=C); 1170*m* (C–O). ^{1}H-NMR: 1.81 (ψs, Me–C(6)); 2.44–2.58 (*m*, 2 H–C(7), 2 H–C(8)); 3.22 (*dd*, *J*(H–C(2), H–C(3)) = 7.4, *J*(H–C(2),H–C(4)) = 1.6, 2 H–C(2)); 3.69 (*s*, MeO); 5.53 (*dt*, *J*(H–C(3),H–C(4)) = 11.1, *J*(H–C(3),H–C(2)) = 7.4, H–C(3)); 6.04 (*d* with f.s., *J*(H–C(5),H–C(4)) = 11.5, H–C(5)); 6.32 (ψtt with f.s., *J*(H–C(4),H–C(5)) = 11.5, *J*(H–C(4), H–C(3)) = 11.1, *J*(H–C(4),H–C(2)) = 1.7, H–C(4)); 9.78 (*t*, *J*(H–C(9),H–C(8)) = 1.3, H–C(9)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (1.0%); H–C(2)/H–C(5) (3.0%); H–C(3)/H–C(2) (1.6%); H–C(3)/H–C(4) (4.0%); H–C(4)/H–C(3) (3.7%); H–C(5)/H–C(5) (4.8%); H–C(5)/Me–C(6′) (3.0%); Me–C(6)/H–C(5) (1.5%); Me–C(6)/H–C(7) (1.6%); H–C(7)/H–C(4) (2.3%). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.42, H 8.21.

1.5. *Irradiation of* rac-**9** (see *Scheme 4*). 1.5.1. *In the Presence of Cyclohexylamine.* A soln. of *rac*-**9** (208 mg; 1.0 mmol; for preparation, see *Exper. 2.5*) and freshly distilled cyclohexylamine (560 µl, 459 mg; 4.62 mmol) in anh. CH_2Cl_2 (50 ml) was irradiated. After 2 h, *rac*-**9** had completely reacted (UV and TLC control). After acidic workup, the obtained residue was purified by FC (30 g of silica gel; hexane/AcOEt 1:4) and semi-prep. HPLC (hexane/1,4-dioxane 5:3; 10 ml/min; refract.) to give 255 mg (86%) of *(2RS,3Z,5E)*-N-*cyclohexyl-4-(hydroxymethyl)-2,6-dimethyl-8-oxonona-3,5-dieneamide* (*rac*-**10a**): TLC (hexane/AcOEt 1:4): R_f 0.20. UV (MeOH): λ_{max} 281.0 (140), 220.0 (6160). IR (film): 3362*s* (NH); 3063*w* (unsat. C–H); 2931*s*, 2854*s* (sat. C–H); 1711*s* (ketone); 1651*s* (amide I); 1532*s* (amide II); 1254*m*, 1122*s* (C–O). ^{1}H-NMR: 0.95–1.85 (*m*, 2 H–C(2′) to 2 H–C(6′)); 1.20 (*d*, *J*(Me–C(2),H–C(2)) = 6.8, Me–C(2)); 1.60 (*d*, *J*(Me–C(6),H–C(5)) = 1.3, Me–C(6)); 2.15 (br. *s*, OH); 2.21 (*s*, 3 H–C(9)); 3.08–3.15 (*m*, H–C(2)); 3.22 (ψs, 2 H–C(7)); 3.64–3.71 (*m*, H–C(1′)); 4.03 (*s*, CH_2–C(4)); 5.59 (ψd, $J \approx 11$, H–C(3)); 5.62 (*s*, H–C(5)); 6.18 (*d*, *J*(N–H,H–C(1′)) = 8.0, NH). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 6.18/3.64–3.71, 4.03/2.15, 3.08–3.15/1.20, 5.62/5.59, 5.62/3.22, 5.62/1.60, 5.59/4.03, 5.59/3.08–3.15. ^{1}H-NMR (C_6D_6): 1.00–2.01 (*m*, 2 H–C(2′) to 2 H–C(6′), OH); 1.39 (*d*, *J*(Me–C(2),H–C(2)) = 6.8, Me–C(2)); 1.51 (*d*, *J*(Me–(6),H–C(5)) = 1.3, Me–C(6)); 1.58 (*s*, 3 H–C(9)); 2.62 (*s*, 2 H–C(7)); 3.26–3.33 (*m*, H–C(2)); 3.96–4.00 (*m*, H–C(1′)); 4.03 (*s*, CH_2–C(4)); 5.51 (*s*, H–C(5)); 5.90 (ψd, $J \approx 9.8$, H–C(3)); 6.40 (*d*, *J*(NH,H–C(1′)) = 7.6, NH). NOEs from difference spectra (C_6D_6, irradiated signal/NOE): H–C(2)/H–C(3) (1.0%); H–C(2)/H–C(5) (1.1%); H–C(2)/Me–C(2) (2.9%); H–C(3)/CH_2–C(4) (1.8%); H–C(3)/Me–C(2) (1.7%); CH_2–C(4)/H–C(3) (1.0%); CH_2–C(4)/H–C(5) (0.5%); H–C(5)/H–C(2) (0.8%); H–C(5)/CH_2–C(4) (0.6%); H–C(5)/Me–C(6) (2.2%); H–C(5)/2 H–C(7) (3.2%); 2 H–C(7)/H–C(2) (0.5%); 2 H–C(7)/H–C(5) (1.5%); 2 H–C(7)/Me–C(6) (0.7%); Me–C(2)/H–C(2) (0.7%); Me–C(2)/H–C(3) (0.7%). ^{13}C-NMR: 17.53 (*Me*–C(2)); 18.61 (*Me*–C(6)); 24.91, 25.51, 32.99, 40.91 (C(2′) to C(6′)); 30.11 (C(9)); 47.99 (C(1′)); 53.34 (C(2), C(7)); 66.14 (CH_2–C(4)); 125.67 (C(4)); 128.75 (C(6)); 134.01 (C(5)); 138.03 (C(3)); 173.46 (C(1)); 207.48 (C(8)). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross signals between 138.03/5.59, 134.01/5.62, 66.14/4.03, 47.99/3.64–3.71, 30.11/2.21, 18.61/1.60, and 17.53/1.20; 53.34/3.08–3.15; 53.34/3.22; 24.91/0.95–1.85; 25.51/0.95–1.85; 32.99/0.95–1.85; 40.91/0.95–1.85. Anal. calc. for $C_{18}H_{29}NO_3$ (307.43): C 70.32, H 9.51, N 4.56; found: C 70.47, H 9.33, N 4.53.

1.5.2. *In MeOH*. A soln. of *rac*-**9** (208 mg; 1 mmol) in abs. MeOH (50 ml) was irradiated for 3 h, when the educt had disappeared (UV and TLC control). The solvent was removed under reduced pressure and the remaining residue purified by FC (30 g of silica gel; hexane/AcOEt 1:4) affording 191 mg (79%) of *methyl (2*RS*,3Z,5E)-2,6-dimethyl-4-(hydroxymethyl)-8-oxonona-3,5-dienoate* (*rac*-**10b**). An anal. sample, after HPLC (hexane/AcOEt 1:2; 10 ml/min; refract.) showed the following properties: TLC (hexane/AcOEt 1:4): R_f 0.48. UV (MeOH): λ_{max} 282.0 (174), 220.0 (6043). IR (film): 3444*m* (OH); 2978*m*, 2952*m*, 2936*m*, 2876*w* (sat. C–H); 1732*s* (C=O); 1163*s*, 1053*m* (C–O). ^{1}H-NMR: 1.22 (*d*, *J*(Me–C(2),H–C(2)) = 2.4, Me–C(2)); 1.61 (*d*, *J*(Me–C(6),H–C(5)) = 1.3, Me–C(6)); 1.91 (br. *s*, OH); 2.17 (*s*, 3 H–C(9)); 3.17 (*s*, 2 H–C(7)); 3.23–3.36 (*m*, H–C(2)); 3.64 (*s*, MeO); 4.05 (*s*, CH_2O); 5.59 (*ψd*, *J*(H–C(3), H–C(2)) ≈ 10, H–C(3)); 5.67 (*s*, H–C(5)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 3.23–3.36/1.22, 5.67/5.59, 5.67/4.05, 5.67/3.17, 5.67/5.59, 5.67/4.05, 5.67/3.17, 5.67/1.61, 5.59/4.05, 5.59/3.23–3.36. NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(5) (1.1%); H–C(3)/Me–C(2) (3.2%); H–C(3)/H–C(4) (2.0%); H–C(3)/Me–C(2) (1.8%); CH_2–C(4)/H–C(3) (1.3%); CH_2–C(4)/H–C(5) (0.5%); H–C(5)/H–C(2) (0.8%); H–C(5)/CH_2–C(4) (1.1%); H–C(5)/2 H–C(7) (3.3%); 2 H–C(7)/H–C(2) (0.5%); 2 H–C(7)/H–C(5) (1.9%); 2 H–C(7)/Me–C(6) (1.3%); Me–C(2)/H–C(2) (0.9%); Me–C(2)/H–C(5) (0.7%). ^{13}C-NMR: 17.75 (*Me*–C(2)); 18.19 (*Me*–C(6)); 29.24 (C(9)); 39.34 (C(2)); 51.75 (MeO); 54.04 (C(7)); 66.15 (CH_2O); 124.73 (C(5)); 126.56 (C(3)); 135.00 (C(4)); 138.33 (C(6)); 175.30 (C(1)); 206.63 (C(8)). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross peaks between 126.56/5.59, 124.73/5.67, 66.15/4.05, 54.04/3.17, 51.75/3.64, 39.34/3.23–3.36, 29.24/2.17, 18.19/1.16, and 17.75/1.22. Anal. calc. for $C_{13}H_{20}O_4$ (240.30): C 64.98, H 8.39; found: C 64.92, H 8.43.

1.6. *Irradiation of* rac-**11** (see *Scheme 5*). 1.6.1. *In the Presence of Cyclohexylamine*. A soln. of *rac*-**11** (195 mg; 1 mmol; for preparation, see *Exper. 2.6*) and cyclohexylamine (0.35 ml; 3 mmol) in anh. Et_2O (100 ml) was irradiated for 90 min. Reaction progress was followed by UV and TLC. Acidic workup and chromatography (25 g of silica gel; hexane/AcOEt 2:1) of the isolated product gave 165 mg (57%) of *(3Z,5E)-6-acetoxy*-N*-cyclohexyl-6-cyclopropylhexa-3,5-dienamide* (*= (1E,3Z)-6-(cyclohexylamino)-1-cyclopropyl-6-oxohexa-1,3-dien-1-yl acetate;* **12**): M.p. 107° (Et_2O). TLC (hexane/AcOEt 2:1): R_f 0.20. IR (KBr): 3293*s* (N–H); 3080*w*, 3018*w* (unsat. C–H, cycloprop.); 2934*m*, 2854*m* (sat. C–H); 1759*s* (acetate); 1640*s* (amide I); 1550*s* (amide II); 1370*m*, 1221*s*, 1170*m*, 1049*m*, 925*m*, 715*m*. UV(MeOH): λ_{max} 246 (26077). ^{1}H-NMR: 0.62–0.71, 0.73–0.83 (2*m*, 2 H–C(8), 2 H–C(9)); 1.03–1.43, 1.56–1.72, 1.83–1.93 (3*m*, 2 H–C(2') to 2 H–C(6'), H–C(7)); 2.13 (*s*, Me); 3.06 (*d*, *J*(H–C(2), H–C(3)) = 7.7, 2 H–C(2)); 3.69–3.77 (*m*, H–C(1')); 5.59 (br. *d*, NH); 5.64 (*dt*, *J*(H–C(3),H–C(2)) = 7.7, *J*(H–C(3),H–C(4)) ≈ 11, H–C(3)); 5.98 (*d*, *J*(H–C(5),H–C(4)) ≈ 11, H–C(5)); 6.52 (*ψt*,*J*(H–C(4), H–C(3)) ≈ 11, *J*(H–C(4),H–C(5)) ≈ 11, H–C(4)). ^{13}C-NMR: 5.54 (C(8), C(9)); 10.68 (C(7)); 20.68 (Me); 24.76, 25.46, 32.95 (C(2') to C(6')); 35.86 (C(2)); 48.21 (C(1')); 113.39 (C(5)); 123.72 (C(3)); 125.92 (C(4)); 151.97 (C(6)); 169.12, 169.21 (C(1), Me*C*OO). The signals were assigned using DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks between 5.58/0.62–0.71, 5.58/0.73–0.83, 10.71/1.83–1.93, 24.79/1.03–1.43, 24.79/1.56–1.72, 25.50/1.56–1.72, 32.99/1.03–1.43, 32.99/183–1.93, 35.91/3.06, 48.25/3.69–3.77, 113.41/5.98, 123.74/5.64 and 125.98/6.52. NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (1.5%); H–C(2)/H–C(5) (3%); H–C(2)/H–N (3.3%); H–C(3)/H–C(2) (3.8%); H–C(3)/H–C(4) (4.3%); H–C(4)/H–C(3) (4.4%); H–C(4)/H–C(5) (1.6%); H–C(4)/H–C(7) (4.2%); H–C(5)/H–C(2) (5.7%), H–C(5)/H–C(4) (1.9%). Anal. calc. for $C_{17}H_{25}O_3N$ (291.39): C 70.07, H 8.65, N 4.81; found: C 69.86, H 8.43, N 4.61.

1.6.2. *In Anh. Et$_2$O*. A soln. of *rac*-**11** (385 mg; 2 mmol) was irradiated for 24 h. After removal of solvent under reduced pressure, a product was isolated which was purified by prep. HPLC (hexane/AcOEt 10:1.5; 2 ml/min; 280 nm) to afford 123 mg (32%) of *2-cyclopropyl-3-hydroxyphenyl acetate* (**13**): M.p. 54°. TLC (hexane/AcOEt 1:1): R_f 0.65. IR (KBr): 3418*m* (OH); 3091*w*, 3074*w*, 3047*w*, 3008*w* (unsat. C–H, cyclopropyl); 1739*s* (acetate); 1619*m*, 1570*m* (C=C); 1466*m*, 1365*m*, 1235*s*, 1034*m*, 803*m*, 736*m*. ^{1}H-NMR: 0.59–0.65 (*m*, H–C(8), H–C(9)); 0.96–1.03 (*m*, H'–C(8), H'–C(9)); 1.44–1.55 (*m*, H–C(7)); 2.33 (*s*, Me); 5.82 (*s*, OH); 6.58 (*dd*, *J*(H–C(4),H–C(5)) = 8.1, *J*(H–C(4),H–C(6)) = 1.2, H–C(4)); 6.79 (*dd*, *J*(H–C(6),H–C(5)) = 8.1, *J*(H–C(6),H–C(4)) = 1.2, H–C(6)); 7.14 (*ψt*, *J*(H–C(5),H–C(4)) = 8.1, *J*(H–C(5),H–C(6)) = 8.1, H–C(5)). ^{13}C-NMR: 5.13 (C(7)); 5.19 (C(8), C(9)); 20.81 (Me); 112.83, 113.83 (C(4), C(6)); 119.26 (C(2)); 128.27 (C(5)); 151.08 (C(3)); 156.68 (C(1)); 169.00 (Me*C*OO). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Cross signals between 5.13/1.44–1.55, 5.19/0.59–0.65, 5.19/0.96–1.03, 112.83/6.79, 113.83/6.58 and 128.27/7.14. NOEs from difference spectra (irradiated signal/NOE): H–O/H–C(6) (0.6%); H–O/H–C(8, 9) (3.1%); H–O/H'–C(8, 9) (1.1%); H–C(7)/H–C(8, 9) (1.3%); H–C(7)/H'–C(8, 9) (3.0%). Anal. calc. for $C_{11}H_{12}O_3$ (192.21): C 68.74, H 6.29; found: C 68.54, H 6.36 and 28.2 mg (10.5%).

2-Cyclopropylphenol (**14**): TLC (hexane/AcOEt 10:1): R_f 0.31. IR (film): 3539*s*, 3445*s* (OH), 3083*m*, 3036*m*, 3004*m* (C–H), 1609*m*, 1581*s* (C=C), 1505*m*, 1491*s*, 1461*s*, 1339*m*, 1257*s*, 1212*s*, 1190*s*, 1091*m*, 1032*m*, 834*m*, 753*s*. ^{1}H-NMR ((D$_6$)DMSO): 0.54–0.60, 0.81–0.88 (2*m*, 2 H–C(8), 2 H–C(9)); 1.99–2.11 (*m*, H–C(7)); 6.64–6.77,

6.90–6.96 (*2m*, H–C(3) to H–C(6)); 9.21 (*s*, in D_2O exchangeable, OH). ^{13}C-NMR: 5.38 (C(8), C(9)); 9.21 (C(7)); 114.56, 120.34, 127.66, 128.55 (C(3) to C(6)); 127.47 (C(2)); 155.33 (C(1)). The signals were assigned by a DEPT spectrum.

1.6.3. *As a Film at −190°*. Compound *rac*-**11** (*ca.* 10 mg) were spread as a thin film between two rock-salt plates in a special cell plate holder. The IR spectra at r.t. and −190° showed characteristic bands, which were very much sharper at the low temp., at 3077*w*, 3046*w*, 1744*s*, 1682*s*, 1637*s*, 1562*m*, 1411*s*, 1370*s*, 1252*s*, 1040*s*, 1006*s*, 886*m*, and 755*s*. The sample was irradiated at −190° using an *Osram HBO 200* high-pressure lamp in combination with a *WG 2* filter, 2 mm of *Jenaer Glaswerke Schott & Genossen*. Spectra were taken after 1, 11, 40, 100, 280, and 460 s. A ketene band developed at 2100, while the C=O band at 1682 became weaker. On warming up to r.t. in the dark, the low-temp. spectrum changed to that one of *rac*-**11** at r.t.

1.7. *Irradiation of* rac-**15** (see *Scheme 6*). 1.7.1. *At r.t.*. 1.7.1.1. *In MeOH*. 1.7.1.1.1. *Preparative*. A soln. of *rac*-**15** (10.09 g; 36.5 mmol; for preparation, see *Exper. 2.7*) in abs. MeOH (1 l) was irradiated for 440 min. Reaction progress was controlled by HPLC (C_6H_6/AcOEt 100:1, 280 and 254 nm). After removal of solvent under reduced pressure, the isolated residue was purified by chromatography (450 g of silica gel; hexane/AcOEt 10:1) to give a solid material (9.84 g) and, after recrystallization, 9.43 g (84%) of *(1*RS,*2Z,4*E*)-5-acetoxy-1-(methoxycarbonyl)cyclotetradeca-2,4-diene* (= *(1*E,*3Z,5*RS*)-5-(methoxycarbonyl)cyclotetradeca-1,3-dien-1-yl acetate*; *rac*-**16a**): M.p. 69–71° (hexane); 70–71° (MeOH). TLC (hexane/AcOEt 1:1): R_f 0.68. IR (KBr): 3005*w*, 2930*s*, 2860*s* (C–H); 1748*s* (enol-acetate); 1732*s* (ester); 1665*w*, 1613*w* (conjug. diene); 1375*s* (CH_3); 1235*s* (enol-acetate); 1198*s* (ester); 1176*s*, 760*m*, 737*m*. UV (hexane): λ_{max} 240 (19900). ^{1}H-NMR: 1.05–1.70 (*m*, 2 H–C(7) through 2 H–C(13)); 1.70–1.85 (*m*, 2 H–C(14)); 2.16 (*s*, $MeCO_2$); 2.30–2.37 (*dt*, *J*(H–C(6),H′–C(6)) = 15.2, *J*(H–C(6),H–C(7)) = *J*(H–C(6),H′–C(7)) = 4.0, H–C(6)); 2.51–2.63 (*ddd*, *J*(H′–C(6), H–C(6)) = 15.2, *J*(H′–C(6),H′–C(7)) = 12.4, *J*(H′–C(6),H–C(7)) = 4.4, H′–C(6)); 3.42–3.52 (*m*, H–C(1)); 3.66 (*s*, $MeCO_2$); 5.38–5.47 (*ψt*, *J*(H–C(2),H–C(3)) = *J*(H–C(2),H–C(1)) = 10.7, H–C(2)); 6.11–6.15 (*d* with f.s., *J*(H–C(4), H–C(3)) = 10.3, H–C(4)); 6.24–6.32 (*ψt*, *J*(H–C(3),H–C(2)) = 10.7, *J*(H–C(3),H–C(4)) = 10.3, H–C(3)). Additional irradiation in the signal at 2.30–2.37 simplified the signals at 1.05–1.70 produced a *dd* at 6.11–6.15 and 2.51–2.63. Decoupling of the signals at 3.42–3.52 caused a *d* at 5.38–5.47 and simplified the signal at 1.70–1.85. Further irradiation into the signal at 5.38–5.47 produced a *d* at 6.24–6.32 and changed the signal at 3.42–3.52. ^{13}C-NMR: 20.99 (*Me*COO); 24.00, 24.44, 25.53, 25.94, 27.20 (C(7) through C(14)); 30.90 (C(6)); 42.69 (C(1)); 51.78 (CO_2*Me*); 114.37 (C(4)); 124.78 (C(3)); 129.77 (C2)); 152.85 (C(5)); 169.28 ($MeCO_2$); 174.57 (*s*, $MeCO_2$). The assignment of the signals due to C(2) to C(4) was performed similarly to *rac*-**19** (see *Exper. 1.8*). Anal. calc. for $C_{18}H_{28}O_4$ (308.42): C 70.10, H 9.15; found: C 69.96, H 9.12.

Crystal-Structure Analysis of rac-**16a** (*Fig. 15*): a = 5.8615(7), b = 22.950(1), c = 12.832(2) Å; β = 95.52(1)°; V = 1718.2(6) Å^3; monoclinic crystals, $P2_1/c$ (No. 14); Z = 4; ρ = 1.192 g/cm^3; quadrant through 2θ = 100°; 1620 indep. reflect. with $I > 0$; 312 variables; $R(F)$ = 0.057; $R_w(F)$ = 0.050.

1.7.1.1.2. *Formal Analysis of Reaction Kinetics*. 1.7.1.1.2.1. *With 365-nm Light*. A soln. of *rac*-**15** ($7.64 \cdot 10^{-5}$ M) in abs. MeOH was irradiated for 108.5 min. The absorption spectra taken after 0, 2, 4.25, 6.75, 10.75, 15, 19.5, 24.75, 33, 48, 85, and 108.5 min intersected at an isosbestic point (λ 268 (1170)). The corresponding ED diagram was linear. The absorption maximum of the soln. after (before) irradiation: λ_{max} 238 (17050) (λ_{max} 307 (3840)).

1.7.1.1.2.2. *With 313-nm-Light*. A soln. of *rac*-**15** ($6.64 \cdot 10^{-5}$ M) in abs. MeOH was irradiated for 93 min. The absorption spectra taken after 0, 2, 4.25, 7.25, 11.5, 17, 23, 33, 48, and 93 min intersected in an isosbestic point (λ 268 (1230)). The corresponding ED diagram was linear. The absorption maximum of the soln. after (before) irradiation: λ_{max} 238 (17390) (λ_{max} 307 (3860)).

1.7.1.2. *In* t-*BuOH*. A soln. of *rac*-**15** (1 g; 3.6 mmol) in abs. *t*-BuOH (120 ml) was irradiated for 145 min. Reaction control by TLC showed that the educt had completely disappeared. The residue obtained after removal of solvent was purified by prep. HPLC (hexane/Et_2O 10:1; 0.1 l/min; refract.) to furnish 752 mg (59%) of *rac*-**16b** and 90 mg (7%) of *rac*-**17** *(1*RS,*2Z,4*E*)-5-acetoxy-1-[(*tert*-butoxy)carbonyl]cyclotetradeca-2,4-diene* (= *(1*E,*3Z,5*RS*)-5-[(*tert*-butoxy)carbonyl]cyclotetradeca-1,3-dien-1-yl acetate; rac*-**16b**): M.p. 58–60° (pentane). TLC (hexane/AcOEt 5:1): R_f 0.41. IR (KBr): 3035*w*, 2920*s*, 2850*s*, (C–H); 1756*s* (enol-acetate); 1722*s* (ester); 1667*w*, 1621*w* (C=C); 1368*s* (CH_3); 1216*s* (enol-acetate); 1162*s* (ester). UV (hexane): λ_{max} 240 (19200). ^{1}H-NMR: 1.05–1.80 (*m*, 2 H–C(7) through 2 H–C(14)); 1.42 (*s*, *t*-Bu); 2.16 (*s*, Me); 2.27–2.38 (*ψdt*, *J*(H–C(6), H′–C(6)) = 14.3, *J*(H–C(6),H′–C(7)) = 3.9, *J*(H–C(6),H–C(7)) = 4.1, H–C(6)); 2.50–2.64 (*ddd*, *J*(H′–C(6), H–C(6)) = 14.3, *J*(H′–C(6), H′–C(7)) = 12.1, *J*(H′–C(6),H–C(7)) = 4.5, H′–C(6)); 3.27–3.39 (*ψdt*, *J*(H–C(1),H–C(14)) = 11.2, *J*(H–C(1),H–C(2)) = 10.8, *J*(H–C(1), H′–C(14)) = 4.0, H–C(1)); 5.35–5.47 (*ψt*, *J*(H–C(2),H–C(3)) = 9.6, *J*(H–C(2),H–C(1)) = 10.8, H–C(2)); 6.10–6.15 (*d*, *J*(H–C(4),H–C(3)) = 10.4, H–C(4)); 6.20–6.30 (*ψt*, *J*(H–C(3),H–C(4)) = 10.4, *J*(H–C(3),H–C(2)) = 0.6, H–C(3)). Anal. calc. for $C_{21}H_{34}O_4$ (350.50): C 71.96, H 9.78; found: C 72.03, H 9.93.

*(1ζ,3Z)-5-Acetoxy-1-[(*tert*-butoxy)carbonyl]cyclotetradeca-1,3-diene* (= *(1*RS,*2Z,4ζ)-5-[(*tert*-Butoxy)carbonyl]cyclotetradeca-2,4-dien-1-yl Acetate; rac-***17***): B.p. 160–165°/0.07 Torr. TLC (hexane/AcOEt 5:1): R_f 0.45. IR (film): 3020*w*, 2920*w*, 2850*s* (C–H); 1736*s* (acetate); 1707*s* (unsat. ester); 1366*s* (CH_3); 1235*s* (acetate); 1155*s*, 1136*s*. UV (hexane): λ_{max} 255 (17860). ^{1}H-NMR: 1.02–1.80 (*m*, 2 H–C(6) through 2 H–C(13)); 1.50 (*s*, *t*-Bu); 2.04 (*s*, Me); 2.14–2.29 (*m*, H–C(14)); 2.58–2.69 (*m*, H′–C(14)); 5.32–5.43 (ψt, *J*(H–C(4),H–C(3)) = 10.0, *J*(H–C(4),H–C(5)) = 9.2, H–C(4)); 5.81–5.91 (ψdt, *J*(H–C(5),H–C(4)) = 9.2, *J*(H–C(5),H–C(6)) = 8.4, *J*(H–C(5),H′–C(6)) = 4.8, H–C(5)); 6.60–6.68 (*d*, *J*(H–C(2),H–C(3)) = 11.2, H–C(2)); 6.86–6.98 (ψt, *J*(H–C(3),H–C(2)) = 11.2, *J*(H–C(3),H–C(4)) = 10.0, H–C(3)). Additional irradiation into the signal at 6.86–6.98 produced a *s* at 6.60–6.68 and a *d* at 5.32–5.43. Decoupling at 2.14–2.29 caused an effective simplification of the signal at 2.58–2.69. Anal. calc. for $C_{21}H_{34}O_4$ (350.50): C 71.96, H 9.78; found: C 72.13, H 9.87.

1.7.2. *At Low Temp.* 1.7.2.1. *IR Spectroscopy.* Following the procedure of *Exper. 1.3.2.2.3*, *rac*-**15** was irradiated at –190°. After 6 s, a ketene band was to be detected at 2078 with a sh at 2069. After 21 s a sharp band at 2976 with two sh at 2066 and 2097 had formed, while the ketone band at 1672 had almost completely disappeared. On warming up, the spectrum did not essentially change before reaching –25°. At r.t., the unchanged spectrum of *rac*-**15** had reformed.

1.7.2.2. *Formal Analysis of Reaction Kinetics.* A soln. of *rac*-**15** ($1.04 \cdot 10^{-4}$ M) in MCI (λ_{max} at r.t. 302.5 (4480); λ_{max} at –185° 308 (5290)) was irradiated for 26.5 min at the low temp. The absorption spectra taken after 1.5, 3.5, 7.67, 11, 17.5, and 26.5 min intersected at an isosbestic point (λ 299 (5570)). In contrast to the EDQ diagram, the corresponding ED diagram was nonlinear. After irradiation, the soln. showed absorption maxima at 281 (9650) and 247 (10620). After warming up to r.t., the newly formed spectrum was substituted by the absorption of *rac*-**15** which had been reformed to 97%.

1.8. *Irradiation of* rac-**18** (see *Scheme 6*) *in MeOH.* A soln. of *rac*-**18** (5.55 g; 19.1 mmol; for preparation, see *Exper. 2.8*) in abs. MeOH (1 l) was irradiated until educt had disappeared (after 4 h; UV control). The residue, obtained after removal of solvent under reduced pressure, was purified by FC (200 g of silica gel; hexane/AcOEt 20:1) and bulb-to-bulb distillation (190°/0.2 Torr) to afford 5.23 g (85%) of *(1*RS,*2Z,4*E*)-5-acetoxy-1-(methoxycarbonyl)cyclopentadeca-2,4-diene* (= *(5*RS,*1*E,*3Z)-5-(methoxycarbonyl)cyclopentadeca-1,3-dien-1-yl acetate*; *rac*-**19**). M.p. 44–45° (Et_2O) ([7]: 42–44° (pentane)). TLC (hexane/AcOEt 8:1): R_f 0.39. UV (hexane): λ_{max} 240 (19870). IR (KBr): 3023*w*, 2930*s*, 2857*s* (C–H); 1757*s* (acetate); 1737*s* (ester); 1663*m*, 1611*w* (C=C); 1369*s* (CH_3); 1230*s* (acetate); 1201*s* (ester); 1162*s*, 1124*s*, 1080*m*, 1042*m*, 1016*m*, 972*w*, 916*m*, 792*m*, 745*m*, 731*m*, 711*m*, 668*m*. ^{1}H-NMR: 1.25–1.63 (*m*, 2 H–C(7) through 2 H–C(14), H–C(15)); 1.76–1.85 (*m*, H′–C(15)); 2.21 (*ddd*, *J*(H–C(6),H′–C(6)) = 14.4, *J*(H–C(6),H–C(7)) = 6.3, *J*(H–C(6), H′–C(7)) = 3.5, H–C(6)); 2.16 (*s*, $MeCO_2$); 2.60 (*ddd*, as 7-line signal, $J_1 \approx 14.2$, $J_2 \approx 9.9$, $J_3 \approx 3.9$, H′–C(6)); 3.40 (ψdt, $J_1 \approx 10.1$, $J_2 \approx 3.6$, H–C(1)); 3.67 (*s*, MeO); 5.58 (ψdt, $J_1 \approx 9.9$, $J_2 \approx 0.8$, H–C(2)); 6.07 (*dd*, *J*(H–C(4),H–C(3)) = 10.9, *J*(H–C(4),H–C(2)) = 0.9, H–C(4)); 6.23 (ψt, $J \approx 10.9$, H–C(3)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross signals between 1.25–1.63/1.76–1.85, 1.25–1.63/2.21, 1.25–1.63/2.60, 1.25–1.63/3.40, 1.76–1.85/3.40, 2.60/2.21, 3.40/5.58, 5.58/6.23, and 6.23/6.07. NOEs from difference spectra (irradiated signal/NOE): H–C(1)/H–C(2) (1%); H–C(1)/H–C(4) (5%); H–C(1)/H–C(6) (1%); H–C(1)/H′–C(15) (3%); H–C(2)/H–C(1) 81.5%); H–C(2)/H–C(3) (4%); H–C(2)/H–C(6) (2%); H–C(2)/H–C(15) (1.5%); H–C(2)/OCH_3 (1%); H–C(3)/H–C(1) (1%); H–C(3)/H–C(2) (3%); H–C(3)/H′–C(6) (5%); H–C(3)/H′–C(15) (1%); H–C(4)/H–C(1) (6%); H–C(6)/H′–C(6) (5%); H′–C(6)/H–C(3) (5%); H′–C(15)/H–C(1) (2%). ^{13}C-NMR: 21.08 ($MeCO_2$); 24.83, 25.57, 25.81, 26.54, 26.59, 26.80, 26.86, 26.95 (C(7) to C(14)); 28.84 (C(15)); 31.93 (C(6)); 43.39 (C(1)); 51.81 (MeO); 114.47 (C(4)); 124.60 (C(3)); 129.46 (C(2)); 152.99 (C(5)); 169.38 (MeCOO); 174.51 (COOMe). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks between 129.46/5.58, 124.0/6.23, 114.47/6.07, 51.81/3.67, 43.39/3.40, 31.93/2.60, 31.93/2.21, 28.84/1.76–1.85, 28.84/1.25–1.63; and 21.08/2.16. Anal. calc. for $C_{19}H_{30}H_4$ (322.44): C 70.78, H 9.37; found: C 70.91, H 9.31.

Crystal-Structure Analysis of rac-**19** *at –160° (Fig. 16)*: Triclinic crystal, obtained by isothermal crystallization from Et_2O at –25°, $P\bar{1}$ (No. 2); a = 10.960(3), b = 16.820(8), c = 21.674(8) Å; α = 93.04(3), β = 103.75(3), γ = 106.52(3)°; V = 3690(6) Å^3; Z = 8 (4 indep. molecules), ρ = 1.164 g/cm^3; hemi-sphere through 2θ = 100°; 5822 indep. reflect. with $I > 0$; 1242 variables; $R(F)$ = 0.068; $R_w(F)$ = 0.103.

Examination of the same crystal at r.t. shows a unit cell half as large as that at –160°. The unit cell constants at r.t. are: a = 11.165(3), b = 13.530, c = 14.145(3)Å; α = 75.31(1), β = 89.08(2), γ = 68.96(1)°, and V = 1922.4(7)Å^3; ρ = 1.114 g/cm^3. Z = 4 (two independent molecules); space group $P\bar{1}$ (No. 2). The r.t. structure contains two independent molecules. Both are appreciably disordered in the polymethylene region. After cooling to –160°, a phase transition had taken place, the result of which was the doubling of the unit cell. The relationship between the cell constants at r.t. and at –160° is:

$$\begin{matrix} a \\ b \\ c_{115\,K} \end{matrix} = \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 1 \\ 0 & -1 & -1 \end{matrix} \cdot \begin{matrix} a \\ b \\ c_{r.t.} \end{matrix}$$

1.9. *Irradiation of* rac-**20** (see *Scheme 7*) *in MeOH*. A soln. of *rac*-**20** (250 mg; 0.76 mmol; for preparation, see *Exper. 2.9*) and LiSCN (494 mg; 7.6 mmol) in abs. MeOH (200 ml) was irradiated for 3 h. The residue remaining after removal of solvent under reduced pressure was purified by FC (10 g of silica gel; hexane/AcOEt 1:1) and prep. HPLC (hexane/AcOEt 10:13) to afford 164 mg (60%) of *methyl (12*RS,*13Z*,*15*E)-16-*acetoxy-1,4,7,10-tetraoxacycloheptadeca-13,15-diene-12-carboxylate* (*rac*-**21**): TLC (hexane/AcOEt 1:3): R_f 0.28. UV (MeOH): λ_{max} 240 (18855). IR (film): 2951*w*, 2868*m*, 2742*w* (C–H); 1738*s* (ester); 1732*s* (acetate); 1614*w*, 1433*m* (C=C); 1368*s* (CH_3); 1211*s*, 1023*s* (acetate); 1154*s*, 1110*s* (C–O). ^{1}H-NMR: 2.16 (*s*, $MeCO_2$); 3.48–3.85 (*m*, 3 OCH_2CH_2O, CO_2Me, H–C(12), 2 H–C(11)); 3.94–4.10 (*d*,*J*(H–C(17),H′–C(17)) = 13.4, H–C(17)); 4.51 (*d*, *J*(H′–C(17),H–C(17)) = 13.4, H′–C(17)); 5.64–5.7 (*m*, H–C(13)); 6.29 (*d*, *J*(H–C(14),H–C(15)) = 11.2, H–C(15)); 6.47 (ψt, *J*(H–C(13),H–C(14)) = *J*(H–C(14),H–C(15)) = 11.2, H–C(14)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. ^{13}C-NMR: 20.91 (*Me*COO); 44.67 (C(12)); 52.04 (C(11)); 67.01 (C(17)); 69.30–71.41 (C(2) to C(9), CO_2(*Me*)); 117.45 (C(15)); 124.88 (C(14)); 128.64 (C(13)); 169.50 (MeCOO); 171.81 (CO_2Me). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Anal. calc. for $C_{17}H_{26}O_8$ (358.39): C 56.97, H 7.31; found: C 56.71, H 7.27.

1.10. *Irradiation of* rac-**22** (see *Scheme 7*) *in MeOH*. A soln. of *rac*-**22** (130 mg; 0.81 mmol; for preparation, see *Exper. 2.10*) and KSCN (800 mg; 8.23 mmol) in abs. MeOH (50 ml) was irradiated for 2.5 h. After concentration, the residue was dissolved in CH_2Cl_2 (50 ml). Neutral workup furnished 163 mg (51%) of *methyl (15*RS,*16Z*,*18*E)-19-acetoxy-*1,4,7,10,13-pentaoxacycloicosa-16,18-diene-1-carboxylate* (*rac*-**23**): M.p. 74° (Et_2O). TLC (CH_2Cl_2/MeOH/NH_3 500:50:1): R_f 0.79. UV (MeOH): λ_{max} 241 (21802). IR (KBr): 2957*w*, 2914*m*, 2885*m*, 2859*m* (C–H); 1742*s* (ester); 1730*s* (acetate); 1613*w*, 1464*m*, 1444*m* (C=C); 1373*s* (CH_3); 1224*s*, 1042*s* (acetate); 1203*s*, 1140*s*, 1112*s* (C–O). ^{1}H-NMR: 2.17 (*s*, $MeCO_2$); 3.54–3.77 (*m*, 4 OCH_2CH_2O, CO_2Me, H–C(15), 2 H–C(14)); 4.09 (*d*, *J*(H–C(20), H′–C(20)) = 13.3, H–C(20)); 4.45 (*d*, J(H′–C(20), H–C(20)) = 13.3, H′–C(20)); 5.64–5.72 (br. m_c, H–C(16)); 6.29 (*d*, *J*(H–C(18), H–C(17)) = 11.6, H–C(18)); 6.48 (ψt, *J*(H–C(17), H–C(16)) = *J*(H–C(17),H–C(4(18)) = 11.6, H–C(17)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 6.48/6.29, 6.48/5.70; 5.70/3.60–3.70. Anal. calc. for $C_{19}H_{30}O_9$ (402.45): C 56.71, H 7.51; found: C 56.67, H 7.46.

1.11. *Irradiation of* rac-**24a** (see *Scheme 8*). 1.11.1. *In the Presence of Cyclohexylamine*. A soln. of *rac*-**24a** (528 mg; 2.0 mmol; for preparation, see *Exper. 2.11*) and freshly distilled cyclohexylamine (2.26 ml; 20.0 mmol) in anh. Et_2O (250 ml) was irradiated. No educt could be detected UV-spectroscopically after 1.5 h. Acidic workup afforded a residue which was purified by FC (100 g of silica gel; hexane/AcOEt 6:1), prep. HPLC (hexane/AcOEt 10:1; refract.) and crystallization (from Et_2O/pentane at −28°) to give 450 mg (62%) of *(2*RS,*3Z*,*5*E)-N-*cyclohexyl-6-acetoxy-2-(*tert-*butyl)-7,7-dimethylocta-3,5-dienamide* (= *(1*E,*3Z)-1,5-di(*tert-*butyl)-6-(cyclohexylamino)-6-oxohexa-1,3-dienyl acetate*; rac-**25a**): M.p. 146–147° (Et_2O). TLC (hexane/AcOEt 8:1): R_f 0.24. UV (MeOH): λ_{max} 242 (24021). IR (KBr): 3280*s* (NH); 2934*s* (C–H); 1764*s* (acetate); 1651*m* (C=C); 1632*s* (amide I); 1542*s* (amide II); 1365*s* (CH_3); 1220*s* (acetate); 1073*s*; 1027*m*. ^{1}H-NMR: 0.99 (*s*, Me_3C–C(6)); 1.08–1.19 (*m*, 2 H–C(3′)); 1.20 (*s*, Me_3C–C(2); 1.22–1.44 (*m*, 2 H–C(2′), 2 H–C(6′)); 1.57–1.93 (*m*, 2 H–C(4′), 2 H–C(5′)); 2.17 (*s*, $MeCO_2$); 2.80 (*dd*, *J*(H–C(2),H–C(3)) = 10.4, *J*(H–C(2),H–C(4)) = 0.7, H–C(2)); 3.73 (*m*, H–C(1′)); 5.40 (ψd, *J*(HN,H–C(1′)) = 8.2, NH); 5.72 (ψdd, *J*(H–C(3),H–C(2)) = 10.6, *J*(H–C(3),H–C(4)) = 11.1, H–C(3)); 5.78 (ψd, *J*(H–C(5),H–C(4)) = 11.2, H–C(5)); 6.56 (*ddd*, *J*(H–C(4),H–C(5)) = 11.2, *J*(H–C(4),H–C(3)) = 11.1, *J*(H–C(4),H–C(2)) = 0.7, H–C(4)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (2.1%); H–C(2)/H–C(5) (8.2%); H–C(2)/^{t}Bu–C(2) (5.6%); H–C(3)/H–C(2) (1.8%); H–C(3)/H–C(4) (4.5%); H–C(3)/^{t}Bu–C(6) (0.8%); H–C(3)/^{t}Bu–C(2) (0.7%); H–C(4)/H–C(3) (4.8%); H–C(4)/H–C(5) (1.7%); H–C(4)/^{t}Bu–C(6) (3.6%); H–C(4)/^{t}Bu–C(2) (2.3%); H–C(5)/H–C(2) (6.3%); H–C(5)/H–C(4) (2.0%); NH/H–C(3) (5.8%). Anal. calc. for $C_{22}H_{37}NO_3$ (363.54): C 72.69, H 10.26, N 3.85; found: C 72.62, H 10.20, N 3.86.

1.11.2. *In MeOH*. A soln. of *rac*-**24a** (528 mg; 2.0 mmol) in anh. MeOH (200 ml) was irradiated for 2 h. Then, by UV-spectroscopic control no educt was to be detected. Evaporation of solvent under reduced pressure furnished 510 mg (86%) of *methyl (2*RS,*3Z*,*5E)-6-acetoxy-2-(*tert-*butyl)-7,7-dimethylocta-3,5-dienoate* (= *(1*E,*3Z)-1,5-di(*tert-*butyl)-6-(methoxycarbonyl)hexa-1,3-dienyl acetate*; *rac*-**25b**). The following data have been obtained after prep. HPLC (hexane/Et_2O 10:1): TLC (hexane/AcOEt 10:1): R_f 0.21. UV (MeOH): λ_{max} 241 (23508). IR (KBr): 2961*s* (C–H); 1760*s* (ester); 1736*s* (acetate); 1432*s* (C=C); 1367*s* (CH_3); 1218*s* (acetate); 1149*m*, 1080*w*. ^{1}H-NMR: 0.97 (*s*, Me_3C–C(6)); 1.22 (*s*, Me_3C–C(2)); 2.16 (*s*, $MeCO_2$); 3.22 (ψd, *J*(H–C(2),

H–C(3)) = 11.5, H–C(2)); 3.65 (*s*, CO_2Me); 5.64 (*dt*, *J*(H–C(3),H–C(2)) = *J*(H–C(3),H–C(4)) = 11.1, *J*(H–C(3),H–C(5)) = 1.3, H–C(3)); 5.83 (*dd*, *J*(H–C(5), H–C(3)) = 1.3, *J*(H–C(5),H–C(4)) = 11.8, H–C(5)); 6.62 (*ddd*, *J*(H–C(4),H–C(5)) = 11.8, *J*(H–C(4),H–C(3)) = 11.1, *J*(H–C(4),H–C(2)) = 0.6, H–C(4)).

1.11.3. *In TFE.* 1.11.3.1. *In the Presence of NMI.* A soln. of *rac*-**24a** (528 mg; 2 mmol) and NMI (1.59 ml; 20 mmol) in anh. TFE (10 ml) was irradiated for 4 h. Reaction progress was followed UV-spectroscopically. After concentration under reduced pressure, the obtained residue was purified by chromatography (80 g of silica gel; hexane/AcOEt 8:1) and prep. HPLC (hexane/Et_2O 10:1) to furnish 140 mg (19%) of *rac*-**25a**, and 80 mg (15%) of **27**.

*2,2,2-Trifluoroethyl (2*RS*,3Z,5*E*)-6-acetoxy-2-(*tert*-butyl)-7,7-dimethylocta-3,5-dienoate* (= *(1*E*,3Z)-1,5-di-(*tert*-butyl)-6-[(2,2,2-trifluoroethoxy)carbonyl]hexa-1,3-dienyl acetate; rac*-**25c**): TLC (hexane/AcOEt 10:1): R_f 0.14. UV (MeOH): λ_{max} 241 (22706). IR (film): 2968*m* (C–H); 1753*s* (C=O); 1651*w*, 1597*w* (C=C); 1369*m* (CH_3); 1279*s* (acetate); 1218*s* (C–F); 978*m*. ^{1}H-NMR: 0.99 (*s*, Me_3C–C(2)); 1.22 (*s*, Me_3C–C(6)); 2.16 (*s*, $MeCO_2$); 3.31 (*dd*, *J*(H–C(2),H–C(3)) = 11.0, *J*(H–C(2),H–C(4)) = 0.8, H–C(2)); 4.48 (*m*, CF_3CH_2); 5.61 (*ψdt*, *J*(H–C(3),H–C(2)) = 11.0, *J*(H–C(3),H–C(4)) = 11.2, *J*(H–C(3),H–C(5)) = 1.3, H–C(3)); 5.82 (*dd*, *J*(H–C(5),H–C(4)) = 1.3, *J*(H–C(5),H–C(4)) = 1.3, *J*(H–C(5),H–C(4)) = 11.8, H–C(5)); 6.66 (*ddd*, *J*(H–C(4),H–C(5)) = 11.8, *J*(H–C(4),H–C(3)) = 11.2, *J*(H–C(4),H–C(2)) = 0.8, H–C(4)). Anal. calc. for $C_{18}H_{27}O_4F_3$ (364.42): C 59.38, H 7.47; found: C 59.31, H 7.55.

*4-Acetoxy-2,6-di(*tert*-butyl)phenol* (**27**). M.p. 92–93° (pentane). TLC (hexane/AcOEt 10:1): R_f 0.37. IR (KBr): 3587*s* (OH); 2957*s* (C–H); 1741*s* (C=O); 1596*w* (C=C); 1369*s* (CH_3); 1224*s* (C–O). ^{1}H-NMR: 1.42 (*s*, 2 *t*-Bu); 2.27 (*s*, $MeCO_2$); 5.09 (*s*, OH); 6.86 (*s*, H–C(3),H–C(5)). Anal. calc. for $C_{16}H_{24}O_3$ (264.37): C 72.68, H 9.15; found: C 72.81, H 9.18.

1.11.3.2. *In the Absence of NMI.* A soln. of *rac*-**24a** (264 mg; 1 mmol) in anh. TFE (10 ml), was irradiated for 2 h. Reaction progress was followed UV-spectroscopically. After removal of solvent under reduced pressure, the obtained residue was purified by chromatography (30 g of silica gel; hexane/AcOEt 10:1) and semi-prep. HPLC (hexane/Et_2O 10:1) to afford traces of *rac*-**25c** (for data, see *Exper. 1.11.3.1*), unchanged *rac*-**24a** (45 mg; 15%), **27** (10 mg; 4%), and 110 mg (41%) of *(5Z)-5-(1-acetoxy-2,2-dimethylpropylidene)-2-(*tert*-butyl)cyclopent-2-en-1-one* (**26a**); *2-acetoxy-3-(*tert*-butyl)-1-(2,2-dimethylpropionyl)cyclopenta-1,3-diene* (**26b**): TLC (hexane/AcOEt 10:1): R_f 0.20. UV (MeOH): λ_{max} 261 (12840). IR (film): 2959*s* (C–H); 1777*s*, 1760*s* (acetate); 1691*s*, 1638*m* (unsat. ketone); 1612*s* (C=C); 1364*s* (acetate); 1319*m*, 1198*s* (C–O); 1120*s*, 1078*s*. ^{1}H-NMR: 1.18 (*s*, Me_3C–C=); 1.24 (*s*, Me_3C–C(2)); 2.34 (*s*, $MeCO_2$); 3.34 (*m*, 2 H–C(4)); 7.01 (*m*, H–C(3)). Anal. calc. for $C_{16}H_{24}O_3$ (264.37): C 72.69, H 9.15; found: C 72.55, H 9.11.

1.12. *Irradiation of* rac-**24b** (see *Scheme 9*). 1.12.1. *In Et_2O in the Presence of Cyclohexylamine.* A soln. of *rac*-**24b** (556 mg; 2 mmol; for preparation, see *Exper. 2.12*) and freshly distilled cyclohexylamine (2.26 ml; 20 mmol) in anh. Et_2O (250 ml) was irradiated for 1.5 h. After the dienone had completely reacted (TLC control; hexane/AcOEt 6:1) acidic workup yielded a residue which was purified by chromatography (100 g of silica gel; hexane/AcOEt 6:1) and crystallization (Et_2O/pentane) to give 582 mg (81%) of *(2*RS*,3Z,5*E*)-6-acetoxy-2-(*tert*-butyl)-*N*-cyclohexyl-4,7,7-trimethylocta-3,5-dienamide* (= *(1*E*,3Z,5*RS*)-1,5-di(*tert*-butyl)-6-(cyclohexylamino)-3-methyl-6-oxohexa-1,3-dienyl acetate*; *rac*-**28**): M.p. 100–101°. TLC (hexane/AcOEt 8:1): R_f 0.26. UV (MeOH): λ_{max} 219 (4727). IR (KBr): 3391*s* (NH); 2952*s*; 2932*s* (C–H); 1736*s* (acetate); 1664*s* (amide I); 1522*s* (amide II); 1362*m* (CH_3); 1230*s* (C–O); 1070*m*; 1021*m*. ^{1}H-NMR: 0.99 (*s*, Me_3C–C(2)); 1.11 (*s*, Me_3C–C(6)); 1.10–1.31, 1.62–1.68, 1.58–1.92 (3*m*, 2 H–C(2′) through 2 H–C(6′)); 1.87 (*s* with f.s., Me–C(4)); 2.18 (*s*, $MeCO_2$); 2.96 (*d*, *J*(H–C(2),H–C(3)) = 10, H–C(2)); 3.73 (*m*, H–C(1′)); 5.38 (br. *s*, NH); 5.56 (*d* with f.s., *J*(H–C(3), H–C(2)) = 10, H–C(3)); 5.97 (*s* with f.s., H–C(5)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Anal. calc. for $C_{23}H_{39}NO_3$ (377.57): C 73.16, H 10.36, N 3.93; found: C 73.18, H 10.23, N 3.93.

Crystal-Structure Analysis of rac-**28** (*Fig. 17*): monoclinic crystals, $P2_1/c$ (No. 14); a = 15.383(2), b = 9.6076(7), c = 17.206(4) Å; β = 111.99(1)°; V = 2358(1) Å^3; Z = 4; ρ = 1.064 g/cm^3; hemisphere through 2θ = 120°; 3386 indep. reflect. with $I > \sigma(I)$; 401 variables; $R(F)$ = 0.048; $R_w(F)$ = 0.059.

1.12.2. *In MeOH in the Presence of DABCO.* A soln. of *rac*-**24b** (556 mg; 2 mmol) and freshly sublimed DABCO (224 mg; 2 mmol) in abs. MeOH (150 ml) was irradiated for 4 h. Although 20% of *rac*-**24b** were still be present (UV control), workup followed because of photochemical instability of primary photoproduct. After neutral workup, the obtained residue was purified by chromatography (80 g of silica gel; hexane/AcOEt 10:1) and crystallization (pentane at –28°) to yield unchanged *rac*-**24b** (110 mg; 20%), 190 mg (34%) of *rac*-**29** and 110 mg (20%) of **30**.

*(*RS*)-exo-6-acetoxy-3,6-di(*tert*-butyl)-5-methylbicyclo[3.1.0]hex-3-en-2-one* (*rac*-**29**): M.p. 95–96° (pentane). TLC (hexane/AcOEt 10:1): R_f 0.17. UV (MeOH): λ_{max} 223 (5675); 267 (1873); 338 (214). IR (KBr): 2971*s* (C–H); 1745*s* (acetate); 1697*s* (unsat. ketone); 1482*s*; 1362*s* (*t*-Bu); 1196*s*; 1161*s*; 1026*s*; 1021*s* (cyclopropane).

^{1}H-NMR: 1.06 (*s*, Me_3C–C(3)); 1.15 (*s*, Me_3C–C(6), 1.41 (*s*, Me–C(5)); 2.04 (*s*, $MeCO_2$); 2.16 (*s*, H–C(1)); 6.86 (*s* with f.s., H–C(4)). The relative configuration at C(6) was determined by difference spectra (irradiated signal/NOE): ^{t}Bu–C(3)/H–C(4) (0.2%); ^{t}Bu–C(3)/^{t}Bu–C(6) (3.6%); H–C(4)/^{t}Bu–C(3) (2.2%); H–C(4)/CH_3–C(5) (0.9%); H–C(4)/^{t}Bu–C(6) (2.5%); H–C(4)/$MeCO_2$ (0.9%); Me–C(5)/H–C(4) (0.6%); ^{t}Bu–C(6)/^{t}Bu–C(3) (2.7%); ^{t}Bu–C(6)/(H–C(4) (0.9%); ^{t}Bu–C(6)/Me–C(5) (1.4%); $MeCO_2$/^{t}Bu–C(3) (0.6%); $MeCO_2$/Me–C(5) (0.2%); $MeCO_2$/H–C(1) (10.4%); $MeCO_2$/^{t}Bu–C(6) (0.6%). Anal. calc. for $C_{17}H_{26}O_3$ (278.39): C 73.33, H 9.33; found: C 73.34, H 9.41 and 110 mg (20%).

4-Acetoxy-2,6-di(tert-*butyl*)*-4-methylcyclohexa-2,5-dien-1-one* (= *3,5-Di*(tert-*butyl*)*-1-methyl-4-oxocyclohexa-2,5-dienyl Acetate*; **30**): M.p. 79–80° (pentane). TLC (hexane/AcOEt 10:1): R_f 0.50. UV (MeOH): λ_{max} 242 (10085). IR (KBr): 2959*s* (C–H); 1753*s* (acetate); 1667*s*, 1647*s* (unsat. ketone); 1236*s* (C–O). ^{1}H-NMR: 1.22 (*s*, 2 *t*-Bu); 1.50 (*s*, Me–C(4)); 2.04 (*s*, $MeCO_2$); 6.59 (*s*, H–C(3), H–C(5)). Anal. calc. for $C_{17}H_{26}O_3$ (278.39): C 73.35, H 9.41; found: C 73.29, H 9.39.

1.12.3. *In TFE.* A soln. of *rac*-**24b** (1.11 g; 4 mmol) in anh. TFE (250 ml) was irradiated. After 3 h, reaction had been completed (UV and TLC control; hexane/AcOEt 10:1). The residue, obtained after neutral workup, was chromatographed (150 g of silica gel; hexane/AcOEt 8:1) to give *rac*-**29** (240 mg; 22%; for data, see *Exper. 1.12.2*) and 610 mg (69%) of *5-acetoxy-2-*(tert-*butyl*)*-4-methylphenol* (**31**). M.p. 102–103° (pentane). TLC (hexane/AcOEt 10:1): R_f 0.21. UV (MeOH): λ_{max} 279 (3182). IR (KBr): 3333*s* (br. OH); 2962*s*; 2953*s* (C–H); 1741*s*; 1728*s* (acetate); 1594*m*; 1594*m* (C=C); 1409*s*; 1255*s*; 1233*s*, 1204*s*; 1133*s*. ^{1}H-NMR: 1.37 (*s*, *t*-Bu); 2.08 (*s*, Me–C(4)); 2.29 (*s*, $MeCO_2$); 4.88 (*s*,OH); 6.39 (*s*, H–C(2)); 7.06 (*s*,H–C(5)). ^{13}C-NMR: 15.5 (*Me*–C(4)); 20.9 (*Me*COO); 29.6 (Me_3C); 34.2 (Me_3C); 110.0 (C(2)); 120.5 (C(4)); 129.2 (C(5)); 134.0 (C(6)); 147.1 (C(3)); 152.8 (C(1)); 169.8 (MeCOO). The signals were assigned by DEPT and GATED spectra. Anal. calc. for $C_{13}H_{18}O_3$ (222.28): C 70.24, H 8.16; found: C 70.10, H 8.15.

1.12.4. *Irradiation of* rac-**29** *in TFE.* A soln. of *rac*-**29** (139 mg) in anh. TFE (25 ml) was irradiated for 3 h. UV Control showed disappearance of educt. The residue isolated after neutral workup was purified by semi-prep. HPLC (hexane/AcOEt 10:1) to afford 85 mg (61%) of *(4*RS*,5Z)-5-(1-acetoxy-2,2-dimethylpropyliden)-2-(*tert-*butyl)-4-methylcyclopent-2-en-1-one* (*rac*-**32**): TLC (hexane/AcOEt 10:1): R_f 0.24. IR (film): 2960*s* (C–H); 1771*s* (acetate); 1661*s*, 1637*s* (unsat. ketone); 1455*m*, 1358*s* (acetate); 1205*s* (C–O); 1105*s*. ^{1}H-NMR: 0.99 (*s*, Me_3C–C(1')); 1.24 (*s*, Me_3C–C(2)); 1.25 (*s*, Me–C(4)); 2.23 (*s*, $MeCO_2$); 6.11 (*s*, H–C(6)); 6.53 (*s*, H–C(3)). Anal. calc. for $C_{17}H_{26}O_3$ (278.39): C 73.35, H 9.41; found: C 72.99, H 9.34. The formation of phenol **31** could be excluded.

1.13. *Irradiation of* rac-**33a** (see *Scheme 10*). 1.13.1. *In the Presence of Cyclohexylamine.* A soln. of *rac*-**33a** (530 mg; 2.55 mmol; for preparation see *Exper. 2.13*) and freshly distilled cyclohexylamine (880 µl; 7.65 mmol) in anh. Et_2O (250 ml) was irradiated for 2 h. After acidic workup, the remaining residue was purified by chromatography (200 g of silica gel; hexane/AcOEt 1:1 through 2:3) to give a colorless solid (516 mg; 66%) which contained the diastereoisomer mixture **34a**/**34c** in a ratio of 85:15 (anal. HPLC). Separation by semi-prep. HPLC (hexane/AcOMe 10:15; 2 ml/min; 254 nm and refr.) afforded 300 mg (38%) of **34a** and 51.4 mg of **34c**.

*(3Z,5*E*)-6-Acetoxy-*N*-cyclohexyl-8-oxonona-3,5-dienamide* (= *(1*E*,3Z)-6-(Cyclohexylamino)-6-oxo-1-(2-oxopropyl)hexa-1,3-dien-1-yl Acetate*; **34a**): M.p. 114° (Et_2O/AcOEt). TLC (hexane/AcOEt 2:3): R_f 0.27. UV (MeOH): λ_{max} 242 (23190). IR (KBr): 3290*s* (N–H, monosubst. amide); 3080*w* (N–H); 1750*s* (acetate); 1715*s* (ketone); 1635*s* (amide I); 1560*m* (amide II); 1210*s* (acetate). ^{1}H-NMR ($CDCl_3$/C_6D_6 3:1): 1.00–1.85 (*m*, 2 H–C(2') to 2 H–C(6')); 2.01 (*s*, $MeCO_2$); 2.06 (*s*, 3 H–C(9)); 2.95 (*dd*, *J*(H–C(2),H–C(3)) = 7.6, *J*(H–C(2),H–C(4)) = 1.4, 2 H–C(2)); 3.33 (*s*, 2 H–C(7)); 3.69–3.75 (*m*, H–C(1')); 5.33 (br. *d*, NH); 5.65 (*dt*, *J*(H–C(3),H–C(4)) = 10.1, *J*(H–C(3),H–C(2)) = 7.6, H–C(3)); 6.07 (ψtt, *J*(H–C(4),H–C(5)) = *J*(H–C(4), H–C(3)) = 11, *J*(H–C(4),H–C(2)) = 1.4, H–C(4)); 6.17 (*d*, *J*(H–C(5),H–C(4)) = 11.7, H–C(5)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(5) (4.5%); H–C(3)/H–C(2) (1.3%); H–C(3)/H–C(4) (3.9%); H–C(3)/H–C(5) (1.4%); H–C(4)/H–C(3) (4.1%); H–C(4)/H–C(7) (2.5%); H–C(5)/H–C(2) (2.9%); H–C(5)/H–C(7) (0.9%); H–C(7)/H–C(4) (5.7%); H–C(7)/H–C(5) (0.7%); H–C(7)/H–C(9) (0.5%); H–C(9)/H–C(7) (0.8%). Anal. calc. for $C_{17}H_{25}NO_4$ (307.39): C 66.43, H 8.20, N 4.56; found: C 66.29, H 8.24, N 4.55.

*(3Z,5Z)-6-Acetoxy-*N*-cyclohexyl-8-oxonona-3,5-dienamide* (= *(1Z,3Z)-6-(Cyclohexylamino)-6-oxo-1-(2-oxopropyl)hexa-1,3-dien-1-yl Acetate;* **34c**): M.p. 98° (Et_2O/pentane). TLC (hexane/AcOEt 2:3): R_f 0.20. UV (MeOH): λ_{max} 242 (24190). IR (KBr): 3310*m* (N–H, monosubst. amide); 3050*w* (NH); 1750*s* (acetate); 1720*m* (ketone); 1645*s* (amide I); 1545*m* (amide II); 1215*m* (acetate). ^{1}H-NMR: 1.03–1.93 (*m*, 2 H–C(2') to 2 H–C(6')); 2.19 (*s*, $MeCO_2$); 2.21 (*s*, 3 H–C(9)); 3.09 (*dd*, *J*(H–C(2),H–C(3)) = 7.8, *J*(H–C(2),H–C(4)) = 1.4, 2 H–C(2)); 3.40 (*s*, 2 H–C(7)); 3.66–3.81 (*m*, H–C(1')); 5.47 (br. *d*, NH); 5.65 (*dt*, *J*(H–C(3),H–C(4)) = 10.9, *J*(H–C(3), H–C(2)) = 7.8, H–C(3)); 5.97 (*d* with f.s., *J*(H–C(5),H–C(4)) = 11.2, H–C(5)); 6.26 (ψtt, *J*(H–C(4),

H–C(5)) = *J*(H–C(4),H–C(3)) = 11.0, *J*(H–C(4),H–C(2)) = 1.4, H–C(4)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(5) (6.3%); H–C(3)/H–C(2) (2.0%); H–C(3)/H–C(4) (5.4%); H–C(4)/H–C(2) (0.6%); H–C(4)/H–C(3) (4.4%); H–C(5)/H–C(2) (3.4%); H–C(5)/H–C(3) (1.1%); H–C(5)/H–C(7) (2.1%); H–C(5)/H–C(9) (0.3%); H–C(9)/H–C(7) (0.4%). Anal. calc. for $C_{17}H_{26}NO_4$ (307.39): C 66.43, H 8.20, N 4.56; found: C 66.32, H 8.19, N 4.64.

1.13.2. *Base-Induced Isomerization of* **34a**. A soln. of **34a** (280 mg; 0.91 mmol) and freshly distilled cyclohexylamine (320 µl; 2.73 mmol) in 100 ml of anh. Et_2O was left for 2 h at r.t. Acidic workup and purification of the obtained residue by chromatography (150 g of silica gel; hexane/AcOEt 1:1 through 2:3) and semi-prep. HPLC (hexane/AcOMe 10:15; 2 ml/min; 254 nm and refract.) afforded **34a** (229 mg; 82%) and **34c** (20 mg; 7%). A soln. of **33a** (4.19 mg; 0.014 mmol) and 1.5 ml of a soln. of 650 µl cyclohexylamine (0.042 mmol) in 200 ml abs. Et_2O was monitored by HPLC. The ratio of **34a**/**34c** was determined (time [min]; ratio [%]): 0, 100:0, 50, 96.5:3.5; 85, 94.3:5.7; 130, 91.5:8.5; 165, 89,2:10.8; 225, 85.9; 14.1. The change paralleled the isomerization taking place during the irradiation of *rac*-**33a** in the presence of cyclohexylamine.

1.13.3. *In MeOH*. A soln. of *rac*-**33a** (517 mg; 2.48 mmol) in abs. MeOH (250 ml) was irradiated until educt had disappeared (after 2 h; UV control). The residue obtained after removal of solvent under reduced pressure was purified by chromatography (40 g of silica gel; hexane/AcOEt 2:1) to yield a colorless oil (484 mg; 81%) an anal. sample of which, after HPLC (hexane/1,4-dioxane 4:1; 2 ml/min; 254 and refract.), showed properties for *(3Z,5E)-ethyl 6-acetoxy-8-oxonona-3,5-dienoate* (= *(1E,3Z)-6-methoxy-6-oxo-1-(2-oxopropyl)hexa-1,3-dien-1-yl acetate*; **34b**): TLC (hexane/AcOEt 1:1): R_f 0.45. UV (MeOH): λ_{max} 240 (18380). IR (film): 3020*w* (unsat. C–H); 1730*s* (enolacetate, ester, ketone); 1660*m* (C=C); 1210*s* (acetate). ^{1}H-NMR: 2.14 (*s*, $MeCO_2$); 2.20 (*s*, 3 H–C(9)); 3.20 (*dd*, *J*(H–C(2),H–C(3)) = 7.5, *J*(H–C(2),H–C(4)) = 1.6, 2 H–C(2)); 3.46 (*s*, 2 H–C(7)); 5.75 (*dt*, *J*(H–C(3),H–C(4)) = 9.8, *J*(H–C(3),H–C(2)) = 7.5, H–C(3)); 6.14 (*ψtt*, *J*(H–C(4),H–C(5)) = 11.6, *J*(H–C(4),H–C(3)) = 9.8, *J*(H–C(4),H–C(2)) = 1.6, H–C(4)); 6.22 (*d*, *J*(H–C(5),H–C(4)) = 11.6, H–C(5)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(5) (4.2%); H–C(3)/H–C(4) (1.1%); H–C(3)/H–C(5) (1.1%); H–C(4)/H–C(2) (0.6%); H–C(4)/H–C(3) (3.4%); H–C(4)/H–C(7) (2.4%); H–C(5)/H–C(2) (2.7%); H–C(5)/H–C(3) (0.9%); H–C(5)/H–C(7) (1.1%); H–C(7)/H–C(4) (4.3%); H–C(7)/H–C(5) (1.1%); H–C(7)/H–C(9) (0.6%); H–C(9)/H–C(7) (0.8%). Anal. calc. for $C_{12}H_{16}O_5$ (240.26): C 59.99, H 6.71; found: C 59.75, H 6.72.

1.14. *Irradiation of* rac-**33b** (see *Scheme 12*). 1.14.1. *In the Presence of* NH_3. To a soln. of *rac*-**33b** (590 mg; 2.36 mmol; for preparation, see *Exper. 2.14*) in anh. Et_2O (700 ml), 30 ml of an ammoniacal Et_2O soln. (*ca.* 0.24M; *ca.* 7.20 mmol) was given. The soln. was irradiated until the dienone had disappeared (90 min; UV control). Acidic workup led to a residue (519 mg) which was purified by chromatography (50 g of silica gel; hexane/AcOEt 2:1) and semi-prep. HPLC (hexane/AcOEt 1:5; 254 nm) to give 210 mg (33%) of **35a** and 110 mg (17%) of *rac*-**36a**.

(3Z,5E)-6-Acetoxy-4-isopropyl-8-oxonona-3,5-dienamide (= *(1E,3Z)-6-Amino-3-isopropyl-6-oxo-1-(2-oxopropyl)hexa-1,3-dien-1-yl Acetate*; **35a**): M.p. 78–79° (CH_2Cl_2/hexane). TLC (hexane/AcOEt 1:2): R_f 0.07. UV (CH_2Cl_2): λ 280.0 (sh, 69). IR (KBr): 3442*s*, 3354*s*, 3200*s* (N–H); 2963*s*, 2872*m* (C–H); 1755*s* (acetate); 1715*s* (ketone); 1674*s* (amide I + II); 1614*m* (C=C); 1213*s*, 1123*s* (C–O). ^{1}H-NMR: 1.03 (*d*, *J*(*H*–CH_2)$_2$CH, Me_2CH) = 6.8, *Me*$_2$CH); 2.16 (*s*, 3 H–C(9), $MeCO_2$); 2.39 (*sept.*, *J*(Me_2CH,(*H*–CH_2)$_2$CH) = 6.8, Me_2CH); 2.99 (*d*, *J*(H–C(2),H–C(3)) = 7.9, 2 H–C(2)); 3.37 (*s*, 2 H–C(7)); 5.43, 5.88 (2br. *s*, NH_2); 5.67 (*t* with f.s., *J*(H–C(3),H–C(2)) = 7.9, H–C(3)); 5.80 (*s*, H–C(5)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (1.2%); H–C(2)/H–C(5) (0.3%); H–C(3)/H–C(2) (5.5); H–C(3)/H–C(7) (0.8%); H–C(3)/^{i}Pr (2.0%); H–C(5)/H–C(2) (1.4%); H–C(5)/H–C(7) (0.5%); H–C(5)/^{i}Pr (1.8%); H–C(7)/H–C(2) (0.4%); H–C(7)/H–C(3) (0.2%), H–C(7)/^{i}Pr (0.8%). Anal. calc. for $C_{14}H_{21}NO_4$ (267.32): C 62.90, H 7.92, N 5.24; found: C 62.71, H 7.79, N 5.20.

(5RS,6SR)-5-Carbamoyl-6-hydroxy-3-isopropyl-6-methylcyclohepta-1,3-dienyl Acetate (*rac*-**36a**): M.p. 103° (hexane). TLC (hexane/AcOEt 1:2): R_f 0.21. UV (MeOH): λ_{max} 244 (5963). IR (KBr): 3348*s*, 3206*s* (O–H, N–H); 2964*s*, 2873*s* (C–H); 1756*s* (acetate); 1674*s* (amide I + II); 1621*m* (C=C); 1215*s*, 1113*s* (C–O). ^{1}H-NMR: 1.06 (*d*, *J*(*H*–CH_2)$_2$CH,Me_2CH) = 6.9, Me_2CH); 1.32 (*s*, Me–C(6)); 2.15 (*s*, $MeCO_2$); 2.38 (*sept.*, *J*(Me_2CH, (*H*–CH_2)$_2$CH) = 6.9, Me_2CH); 2.42 (*dd*, *J*(H′–C(7),H–C(7)) = 17.4, *J*(H′–CC(7),H–C(2)) = 1.6, H′–C(7)); 2.79 (*d* with f.s., *J*(H–C(7),H′–C(7)) = 17.4, H–C(7)); 3.13 (*d* with f.s., *J*(H–C(5),H–C(4)) = 7.9, H–C(5)); 5.17 (br. *s*, OH); 5.65 (*d*, *J*(H–C(2),H′–C(7)) = 1.6, H–C(2)); 5.77 (*d*, *J*(H–C(4),H–C(5)) = 7.9, H–C(4)); 5.92, 6.10 (2 br. *s*, NH_2). NOEs from difference spectra (irradiated signal/NOE): Me/OH (0.2%), Me/H–C(5) (0.5%); Me/H′–C(7) (0.6%); OH/Me (0.6%); OH/H–C(5) (0.9%); OH/H–C(7) (1.1%); H–C(5)/Me (1.7%); H–C(5)/OH (0.7%); H–C(7)/Me (0.9%); H–C(7)/OH (2.7%); H–C(7)/H–C(5) (1.1%); H–C(7)/H′–C(7) (9.6%). ^{13}C-NMR: 21.0 (*Me*CO_2); 21.5, 21.7 (*Me*$_2$CH); 27.6 (*Me*–C(6)); 36.1 (Me_2CH); 45.8 (C(7)); 54.7 (C(5)); 77.1 (C(6)); 116.4 (C(2)); 120.1 (C(4)); 144.9 (C(3)); 150.7 (C(1)); 169.3 ($MeCO_2$); 176.7 (NH_2CO). Anal. calc. for $C_{14}H_{21}NO_4$ (267.32): C 62.90, H 7.92, H 5.24; found: C 62.74, H 8.07, N 5.33.

1.14.2. *In the Presence of $PhCH_2NH_2$.* A soln. of *rac*-**33b** (240 mg; 0.96 mmol) and freshly distilled $PhCH_2NH_2$ (0.32 ml; 2.88 mmol) in anh. Et_2O (320 ml) was irradiated for 45 min, when *rac*-**33b** had completely reacted (UV control). Acidic workup afforded an orange oil (360 mg) which was purified by chromatography (50 g of silica gel; hexane/AcOEt 2:1) and semi-prep. HPLC (hexane/AcOEt 5:3; 254 nm) to give 85.3 mg (25%) of **35b** and 124 mg (36%) of *rac*-**36b**.

*(3Z,5E)-6-Acetoxy-*N*-benzyl-4-isopropyl-8-oxonona-3,5-dieneamide* (= *(1E,3Z)-6-(Benzylamino)-3-isopropyl-6-oxo-1-(2-oxopropyl)hexa-1,3-dien-1-yl Acetate*; **35b**): M.p. 76° (Et_2O/hexane). TLC (hexane/AcOEt 2:1): R_f 0.05. UV (MeOH): λ 229.9 (sh, 4383); λ 284.9 (sh, 318). IR (KBr): 3364*s*, 3037*w* (N–H); 2956*m*, 2926*m*, 2867*w* (C–H); 1750*s* (acetate); 1707*s* (ketone); 1667*s* (amide I); 1535s (amide II); 1215*s*, 1122*s* (C–O). ^{1}H-NMR (C_6D_6): 0.95 (*d*, $J((H\text{–}CH_2)_2CH, (CH_3)_2C\text{–}H)$ = 6.9, Me_2CH); 1.64, 1.68 (2*s*, 3 H–C(9), $MeCO_2$); 2.23 (*sept.*, $J(Me_2CH,(H\text{–}CH_2)_2CH)$ = 6.9, Me_2CH); 2.90 (*d*, J(H–C(2),H–C(3)) = 7.6, 2 H–C(2)); 3.25 (*s*, 2 H–C(7)); 4.25 (*d*, J(H–CHN, NH) = 5.8, CH_2N); 5.47 (br. *t*, J(NH, H–CHN) = 5.8, NH); 5.69 (*s*, H–C(5)); 5.78 (*t* with f.s., J(H–C(3),H–C(2)) = 7.6, H–C(3)); 7.00–7.19 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (1.1%); H–C(2)/H–C(5) (0.3%); H–C(2)/H–C(7) (0.4%); H–C(2)/^{i}Pr (1.9%); H–C(3)/H–C(2) (2.7%); H–C(3)/H–C(7) (0.6%); H–C(5)/H–C(2) (1.5%); H–C(5)/H–C(7) (0.5%); H–C(5)/^{i}Pr (2.4%); H–C(7)/H–C(2) (0.7%); H–C(7)/H–C(5) (< 0.1%); H–C(7)/^{i}Pr (0.8%). Anal. calc. for $C_{21}H_{27}NO_4$ (357.45): C 70.56, H 7.61, N 3.92; found: C 70.35, H 7.50, N 3.94.

*(5RS,6SR)-5-(*N*-Benzylcarbamoyl)-6-hydroxy-3-isopropyl-6-methylcyclohepta-1,3-dien-1-yl Acetate (rac-***36b**): M.p. 99° (Et_2O/hexane). TLC (hexane/AcOEt 2:1): R_f 0.15. UV (MeOH): λ_{max} 243.5 (6.121). IR (KBr): 3322*s* (O–H, N–H); 3089*w*, 3064*w* (N–H); 2962*s*, 2930*m*, 2872*m* (C–H); 1756*s* (amide I); 1538*m* (amide II); 1213*s*, 1120*s* (C–O). ^{1}H-NMR: 0.99, 1.00 (2*d*, $J((H\text{–}CH_2)_2CH,Me_2CH)$ = 6.8, Me_2CH); 1.29 (*s*, Me–C(6)); 2.15 (*s*, $MeCO_2$); 2.34 (*sept.*, $J(Me_2CH,(H\text{–}CH_2)_2CH)$ = 6.8, Me_2CH); 2.43 (*d* with f.s., J(H′–C(7),H–C(7)) = 17.7, H′–C(7)); 2.80 (*d* with f.s., J(H–C(7),H′–C(7)) = 17.7, H–C(7)); 3.16 (*d* with f.s., J(H–C(5),H–C(4)) = 8.1, H–C(5)); 4.43 (*d*, J(H–CHN, NH) = 5.5, CH_2N); 5.49 (*s*, OH); 5.61 (*s* with f.s., H–C(2)); 5.73 (*d*, J(H–C(4),H–C(5)) = 8.1, H–C(4)); 6.42 (br. *t*, J(NH, H–CHN) = 5.5, NH); 7.23–7.36 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): Me/OH (0.2%); Me/H–C(5) (0.7%); OH/H–C(5) (1.6%); OH/H–C(7) (2.0%); H–C(5)/OH (1.4%); H–C(7)/OH (1.6%); H–C(7)/H′–C(7) (14.3%); H′–C(7)/Me (1.5%); H′–C7)/H–C(7) (15.9%). ^{13}C-NMR: 21.0 ($MeCO_2$); 21.5, 21.6 (Me_2CH); 27.6 (*Me*–C(6)); 36.1 (Me_2CH); 43.6 (C(7)); 45.9 (CH_2N); 55.1 (C(5)); 76.5 (C(6)); 116.1 (C(2)); 119.7 (C(4)); 127.5, 127.6, 128.7 (5 arom. C); 137.6 (C_{ipso}); 145.1 (C(3)); 159.9 (C(1)); 169.2 (MeCOO); 173.5 (HNCO). Anal. calc. for $C_{21}H_{27}NO_4$ (357.45): C 70.56, H 7.61, N 3.92; found: C 70.65, H 7.84, N 3.63.

Crystal-Structure Analysis of rac-**36b** (*Fig. 18*): monoclinic crystals, $P2_1/n$ (No. 14); a = 9.677(1), b = 10.837(3), c = 19.843(3) Å; β = 100.67(1)°; V = 2045(1) Å^3; Z = 4; ρ = 1.161 g/cm^3; hemisphere through 2θ = 120°; 2293 indep. reflect. with $I > \sigma(I)$; 236 variables; $R(F)$ = 0.104; $R_w(F)$ = 0.129.

1.15. *Irradiation of* rac-**33c** (see *Scheme 13*). 1.15.1. *In Anh. Et_2O.* 1.15.1.1. *In the Presence of NH_3.* A soln. of *rac*-**33c** (100 mg; 0.37 mmol; for preparation, see *Exper. 2.15*) in anh. Et_2O (250 ml) was irradiated for 30 min. A gentle stream of dry NH_3 was passed through the soln. during, and of N_2, after the reaction. The residue left after the removal of solvent at reduced pressure was purified by chromatography (30 g of silica gel; hexane/AcOEt 1:2 through 1:4) and crystallization (from Et_2O/pentane) to give 48 mg (45%) of *(5RS,6SR)-3-(*tert*-butyl)-5-carbamoyl-6-hydroxy-6-methylcyclohepta-1,3-dien-1-yl acetate* (*rac*-**38a**): M.p. 142–144°. TLC (hexane/AcOEt 1:2): R_f 0.22. UV (MeOH): λ_{max} 238.0 (5850). IR (KBr): 3441*s*, 3343*s*, 3204*s* (OH, NH); 1764*s* (acetate); 1573*s* (amide I); 1652*s* (amide II); 1616*m* (C=C); 1209*s* (acetate). ^{1}H-NMR: 1.09 (*s*, *t*-Bu); 1.35 (*s*, Me–C(6)); 2.18 (*s*, $MeCO_2$); 2.26 (*d*, J(H–C(7),H′–C(7)) = 15.4, H–C(7)); 2.61 (*d*, J(H′–C(7),H–C(7)) = 15.3, H′–C(7)); 3.06 (*d*, J(H–C(5),H–C(4)) = 7.1, H–C(5)); 5.02 (*s*, in D_2O exchangeable, OH); 5.83–5.92 (*m*, J(H–C(4), H–C(5)) ≈ 7.3, H–C(4), H–C(2), NH_2). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. ^{13}C-NMR: 21.11 ($MeCO_2$); 28.06 (*Me*–C(6)); 29.12 (Me_3C); 35.82 (Me_3C); 45.98 (C(7)); 53.83 (C(5)); 84.91 (C(6)); 116.64 (C(2)); 121.06 (C(4)); 149.21 (C(3)); 150.99 (C(1)); 169.34 ($MeCO_2$); 177.25 (NHCO). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Anal. calc. for $C_{15}H_{23}O_4N$ (281.35): C 64.04, H 8.24, N 4.98; found: C 64.24, H 8.26, N 5.26.

Crystal-Structure Analysis of rac-**38a** (*Fig. 19*): monoclinic, $P2_1/n$ (No. 14); a = 10.744(2), b = 16.881(2), c = 18.077(2) Å; β = 104.47(1)°; V = 3174(1) Å^3; Z = 8 (two indep. molecules); ρ = 1.177 g/cm^3; hemisphere through 2θ = 110°; 3640 indep. reflect. wtih $I > \sigma(I)$; 546 variables; $R(F)$ = 0.056; $R_w(F)$ = 0.068.

1.15.1.2. *In the Presence of Cyclohexylamine.* A soln. of *rac*-**33c** (180 mg; 0.70 mmol) and freshly distilled cyclohexylamine (240 µl; 2.1 mmol) in anh. Et_2O (100 ml) was irradiated for 1 h. After usual workup, the obtained product was purified by chromatography (30 g of silica gel; hexane/AcOEt 1:1) to give 132 mg (53%) of *(5RS,6SR)-3-(*tert*-butyl)-5-(*N*-cyclohexylcarbamoyl)-6-hydroxy-6-methylcyclohepta-1,3-dienyl acetate* (*rac*-**38b**):

M.p. 41–46°. TLC (hexane/AcOEt 1:1): R_f 0.58. UV (MeOH): λ_{max} 237.5 (5720). IR (KBr): 3302*s* (br., NH, OH); 3080*w* (N–H); 1758*s* (acetate); 1644*s* (amide I); 1548*s* (amide II); 1212*s* (C–O). ^{1}H-NMR: 1.09 (*s*, *t*-Bu); 1.29 (*s* with f.s., Me–C(6)); 1.06–1.08, 1.12–1.28, 1.35–1.91 (3*m*, 2 H–C(2') to 2 H–C(6')); 2.17 (*s*, MeCOO); 2.27 (*d*, *J*(H–C(7),H'–C(7)) = 15.8, H–C(7)); 2.63 (*d* with f.s., *J*(H'–C(7),H–C(7)) ≈ 16.7, H'–C(7)); 2.96 (*d*, *J*(H–C(5),H–C(4)) = 7.3, H–C(5)); 3.62–3.84 (*m*, H–C(1')); 5.54 (*s*, in D_2O exchangeable, OH); 5.72–5.75 (*m*, NH); 5.85–5.88 (*m*, *J*(H–C(4),H–C(5)) ≈ 7.4, H–C(4), H–C(2)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. NOEs from difference spectra (irradiated signal/NOE): Me/H–C(5) (0.7%); Me/H–C(7) (1.0%); H–C(5)/Me (1.7%); H–C(5)/OH (0.6%); H–C(7)/Me (0.5%); H–C(7)/H'–C(7)/OH (0.5%); OH/Me (1.5%); OH/H–C(5) (1.3%); OH/H'–C(7) (1.3%). ^{13}C-NMR: 21.12 (*Me*CO_2); 24.60, 25.43, 32.61, 32.91 (C(2')–C(6')); 28.04 (*Me*–C(6)); 29.15 (*Me*$_3$C); 35.89 (Me$_3$*C*); 45.94 (C(7)); 48.21 (C(1')); 54.53 (C(5)); 83.65 (C(6)); 116.39 (C(2)); 121.04 (C(4)); 148.63 (C(3)); 151.00 (C(1)); 169.33 (Me*C*O$_2$); 173.46 (NHCO)). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Anal. calc. for $C_{21}H_{33}O_4N$ (3.63.50): C 69.39, H 9.15, N 3.85; found: C 69.24, H 9.22, N 3.87.

1.15.2. *In the Presence of PhCH$_2$NH$_2$.* 1.15.2.1. *In Hexane.* A soln. of *rac*-**33c** (132 mg; 0.5 mmol) and freshly distilled $PhCH_2NH_2$ (0.17 ml; 1.5 mmol) in hexane (200 ml) was irradiated until the dienone had completely reacted (30 min; TLC control). The residue (190 mg) obtained after acidic workup was purified by chromatography (10 g of silica gel; hexane/AcOEt 1:1) to give 70.6 mg (38%) of *(3Z,5E)-6-acetoxy*-N-*benzyl-4-(*tert-*butyl)-8-oxonona-3,5-dienamide* (= *(1E,3Z)-6-(benzylamino)-3-(*tert-*butyl)-6-oxo-1-(2-oxopropyl)hexa-1,3-dien-1-yl acetate*; **37a**): M.p. 50–51°. TLC (hexane/AcOEt 1:1): R_f 0.42. UV (MeOH): λ 229.9 (sh, 3538); 289.9 (376). IR (KBr): 3308*m* (br., N–H); 3963*w* (N–H); 3031*w* (= C–H); 2964*s*, 2869*m* (–C–H); 1754*s* (acetate); 1721*s* (ketone); 1659*s* (amide I); 1538*s* (amide II); 1362*s* (*t*-Bu); 1211*s*, 1117*s* (C–O). ^{1}H-NMR (C_6D_6): 1.02 (*s*, *t*-Bu); 1.66, 1.68 (2*s*, MeCO$_2$, 3 H–C(9)); 2.97 (*d* with f.s., *J*(H–C(2),H–C(3)) = 7.2, 2 H–C(2)); 3.26 (*s*, 2 H–C(7)); 4.26 (*d*, *J*(H–CHN, NH) = 6.0, CH$_2$N); 5.55 (br. *t*, *J*(NH, H–CHN) = 6.0, NH); 5.81 (*s*, H–C(5)); 5.89 (*t* with f.s., *J*(H–C(3), H–C(2)) = 7.2, H–C(3)); 6.99–7.13 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (1.2%); H–C(2)/H–C(5) (0.4%); H–C(2)/^{t}Bu (9%); H–C(3)/H–C(2) (4.0%); H–C(3)/H–C(7) (0.8%); H–C(3)/^{t}Bu (5.4%); H–C(5)/H–C(2) (1.1%); H–C(5)/H–C(7) (0.4%); H–C(5)/^{t}Bu (3.0%); H–C(7)/H–C(3) (0.3%); H–C(7)/H–C(5) (0.2%); H–C(7)/^{t}Bu (1.1%). Anal. calc. for $C_{22}H_{29}NO_4$ (371.48): C 71.13, H 7.87, N 3.77; found: C 70.92, H 7.89, N 3.77.

1.15.2.2. *In Et$_2$O.* A soln. of *rac*-**33c** (264 mg; 1 mmol) and freshly distilled $PhCH_2NH_2$ (0.33 ml; 3 mmol) in anh. Et$_2$O (35 ml) was irradiated. After 4 h, all the dienone had reacted (UV and TLC control). Acidic workup led to an oily product (260 mg) which was fractionated by chromatography (25 g of silica gel; hexane/AcOEt 2:1)[24]. Anal. samples of the compounds after HPLC (hexane/AcOEt 30:13 + 30% CH_2Cl_2; 254 nm): **37a** (110 mg; 30%; for data, see *Exper. 1.15.2.1*). *rac*-**38c** (10.7 mg; 3%), and **39** (40.2 mg; 19%).

*(5*RS*,6*SR*)-5-(*N*-Benzylcarbamoyl)-3-(*tert*-butyl)-6-hydroxy-6-methylcyclohepta-1,3-dienyl Acetate* (*rac*-**38c**): M.p. 78°. TLC (hexane/AcOEt 2:1): R_f 0.25. UV (MeOH): λ_{max} 238.4 (6299); 329.0 (217). IR (KBr): 3240*s* (O–H); 3069*s* (N–H); 2953*s*, 2869*m* (C–H); 1764*s* (acetate); 1641*s* (amide I); 1566*s* (amide II); 1372*s* (*t*-Bu); 1195*s*, 1111*s* (C–O). ^{1}H-NMR: 1.06 (*s*, *t*-Bu); 1.31 (*s*, Me–C(6)); 2.16 (*s*, MeCO$_2$); 2.26 (*d*, *J*(H'–C(7), H–C(7)) = 15.7, H'–C(7)); 2.63 (*d* with f.s., *J*(H–C(7),H'–C(7)) = 15.7, H–C(7)); 3.04 (*d*, *J*(H–C(5), H–C(4)) = 7.2, H–C(5)); 4.45 (*AB* system, *J*(H$_a$,H$_b$) = 15.7, *J*(H$_a$, NH) = *J*(H$_b$, NH) = 5.3, CH$_2$N); 5.41 (br. *s*, D_2O exchangeable, OH); 5.84 (*s* with f.s., H–C(2)); 5.89 (*d*, *J*(H–C(4),H–C(5)) = 7.2, H–C(4)); 6.25 (br. *t*, *J*(NH, H–HN) = 5.3, NH); 7.23–7.36 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): Me/H–C(5) (0.7%); Me/H'–C(7) (0.7%); OH/H–C(5) (0.7%); OH/H–C(7) (1.0%); H–C(5)/Me (2.4%); H–C(5)/OH (0.9%); H–C(5)/H'–C(7) (0.8%); H–C(7)/OH (2.2%); H–C(7)/H'–C(7) (9.9%); H'–C(7)/H–C(7) (7.8%). ^{13}C-NMR: 21.0 (*Me*CO_2); 28.1 (*Me*–C(6)); 29.0 (*Me*$_3$C); 35.8 (Me$_3$*C*); 43.5 (C(7)); 46.0 (CH_2N); 54.4 (C(5)); 84.3 (C(6)); 116.5, 120.9 (C(2), C(4)); 127.6, 127.6, 128.7 (5 arom. C); 137.6 (C_{ipso}); 149.0, 151.0 (C(1), C(3)); 169.2 (Me*C*O$_2$); 174.3 (NHCO). Anal. calc. for $C_{22}H_{29}NO_4$ (371.48): C 71.13, H 7.87, N 3.77; found: C 70.86, H 7.83, N 3.80.

*[5-(*tert*-Butyl)-2-hydroxyphenyl]propan-2-one* (**39**): M.p. 97°. TLC: (hexane/AcOEt 4:1): R_f 0.40. IR (KBr): 3430*s* (O–H); 1707*s* (ketone); 1611*m* (C=C); 1360*m* (*t*-Bu). ^{1}H-NMR: 1.28 (*s*, *t*-Bu); 2.28 (*s*, 3 H–C(3)); 3.73 (*s*, 2 H–C(1)); 6.74 (*s*, in D_2O, OH); 6.84 (*d*, *J*(H–C(3'),H–C(4')) = 8.4, H–C(3')); 7.05 (*d*, *J*(H–C(6'), H–C(4')) = 2.4 H–C(5')); 7.18 (*dd*, *J*(H–C(4'),H–C(3')) = 8.4, *J*(H–C(4'),H–C(6')) = 2.4, H–C(4')). Anal. calc. for $C_{13}H_{18}O_2$ (206.29): C 75.69, H 8.80; found: C 75.75, H 8.75.

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[24]) Irradiation of *rac*-**33c** in 350 ml of anh. Et$_2$O under the same conditions as described in *Exper. 1.15.2.2* gives only the carbocyclic compound *rac*-**38c**. Phenol **39** and acyclic compund **37a** could not be detected.

1.15.3. *In MeOH.* A soln. of *rac*-**33c** (300 mg; 1.1 mmol) in abs. MeOH (200 ml) was irradiated for 2 h. After evaporation of solvent under reduced pressure, the remaining residue was filtered through silica gel (30 g; hexane/AcOEt 1:1) and purified by prep. HPLC (hexane/AcOEt 1:1; 254 nm) to give **37b** (226 mg; 67%) and *rac*-**38d**/*rac*-**40** (31 mg; 9%).

*Methyl (3Z,5E)-6-Acetoxy-4-(*tert*-butyl)-8-oxonona-3,5-dienoate (= (1E,3Z)-4-(*tert*-Butyl)-6-methoxy-6-oxo-1-(2-oxopropyl)hexa-1,3-dien-1-yl Acetate*; **37b**): TLC (hexane/AcOEt 1:1): R_f 0.49. UV (MeOH): λ_{max} 285.0 (120). IR (film): 1739*s* (br., acetate, ketone, ester); 1672*w* (C=C); 1211*s* (C–O). ^{1}H-NMR: 1.03 (*s*, *t*-Bu); 2.08 (*s*, MeCOO); 2.09 (*s*, 3 H–C(9)); 3.09 (*dd*, *J*(H–C(2),H–C(3)) = 7.2, *J*(H–C(2),H–C(5)) = 1.2, 2 H–C(2)); 3.31 (*s*, 2 H–C(7)); 3.62 (*s*, MeO); 5.56 (*dt*, *J*(H–C(3),H–C(2)) = 7.2, *J*(H–C(3),H–C(5)) = 1.4, H–C(3)); 5.79 (*d* with f.s., *J*(H–C(5),H–C(3)) = 1.3, H–C(5)). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (1.2%); H–C(2)/H–C(5) (0.5%); H–C(2)/^{t}Bu (5.1%); H–C(3)/H–C(2) (2.2%); H–C(3)/^{t}Bu (15.3%); H–C(5)/H–C(2) (1.4%); H–C(5)/H–C(7) (0.9%); H–C(5)/^{t}Bu (12.9%); H–C(7)/^{t}Bu (5.2%). Anal. calc. for $C_{16}H_{24}O_5$ (296.37): C 64.84, H 8.16; found: C 64.81, H 8.17.

*(5RS,6SR)-/(5RS,6RS)-3-(*tert*-Butyl)-6-hydroxy-5-(methoxycarbonyl)-6-methylcyclohepta-1,3-dien-1-yl Acetate* (*rac*-**38d**/*rac*-**40**, resp.): M.p. 103–110°. TLC (hexane/AcOEt 1:1): R_f 0.49. IR (KBr): 3501*s* (OH); 1734*s* (acetate); 1728*s* (ester); 1686*w*, 1656*m* (C=C); 1372*s* (*t*-Bu); 1228s (acetate). ^{1}H-NMR: 1.05, 1.06 (2*s*, *t*-Bu); 1.18; 1.19, 1.21 (3*s*, Me–C(6)); 2.02, 2.22, 2.24 (3*s*, $MeCO_2$); 2.08 (ψd, *J*(H–C(7),H′–C(7)) = 14.7, H–C(7)); 2.35 (ψd, *J*(H′–C(7),H–C(7)) = 14.7, H′–C(7)); 3.11, 3.27, 4.45 (3*d*, *J*(H–C(5),H–C(4)) = 6.4, H–C(5)); 3.68, 3.75, 4.27 (3*s*, MeO); 5.61 (*s*, in D_2O exchangeable; OH); 6.04 (*s*, H–C(2)); 6.09 (*d*, *J*(H–C(4),H–C(5)) = 6.4, H–C(4)). *rac*-**38d**/*rac*-**40**, according to ^{1}H-NMR, are formed in a ratio of 5:1 or 1:5, respectively. Anal. calc. for $C_{16}H_{24}O_5$ (296.37): C 64.84, H 8.16; found: C 64.75, H 8.23.

1.16. *Irradiation of* rac-**33d** (see *Scheme 14*). 1.16.1. *In the Presence of NH_3.* To a soln. of *rac*-**33d** (2.84 mg; 1 mmol; for preparation, see *Exper. 2.16*) in anh. Et_2O (330 ml), an ammoniacal soln. (16 ml of a *ca.* 0.21M soln. in Et_2O; *ca.* 3 mmol) was added. The soln. was irradiated until the dienone had completely reacted (1 h). Acidic workup yielded an orange oil (420 mg) which was purified by chromatography (30 g of silica gel; hexane/AcOEt 1:2) and separated by HPLC (hexane/AcOEt 1:5; 254 nm) to afford after crystallization 87.1 mg (29%) of **41a** and 30.8 mg (11%) of *rac*-**42a**.

(3Z,5E)-6-Acetoxy-8-oxo-4-phenylnona-3,5-dieneamide (= (1E,3Z)-5-Carbamoyl-3-phenyl-1-(2-oxopropyl)-hexa-1,3-dien-1-yl Acetate; **41a**): M.p. 91° (MTB). TLC (hexane/AcOEt 1:2): R_f 0.12. UV (MeOH): λ_{max} 250.3 (13794). IR (KBr): 3439*s*, 3339*m*, 3315*m*, 3212*m* (N–H); 2914*m* (C–H); 1745*s* (acetate); 1715*s* (ketone); 1666*s* (amide I + II); 1616*m* (C=C); 1230*s*, 1213*s*, 1124*s* (C–O); 753*s*, 689*m* (Ph). ^{1}H-NMR: 1.52, 1.67 (2*s*, 3 H–C(9), $MeCO_2$); 2.98 (*d* with f.s., *J*(H–C(2),H–C(3)) = 7.8, 2 H–C(2)); 3.08 (*s*, 2H–C(7)); 5.08, 5.23 (2br. *s*, NH_2); 5.92 (*s* with f.s., H–C(5)); 6.32 (*t* with f.s., *J*(H–C(3),H–C(2)) = 7.8, H–C(3)); 7.01–7.14, 7.43–7.47 (2*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (2.1%); H–C(2)/H–C(5) (0.6%); H–C(3)/H–C(2) (1.9%); H–C(3)/H–C(7) (0.9%); H–C(5)/H–C(2) (1.3%); H–C(5)/H–C(7) (0.6%); H–C(5)/Ph (5.9%); H–C(7)/H–C(3) (0.2%); H–C(7)/H–C(5) (0.2%); H–C(7)/Ph (2.1%). Anal. calc. for $C_{17}H_{19}NO_4$ (301.34): C 67.76, H 6.35, N 4.65; found: C 67.67, H 6.31, N 4.66.

(5RS,6SR)-5-Carbamoyl-6-hydroxy-6-methyl-3-phenylcyclohepta-1,3-dien-1-yl Acetate (*rac*-**42a**): M.p. 154° (Et_2O/pentane at –30°). TLC (hexane/AcOEt 1:2): R_f 0.30. UV (MeOH): λ_{max} 229.1 (19403); 260.8 (9107). IR (KBr): 3469*s*, 3335*m*, 3194*m* (O–H, N–H); 2977*w* (=C–H); 1757*s* (acetate); 1660*s* (amide I + II); 1610*s* (C=C); 1206*s*, 1112*s* (C–O); 764*s*, 698*s* (Ph). ^{1}H-NMR: 1.41 (*s*, Me–C(6)); 2.19 (*s*, $MeCO_2$); 2.46 (*d*, *J*(H′–C(7),H–C(7)) = 16.4, H′–C(7)); 2.81 (*d* with f.s., *J*(H–C(7),H′–C(7)) = 16.4, H–C(7)); 3.31 (*d*, *J*(H–C(5), H–C(4)) = 7.5, H–C(5)); 5.12 (*s*, OH); 5.88, 6.16 (2 br. *s*, NH_2); 6.01 (*s* with f.s. H–C(2)); 6.35 (*d*, *J*(H–C(4),H–C(5)) = 7.5, H–C(4)); 7.30–7.40 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): Me/OH (> 0.5%); Me/H–C(5) (0.7%); Me/H′–C(7) (0.6%); OH/Me (> 0.5%); OH/H–C(5) (1.1%); OH/H–C(7) (0.8%); H–C(5)/Me (1.8%); H–C(5)/OH (0.4%); H–C(7)/Me (0.8%); H–C(7)/H′–C(7) (10.0%); H′–C(7)/Me (2.1%); H′–C(7)/OH (> 0.5%); H′–C(7)/H–C(7) (12.7%). ^{13}C-NMR: 21.1 (*Me*CO_2); 28.0 (*Me*–C(6)); 46.3 (C(7)); 55.0 (C(5)); 82.2 (C(6)); 117.4 (C(2)); 125.6 (C(4)); 126.3, 128.0, 128.5 (5 arom. C); 139.7, 140.2, 152.1 (C(1), C(3), C_{ipso}); 169.3 ($MeCO_2$); 176.3 (NH_2CO). Anal. calc. for $C_{17}H_{19}NO_4$ (301.34); C 67.76, H 6.35, N 4.65; found: C 67.72, H 6.34, N 4.64.

1.16.2. *In the Presence of Cyclohexylamine.* A soln. of *rac*-**33d** (2.84 mg; 1 mmol) and freshly distilled cyclohexylamine (0.34 ml; 3 mmol) were dissolved in anh. CH_2Cl_2 (5 ml) and filled to a volume of 350 ml with abs. Et_2O. After irradiation for 1 h, no dienone was to be detected UV-spectroscopically. Acidic workup afforded an oily product (430 mg) which was purified by semi-prep. HPLC (hexane/AcOMe 10:3; 254 nm) to give a solid fraction containing *rac*-**42b** (141 mg; 37%) and an oily fraction from which, after a second HPLC (hexane/AcOEt 1:1; 254 nm), 80.4 mg (21%) of **41b** could be isolated.

(3Z,5E)-6-Acetoxy-N-cyclohexyl-8-oxo-4-phenylnona-3,5-dieneamide (= *(1E,3Z)-6-(Cyclohexylamino)-6-oxo-3-phenyl-1-(2-oxopropyl)hexa-1,3-dien-1-yl Acetate*; **41b**): M.p. 104° (CH_2Cl_2/hexane). TLC (hexane/AcOEt 1:1): R_f 0.28. UV (MeOH): λ_{max} 251.0 (13985). IR (KBr): 3309*s*, 3078*w* (N–H); 3060*w* (=C–H); 2934*s*, 2854*m* (–C–H); 1749*s* (acetate); 1714*s* (ketone); 1677*w* (C=C); 1635*s* (amide I); 1539*s* (amide II); 1224*s*, 1162*m*, 1128*s* (C–O); 767*s*, 695*s* (Ph). ^{1}H-NMR: 1.08–1.22, 1.28–1.39, 1.58–1.75, 1.86–1.92 (4*m*, 2 H–C(2') to 2 H–C(6')); 1.96 (*s*, 3 H–C(9)); 2.19 (*s*, $MeCO_2$); 3.15 (*d* with f.s., *J*(H–C(2),H–C(3)) = 7.7, 2 H–C(2)); 3.23 (*s*, 2 H–C(7)); 3.75 (m_c, H–C(1')); 5.91 (br. *d*, *J*(NH,H–C(1')) = 7.7, NH); 6.14 (*s* with f.s., H–C(5)); 6.28 (*td*, *J*(H–C(3),H–C(2)) = 7.7, *J*(H–C(3),H–C(5)) = 1.6, H–C(3)); 7.28–7.36, 7.42–7.46 (2*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (2.9%); H–C(2)/H–C(9 (1.8%); H–C(3)/H–C(2) (2.0%); H–C(3)/Ph (2.7%); H–C(5)/H–C(2) (1.5%); H–C(5)/H–C(7) (0.90%); H–C(5)/Ph (1.6%); H–C(7)/H–C(3) (0.4%); H–C(7)/H–C(5) (0.2%); H–C(7)/Ph (0.4%). Anal. calc. for $C_{23}H_{29}NO_4$ (383.49): C 72.03, H 7.62, N 3.65; found: C 71.94, H 7.64, N 3.49.

(5RS,6SR)-5-(Cyclohexylcarbamoyl)-6-hydroxy-6-methyl-3-phenylcyclohepta-1,3-dien-1-yl Acetate (*rac*-**42b**): M.p. 137–138° (Et_2O/pentane). TLC (hexane/AcOEt 1:1): R_f 0.35. UV (MeOH): λ_{max} 228.5 (18889); 261.5 (9361). IR (KBr): 3300*m* (br., O–H, N–H); 3080*w* (N–H); 3059*w* (=C–H); 2931*s*, 2854*m* (–C–H); 1759*s* (acetate); 1641*s* (amide I); 1546*m* (amide II); 1210*s*, 1161*m*, 1119*m* (C–O); 762*s*, 697*s* (Ph). ^{1}H-NMR: 1.38 (*s*, Me–C(6)); 1.09–1.41, 1.58–1.66, 1.86–1.95 (3*m*, 2 H–C(2') to 2 H–C(6')); 2.19 (*s*, $MeCO_2$); 2.43 (*d*, *J*(H'–C(7), H–C(7)) = 16.5, H'–C(7)); 2.80 (*d* with f.s., *J*(H–C(7),H'–C(7)) = 16.5, H–C(7)); 3.21 (*d*, *J*(H–C(5),H–C(4)) = 7.6, H–C(6)); 3.77–3.83 (*m*, H–C(1')); 5.55 (*s*, OH); 5.99 (*d*, *J*(H–C(2),H–C(7)) = 1.9, H–C(2)); 5.95–5.99 (*d*, partly hidden, NH); 6.31 (*d*, *J*(H–C(4),H–C(5)) = 7.6, H–C(4)); 7.29–7.36 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): Me/OH (0.3%); Me/H–C(5) (0.9%); Me/H'–C(7) (0.9%); OH/Me (0.6%); OH/H–C(5) (0.7%); OH/H–C(7) (1.3%); H–C(5)/Me (2.9%); H–C(5)/OH (0.5%); H–C(7)/OH (1.0%); H–C(7)/H'–C(7) (6.1%); H'–C(7)/Me (2.5%); H'–C(7)/OH (3.9%); H'–C(7)/H–C(7) (9.0%). ^{13}C-NMR: 21.1 ($MeCO_2$); 24.6, 25.4, 32.7, 32.9 (C(2') to C(6')); 28.0 (*Me*–C(5)); 46.3 (C(7)); 48.4 (C(1')); 55.5 8C(5)); 81.9 (C(6)); 117.2 (C(2)); 125.8 (C(4)); 126.3, 127.9, 128.5 (5 arom. C); 139.6, 140.5 (C(3), C_{ipso}); 169.2 ($MeCO_2$); 172.6 (NHCO). The signals were assigned by a ^{1}H,^{13}C-COSY spectra. Cross signals between: 1.38/28.0; 1.09–1.41/24.6, 25.4, 32.7, 32.9; 1.58–166/24.6, 25.4; 1.86–1.95/32.7, 32.9; 2.19/21.1; 2.43, 2.80/46.3; 3.21/55.5; 3.77–3.83/48.4; 5.99/117.2; 6.31/125.8; 7.29–7.36/126.3, 127.9, 128.5. Anal. calc. for $C_{23}H_{29}NO_4$ (383.49): C 72.03, H 7.62, N 3.65; found: C 71.87, H 7.45, N 3.48.

1.16.3. *In the Presence of $PhCH_2NH_2$.* A soln. of *rac*-**33d** (284 mg; 1 mmol) and freshly distilled $PhCH_2NH_2$ (0.33 ml; 3 mmol) in anh. CH_2Cl_2 (5 ml) was filled up with abs. Et_2O to a volume of 350 ml and irradiated for 1 h. UV Monitoring showed that dienone had completely reacted. Acidic workup led to an oily product (620 mg) which was separated by chromatography (30 g of silica gel; hexane/AcOEt 1:1) into two fractions, further purified by recrystallization from MTB/hexane or semi-prep. HPLC (hexane/AcOEt 3:2; 254 nm) to furnish **41c** (105 mg; 27%) and *rac*-**42c** (81.2 mg; 21%).

(3Z,5E)-6-Acetoxy-N-benzyl-8-oxo-4-phenylnona-3,5-dieneamide (= *(1E,3Z)-6-(Benzylamino)-6-oxo-3-phenyl-1-(2-oxopropyl)hexa-1,3-dien-1-yl Acetate*; **41c**): M.p. 88° (MTP/hexane). TLC (hexane/AcOEt 1:1): R_f 0.35. UV (MeOH): λ_{max} 251.6 (14610). IR (KBr): 3323*s*, 3061*w* (N–H); 3030*w* (unsat. C–H); 2948*w* (sat. C–H); 1755*s* (acetate); 1708*s* (ketone); 1637*s* (amide I); 1540*m* (amide II); 1228*s*, 1208*s*, 1133*s* (C–O); 757*m*, 696*m* (Ph). ^{1}H-NMR: 1.84 (*s*, 3 H–C(9)); 2.17 (*s*, $MeCO_2$); 3.07 (*s*, 2 H–C(7)); 3.23 (*d* with f.s., *J*(H–C(2),H–C(3)) = 7.2, 2 H–C(2)); 4.44 (*d*, *J*(H–CHN, NH) = 5.9, CH_2N); 6.15 (*s* with f.s., H–C(5)); 6.30 (*t* with f.s., *J*(H–C(3),H–C(2)) = 7.2, H–C(3)); 6.48 (br. *t*, *J*(NH,H–CHN) = 5.9, NH); 7.24–7.44 (*m*, 10 arom. H). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (2.0%); H–C(2)/H–C(5) (1.3%); H–C(3)/H–C(2) (5.4%); H–C(3)/H–C(7) (0.3%); H–C(3)/Ph (3.2%); H–C(5)/H–C(2) (2.9%); H–C(5)/H–C(7) (0.3%); H–C(5)/Ph (1.8%); H–C(7)/H–C(5) (0.2%); H–C(7)/Ph (1.0%). Anal. calc. for $C_{24}H_{25}NO_4$ (391.47): C 73.63, H 6.44, N 3.58; found: C 73.38, H 6.55, N 3.51.

(5RS,6SR)-5-(N-Benzylcarbamoyl)-6-hydroxy-6-methyl-3-phenylcyclohepta-1,3-dien-1-yl Acetate (*rac*-**42c**): M.p. 98° (Et_2O/hexane). TLC (hexane/AcOEt 1:1): R_f 0.59. UV (MeOH): λ_{max} 228.5 (19684); 261.5 (9957). IR (KBr): 3348*s* (br., O–H, N–H); 3086*w* (N–H); 3031*w* (C=C); 2979*m*, 2938*m* (sat. C–H); 1758*s* (acetate); 1645*s* (amide I); 1545*m* (amide II); 1213*s*, 1121*s*, 1084*s* (C–O); 759*m*, 700*s* (Ph). ^{1}H-NMR: 1.38 (*s*, Me–C(6)); 2.17 (*s*, $MeCO_2$); 2.44 (*d*, *J*(H'–C(7),H–C(7)) = 16.5, H'–C(7)); 2.80 (*d* with f.s., *J*(H–C(7),H'–C(7)) = 16.5, H–C(7)); 3.29 (*d*, *J*(H–C(5),H–C(4)) = 7.5, H–C(5)); 4.44, 4.51 (*AB* system, *J*(H_a,H_b) = 14.8, *J*(H_a,NH) = *J*(H_b, NH) = 5.7, CH_2N); 5.42 (*s*, OH); 5.98 (*d*, *J*(H–C(2),H–C(7)) = 1.6, H–C(2)); 6.32 (*d*, *J*(H–C(4),H–C(5)) = 7.5, H–C(4)); 6.50 (br. *t*, *J*(NH, H–CHN) = 5.7, NH); 7.23–7.37 (*m*, 10 arom. H). NOEs from difference spectra (irradiated signal/NOE): MeOH (10.4%); Me/H–C(5) (1.3%); Me/H'–C(7) (1.1%); OH/H–C(5) (0.6%); OH/H–C(7) (1.5%); H–C(5)/Me (2.8%); H–C(7)/Me (0.8%); H–C(7)/H'–C(7)

(11.7%); H′–C(7)/Me (1.5%); H′–C(7)/H–C(7) (13.7%). ^{13}C-NMR: 21.0 (*Me*CO_2); 28.1 (*Me*–C(6)); 43.6 (CH_2N); 46.3 (C(7)); 55.5 (C(5)); 82.3 (C(6)); 117.3 (C(2)); 125.5 (C(4)); 126.2, 127.6, 127.7, 127.9, 128.5, 128.7, (10 arom. C); 137.6, 139.8, 140.2, 152.2 (C(1), C(3), 2C_{ipso}); 169.2 (Me*C*O_2); 173.5 (NHCO). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross signals between: 1.38/28.1; 2.17/21.0; 2.44, 2.80/46.3; 3.29/55.5; 4.44, 4.51/43.6; 5.98/117.3; 6.32/125.5. Cross signals between nuclei of the Ph groups are left unnoticed. Anal. calc. for $C_{24}H_{25}NO_4$ (391.47): C 73.63, H 6.44, N 3.57; found: C 73.56, H 6.35, N 3.48.

1.16.4. *In MeOH.* A soln. of *rac*-**33d** (284 mg; 1 mmol) in abs. MeOH (200 ml) was irradiated. After 45 min, the educt had disappeared (UV control). The residue (300 mg) obtained after evaporation of solvent under reduced pressure was purified by chromatography (25 g of silica gel; hexane/AcOEt 4:1) and crystallization (Et_2O/hexane) to yield 272 mg (86%) of *methyl (3Z,5E)-6-acetoxy-8-oxo-4-phenylnona-3,5-dienoate* (= *(1E,3Z)-6-methoxy-6-oxo-3-phenyl-1-(2-oxopropyl)hexa-1,3-dien-1-yl acetate*; **41d**): M.p. 64° (Et_2O/hexane). TLC hexane/AcOEt 4:1): R_f 0.19. UV (MeOH): λ_{max} 249.0 (13308). IR (KBr): 3003*m* (unsat. C–H); 2954*m* (sat. C–H); 1759*s* (acetate); 1729*s* (ester); 1717*s* (ketone); 1667*s* (C=C); 1290*s*, 1160*s*, 1113*s* (C–O); 754*s*, 699*s* (Ph). ^{1}H-NMR: 1.58, 1.67 (2*s*, $MeCO_2$, 3 H–C(9)); 3.14 (*s*, 2 H–C(7)); 3.25 (*d* with f.s., *J*(H–C(2),H–C(3)) = 7.4, 2 H–C(2)); 3.34 (*s*, MeO); 5.94 (*d*, *J*(H–C(5),H–C(3)) = 1.4, H–C(5)); 6.20 (*td*, *J*(H–C(3),H–C(2)) = 7.4, *J*(H–C(3), H–C(5)) = 1.4, H–C(3)); 6.98–7.14, 7.47–7.52 (2*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (1.7%); H–C(2)/H–C(5) (0.4%); H–C(2)/Ph (0.9%); H–C(3)/H–C(2) (3.1%); H–C(3)/H–C(5) (1.2%); H–C(3)/Ph (4.1%); H–C(5)/H–C(2) (3.7%); H–C(5)/H–C(7) (1.0%); H–C(5)/Ph (2.6%); H–C(7)/H–C(5) (0.3%); H–C(7)/Ph (1.2%). Anal. calc. for $C_{18}H_{20}O_5$ (316.35): C 68.34, H 6.37; found: C 68.49, H 6.29.

1.17. *Irradiation of* rac-**43** (see *Scheme 15*). 1.17.1. *In the Presence of* NH_3. A soln. of *rac*-**43** (250 mg; 1 mmol; for preparation see *Exper. 2.17*) in abs. Et_2O (350 ml) was irradiated, while an ammoniacal Et_2O soln. (10 ml, *ca.* 0.13M; *ca.* 1.3 mmol) was slowly added. After 45 min, no educt was left (UV control). Acidic workup afforded an oily product (280 mg) which was filtered through silica gel (10 g; AcOEt) and purified by recrystallization from MTB/hexane to yield 126 mg (47%) of *(5RS,6RS)-3-(*tert*-butyl)-5-carbamoyl-6-hydroxycyclohepta-1,3-dien-1-yl acetate* (*rac*-**44a**): M.p. 153°. TLC (hexane/AcOEt 1:1): R_f 0.07. UV (MeOH): λ_{max} 236.0 (5946). IR (KBr): 3426*s*, 3210sh (br. sh, O–H, N–H); 2963*s*, 2870*m* (sat. C–H); 1735*s* (acetate); 1670*s* (amide I + II); 1617*m* (C=C); 1367*s* (*t*-Bu); 1238*s*, 1115*s* (C–O). ^{1}H-NMR: 1.06 (*s*, *t*-Bu); 2.14 (*d*, *J*(H–C(7),H′–C(7)) = 15.0, H–C(7)); 2.24 (*s*, $MeCO_2$); 2.60 (*dd* with f.s., *J*(H′–C(7),H–C(7)) = 15.0, *J*(H′–C(7),H–C(6)) = 6.0, H′–C(7)); 2.87 (*dd*, *J*(H–C(5), H–C(6)) = 10.0, *J*(H–C(5),H–C(4)) = 5.7, H–C(5)); 4.37–4.47 (*m*, H–C(6)); 4.59 (*d*, *J*(OH, H–C(6)) = 10.4, OH); 5.84, 6.76 (2 br. *s*, NH_2); 6.08 (*s* with f.s., H–C(2)); 6.24 (*d*, *J*(H–C(4),H–C(5)) = 5.7, H–C(4)). NOEs from difference spectra (irradiated signal/NOE): OH/H–C(5) (3.3%), OH/H–C(6) (3.8%); OH/H′–C(7) (1.1%); OH/H–C(7) (2.7%); H–C(5)/OH (3.4%); H–C(5)/H–C(6) (2.0%); H–C(5)/H–C(7) (2.3%); H–C(6)/OH (3.2%); H–C(6)/H–C(5) (5.0%); H–C(6)/H′–C(7) (4.6%); H–C(6)/H–C(7) (4.6%); H′–C(7)/OH (1.8%); H′–C(7)/H–C(5) (2.5%); H′–C(7)/H–C(6) (6.1%); H′–C(7)/H–C(7) (16.0%); H–C(7)/OH (2.7%); H–C(7)/H–C(5) (1.9%); H–C(7)/H–C(6) (3.5%), H–C(7)/H′–C(7) (17.2%). ^{13}C-NMR: 21.0 (*Me*CO_2); 29.0 (*Me*$_3$C); 35.5 (Me$_3$*C*); 39.3 (C(7)); 52.8 (C(5)); 84.0 (C(6)); 118.3 (C(2)); 121.6 (C(4)); 147.5, 151.3 (C(1), C(3)); 171.6, 175.8 (Me*C*O_2, NH_2*C*O). Anal. calc. for $C_{14}H_{21}NO_4$ (267.32): C 62.90, H 7.92, N 5.24; found: C 62.78, H 7.87, N 5.40.

1.17.2. *In the Presence of* $PhCH_2NH_2$. A soln. of *rac*-**43** (125 mg; 0.5 mmol) in anh. Et_2O (165 ml) was irradiated, while a soln. of freshly distilled $PhCH_2NH_2$ (0.06 ml; 0.55 mmol) in Et_2O (10 ml) was slowly added. After 30 min, all the dienone had reacted (UV control). Acidic workup gave a brown oil (200 mg), which was filtered through silica gel (10 g; hexane/AcOEt 1:1) and purified by semi-prep. HPLC (hexane/AcOEt 3:2; 254 nm) to furnish *rac*-**44b** (45.5 mg; 25%) and *rac*-**45** (60.7 mg; 34%).

*(5RS,6RS)-3-(*tert*-Butyl)-5-(*N*-benzylcarbamoyl)-6-hydroxycyclohepta-1,3-dien-1-yl Acetate* (*rac*-**44b**): M.p. 107° (Et_2O/hexane). TLC (hexane/AcOEt 2:1): R_f 0.14. UV (MeOH): λ_{max} 236.0 (6600). IR (KBr): 3487 (sh), 3325*s* (O–H, N–H); 3065*w* (N–H); 2964*s*, 2870*m* (sat. C–H); 1738*s* (acetate); 1659*s*, 1538*s* (amide I + II); 1366*s* (*t*-Bu); 1239*s*, 1116*s* (C–O). ^{1}H-NMR: 1.06 (*s*, *t*-Bu); 2.11 (*dd*, *J*(H–C(7),H′–C(7)) = 15.0, *J*(H–C(7),H–C(2)) = 1.7, H–C(7)); 2.22 (*s*, $MeCO_2$); 2.60 (*dd* with f.s., *J*(H′–C(7),H–C(7)) = 15.0, *J*(H′–C(7),H–C(6)) = 5.7, H′–C(7)); 2.84 (*dd*, *J*(H–C(5),H–C(6)) = 9.4, *J*(H–C(5),H–C(4)) = 5.7, H–C(5)); 4.44–4.55 (*m*, OH, CH_2N, H–C(6)); 6.07 (m_c, H–C(2)); 6.32 (*d* with f.s., *J*(H–C(4), H–C(5)) = 5.7, H–C(4)); 7.02 (br. *t*, *J*(NH, H–CHN) = 5.0, NH); 7.22–7.35 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): OH/H–C(7) (3.7%); H–C(5)/OH (0.8%); H–C(6)/OH (1.1%); H′–C(7)/OH (1.3%); H′–C(7)/H–C(7) (11.0%); H–C(7)/H′–C(7) (19.0%). ^{13}C-NMR: 21.0 (*Me*CO_2); 29.0 (*Me*$_3$); 35.6 (Me$_3$*C*); 39.4 (C(7)); 43.5 (CH_2N); 53.5 (C(5)); 84.2 (C(6)); 118.3 (C(2)); 122.0 (C(4)); 127.2, 127.5, 128.5 (5 arom. C); 138.5 (C_{ipso}); 147.3 (C(1), C(3)); 171.9, 173.1 (Me*C*O_2, HN*C*O). Anal. calc. for $C_{21}H_{27}NO_4$ (357.45): C 70.56, H 7.61, N 3.92; found: C 70.58, H 7.73, N 4.15.

*(5RS,6RS)-3-(*tert*-Butyl)-5-(N-benzylcarbamoyl)-6-hydroxycyclohepta-1,3-dien-1-yl Acetate* (*rac*-**45**): M.p. 101° (Et_2O/pentane). TLC (hexane/AcOEt 2:1): R_f 0.20. UV (MeOH): λ_{max} 237.0 (6168). IR (KBr): 3492*s*, 3290*s* (O–H, N–H); 3066*w* (N–H); 3026*w* (=C–H); 2962*s*, 2927*s*, 2868*m* (stat. C–H); 1736*s* (acetate); 1653*s*, 1543*s* (amide I + II); 1363*s* (*t*-Bu); 1236*s*, 1211*s*, 1100*s* (C–O). ^{1}H-NMR: 1.08 (*s*, *t*-Bu); 2.16 (*s*, $MeCO_2$); 2.32 (*dd* with f.s., *J*(H–C(7),H′–C(7)) = 14.9, *J*(H–C(7),H–C(6)) = 6.9, H–C(7)); 3.25 (*dd*, *J*(H–C(5),H–C(4)) = 6.6, *J*(H–C(5),H–C(6)) = 3.4, H–C(5)); 4.38 (*d*, *J*(OH, H–C(6)) = 4.0, OH); 4.47 (*d*, *J*(H–CHN, NH) = 5.7, CH_2N); 4.81 (m_c, H–C(6)); 5.81 (m_c, H–C(2)); 5.95 (*d*, *J*(H–C(4),H–C(5)) = 6.6, H–C(4)); 6.00 (br. *t*, *J*(NH, H–CHN) = 5.7, NH); 7.30–7.38 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): H–C(6)/OH (2.2%); H–C(6)/H–C(5) (3.6%); H–C(6)/H–C(7) (3.3%); H–C(6)/H′–C(7) (2.5%); H–C(7)/H′–C(7) (7.5%); H′–C(7)/OH (2.0%); H′–C(7)/H–C(6) (4.4%); H′–C(7)/H–C(7) (11.6%). ^{13}C-NMR: 20.9 ($MeCO_2$); 29.1 (Me_3C); 35.8 (Me_3C); 39.3 (C(7)); 43.6 (CH_2N); 49.9 (C(5)); 81.0 (C(6)); 116.0 (C(2)); 120.3 (C(4)); 127.6, 127.7, 128.8 (5 arom. C); 137.7 (C_{ipso}); 149.8, 151.6 (C(1), C(3)); 169.5 ($MeCO_2$); 174.2 (HNCO). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross peaks between 1.08/29.1; 2.16/20.9; 2.32/39.3, 2.49/39.3; 3.25/49.9; 4.47/43.6; 4.81/81.0; 5.81/116.0; 5.95/120.3; 7.30–7.38/127.6, 127.7, 128.8. Anal. calc. for $C_{21}H_{27}NO_4$ (357.45): C 70.56, H 7.61, N 3.92; found: C 70.85, H 7.77, N 3.90.

1.18. *Irradiation of* rac-**46** (see *Scheme 16*). 1.18.1. *In MeOH.* A soln. of *rac*-**46** (496 mg; 2.00 mmol; for preparation, see *Exper. 2.18*) in abs. MeOH (200 ml) was irradiated until educt had dissapeared (after 45 min, UV control). The greenish, oily residue obtained after removal of solvent under reduced pressure was purified by semi-prep. HPLC (hexane/AcOMe 20:7; 254 nm) to afford 27.4 mg (5%) of **48** and 33.4 mg (9%) of **47** (see *Exper. 2.18*).

Methyl (3Z)-3-[(2E)-2-(1-acetoxy-3-oxobutylidene)cyclopentylidene]propionate (**48**): M.p. 73° (CH_2Cl_2/hexane). TLC (hexane/AcOEt 2:1): R_f 0.36. UV (MeOH): λ_{max} 236.5 (8955). IR (KBr): 3001*w* (unsat. C–H); 2970*w*, 2887*w* (sat. C–H); 1740*s* (acetate, ester, ketone); 1676*m* (C=C); 1202*s*, 1168*s*, 1142*s*, 1142*s* (C–O). ^{1}H-NMR: 1.70 (m_c, 2 H–C(4′)); 2.13 (*s*, $MeCO_2$, 3 H–C(4″)); 2.30–2.40 (*m*, 2 H–C(3′), 2 H–C(5′)); 3.04 (*dt*, *J*(H–C(2),H–C(3)) = 7.4, *J*(H–C(2),H–C(5′)) = 1.2, 2 H–C(2)); 3.43 (*s* with f.s., 2 H–C(2″)); 3.68 (*s*, MeO); 5.55 (*tt*, *J*(H–C(3),H–C(2)) = 7.4, *J*(H–C(3),H–C(5′)) = 1.4, H–C(3)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 1.70/2.30–2.40; 2.30–2.40/1.70, 3.04, 3.43, 5.55; 3.04/2.30–2.40, 5.55; 3.43/2.30–2.40; 5.55/2.30–2.40, 3.04. NOEs from difference spectra (irradiated signal/NOE): H–C(3)/H–C(2) (2.4%); H–C(3)/H–C(5′) (3.0%); H–C(3)/H–C(2″) (0.1%); H–C(2″)/H–C(2) (2.9%). Anal. calc. for $C_{15}H_{20}O_5$ (280.32): C 64.27, H 7.19; found: C 64.54, H 7.25.

1.18.2. *In the Presence of* $PhCh_2NH_2$. A soln. of *rac*-**46** (248 mg; 2.00 mmol) and freshly distilled $PhCH_2NH_2$ (0.33 ml; 3.00 mmol) in 1 ml of anh. CH_2Cl_2 was filled up with abs. Et_2O to a volume of 350 ml and irradiated for 45 min (UV control, no educt could be deteceted). Acidic workup led to an dark, oily product (280 mg) which was seperated by semi-prep. HPLC (hexane/AcOEt 3:2 + 30% CH_2Cl_2, 254 nm), after filtration through silica gel (10 g; hexane/AcOEt 1:2), to furnish 50.4 mg (14%) *rac*-**49** and 40.2 g (21%) phenol **47** (for anal. data, see *Exper. 2.18*).

(6RS,7SR)-7-(N-Benzylcarbamoyl)-1,2,3,5,6,7-hexahydro-6-hydroxy-6-methylazulen-4-yl Acetate (*rac*-**49**): TLC (hexane/AcOEt 1:1): R_f 0.46. UV (MeOH): λ_{max} 260.5 (8237). IR (film): 3369*s* (O–H, N–H); 3063*w* (N–H); 2958*s*, 2932*s*, 2872*m*, 2848*m* (sat. C–H); 1738*s* (acetate); 1643*s* (amide I); 1526*s* (amide II); 1227*s*, 1203*s* 1122*s* (C–O). ^{1}H-NMR: 1.31 (*s*, Me–C(6)); 1.45–1.75 (*m*, 2 H–C(2)); 2.15 (*s*, $MeCO_2$); 2.32–2.55 (*m*, H′–C(5), 2 H–C(1), 2 H–C(3)); 2.88 (*d* with f.s., *J*(H–C(5),H′–C(5)) = 18.7, H–C(5)); 3.22 (*dd*, *J*(H–C(7),H–C(8)) = 8.0, *J*(H–C(7),H–C(1)) = 2.5, H–C(7)); 4.40, 4.49 (*AB* system, *J*(H_a,H_b) = 14.9, *J*(H_a, NH) = *J*(H_b, NH) = 5.8, CH_2N); 5.42 (*s*, OH); 5.70 (*d* with f.s., *J*(H–C(8),H–C(7)) = 8.0, H–C(8)); 6.63 (br. *t*, *J*(NH, H–CHN) = 5.8, NH); 7.22–7.37 (*m*, 5 arom. H). NOEs from difference spectra (irradiated signal/NOE): Me/OH (1.2%); Me/H′–C(5) (0.8%); Me/H–C(7) (1.1%); OH/Me (27.9%); OH/H′–C(5) (1.7%); OH/H–C(7) (1.9%); H′–C(5) (6.6%); H–C(7)/Me (1.5%). ^{13}C-NMR: 20.7 (*Me*COO); 23.4 (C(2)); 27.2 (*Me*–C(6)); 31.3, 36.6 (C(1), C(3)); 43.5 (CH_2N); 45.6 (C(5)); 56.1 (C(7)); 69.7 (C(6)); 115.8 (C(8)); 127.4, 127.5, 128.7, (5C, Ph); 127.7 (C_{ipso}); 137.7, 142.9, 143.1 (C(4), C(9), C(10)); 168.5 ($MeCO_2$); 173.2 (NHCO). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross peaks between 1.31/27.2; 1.45–1.75/23.4; 2.15/20.7; 2.32–2.53/31.3, 36.6, 45.6; 2.88/45.6; 3.22/56.1; 4.40, 4.49/43.5; 5.70/115.8; 7.22–7.37/127.4, 127.5, 128.7. Anal. calc. for $C_{21}H_{25}NO_4$ (355.43): C 70.96, H 7.09, N 3.94; found: C 70.77, H 7.36, N 3.66.

1.19. *Irradiation of* rac-**50** (see *Schemes 17* and *18*). 1.19.1. *In the Presence of* N-*(Phenylmethylidene)aniline* (**52a**). *rac*-**50** (174 mg; 1.00 mmol; for preparation, see [49]) and **52a** [45] [47] (393 mg; 2.00 mmol) were dissolved in 100 ml of abs. hexane and irradiated for 5 h with light of wavelength > 340 nm. TLC Control (hexane/AcOEt 4:1) indicated that no detectable reaction had occured. The solvent was removed in a rotary evaporator under reduced pressure, and the obtained residue was seperated and purified by FC (20 g of silica gel; hexane/AcOEt 4:1). This afforded 215 mg (55%) of **52a** [45][47] and 167 mg (96%) of *rac*-**50**.

1.19.2. *In the Presence of* N-*(Benzylidene)cyclohexylamine* (**52b**). A soln. of *rac*-**50** [49] (166 mg; 1.0 mmol) and **52b** [48] (187 mg; 1.0 mmol) in anh. hexane/CH_2Cl_2 9:1 was irradiated for 120 min with light > 340 nm. The solid residue, obtained after removal of solvents by rotary evaporation under reduced pressure, was recrystallized (Et_2O/hexane) to give 340 mg (98%) of *(3*RS,*4*RS*)-3-[(1*Z,*3*E*)-4-acetoxypenta-1,3-dienyl]-1-cyclohexyl-4-phenylazetidin-2-one* (= *(1*E,*3*Z*)-4-[(3*RS,*4*RS*)-1-cyclohexyl-2-oxo-4-phenylazetidin-3-yl]-1-methylbuta-1,3-dien-1-yl acetate*; *rac*-**54**): M.p. 71–72° (Et_2O/hexane). TLC (hexane/AcOEt 4:1): R_f 0.45. UV (MeOH): λ_{max} 245.5 (23048). IR (KBr): 1750*s* (sh; acetate, β-lactam); 1665*m*, 1610*w* (C=C); 1210*s*, 1145*s* (C–O); 750*s*, 705*s* (Ph). ^{1}H-NMR: 1.02–1.29 (*m*, 2 H–C(3′) through 2 H–C(5′)); 1.48–1.64 (*m*, H–C(2′),H–C(6′)); 1.70–1.77 (*m*, H′–C(2′),H′–C(6′)); 1.96 (*s*, 3 H–C(5″)); 2.07 (*s*, $MeCO_2$); 3.36–3.45 (*m*, H–C(1′)); 3.79 (ψ*dt*, *J*(H–C(3), H–C(1″)) = 8.5, *J*(H–C(3),H–C(4)) = *J*(H–C(3),H–C(2″)) ≈ 1.8, H–C(3)); 4.30 (*d*, *J*(H–C(4),H–C(3)) = 2.1, H–C(4)); 5.63 (*dd*, *J*(H–C(2″),H–C(1″)) = 10.7, *J*(H–C(2″),H–C(3″)) = 9.6, H–C(2″)); 5.72 (ψ*dt*, *J*(H–C(3″),H–C(2″) = 9.6, *J*(H–C(3″),H–C(1″)) = *J*(H–C(3″),H–C(5″)) ≈ 1.1, H–C(3″)); 6.23 (*ddd*, *J*(H–C(1″),H–C(2″)) = 10.7, *J*(H–C(1″),H–C(3)) = 8.5, *J*(H–C(1″),H–C(3″)) = 1.3, H–C(1″)); 7.30–7.41 (*m*, 5 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Configuration was determined by NOE. NOEs from difference spectra (irradiated signal/NOE): H–C(4)/H–C(3) (0.5%); H–C(4)/H–C(2′) (1.7%); H–C(4)/H–C(3) (1.7%); H–C(4)/Ph (4.9%); H–C(3)/H–C(4) (0.7%); H–C(3)/H–C(1″) (1.0%); H–C(3)/H–C(2″) (3.0%); H–C(3)/H–C(3″) (8.6%); H–C(3)/Ph (3.8%); H–C(1″)/H–C(2″) (6.0%); H–C(2″)/H–C(4) (2.3%); H–C(2″)/H–C(3) (2.4%); H–C(2″)/H–C(1″) (4.6%); H–C(2″)/Ph (1.0%); H–C(3″)/H–C(4) (1.2%); H–C(3″)/H–C(3) (2.8%); H–C(3″)/H–C(1″) (3.2%); H–C(3″)/H–C(5″) (0.3%); H–C(3″)/Ph (2.5%). ^{13}C-NMR: 15.76 (*Me*–C(4″)); 20.89 (*Me*CO_2); 24.94, 25.10, 25.14, 30.62, 31.39 (C(2′) through C(6′)); 52.81 (C(1′)); 58.87 (C(3)); 61.32 (C(4)); 114.12 (C(3″)); 124.04 (C(1″)); 126.52 (C(2″)); 126.64, 128.45, 128.80 (5 arom. C); 138.96 (C_{ipso}); 149.57 (C(4″)); 168.07 (C(2)); 169.14 ($MeCO_2$). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Anal. calc. for $C_{22}H_{27}NO_3$ (353.46): C 74.76, H 7.70, N 3.96; found: C 74.80, H 7.68, N 4.17.

Crystal-Structure Analysis of rac-**54** (*Fig. 20*): monoclinic crystals; $P2_1/c$ (No. 14); a = 11.1413(6), b = 6.6420(3), c = 27.538(1) Å; β = 91.578(4)°; V = 2037.0(3) Å^3; Z = 4; ρ = 1.152 g/cm^3; hemisphere through 2θ = 120°; 2972 indep. reflect. with $I > \sigma$; 344 variables; $R(F)$ = 0.043; $R_w(F)$ = 0.063.

1.19.3. *In the Presence of* N-*[(Methylsulfanyl)methylidene]benzylamine* (**53**). *rac*-**50** [49] (0.5 g; 3.00 mmol) and **53** (amount freshly prepared as described in *Exper. 3.1*) were dissolved in 240 ml of anh. CH_2Cl_2/acetone 9:1 and irradiated under bubbling a continuous stream of dry N_2 through the soln. for 2 h. The solvents were removed under reduced pressure, and the obtained residue was purified by FC (80 g of silica gel, hexane/AcOEt 2:1). This afforded 0.8 g of a brown oil which was recrystallized from Et_2O/pentane yielding 0.6 g (60%) of *rac*-**55** an anal. sample of which was obtained by prep. HPLC (hexane/AcOEt 5:1 + 30% CH_2Cl_2; 254 nm).

*(3*RS,*4*RS*)-3-[(1*Z,*3*Z*)-4-Acetoxypenta-1,3-dienyl]-1-benzyl-4-(methylsulfanyl)azetidin-2-one* (= *(1*E,*3*Z*)-4-[(3*RS,*4*RS*)-1-Benzyl-2-oxo-4-(methylsulfanyl)azetidin-3-yl]-1-methylbuta-1,3-dienyl Acetate*; *rac*-**55**): M.p. 59–61° (Et_2O/pentane). TLC (hexane/AcOEt 2:1): R_f 0.3. UV (MeOH): λ_{max} 248 (34370). IR (film): 3030*w* (unsat. C–H); 2920*w* (sat. C–H); 1754*s* (acetate, lactam); 1672*s* (C=C); 1385*m*; 1217*m*; 1149*m*. ^{1}H-NMR: 1.98 (*s*, $MeCO_2$); 1.99 (*s*, Me–C(4″)); 2.14 (*s*, Me); 3.79 (ψ*d*, *J*(H–C(1′),H′–C(1′)) = 14.9, H–C(1)); 4.15 (ψ*d*, *J*(H–C(3),H–C(1″)) = 10.9, H–C(3)); 4.23 (*d*, *J*(H–C(4),H–C(3)) = 2.0, H–C(4)); 4.70 (*d*, *J*(H′–C(1′), H–C(1′)) = 15.1, H′–C(1)); 5.51 (*t*, *J*(H–C(1″),H–C(2″)) = *J*(H–C(1″),H–C(3)) ≈ 10.5, H–C(1″)); 6.02 (*dt*, *J*(H–C(3″),H–C(2″)) = 11.7, H–C(3″)); 6.25 (ψ*t*, *J*(H–C(2″),H–C(3″)) = *J*(H–C(2″),H–C(1″)) = 11.2, H–C(2″)); 7.26–7.38 (*m*, 5 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 4.15/4.70 and 5.51; 5.51/6.25; 6.25/6.02. ^{13}C-NMR: 10.44 (*Me*CO_2); 15.38 (*Me*–C(4″)); 21.00 (MeS); 43.97 (C(1′)); 55.92 (C(3)); 63.44 (C(4)); 113.63 (C(3″)); 122.36 (C(1″)); 127.24 (C(2″)); 127.82, 128.34, 135.82 (5 arom. C); 150.27 (C_{ipso}); 166.23 ($MeCO_2$); 169.16 (C(2)). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks between 10.44/1.98; 15.38/1.99; 21.00/2.14; 43.97/3.79; 55.92/4.15; 63.44/4.23; 113.63/6.02; 122.36/5.51; 127.24/6.25; 127.82/7.2–7.38; 128.34/7.26–7.38; 135.82/7.26–7.38. Anal. calc. for $C_{18}H_{21}NO_3S$ (331.43): C 65.23, H 6.39, N 4.23, S 9.68; found: C 65.21, H 6.43, N 4.24, S 9.61.

Crystal-Structure Analysis of rac-**55** (*Fig. 21*): monoclinic crystals; $P2_1/c$ (No. 14); a = 7.527(3), b = 30.624(2), c = 8.097(1) Å; β = 102.18(2)°; V = 1824(1) Å^3; Z = 4; ρ = 1.207 g/cm^3; quadrant through 2θ = 120°; 2570 indep. reflect. with $I > 0$; 293 variables; $R(F)$ = 0.056; $R_w(F)$: 0.062.

1.19.4. *In the Presence of (2*RS*)-*N-*Benzylidenebicyclo[2.2.1]heptan-2-amine* (*rac*-**56**). A soln. of *rac*-**56** (2.51 g; 13 mmol; for preparation, see *Exper. 3.2*) and *rac*-**50** [49] (0.42 g; 25 mmol) in anh. CH_2Cl_2(70 ml) was irradiated for 150 min with light > 340 nm. The reaction was monitored UV-spectroscopically. The residue, obtained after removal of solvent by rotary evaporation under reduced pressure, was purified by FC (60 g of silica gel; hexane/AcOEt 2:1) to give a product (0.74 g; 80%) which proved to be a complex mixture (HPLC: hexane/AcOEt 2:1 + 30% CH_2Cl_2). Prep. HPLC afforded 0.13 g (14%) of *rac*-**58** and 0.15 g (16%) of *rac*-**59**.

(3RS,4RS)-3-[(1Z,3E)-4-Acetoxypenta-1-[(2RS)-bicyclo[2.2.1]hept-2-yl]-1,3-dienyl]-4-phenylazetidin-2-one (= *(1E,3Z)-4-{(3RS,4RS)-1-[(2RS)-bicyclo[2.2.1]hept-2-yl]-2-oxo-4-phenylazetidin-3-yl}-1-methylbuta-1,3-dienyl Acetate*, *rac*-**58**): M.p. 90° (Et_2O/pentane). TLC (hexane/AcOEt 2:1): R_f 0.34. UV (MeOH): λ_{max} 246.5 (24537). IR: (KBr): 3067*w* (unsat. C–H); 2955*m*, 2873*w* (sat. C–H); 1747*s* (lactam); 1668*m* (C=C); 1455*m*; 1368*m*; 1217*m*; 1150*m*. ^{1}H-NMR: 0.83–1.71 (*m*, 2 H–C(3'), 2 H–C(5'), 2 H–C(6'), 2 H–C(7)); 1.96 (*s*, Me–C(4'')); 2.07 (*s*, $MeCO_2$); 2.15 (ψs, H–C(4')); 2.25 (ψs, H–C(1')); 3.28 (*ddd*, *J*(H–C(2'),H–C(1')) = 3.8, *J*(H–C(2'),H–C(3')) = 4.1, *J*(H–C(2'),H'–C(3')) = 8.1, H–C(2')); 3.73 (ψd, *J*(H–C(3),H–C(1'')) = 8.4, H–C(3)); 4.27 (*d*, *J*(H–C(4),H–C(3)) = 2.0, H–C(4)); 5.63 (*dd*, *J*(H–C(1''),H–C(3)) = 8.6, *J*(H–C(1''), H–C(2'') = 9.8, H–C(1'')); 5.74 (*dd*, *J*(H–C(3''),H–C(2'')) = 11.8, *J*(H–C(3''),H–C(1'')) = 1.0, H–C(3'')); 6.23 (*ddd*, *J*(H–C(2''),H–C(3'')) = 11.8, *J*(H–C(2''),H–C(1'')) = 9.9, *J*(H–C(2''),H–C(3)) = 1.4, H–C(2'')); 7.26–7.42 (*m*, 5 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 9.83–1.71/2.15 and 3.28; 3.73/4.27 and 5.63; 5.63/5.74 and 6.23. ^{13}C-NMR: 15.79 (*Me*–C(4'')); 20.93 (*Me*CO_2); 26.81 (C(5')); 28.37 (C(6)); 35.64 (C(4')); 35.74 (C(7')); 36.14 (C(3')); 40.74 (C(1')); 57.15 (C(2')); 58.85 (C(3)); 62.13 (C(4)); 114.15 (C(3'')); 124.11 (C(1'')); 126.55 (C(2'')); 126.63, 128.46, 128.92 (5 arom. C); 138.61 (C_{ipso}); 149.58 (C(4'')); 168.33 ($MeCO_2$); 169.16 (C(2)). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks between 15.79/1.96; 20.93/2.07; 26.81/0.83–1.71; 28.37/0.83–1.71; 35.74/0.83–1.71; 35.64/2.15; 40.75/2.25; 57.15/3.28; 58.85/3.73; 62.13/4.27; 114.15/5.74; 124.11/5.63. Anal. calc. for $C_{23}H_{27}NO_3$ (365.47): C 75.59, H 7.45, N 3.83; found: C 75.34, H 7.44, N 3.97.

(3RS,4SR)-3-[(1Z,3E)-Acetoxypenta-1,3-dienyl]-1-[(2RS)-bicyclo[2.2.1]hept-2-yl]-4-phenylazetidin-2-one (= *(1E,3Z)-4-{(3RS,4SR)-1-[(2RS)-bicyclo[2.2.1]hept-2-yl]-2-oxo-4-phenylazetidin-3-yl}-1-methylbuta-1,3-dienyl Acetate*, *rac*-**59**): M.p. 104° (Et_2O/pentane). TLC (hexane/AcOEt 2:1): R_f 0.34. IR: (KBr): 3064*w*, 3029*w* (unsat. C–H); 2955*m*, 2869*m* (sat. C–H); 1747*s* (lactam); 1660*m* (C=C); 1460*m*, 1390*m*, 1215*m*, 1144*m*. ^{1}H-NMR: 0.83–1.58 (*m*, 2 H–C(3'), 2 H–C(5'), 2 H–C(6'), 2 H–C(7')); 1.97 (*s*, Me–C(4'')); 2.07 (*s*, $MeCO_2$); 2.17 (ψs, H–C(4')); 2.68 (ψs, H–C(1')); 3.39–3.44 (*m*, H–C(2')); 3.71 (ψd, *J*(H–C(3),H–C(1'')) = 8.5 H–C(3)); 4.27 (*d*, *J*(H–C(4),H–C(3)) = 2.0, H–C(4)); 5.64 (*d*, *J*(H–C(1''),H–C(3)) = 8.7, *J*(H–C(1''),H–C(2'')) = 10.5, H–C(1'')); 5.73 (*dd*, *J*(H–C(3''),H–C(1'')) = 1.1, *J*(H–C(3''), H–C(2'')) = 11.8, H–C(3'')); 6.23 (*ddd*, *J*(H–C(2''),H–C(3'')) = 12.0, *J*(H–C(2''), H–C(1'')) = 10.8, *J*(H–C(2''),H–C(3)) = 1.5, H–C(2'')); 7.26–7.40 (*m*, 5 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 0.83–1.58/2.17, 2.68, and 3.39–3.44; 3.71/4.27 and 5.64; 5.64/5.73 and 6.23. ^{13}C-NMR: 15.80 (*Me*–C(4'')); 20.93 ($MeCO_2$); 26.97 (C(5')); 28.31 (C(6')); 35.72 (C(4')); 35.82 (C(7')); 36.33 (C(3')); 41.03 (C(1')); 57.02 (C(2')); 58.42 (C(3)); 62.50 (C(4)); 114.14 (C(3'')); 124.16 (C(1'')); 126.56, 128.40, 128.89 (5 arom. C); 138.75 (C(4'')); 167.97 ($MeCO_2$); 169.16 (C(2)). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks between 15.80/1.97; 20.93/2.07; 26.97/0.83–1.58; 28.31/0.83–1.58; 36.33/0.83–1.58; 35.82/0.83–1.58; 35.72/2.17; 41.03/2.68; 57.02/3.39–3.44; 58.42/3.71; 62.50/4.27; 114.14/5.73; 124.16/5.64; 126.56/6.23. Anal. calc. for $C_{23}H_{27}NO_3$ (365.47): C 75.59, H 7.45, N 3.83; found: C 75.48, H 7.34, N 3.65.

1.19.5. *In the Presence of* N-*(1-Phenylethylidene)benzylamine* (**57b**). A soln. of *rac*-**50** [53] (0.5 g; 3 mmol) and **57b** [45] [50] (5.7 g; 27.2 mmol) in anh. CH_2Cl_2 (100 ml) was irradiated for 5.5 h with light > 340 nm. The reaction was monitored UV-spectroscopically. After removal of solvent by rotary evaporation under reduced pressure, a residue remained which was purified by FC (70 g of silica gel; hexane/AcOEt 2:1) to give an oily product (0.78 g; 69%) which was fractionated by prep. HPLC (hexane/AcOEt 2:1 + 30% CH_2Cl_2) to afford 160 mg (13%) *rac*-**60** and 73 mg (86.4%) of *rac*-**61**.

(3RS,4RS)-3-[(1Z,3E)-4-Acetoxypenta-1,3-dienyl]-1-benzyl-4-methyl-4-phenylazetidin-2-one (= *(1E,3Z)-4-[(3RS,4RS)-1-Benzyl-4-methyl-2-oxo-4-phenylazetidin-3-yl]-1-methylbuta-1,3-dien-1-yl Acetate*; *rac*-**60**): M.p. 98° (Et_2O/pentane). TLC (hexane/AcOEt 2:1): R_f 0.32. IR (KBr): 3028*w* (unsat. C–H); 2981*w* (sat. C–H); 1756*s* (acetate, lactam); 1662*m* (C=C); 1393*m*; 1219*s*. ^{1}H-NMR: 1.39 (*s*, Me–C(4)); 1.96 (*s*, Me–C(4'')); 2.06 (*s*, $MeCO_2$); 3.95 (*d*, *J*(H–C(1'),H'–C(1')) = 15.1, H–C(1)); 3.98 (ψd,*J*(H–C(3),H–C(1'')) = 8.6, H–C(3)); 4.83 (*d*, *J*(H'–C(1'),H–C(1')) = 15.1, H'–C(1')); 5.57–5.62 (*m*, H–C(1'')); 5.61 (ψt, *J*(H–C(3''),H–C(2'')) = 11.8, H–C(2'')); 6.30 (ψt, *J*(H–C(2''),H–C(3'')) = 11.3, H–C(3'')); 7.25–7.38 (*m*, 10 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 3.95/4.73; 3.98/5.57–5.62; 5.61/6.30. ^{13}C-NMR: 15.84 (*Me*–C(4'')); 20.69 (*q*, *Me*CO_2); 20.91 (*Me*–C(4)); 44.33 (C(1')); 60.42 (C(3)); 63.1 (C(3)); 114.06 (C(1'')); 121.75 (C(2'')); 125.3, 127.66, 127.65, 127.81 (10 arom. C); 128.54 (C(3'')); 128.68, 128.80 (2 C_{ipso}); 149.88 (C(4'')); 168.70 (MeCOO); 169.04 (C(2)). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. NOEs from difference spectra (irradiated signal/NOE): H–C(3)/H–C(1') (6.3%); H–C(1')/H–C(2') (4.6%); H–C(2')/H–C(3) (4.6%); H–C(2')/H–C(3') (2.0%); H–C(3')/H–C(2') (4.7%). Anal. calc. for $C_{24}H_{25}NO_3$ (375.47): C 76.77, H 6.71, N 3.73; found: C 76.63, H 6.66, N 3.77.

(3RS,4SR)-3-[(1Z,3E)-4-Acetoxypenta-1,3-dienyl]-1-benzyl-4-methyl-4-phenylazetidin-2-one (= *(1E,3Z)-4-[(3RS,4SR)-1-Benzyl-4-methyl-2-oxo-4-phenylazetidin-3-yl]-1-methylbuta-1,3-dien-1-yl Acetate*; *rac*-**61**): TLC (hexane/AcOEt 2:1): R_f 0.31. UV (MeOH): λ_{max} 245.5 (23612). IR: (film); 3030*w* (unsat. C–H); 2969*w* (sat. C–H); 1749*s* (acetate, lactam); 1665*m* (C=C); 1384*m*; 1217*m*. ^{1}H-NMR: 1.61 (*s*, Me–C(4)); 1.89 (*s*, Me–C(4″)); 2.04 (*s*, MeCOO); 4.05 (*d*, *J*(H–C(1′),H′–C(1′)) = 14.7, H–C(1′)); 4.01–4.16 (*m*, H–C(3)); 4.84 (*d*, *J*(H′–C(1′), H–C(1′)) = 14.6, H′–C(1′)); 4.86 (*ψt*, *J*(H–C(1″),H–C(2″)), *J*(H–C(1″),H–C(3)) = 9.8, H–C(1″)); 5.90–6.10 (*m*, H–C(2″),H–C(3″)); 7.15–7.38 (*m*, 10 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 4.05/4.84; 4.86/4.01–4.16 and 5.90–6.08. ^{13}C-NMR: 15.75 (*Me*–C(4″)); 21.06 (*MeCO*$_2$); 24.78 (*Me*–C(4)); 44.46 (C(1′)); 61.86 (C(3)); 113.64 (C(3″)); 122.43 (C(1″)); 122.43 (C(1″)); 126.55 (C(2″)); 127.61, 128.53, 128.60, 128.71 (10 arom. C); 136.89, 139.47 (2 C_{ipso}); 149.73 (C(4″)); 167.94 (MeCOO); 169.22 (C(2)). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross peaks between 15.75/1.89; 21.06/2.04; 24.78/2.17; 44.46/4.05 and 4.84; 62.86/4.01–4.16; 113.64/5.90–6.05; 122.43/4.86; 126.55/5.90–6.05; 127.61/7.15–7.38; 128.53/7.15–7.38; 128.60/7.15–7.38; 128.71/7.15–7.38. NOEs from difference spectra (irradiated signal/NOE): H–C(3)/H–C(3′) (5.1%); H–C(3)/Me–C(4) (0.1%); H–C(1′)/H–C(2′) (4.2%); H–C(2′)/H–C(1′) (4.4%); H–C(3′)/H–C(3) (5.7%); Me–C(4)/H–C(3) (2.1%). Anal. calc. for $C_{24}H_{25}NO_3$ (375.47): C 76.77, H 6.71, N 3.73; found: C 76.72, H 6.56, N 3.55.

1.20. *Transformations of the 2-Acetyl-*o*-quinolacetate* rac-**62** *and Its Photoproduct* rac-**63** (see *Scheme 20*). 1.20.1 *Irradiation in the Presence of* **52b**. *rac*-**62** (220 mg; 1.00 mmol; for preparation see *Exper. 2.19*) and **52b** [48] (370 mg; 1.00 mmol) were dissolved in 50 ml of anh. hexane/CH_2Cl_2 9:1 and irradiated for 6 h at −60° with light of wavelength > 340 nm (UV control). The residue, obtained after removal of solvents by rotary evaporation under reduced pressure, was purified by FC (20 g of silica gel; hexane/AcOEt 4:1 through 1:1) followed by crystallization from Et_2O/pentane to furnish 120 mg (30%) of *rac*-**63**.

(2RS)-5-[(1Z,3E)-4-Acetoxy-2-methylpenta-1,3-dienyl]-3-cyclohexyl-3,4-dihydro-6-methyl-2-phenyl-1,3-oxazin-4-(2H)-on (= *(1E,3Z)-4-[(2RS)-3-Cyclohexyl-6-methyl-4-oxo-2-phenyl-3,4-dihydro-2H-[1,3]oxazin-5-yl]-1,3-dimethylbuta-1,3-dien-1-yl Acetate*; *rac*-**63**): M.p. 138–139°. TLC (hexane/AcOEt 4:1): R_f 0.1. UV (MeOH): λ_{max} 250.5 (13774). IR (KBr): 1735*s* (acetate); 1650*s* (oxazine); 1610*m*, 1585*w* (C=C); 1220*s* (acetate); 745*s* (Ph). ^{1}H-NMR: 1.02–1.22 (*m*, 2 H–C(3′) through 2 H–C(5′)); 1.38–1.56 (*m*, H–C(2′), H–C(6′)); 1.64 (*s* with f.s., Me–C(2″)); 1.70–1.77 (*m*, H′–C(2′), H′–C(6′)); 1.83 (*s* with f.s., Me–C(6)); 1.96 (*d*, *J*(H–C(5″), H–C(3″)) = 1.4, 3 H–C(5″)); 2.07 (*s*, $MeCO_2$); 4.44–4.51 (*m*, H–C(1′)); 4.53 (*s* with f.s., H–C(1″)); 6.15 (*s*, H–C(2)); 6.29 (*s*, H–C(3″)); 7.30–7.35, 7.38–7.42 (2*m*, 5 arom. H). ^{13}C-NMR: 17.53 (*Me*–C(2″)); 18.53 (*C*(5′)); 21.06 (*MeCO*$_2$); 23.28 (Me–C(6)); 25.38, 25.72, 30.92, 31.60 (C(2′) through C(6′)); 51.99 (C(1′)); 82.59 (C(3″)); 111.38 (C(2″)); 118.90 (C(1″)); 123.07 (C(2)); 127.19, 128.01, 128.51 (5 arom. C); 132.57 (C_{ipso}); 138.57 (C(4″)); 147.08 (C(6)); 160.04 (C(5)); 162.08 (*MeCO*$_2$); 169.01 (C(4)). Anal. calc. for $C_{25}H_{31}NO_4$ (409.53): C 73.32, H 7.63, N 3.42; found: C 73.15, H 7.79, N 3.62.

Crystal-Structure Analysis of rac-**63** (*Fig. 22*): orthorhombic crystal; $P2_12_12_1$ (No. 19); a = 9.4477(6), b = 14.272(1), c = 16.526(1) Å; V = 2228.3(4) Å^3; Z = 4; ρ = 1.221 g/cm^3; hemisphere through 2Θ = 120°; 1898 indep. reflect. with $I > \sigma$; 396 variables; $R(F)$ = 0.029; $R_w(F)$ = 0.039.

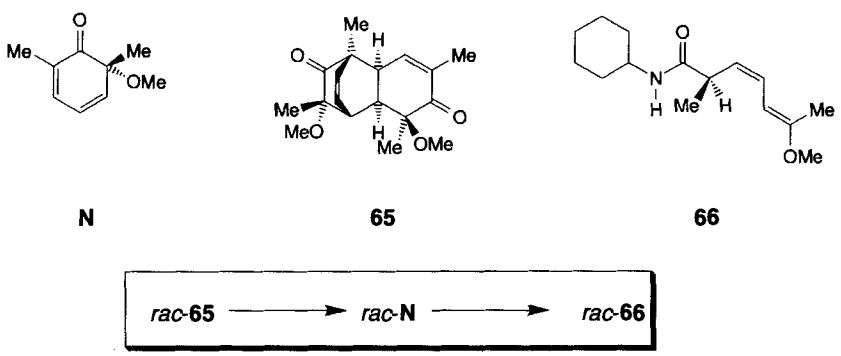
1.20.2. *Irradiation in the Presence of Cyclohexylamine*. A soln. of *rac*-**62** (220 mg; 1 mmol; for preparation, see *Exper. 2.20*) and cyclohexylamine (3 g; 33 mmol) in 30 ml of anh. CH_2Cl_2 was irradiated for 3 h with light of wavelength > 340 nm until no more educt could be detected (UV control). After removal of solvents by rotary evaporation under reduced pressure, a residue was obtained which was purified by FC (2×, 20 g silica gel; hexane/AcOEt 4:1 through 1:1) followed by crystallization. This procedure furnished 127 mg (40%) of *(2RS,3Z,5E)-6-acetoxy*-N-*cyclohexyl-2-acetyl-4-methylhepta-3,5-dienamide* (= *(1E,3Z,5RS)-5-acetyl-6-(cyclohexylamino)-1,3-dimethyl-6-oxohexa-1,3-dien-1-yl acetate*; *rac*-**64**): M.p. 104–105° (Et_2O). TLC (hexane/AcOEt 1:2): R_f 0.6. UV (MeOH): λ_{max} 235 (16894; not stable). UV (MeCN): λ_{max} 235 (17001). IR (KBr): 3310*s* (NH); 1750*s* (acetate); 1665*m* (C=C); 1610*s*, 1590*s* (ketone, amide I); 1536*s* (amide II); 1215*s* (acetate). ^{1}H-NMR: 1.09–1.41 (*m*, 2 H–C(3′) through 2 H–C(5′)); 1.57–1.73 (*m*, H–C(2′), H–C(6′)); 1.80–1.92 (*m*, H′–C(2′), H′–C(6′)); 1.84 (*s*, Me–C(4)); 2.05 (*s*, 3 H–C(7)); 2.09 (*s*, $MeCO_2$, MeCO); 5.31 (*d*, *J*(NH, H–C(1′)) = 8.1, NH); 5.76 (2*s*, H–C(3), H–C(5)); 14.80 (*s* with f.s., H–C(2)). Anal. calc. for $C_{18}H_{27}NO_4$ (321.42): C 67.26, H 8.47, N 4.36; found: C 67.24, H 8.49, N 4.62.

1.20.3. *Hydrolysis of* rac-**63**. To a soln. of *rac*-**63** (40 mg; 0.1 mmol; for preparation see *Exper. 1.20.1*) in 2 ml of abs. MeOH was added 1 ml of 1N aq. HCl soln. After stirring overnight, the solvent was removed by rotary evaporation under reduced pressure. The obtained residue was purified by FC (20 g of silica gel; hexane/AcOEt 1:1) and crystallization from Et_2O to furnish 20 mg (63%) of *rac*-**64**, whose anal. data were identical with that obtained for *rac*-**64** in *Exper. 1.20.2*.

1.21. *Irradiation of* rac-N *in the Presence of Cyclohexylamine* (see *Scheme 22*). A sample of dimer *rac*-**65** was prepared following a known procedure [51] and monomerized leading to a crude product[25]) (160 mg; 1.05 mmol)

which was dissolved in anh. Et_2O (80 ml). After freshly distilled cyclohexylamine (593 µl; 5.3 mmol) had been added, the soln. was irradiated for 75 min (UV and TLC control (hexane/AcOEt 6:1)). Acidic workup and carful removal of solvent under reduced pressure, avoiding rising of the temp. above 35°, gave a residue which was filtered through silica (20 g; hexane/AcOEt 4:1) to afford a mixture (according to HPLC (hexane/AcOEt 1:1; 2 ml/min; refract.)) of *rac*-**65** (44 mg; 13%) and *(2*RS*,3Z,5*E*)-N-cyclohexyl-6-methoxy-2-methylhepta-3,5-dienamide* (*rac*-**66**) (220 mg; 83%). Crystallized from Et_2O/hexane. M.p. 103–104° (Et_2O/hexane). TLC (hexane/AcOEt 4:1): R_f 0.31. UV (MeOH): λ_{max} 249 (20773). IR (KBr): 3282*s* (NH); 2930*s*, 2852*s* (C–H); 1634*s* (amide I); 1063*m* (C=C); 1545*s* (amide II); 1441*m*; 1218*s*; 1146*w*; 1100*m*; 1069*m*, 1033*m*; 972*w* ((*E*)-CH=CH); 939*w* ((*Z*)–CH=CH). ^{1}H-NMR: 1.02–1.44 (*m*, 2 H–C(3'), 2 H–C(5')); 1.28 (*d*, *J*(Me–C(2),H–C(2)) = 7.1, Me–C(2)); 1.54–1.70 (*m*, 2 H–C(2'), 2 H–C(6')); 1.82–1.88 (*m*, 2 H–C(4')); 1.94 (*s*, 3 H–C(7)); 3.57 (*s*, MeO); 3.73 (*m*, H–C(1')); 5.13 (ψt, $J \approx 9.9$, H–C(3)); 5.32 (*d*, *J*(H–C(5),H–C(4)) = 11.3, H–C(5)); 5.68 (br., NH); 6.24 (ψt, $J \approx 11.0$, H–C(4)). The configuration was determined by interpretation of NOE difference spectra (irradiated signal/NOE): H–C(2)/H–C(3) (2.7%); H–C(2)/H–C(5) (2.3%); H–C(2)/Me–C(2) (2.8%); H–C(3)/H–C(2) (3.2%); H–C(3)/H–C(4) (6.3%); H–C(3)/Me–C(2) (2.2%); H–C(4)/H–C(3) (1.9%); H–C(4)/H–C(7) (7.0%); H–C(5)/H–C(2) (2.3%); H–C(5)/H–C(7) (1.2%); H–C(5)/MeO (2.6%); H–C(5)/Me–C(2) (2.8%); H–C(7)/H–C(4) (1.0%); H–C(7)/Me–C(2) (0.2%); MeO/H–C(5) (1.5%); MeO/H–C(7) (0.5%). Anal. calc. for $C_{15}H_{25}NO_2$ (251.37): C 71.67, H 10.02, N 5.57; found: C 71.70, H 9.81, N 5.56.

Scheme 22

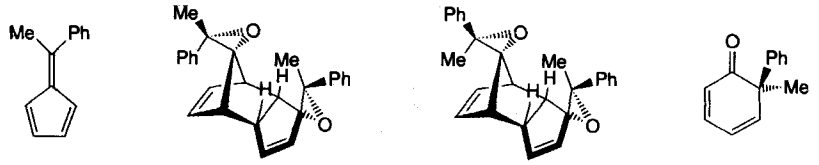


2. Preparation of Individual Cyclohexa-2,4-dien-1-ones. – 2.1. *(*RS*)-6-Methyl-6-phenylcyclohexa-2,4-dien-1-one* (*rac*-**1**; *Scheme 23*). On epoxidizing **P** [52] a product was formed [53], a sample of which could be purified by prep. HPLC (hexane/AcOEt 40:1 + 20% CH_2Cl_2; 10 ml/min; refract.). After evaporation of the solvent, two fractions of solid components were obtained each of which was crystallized from CH_2Cl_2/pentane to give *rac*-**67** and *rac*-**68**, respectively.

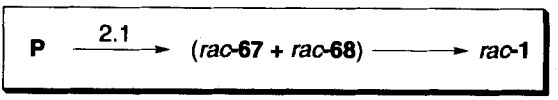
*(1'*RS*,3*RS*,3''*RS*,3a'*RS*,4'*SR*,7'*RS*,7a'*RS*,8'*RS*)-3,3''-Dimethyl-3,3''-diphenyl-3a',4',7',7a'-tetrahydrodispiro[oxiran-2,1'-(4,7-methanoinden)]-8',2''-oxiran* (*rac*-**67**): M.p. 172°. TLC (hexane/AcOEt 10:1): R_f 0.24. IR (KBr): 3079*w*, 3066*w*, 3024*w* (unsat. C–H); 2994*m*, 2988*s*, 2962*m*, 2904*m* (sat. C–H); 1604*w* (C=C); 1496*s*, 1441*s*; 1374*s* (C–O (oxirane)). ^{1}H-NMR: 1.58, 1.64 (2*s*, Me–C(3), Me–C(3'')); 2.05 (*dd*, *J*(H–(7'),H–C((7a')) = 4.4, *J*(H–C(7'),H–C(6')) = 3.6, H–C(7')); 2.79–2.83 (*m*, H–C(4')); 3.20 (*dd*, *J*(H–C(7a'),H–C(7')) = 4.6, *J*(H–C(7a'),H–C(3a')) = 7.6, H–C(7a')); 3.71 (*ddd*, *J*(H–C(3a'),H–C(7a')) = 7.6, *J*(HH–C(3a'),H–C(4')) = 4.7, *J*(H–C(3a'),H–C(3')) = 2.3, H–C(3a')); 4.93 (*dd*, *J*(H–C(2'),H–C(3')) = 5.8, *J*(H–C(2'),H–C(3a')) = 1.6, H–C(2')); 5.82 (*dd*, *J*(H–C(3'),H–C(2')) = 5.8, *J*(H–C(3'),H–C(3a')) = 1.9, H–C(3')); 5.99 (*ddd*, *J*(H–C(5'), H–C(6')) = 6.3, *J*(H–C(5'),H–C(4')) = 3.4, *J*(H–C(5'),H–C(7')) = 0.9, H–C(5')); 6.25 (*ddd*, *J*(H–C(6'), H–C(5')) = 6.3, *J*(H–C(6'),H–C(7')) = 3.5, *J*(H–C(6'),H–C(4')) = 1.0, H–C(6')); 7.19–7.33 (*m*, 10 arom. H). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 5.82/2.13 and 3.31/2.73, 6.40/5.82, 6.40/2.73, 5.69/4.91, 5.69/3.57–3.63, 3.57–3.63/3.31 and 3.57–3.63/2.13. The relative configuration follows from NOE difference spectra (irradiated signal/NOE): H–C(2')/H–C(3') (25.7%); H–C(3')/H–C(2') (22%);

[25]) As monomer *rac*-**N** rapidly dimerizes at r.t., a mixture of *rac*-**N**/*rac*-**65** was used.

Scheme 23



P **67** **68** **1**



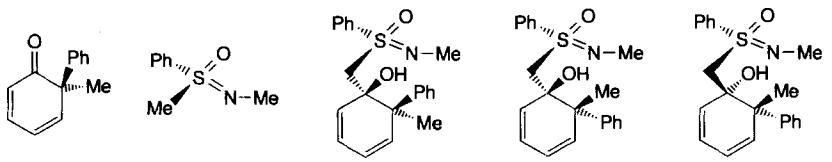
H–C(3')/H–C(3a') (15.9%); H–C(3')/H–C(4') (5.1%); H–C(3a')/H–C(3') (17.8%); H–C(3a')/H–C(4') (26.6%); H–C(3a')/H–C(7a') (27.8%); H–C(4')/H–C(3') (7.25); H–C(4')/H–C(3a') (26.5%); H–C(5') (15.1%); H–C(5')/H–C(4') (3.4%); H–C(5')/H–C(6') (3.9%); H–C(6')/H–C(5') (10.5%); H–C(6')/H–C(7') (7.4%); H–C(7')/H–C(6') (18.6%); H–C(7')/H–C(7a') (26.6%); H–C(7a')/H–C(3a') (24.7%); H–C(7a)/H–C(7') (20.4%); CH_3–C(3)/H–C(6) (3.7%); Me–C(3)/H–C(7') (7.5%); Me–C(3)/H–C(7a') (14.2%); Me–C(3'')/H–C(6') (4.2%); Me–C(3'')/H–C(7') (15.5%); Me–C(3'')/H–C(7a') (2.1%). Anal. calc. for $C_{26}H_{24}O_2$ (368.47): C 84.75, H 6.56; found: C 84.61 H 6.57.

(1'RS,3RS,3''RS,3a'RS,4'SR,7'RS,7a'RS,8'RS)-3,3''-Dimethyl-3,3''-diphenyl-3a',4',7',7a'-tetrahydrodispiro[oxirane-2,1'-(4,7-methanoinden)]-8',2''-oxiran (*rac*-**68**): M.p. 189–190°. TLC (hexane/AcOEt 10:1): R_f 0.24. IR (KBr): 3072*w*, 3036*w*, 3027*w*, 3001*m* (unsat. C–H); 2990*m* (sat. C–H); 1604*m* (C=C); 1498*s*, 1443*s*, 1376*s* (C–O (oxirane)). ^{1}H-NMR: 1.65, 1.73 (2*s*, Me–C(3), Me–C(3')); 2.13 (*dd*, *J*(H–C(4'),H–C(3a')) = 4.3, *J*(H–C(4'), H–C(5')) = 3.4, H–C(4')); 2.73 (ψt, $J \approx 3.9$, H–C(7')); 3.31 (*dd*, *J*(C–H(7a'),H–C(7')) = 4.6, *J*(H–C(7a'), H–C(3a')) = 7.6, H–C(7a')); 3.57–3.63 (*m*, H–C(3a')); 4.91 (*dd*, *J*(H–C(2'),H–C(3')) = 5.9, *J*(H–C(2'), H–C(3a')) = 1.6, H–C(2')); 5.69 (*dd*, *J*(H–C(3'), H–C(2')) = 5.9, *J*(H–C(3'),H–C(3a')) = 2.3, H–C(3')); 5.82 (*dd*, *J*(H–C(5'),H–C(4')) = 3.4, *J*(H–C(5'),H–C(6')) = 6.2, H–C(5')); 6.40 (*ddd*, *J*(H–C(6'),H–C(5')) = 6.2, *J*(H–C(6'),H–C(7')) = 3.3, *J*(H–C(6'),H–C(4')) = 0.9, H–C(6')): 7.21–7.35 (*m*, 10 arom. H). The signals were assigned using a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 3.20/2.05; 6.25/5.99, 6.25/2.79–2.83; 5.99/2.79–2.83, 6.25/2.05; 5.82/4.93, 5.82/3.71; 3.71/3.20 and 3.71/2.79–2.83. The relative configuration follows from NOE difference spectra (irradiated signal/NOE): H–C(3')/H–C(3') (27.8%); H–C(3')/H–C(2') (26.3%); H–C(3')/H–C(3a') (15.1%); H–C(3a')/H–C(3) (20.4%); H–C(3a')/H–C(4') (28.7%); H–C(3a')/H–C(7a') (29.6%); H–C(4')/H–C(3') (7.9%); H–C(3')/H–C(3a) (30.2%); H–C(4')/H–C(5') (15.9%); H–C(5')/H–C(4') (18.5%); H–C(5')/H–C(6') (16.6%); H–C(6')/H–C(5') (2.9%); H–C(6')/H–C(7') (13.9%); H–C(7')/H–C(6') (21.5%); H–C(7')/H–C(7a') (24.6%); H–C(7a')/H–C(3a') (31.0%); H–C(7') (20.7%); H–C(7a')/Me–C(3) (19.5%); Me–C(3)/H–C(7') (5.2%); Me–C(3)/H–C(7a') (12.9%); Me–C(3'')/H–C(4') (15.5%). Anal. calc. for $C_{26}H_{24}O_2$ (368.47): C 84.75, H 6.56; found: C 84.70, H 6.45. The major part of the mixture *rac*-**67**/*rac*-**68** was pyrolyzed [51] and afforded *rac*-**1** (*ca.* 40%). For the properties of *rac*-**1**, see [49].

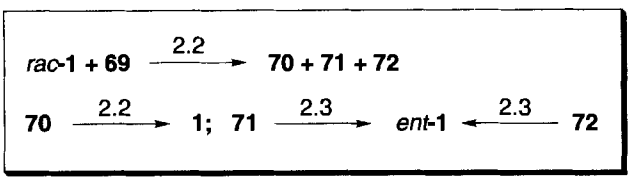
2.2. *(R)-6-Methyl-6-phenylcyclohexa-2,4-dien-1-one* (**1**; *Scheme 24*). In a 100-ml, three-necked, round-bottomed flask, a 2.5M BuLi soln. in hexane (2.96 ml; 7.40 mmol, 1.05 equiv.) was added at 0° to a soln. of (*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine **69**[26]) (1.32 g; 7.70 mmol; 1.1 equiv.) in dry THF (21 ml). The mixture was stirred for 45 min at r.t. After cooling to –80°, a soln. of *rac*-**1** (1.30 g; 7.05 mmol) in dry THF (6.5 ml) was added dropwise. The mixture was stirred at –80° for 6 h. After usual workup, the diastereoisomers were separated by FC (150 g of silica gel; hexane/AcOEt 1:1; twice) and crystallized from CH_2Cl_2/pentane to give **70** (1.02 g, 41%), **71** (578 mg, 23%), and **72** (501 mg, 20%). The ratio of **70**/**71**/**72** was determined as 1.6:1:1.1 by anal. HPLC (hexane/AcOEt 10:3, 2 ml/min, refrac.) from an experiment carried out under identical conditions.

[26]) Prepared according to [54].

Scheme 24



1 **69** **70** **71** **72**



(1R,6R)-6-Methyl-1-{[(S)-N-methyl-S-phenylsulfonimido]methyl}-6-phenylcyclohexa-2,4-dien-1-ol (**70**): M.p. 114–115°. TLC (hexane/Et_2O 1:1): R_f 0.32. $[\alpha]_{589} = +251.5$ ($c = 0.777$, CH_2Cl_2); $[\alpha]_{578} = +265.0$; $[\alpha]_{546} = +310.8$; $[\alpha]_{436} = +644.5$; $[\alpha]_{365} = +1376.9°$. UV (MeOH): λ_{max} 272.5 (5840); 266.5 (6085); 260.0 (5647). IR (KBr): 3170*m* (br., OH); 3055*m*, 3045*w* (unsat. C–H); 2945*m*, 2855*w* (sat. C–H); 1645*w*, 1600*w*, 1500*w*, 1465*m* (C=C); 1235*s*, 1150*s* (O=S=N). ^{1}H-NMR: 1.42 (*s*, Me–C(6)); 2.54 (*s*, MeN); 3.36 (*d*, *J*(H–C(S),H′–C(S)) = 13.2, H–C(S)); 3.59 (*d*, *J*(H′–C(S),H–C(S)) = 13.2, H′–C(S)); 5.73 (*ψd*, *J*(H–C(2), H–C(3)) = 9.5, H–C(2)); 6.02 (*ddd*, *J*(H–C(4),H–C(5)) = 9.6, *J*(H–C(4),H–C(3)) = 5.1, *J*(H–C(4),H–C(2)) = 1.2, H–C(4)); 6.17 (*ddd*, *J*(H–C(3),H–C(2)) = 9.5, *J*(H–C(3),H–C(4)) = 5.1, *J*(H–C(3),H–C(5)) = 1.1, H–C(3)); 7.18–7.31 (*m*, 3 arom. H); 7.34 (*s*, OH); 7.43–7.66 (*m*, 5 arom. H); 7.80–7.84 (*m*, 2 arom. H). The relative configuration at C(1), and C(6) follows from NOE difference spectra (irradiated signal/NOE): H–C(S)/H′–C(S) (13.6%); H–C(S)/Me–C(6) (5.6%); H′–C(S)/H–C(S) (15.3%); H′–C(S)/Me–C(6) (6.0%); Me–C(6)/H–C(S) (2.2%); MeC(6)/H′–C(S) (1.6%). ^{13}C-NMR: 20.43 (Me–C(6)); 28.65 (MeN); 47.36 (C(6)); 60.32 (CH_2S); 75.20 (C(1)); 123.26 (C(4)); 123.58 (C(3)); 126.65, 127.31, 128.92, 129.60, 132.43 (10 arom. C); 133.14 (C(5)); 137.24 (C(2)); 139.02, 139.30 (2 C_{ipso}). Anal. calc. for $C_{21}H_{23}NO_2S$ (353.48): C 71.36, H 6.59, N 3.96, S 9.07; found: C 71.51, H 6.58, N 3.95, S 9.20.

For the crystal-structure analysis of **70**, see *Fig. 28*: trigonal crystals; $P3_2$ (No. 145); $a = b = 12.1676(6)$, $c = 11.0721(8)$ Å; $V = 1419.6(2)$ Å^3; $Z = 3$; $\rho = 1.240$ g/cm^{-3}. Hemisphere up to $2\Theta = 130°$; 2590 independent reflections with $I > 0$; 318 variables; $R(F) = 0.034$, $R_w(F) = 0.044$.

A 50-ml, three-necked, round-bottomed flask, equipped with a condenser, a thermometer, and a glass stopper was charged with **70** (300 mg, 0.85 mmol) in i-BuOH (6 ml) and heated to 80° for 1 h. After usual workup the obtained residue was purified by FC (30 g of silica gel, hexane/Et_2O 1:1) to afford **1** (147 mg; 94%). TLC (hexane/Et_2O 1:1): R_f 0.26. UV (MeOH): λ_{max} 307.5 (3765). $[\alpha]_{589} = +110.1$ ($c = 0.942$ in CH_2Cl_2); $[\alpha]_{578} = 114.5$; $[\alpha]_{546} = +127.6$; $[\alpha]_{436} = -73.3$. CD ($c = 0.0286$ in MeOH): −5602 (364); +24625 (313); −15252 (253). IR and ^{1}H-NMR spectra were identical with those of *rac*-**1** [49] and *ent*-**1** (see *Exper. 2.3*). Anal. calc. for $C_{13}H_{12}O$ (184.24): C 84.75, H 6.56; found: C 84.65, H 6.61.

2.3. *(S)-6-Methyl-6-phenylcyclohexa-2,4-dien-1-one* (*ent*-**1**; *Scheme 24*). *(1R,6S)-6-Methyl-1-{[(S)-N-methyl-S-phenylsulfonimido]methyl}-6-phenylcyclohexa-2,4-dien-1-ol* (**71**; for preparation, see *Exper. 2.2*): M.p. 105–106° (CH_2Cl_2/pentane). TLC (hexane/Et_2O 1:1): R_f 0.41. $[\alpha]_{589} = +489$ ($c = 0.720$, CH_2Cl_2), $[\alpha]_{578} = +515$, $[\alpha]_{546} = +602.5$, $[\alpha]_{436} = +1227$, $[\alpha]_{365} = +2542$. UV (MeOH): λ_{max} 272.5 (4080); 266 (4470); 260 (4190). IR (KBr): 3186*w* (br., OH); 3064*w*, 3048*w* (unsat. C–H); 2976*w*, 2932*w*, 2872*w*, 2802*w* (sat. C–H); 1599*w*, 1580*w*, 1494*w* (C=C); 1242*s*, 1148*s* (O=S=N). ^{1}H-NMR: 1.57 (*s*, Me–C(6)); 2.48 (*d J*(H–C(S),H′–C(S)) = 13.4, H–C(S)); 2.49 (*s*, MeN); 3.35 (*d*, *J*(H′–C(S),H–C(S)) = 13.5, H′–C(S)); 5.90–6.08 (*m*, 3 H, olefin.); 6.25 (*ψd*, *J* = 8.2, 1 H, olefin.); 7.16–7.29 (*m*, 4 arom. H, OH); 7.40–7.61 (*m*, 7 arom. H). ^{1}H-NMR ($CDCl_3/C_6D_6$ 1:1): 1.60 (*s*, Me–C(6)); 2.45 (*s*, MeN); 2.50 (*d*, *J*(H–C(S),H′–C(S) = 13.4,H–C(S)); 3.36 (*d*, *J*(H′–C(S), H–C(S)) = 13.4, H′–C(S)); 5.88–6.02 (*m*, 3 H, olefin.); 6.29–6.33 (*m*, 1 H, olefin.); 7.12–7.35 (*m*, 8 arom. H, OH); 7.43–7.52 (*m*, 3 arom. H). The relative configuration at C(1) and C(6) follows from NOE difference

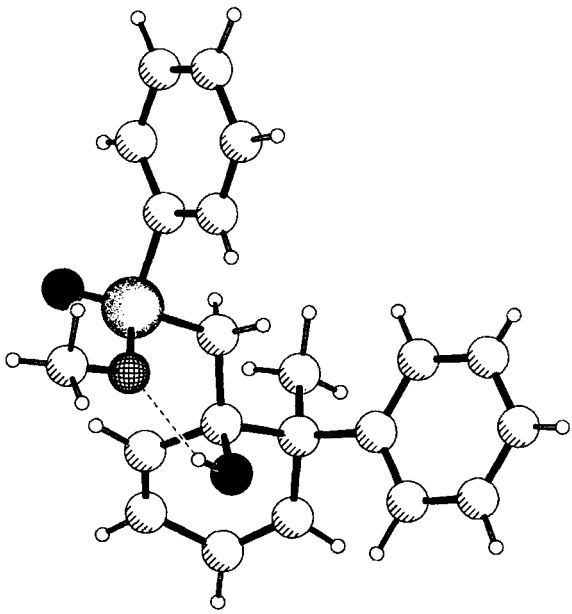


Fig. 28. *Representation of single-crystal X-ray structure of* rac-**70**

spectra (irradiated signal/NOE): H–C(S)/H′–C(S) (8.5%); H′–C(S)/H–C(S) (10.3%). ^{13}C-NMR: 18.81 (*Me*–C(6)); 28.68 (MeN); 50.11 (C(6)); 60.98, (CH_2S); 76.07 (C(1)); 121.83, 122.55 (C(3), C(4)); 126.86, 127.91, 128.54, 128.69, 129.35, 132.88 (10 arom. C); 137.07 (C(2), C(5)); 138.56, 142.94 (2 C_{ipso}). Anal. calc. for $C_{21}H_{23}NO_2S$ (353.48): C 71.36, H 6.59, N 3.96, S 9.07; found: C 71.27, H 6.52, N 3.93, S 9.08.

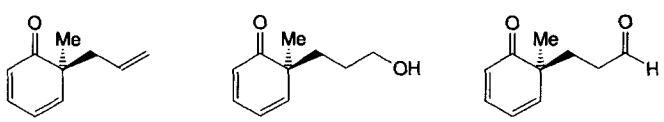
A 50-ml, three-necked, round-bottomed flask, equipped with a condenser, a thermometer, and a glass stopper was charged with **71** (300 mg) in i-BuOH (6 ml) and heated to 80° for 1 h. After usual workup, the obtained residue was purified by FC (30 mg of silica gel, hexane/Et_2O 1:1) to afford *ent*-**1** (148 mg, 95%). TLC (hexane/Et_2O 1:1): R_f 0.26. UV (MeOH): λ_{max} 307.5 (3705). $[\alpha]_{589} = -109.6$ ($c = 0.307$, CH_2Cl_2); $[\alpha]_{578} = -113.8$; $[\alpha]_{546} = -126.4$; $[\alpha]_{436} = +75.9$. Anal. calc. for $C_{13}H_{12}O$ (184.24): C 84.75, H 6.56; found: C 84.62, H 6.73. The IR and ^{1}H-NMR spectra were identical with those of **1** (from **70**; see *Exper. 2.2*) and *ent*-**1** (from **72**; *vide infra*).

*(1S,6S)-6-Methyl-1-{[(S)-*N*-methyl-*S*-phenylsulfonimido]methyl}-6-phenylcyclohexa-2,4-dien-1-ol* (**72**, for preparation, see *Exper. 2.2*): M.p. 96–97° (CH_2Cl_2/pentane). TLC (hexane/Et_2O 1:1): R_f 0.21. $[\alpha]_{589} = -160.9$ ($c = 0.453$, CH_2Cl_2), $[\alpha]_{578} = -170.5$, $[\alpha]_{546} = -205$, $[\alpha]_{436} = -483$, $[\alpha]_{365} = -1249$. UV (MeOH): λ_{max} 272.5 (3775); 266 (4280); 260 (5000). IR (KBr): 3317*m* (br. OH); 3053*w*, 3042*w* (unsat. C–H); 2993*w*, 2979*w*, 2948*w*, 2872*w* (sat. C–H); 1638*w*, 1496*w*, 1444*m* (C=C); 1231*s*, 1138*s* (O=S=N). ^{1}H-NMR: 1.48 (*s*, Me–C(6)); 2.70 (*s*, MeN); 3.53 (*d*, *J*(H–C(S)/H′–C(S)) = 14.1, H–C(S)); 3.83 (*d*, *J*(H′–C(S),H–C(S)) = 14.1, H′–C(S)); 5.51 (*ddd*, *J*(H–C(3),H–C(2)) = 9.7, *J*(H–C(3),H–C(4)) = 4.9, *J*(H–C(3),H–C(5)) = 0.9, H–C(3)); 5.69 (*m*, H–C(2),H–C(5)); 5.96 (*ddd*, *J*(H–C(4),H–C(5)) = 9.6, *J*(H–C(4),H–C(3)) = 4.9, *J*(H–C(4),H–C(2)) = 0.9, H–C(4)); 6.36 (*s*, OH); 7.16–7.29, 7.39–7.60, 7.73–7.77 (3*m*, 10 arom. H). The relative configuration at C(1), and C(6) follows from NOE difference spectra (irradiated signal/NOE): H–C(S)/H′–C(S) (20%); H–C(S)/Me–C(6) (16.1%); H′–C(S)/H–C(S) (4.3%); H′–C(S)/Me–C(6) (11.5%); Me–C(6)/H–C(S) (2.2%); Me–C(6)/H′–C(S) (1.5%). ^{13}C-NMR: 20.50 (*Me*–C(6)); 29.04 (MeN); 44.97 (C(6)); 61.54 (CH_2S); 73.64 (C(1)); 123.20 (C(3)); 123.33 (C(4)); 152.12, 126.60, 126.66, 128.65, 128.72, 129.44, 132.84, 132.88 (10 arom. C); 133.44, 137.56 (C(2), C(5)); 138.82, 139.62 (2 C_{ipso}). Anal. calc. for $C_{21}H_{23}NO_2S$ (353.48): C 71.36, H 6.59, N 3.96, S 9.07; found: C 71.32, H 6.56, N 3.96, S 9.10.

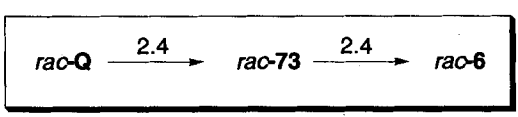
A 50-ml, three-necked, round-bottomed flask, equipped with a condenser, a thermometer, and a glass stopper was charged with **72** (173 mg) in i-BuOH (5 ml) and heated to 80° for 1 h. After usual workup, the obtained residue was purified by FC (20 mg of silica gel, hexane/Et_2O 1:1) to give *ent*-**1** (85 mg, 94%). UV (MeOH): λ_{max} 308 (3770). $[\alpha]_{589} = -107.5$ ($c = 0.800$, CH_2Cl_2); $[\alpha]_{578} = -111.8$; $[\alpha]_{546} = -124.5$; $[\alpha]_{436} = +72.0$. The IR and ^{1}H-NMR spectra were identical with those of **1** (see *Exper. 2.2*) and *ent*-**1** from **71** (*vide supra*).

2.4. *(RS)-6-Methyl-6-(3-oxopropyl)cyclohexa-2,4-dien-1-one* (*rac*-**6**) (*Scheme 25*). A 1-l, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, a pressure-equalizing dropping funnel, a thermometer, and a N_2 inlet was purged with dry N_2 and charged with *rac*-**Q** [55] (12.7 g, 85.7 mmol) and dry THF (100 ml). To the soln., cooled to 3°, 9-BBN (40 ml of a 0.5M soln. in THF, 205 mmol, 2.4 equiv.) Was added during a period of 1 h. After stirring for 10 h at r.t., the mixture was cooled to 3°, and NaOH (85.7 ml of a 3M aq. soln.) and H_2O_2 (68 ml of a 30% aq. soln.; 7 equiv.) were added successively, taking care of the temp. not exceeding 25°. After stirring for 30 min and usual workup the resulting residue was purified by FC (400 g of silica gel, hexane/AcOEt 1:1) to give a colorless oil (9.53 g; TLC (hexane/AcOEt 1:1): R_f 0.17) which was dissolved in dry CH_2Cl_2 (300 ml) in a 500-ml, round-bottomed flask of brown glass. To the vigorously stirred soln. was added, *via* solid addition funnel, freshly precipitated MnO_2 (60 g)[27]. After 1.5 h (TLC control, hexane/AcOEt 1:1), the reaction had been completed. The suspension was filtered through *Celite* and the residue obtained after removal of solvent purified by FC (250 g of silica gel; hexane/AcOEt 1:1) to give *rac*-**73** (6.20 g; 44% related to *rac*-**Q**) as a yellow oil which crystallized at −20°. An anal. sample of *(6RS)-6-(3-hydroxypropyl)-6-methylcyclohexa-2,4-dien-1-one* (*rac*-**73**) was obtained by bulb-to-bulb distillation (90°/0.1 Torr): TLC (hexane/AcOEt 1:1): R_f 0.25. UV (hexane): λ_{max} 296 (4710). UV (MeOH): λ_{max} 304 (4710). UV (TFE): λ_{max} 308 (4650). IR (film): 3430*s* (br., OH); 1660*s* (unsat. ketone); 1630*s* (C=C). ^{1}H-NMR: 1.19 (*s*, Me–C(6)); 1.13–1.60 (*m*, 2 H–C(2'), H–C(1')); 1.96–2.08 (*m*, H'–C(1')); 2.83 (*s*, OH, exchangeable in D_2O); 3.39–3.51 (*m*, 2 H–C(3')); 6.03 (*d* with f.s., *J*(H–C(2),H–C(3)) = 9.7, H–C(2)); 6.28 (*ddd*, *J*(H–C(4),H–C(5)) = 9.4, *J*(H–C(4),H–C(3)) = 5.4, *J*(H–C(4),H–C(2)) = 0.8, H–C(4)); 6.34 (*ddd*, *J*(H–C(5),H–C(4)) = 9.4, *J*(H–C(5),H–C(3)) = 2.3, *J*(H–C(5), H–C(2)) = 0.8, H–C(5)); 7.07 (*ddd*, *J*(H–C(3),H–C(2)) = 9.7, *J*(H–C(3),H–C(5)) = 2.3, *J*(H–C(3),H–C(4)) = 5.4, H–C(3)). ^{13}C-NMR: 25.47 (*Me*–C(6)); 28.29 (C(2')); 36.49 (C(1')); 51.39 (C(6)); 62.35 (C3')); 120.70 (C(4)); 152.92 (C(2)); 141.96 (C(3)); 147.96 (C(5)); 206.22 (C(1)). The signals werde assigned using DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks between 147.96/6.34, 152.92/6.03, 120.70/6.28 and between 36.49/1.13–1.60, 36.49/1.96–2.08, 28.29/1.13–1.60, 25.47/1.19. Anal. calc. for $C_{10}H_{14}O_2$ (166.22): C 72.26, H 8.49; found: C 72.04, H 8.56.

Scheme 25



Q **73** **6**



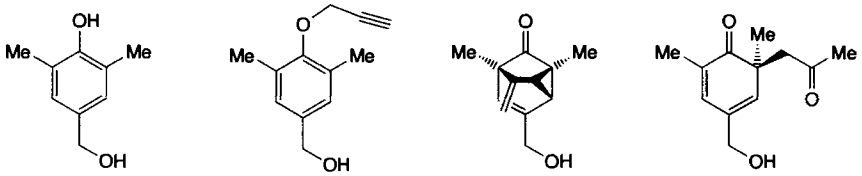
A 100-ml *Löwenthal* flask equipped with a thermometer, a pressure-equalizing dropping funnel with a $CaSO_4$-filled drying tube, and a magnetic stirring bar was charged at −60° with dry CH_2Cl_2 (50 ml) and oxalyl chloride (0.82 ml; 9.4 mmol). After dropwise addition of dry DMSO (1.28 ml; 18 mmol), the mixture was stirred at −60° for 3 min, taking care to release any pressure built up. A soln. of *rac*-**73** (1.24 g; 7.5 mmol) in dry CH_2Cl_2 (20 ml) was added. After stirring the cloudy soln. for 15 min at −50° and addition of Et_3N (5.0 ml; 36 mmol), the mixture was warmed up to r.t. within 30 min. After usual workup, the resulting crude product was purified by FC (100 g of silica gel; hexane/AcOEt 1:1) to furnish *rac*-**6** (1.12 g; 91%) as a yellow oil which crystallized at −20° and was recrystallized from Et_2O at −20°: M.p. 32–34° (Et_2O). TLC (hexane/AcOEt 1.1): R_f 0.49. UV (hexane): λ_{max} 296 (4830). UV (MeOH): λ_{max} 304 (4870). UV (TFE): λ_{max} 307 (4770). IR (film): 1720*s* (aldehyde); 1660*s* (unsat. ketone); 1630*s* (C=C). ^{1}H-NMR: 1.23 (*s*, Me–C(6)); 1.82 (*m*, H'–C(1')); 2.23 (*m*, 2 H–C(2'), H–C(1')); 6.07 (*d* with f.s., *J*(H–C(2),H–C(3)) = 9.7, H–C(2)); 6.25 (*ddd*, *J*(H–C(5), H–C(4)) = 9.5, *J*(H–C(5),H–C(3)) = 2.2, *J*(H–C(5), H–C(2)) = 0.8, H–C(5)); 6.31 (*ddd*, *J*(H–C(4),

[27]) By temporary removal of the C=O group, epoxidation could be circumvented.

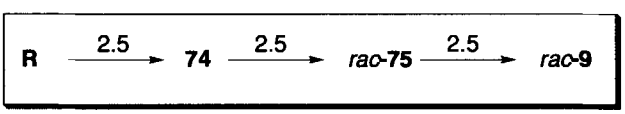
H–C(5)) = 9.5, *J*(H–C(4),H–C(3)) = 5.5, *J*(H–C(4),H–C(2)) = 0.8, H–C(4)); 7.07 (*ddd*, *J*(H–C(3), H–C(2)) = 9.7, *J*(H–C(3),H–C(5)) = 2.2, *J*(H–C(3),H–C(4)) = 5.5, H–C(3)); 9.66 (*t*, *J*(H–C(3'), H–C(2')) = 1.0, H–C(3')). ^{13}C-NMR: 25.17 (*Me*–C(6)); 31.88 (C(1')); 39.53 (C(2')); 50.67 (C(6)); 121.34 (C(4)); 126.22 (C(2)); 141.78 (C(3)); 146.86 (C(5)); 201.10 (C(3')); 205.0 (C(1)). The signals were assigned using DEPT and ^{1}H, ^{13}C-COSY spectra. Cross peaks between 201.10/9.66, 146.86/6.25, 141.78/7.07, 126.22/6.07, 121.34/6.31, 39.53/2.23, 25.17/1.23, 31.88/1.82, and 31.88/2.23. Anal. calc. for $C_{10}H_{12}O_2$ (164.20): C 73.15, H 7.37; found: C 73.13, H 7.35.

2.5. *(RS)-4-(Hydroxymethyl)-2,6-dimethyl-6-(2-oxopropyl)cyclohexa-2,4-dien-1-one* (*rac*-**9**; *Scheme 26*). A 50-ml *Löwenthal* flask equipped with a magnetic stirring bar, a dropping funnel, a gas inlet, and a drying tube was flushed with Ar, flame dried, cooled to 0°, maintained under a positive pressure of Ar, and charged with **R** [56] (1.0 g; 6.57 mmol) and anh. THF (20 ml). NaH (263 mg of a 55-to-65% dispersion in oil; *ca.* 6.57 mmol) was added within 30 min and the mixture warmed up to r.t. After propargyl bromide (7.30 ml of a 80% soln. in toluene; 6.57 mmol) had been added within 30 min, the mixture was stirred for 3 d at r.t. Usual workup gave a solid product which was recrystallized from Et_2O/pentane to furnish *3,5-dimethyl-4-(prop-2-ynyloxy)benzene-1-methanol* (**74**) (1.19 g; 95%): M.p. 81° (Et_2O/pentane). TLC (hexane/Et_2O 1:1): R_f 0.21. IR (KBr): 3511*s* (OH); 3208*s* (≡C–H); 3006*w* (unsat. C–H); 2951*m*, 2924*s*, 2876*m* (sat. C–H); 2116*m* (C≡C); 1600*w*, 1481*s*, 1462*s* (C=C); 1397*s*, 1362*s*, 1307*s*, 1204*s*, 1142*s* 1044*s* (ether), 724*s* (1,2,3-trisubst. benzene). ^{1}H-NMR: 1.65 (*t*, *J*(OH,CH_2–C(4)) = 5.8, OH); 2.32 (*s*, Me–C(2), Me–C(6)); 2.51 (*t*, *J*(H–C(3'),H–C(1')) = 2.4, H–C(3')); 4.49 (*d*, *J*(H–C(1'),H–C(3')) = 2.4, 2 H–C(1')); 4.58 (*d*, *J*(CH_2–C(4),OH) = 5.7, CH_2–C(4)); 7.02 (*s*, H–C(3), H–C(5)). Anal. calc. for $C_{12}H_{14}O_2$ (190.24): C 75.76, H 7.42; found: C 75.74, H 7.31.

Scheme 26



R **74** **75** **9**



A soln. of **74** (5.0 g; 26.3 mmol) in *N,N*-dimethylaniline was added dropwise within 5 h, under a N_2 atmosphere, into boiling *N,N*-dimethylaniline, which had been given into a 250-ml, three-necked, round-bottomed flask equipped with a reflux condenser, a dropping funnel, and a N_2 inlet. After stirring for another 2.5 h at boiling temp., the cooled mixture was worked up to afford a crude product which was purified by chromatography (150 g of silica gel; CH_2Cl_2/Et_2O 3:1) and bulb-to-bulb distillation (130°/0.1 Torr).: *rac*-**75** (3.69 g; 74%).

(1RS,2RS,5SR,7RS)-3-(Hydroxymethyl)-1,5-dimethyl-6-methylenetricyclo[3.2.1.0^{2,7}]oct-3-en-8-one (*rac*-**75**)[28]: TLC (CH_2Cl_2/Et_2O 3:1): R_f 0.40. UV (MeOH): λ_{max} 304.5 (272), 229.0 (3010). IR (film): 3434*s* (br., OH); 3084*w* (unsat. C–H); 2972*m*, 2931*m*, 2870*m* (sat. C–H); 1738*s* (unsat. ketone); 1660*s*, 1453*m* (C=C). ^{1}H-NMR: 1.17 (*s*, Me–C(5)); 1.30 (*s*, Me–C1)); 2.09 (br. *s*, OH); 2.37 (*dd*, *J*(H–C(2),H–C(7)) = 7.2, *J*(H–C(2),H–C(4)) = 3.7, H–C(2)); 2.56 (*d*, *J*(H–C(7),H–C(2)) = 7.2, H–C(7)); 4.17 (*s*, 2 H–C(10)); 4.77 (*s*, H–C(9)); 4.86 (*s*, H'–C(9)); 5.42 (*m*, H–C(4)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks at 4.77/2.56, 4.17/2.09 and 2.56/2.37. The signal at 5.42 showed cross peaks at 4.17 and 2.37. ^{13}C-NMR: 11.78 (*Me*–C(1)); 12.31 (*Me*–C(5)); 30.53 (C(1)); 37.32 (C(2)); 37.61 (C(7)); 50.64 (C(5)); 63.19 (C(10)); 100.60 (C(9)); 125.84 (C(4)); 138.00 (C(3)); 147.64 (C(6)); 212.58 (C(8)). The signals were assigned by a ^{1}H,^{13}C-COSY

[28]) Compound *rac*-**75** arises by *Claisen* rearrangement from **74** [57] and furnishes *rac*-**9** on hydromercuration [58].

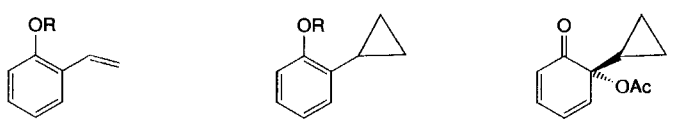
spectrum. Cross peaks at 125.84/5.42, 100.60/4.77 and 4.86, 63.19/4.17, 37.61/2.56, 37.32/2.37, 12.31/1.17 and 11.78/1.30. Anal. calc. for $C_{12}H_{14}O_2$ (190.24): C 75.76, H 7.42; found: C 75.69, H 7.49.

Hg(II) trifluoroacetate (5.97 g; 14.0 mmol) was added at 0° within 1 h portionwise to a stirred soln. of *rac*-**75** (2.66 g; 14.0 mmol) in THF/H_2O 4:1 (70 ml). To the soln., which had been stirred for 1 h at r.t. and afterwards cooled down to 0°, again an aq. soln. of 3N aq. NaOH (20 ml) and a 3N soln. (10 ml) of $NaBH_4$ (265 mg; 7.0 mmol) in aq. NaOH were added successively. After stirring for 30 min at 0° and usual workup, a crude product was isolated and purified by FC (100 g of silica gel; hexane/AcOEt 4:1) and crystallization (Et_2O/pentane) to give *rac*-**9** (1.76 g; 60%). An anal. sample obtained by semi-prep. HPLC (hexane/AcOEt 1:4; 10 ml/min; refract.) showed the following properties: M.p. 74–75°. TLC (hexane/AcOEt 1:4): R_f 0.18. UV (hexane + 1% CH_2Cl_2): λ_{max} 300.8 (4735). UV (MeOH): λ_{max} 306.3 (4762). UV (TFE): λ_{max} 306.8 (4861). IR (KBr): 3434*s* (OH); 3059*w* (unsat. C–H); 2985*w*, 2966*w*, 2832*m* (sat. C–H); 1713*s* (sat. ketone); 1665*m*, 1629*s* (unsat. ketone); 1449*m* (C=C); 1243*m*, 1166*m*, 1031*s* (C–O). ^{1}H-NMR: 1.11 (*s*, Me–C(2)); 1.94 (*d*, *J*(Me–C(6),H–C(5)) = 0.9, Me–C(6)); 2.04 (*s*, (Me–C(2')); 2.04 (ψt, *J*(HO,CH_2–O) ≈ 6.1, OH); 2.70 (*d*, *J*(H–C(1'),H'–C(1')) = 17.7, H–C(1')); 3.40 (*d*, *J*(H'–C(1'),H–C(1')) = 17.7, H'–C(1')); 4.23 (ψd, *J*(CH_2O, OH) = 5.9, CH_2O); 6.00 (*m*, H–C(5)); 6.90 (*m*, H–C(3)). ^{13}C-NMR: 15.63 (*Me*–C(2)); 25.57 (*Me*–C(6)); 29.56 (*Me*–C(2')); 47.12 (C(6)); 54.25 (C(1')); 64.65 (CH_2O); 132.05 (C(4)); 133.43 (C(2)); 138.12 (C(3)); 138.56 (C(5)); 204.54 (C(2')); 205.51 (C(1)). Anal. calc. for $C_{12}H_{16}O_3$ (208.26): C 69.21, H 7.74; found: C 69.00, H 7.83.

2.6. *(RS)-6-Acetoxy-6-cyclopropylcyclohexa-2,4-dien-1-one* (= *(RS)-1-Cyclopropyl-6-oxocyclohexa-2,4-dienyl Acetate*; *rac*-**11**; *Scheme 27*)[29]. A 100-ml, three-necked, round-bottomed flask equipped with a magnetic stirring bar, pressure-equalizing addition funnel, and N_2 inlet, was flame-dried under a stream of dry N_2. The apparatus was charged with *2-vinylphenol* (**76a**) [61] (6.41 g; 53 mmol), anh. pyridine (4.5 ml; 55.0 mmol), and dry Et_2O (40 ml). The dropping funnel was charged with a soln. of freshly distilled Me_3SiCl (7.0 ml; 55 mmol) in dry Et_2O (7 ml). Magnetic stirring was initiated and the Me_3SiCl soln. added dropwise at r.t. After standing overnight and usual workup, the obtained residue was purified by bulb-to-bulb distillation (55°/0.5 Torr) to give 8.42 g (83%) of *1-[(trimethylsilyl)oxy]-2-vinylbenzene* (**76b**): TLC (hexane): R_f 0.38. IR (film): 3069*w*, 3031*w* (unsat. C–H); 2960*s* (sat. C–H); 1625*m*, 1598*m*, 1571*m* (C=C); 1103*m* (C–O); 1484*s*, 1452*s*, 1252*s*, 921*s*, 845*s*, 761*m*. ^{1}H-NMR ((D_6)DMSO): 0.24 (*s*, Me_3Si); 5.25 (*dd*, *J*(H–C(8),H'–C(8) = 1.5, *J*(H–C(8),H–C(7)) = 11.2, H–C(8)); 5.77 (*dd*, *J*(H'–C(8),H–C(8)) = 1.5, *J*(H'–C(8),H–C(7)) = 17.8, H'–C(8)); 6.90 (*dd*, *J*(H–C(7), H–C(8)) = 11.2, *J*(H–C(7),H'–C(8)) = 17.8, H–C(7)); 6.83–6.99, 7.15–7.22, 7.52–7.55 (3*m*, H–C(3) to H–C(6)). ^{13}C-NMR ((D_6)DMSO): 0.15 (Me_3); 114.27 (C(8)); 119.69, 121.57, 126.13, 128.90, 131.41 (C(3) through C(7)); 128.10 (C(2)); 152.09 (C(1)). The signals were assigned by a DEPT spectrum. Anal. calc. for $C_{11}H_{16}OSO$ (192.33): C 68.69, H 8.38; found: C 68.79, H 8.26.

A 500-ml, round-bottomed flask equipped with a magnetic stirring bar and a pressure-equalizing dropping funnel was charged with **76b** (8.22 g; 43 mmol), $Pd(OAc)_2$ (75.0 mg; 0.43 mmol) and dry Et_2O (100 ml) and cooled to 0°. A soln. of CH_2N_2 in Et_2O (150 ml of a 0.60M soln.) was added dropwise over 30 min under stirring. The

Scheme 27



76a R = H **77a** R = H (= **14**) **11**

b R = $SiMe_3$ **b** R = $SiMe_3$

76a —2.6→ **76b** —2.6→ **77b** —2.6→ **77a** —2.6→ *rac*-**11**

[29]) Rather than oxidizing cyclopropyl benzene [59], we preferred to make use of the $Pd(OAc)_2$-mediated cyclopropanation [60] of **76b**.

dark suspension was filtered through *Celite*. Usual workup afforded a residue which was purified by bulb-to-bulb distillation (75°/0.5 Torr) to give 7.91 g (89%) of *1-cyclopropyl-2-[(trimethylsilyl)oxy]benzene* (**77b**): TLC (hexane): R_f 0.36. IR (film): 3081*w*, 3030*w* (unsat. C–H, cyclopropyl); 2960*s*, 2900*w* (sat. C–H); 1601*m*, 1577*m* (C=C); 1097*m* (C–O); 1493*s*, 1449*s*, 1369*m*, 1252*s*, 1202*m*, 1034*m*, 928*s*, 898*s*, 842*s*, 753*s*. ^{1}H-NMR: 0.28 (*s*, Me_3Si); 0.60–0.66, 0.87–0.95 (2*m*, 2 H–C(8), 2 H–C(9)); 2.06–2.16 (*m*, H–C(7)); 6.76–6.79, 6.85–6.90, 6.99–7.05 (3*m*, H–C(3) to H–C(6)). Anal. calc. for $C_{11}H_{16}OSi$ (192.33): C 69.84, H 8.79; found: C 69.88, H 8.68.

A soln. of **77b** (11.9 g; 57.7 mmol) and PTS · H_2O (11.0 g; 57.7 mmol) in CH_2Cl_2 (300 ml) was refluxed for 5 h. After the mixture had been allowed to cool down to r.t., usual workup gave a residue which was purified by FC (200 of silica gel; hexane/AcOEt 10:1). The resulting oily product (**77a** = **14**; 7.20 g; for characteristic data, see *Exper. 1.6.2*) was dissolved in dry $CHCl_3$ (15 ml) without further purification and added dropwise, over 10 min, to a stirred suspension of $Pb(OAc)_4$ (35.8 g; 80.4 mmol) in dry $CHCl_3$ (120 ml) at 0°. Stirring had been continued for 3 h at 0°, before excessive oxidant was removed by added ethylene glycol (25 ml). Usual workup (see *Exper. 2.13*) furnished a crude product which was purified by FC (400 g of silica gel; hexane/AcOEt 4:1) to give 5.67 g of crystalline *rac*-**11** (55%). M.p. 68° (CH_2Cl_2/hexane). TLC (hexane/AcOEt 4:1): R_f 0.26. UV (hexane): λ_{max} 293.3 (4120). UV (MeOH): λ_{max} 299.4 (3950). UV (TFE): λ_{max} 302.2 (3820). IR (KBr): 3077*w*, 3046*w*, 3014*w* (unsat. C–H, cyclopropyl); 1744*s* (acetate); 1682*s* (ketone); 1637*s* (C=C); 1562*m*, 1411*s*, 1370*s*, 1252*s*, 1040*s*, 1006*s*, 866*m*, 755*s*. ^{1}H-NMR: 0.39–0.61 (*m*, 2 H–C(8), 2 H–C(9)); 1.05–1.15 (*m*, H–C(7)); 2.11 (*s*, $MeCO_2$); 6.05 (*dd*, *J*(H–C(5),H–C(4)) = 9.7, *J*(H–C(5),H–C(3)) = 1.7, H–C(5)); 6.20 (*dd*, *J*(H–C(2),H–C(3)) = 9.8, *J*(H–C(2),H–C(4)) ≈ 1.0, H–C(2)); 6.29 (*ddd*, *J*(H–C(4),H–C(5)) = 9.7, *J*(H–C(4),H–C(3)) = 5.8, *J*(H–C(4), H–C(2)) ≈ 1.0, H–C(4)); 6.95 (*ddd*, *J*(H–C(3),H–C(2)) = 9.8, *J*(H–C(3),H–C(4)) = 5.8, *J*(H–C(3),H–C(5)) = 1.7, H–C(3)). ^{13}C-NMR: –0.07, 0.94 (C(8), C(9)); 16.78 (C(7)); 20.50 ($MeCO_2$); 80.94 (C(6)); 123.57 (C(4)); 127.08 (C(2)); 139.00 (C(5)); 139.94 (C(3)); 169.58 ($MeCO_2$); 197.84 (C(1)). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks between –0.07/0.39–0.61, 0.94/0.39–0.61, 16.78/1.05–1.15, 20.50/2.11, 123.57/6.29, 127.08/6.20, 139.00/6.05, and 139.94/6.95. Anal. calc. for $C_{11}H_{12}O_3$ (192.21): C 68.74, H 6.29; found: C 68.50, H 6.32.

2.7. *(RS)-1-Acetoxybicyclo[9.3.1]pentadeca-11,13-dien-15-one* (= *(RS)-15-oxobicyclo[9.3.1]pentadeca-2,4-dienyl Acetate*; *rac*-**15**; see *Scheme 28*). Phenol **78**, obtained through dehydrogenation of *rac*-**S**[30]) (26.20 g; 120 mmol) in anhydrous $CHCl_3$ (100 ml), was added slowly to a stirred slurry of $Pb(OAc)_4$ (87%; 86.6 g; 170 mmol) and $CHCl_3$ (10 ml). Following the usual workup procedure (see *Exper. 2.6*) together with prep. HPLC (benzene/AcOEt 100:1; 0.1 l/min); afforded *rac*-**15** (16.8 g; 51%) as a solid material: M.p. 104.5–105.5° (benzene/hexane). TLC (hexane/acetone 4:1): R_f 0.39. UV (hexane): λ_{max} 303 (4510). UV (MeOH): λ_{max} 307 (3830). UV (TFE): λ_{max} 309 (3680). IR (KBr): 3035*m* (unsat. C–H); 2930*s*, 2855*s* (sat. C–H); 1739*s* (ester); 1672*s* (ketone); 1640*w* (C=C); 1371*s* (CH_3); 1244*s* (C–O); 729*s*. ^{1}H-NMR: 1.0–2.0 (*m*, 2 H–C(3) to 2 H–C(10), H–C(2)); 2.13 (*s*, $MeCO_2$); 2.85–3.00 (*m*, H′–C(2)); 6.05–6.15 (*dd*, *J*(H–C(13),H–C(14)) = 9.8, *J*(H–C(13), H–C(12)) = 5.6, H–C(13)); 6.15–6.20 (*dd*, *J*(H–C(14),H–C(13)) = 9.8, *J*(H–C(14),H–C(12)) = 1.7, H–C(14)); 6.60–6.70 (*dt*, *J*(H–C(12),H–C(13)) = 5.6, *J*(H–C(12),H–C(14)) = *J*(H–C(12),H–C(10)) = 1.7, H–C(12)). Additional irradiation into the signal at 6.60–6.70 simplified the signals at 6.15–6.20 and 6.05–6.15 in each case showing a *d*. ^{13}C-NMR: 20.59 ($MeCO_2$); 17.41, 22.47, 22.58, 23.40, 23.85, 26.29, 26.37 (C(3) to C(9)); 29.44 (C(2)); 34.61 (C(10)); 85.18 (C(1)); 120.91 (C(13)); 137.04 (C(12)); 139.09 (C(11)); 141.79 (C(14)); 169.63 ($MeCO_2$); 199.32 (C(15)). Anal. calc. for $C_{17}H_{24}O_3$ (276.38): C 73.88, H 8.75; found: C 73.89, H 8.65.

The second compound isolated not quantitatively by HPLC was *15-hydroxybicyclo[9.3.1]pentadeca-1(15),11,13-trien-13-yl acetate* (*rac*-**79**): M.p. 160–161° (hexane). TLC (hexane/acetone 4:1): R_f 0.31. UV (EtOH): λ_{max} 283 (2000). IR (KBr): 3475*s* (OH); 3030*w* (unsat. C–H); 2980*s*, 2920*s*, 2855*s* (sat. C–H); 1741*s* (acetate); 1612*w*, 1598*w* (C=C); 1373*m* (CH_3); 1225*s* (C–O); 1025*m*. ^{1}H-NMR: 0.37–0.58, 0.83–1.52 (2*m*, 2 H–C(3) to 2 H–C(9)); 2.27 (*s*, $MeCO_2$); 2.22–2.39 (*ddd* as 7-line signal, *J*(H–C(2),H′–C(2)) = *J*(H–C(10),H′–C(10)) = 13.8, *J*(H–C(2),H–C(3)) = *J*(H–C(10),H–C(9)) = 6.9, *J*(H–C(2),H′–C(3)) = *J*(H–C(10),H′–C(9)) = 4.8, H–C(2), H–C(10)); 2.87–3.01 (*ddd*, *J*(H′–C(2),H–C(2)) = *J*(H′–C(10), H–C(10)) = 13.8, *J*(H′–C(2),H′–C(3)) = *J*(H′–C(10),H′–C(9)) = 9.1, *J*(H′–C(2),H–C(3)) = *J*(H′–C(10), H–C(9)) = 4.8, H′–C(2), H′–C(10)); 4.97 (*s*, exchangeable with D_2O, OH); 6.63 (*s*, H–C(12),H–C(14)). Anal. calc. for $C_{17}H_{24}O_3$ (276.38): C 73.88, H 8.75; found: C 73.86, H 8.70.

2.8. *(RS)-1-Acetoxybicyclo[10.3.1]hexadeca-12,14-dien-16-one* (= *(RS)-16-Oxobicyclo[10.3.1]hexadeca-2,4-dienyl Acetate*; *rac*-**18**; see *Scheme 29*). A 1-l, three-necked, round-bottomed flask, equipped with a reflux

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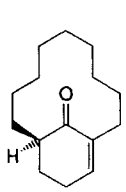
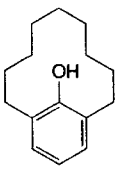
[30]) The ene-amine, accessible from 1-(morpholin-4-yl)cyclododecene and acrolein leads to a dihydropyran derivative, which, after isomerization and hydrolysis, furnishes *rac*-**S** in 47% overall yield [7].

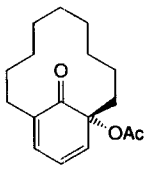
Scheme 28



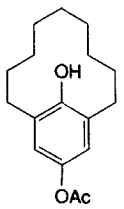
S



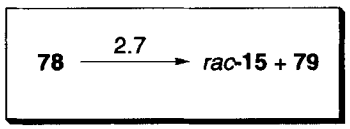
78



15



79

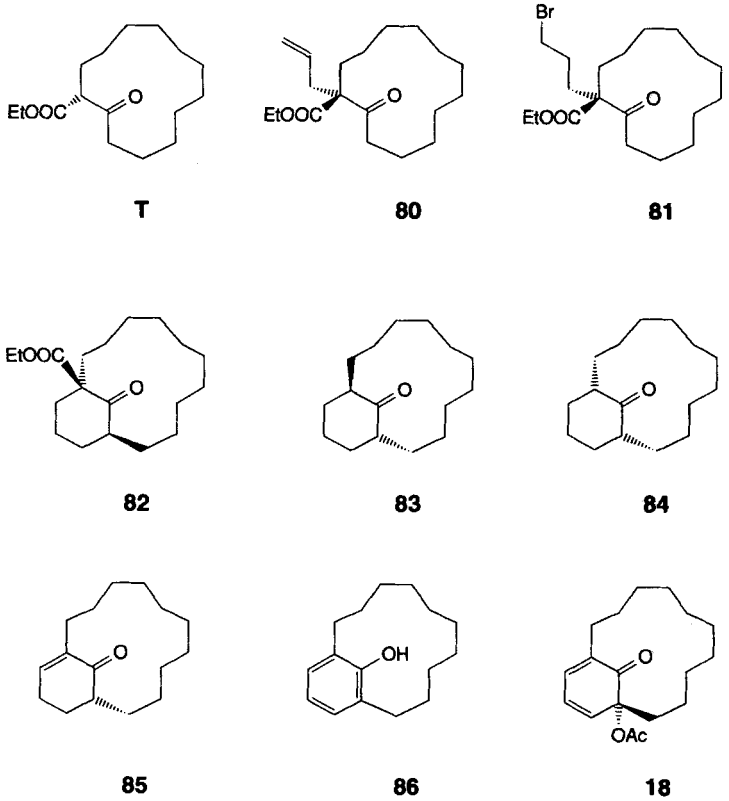


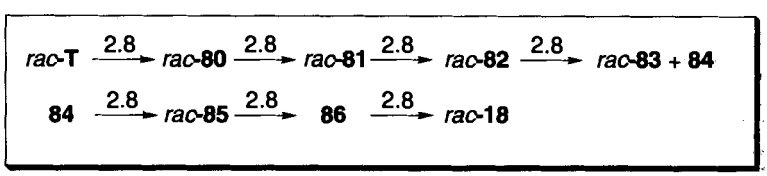
condenser fitted with a NaOH-filled tube, a thermometer, a pressure-equalizing addition funnel, and a magnetic stirring bar was purged with Ar and charged with *rac*-**T** [62] (31.5 g; 117 mmol) and dry THF (500 ml). To the stirred soln., NaH (5.9 g of a 60% dispersion in mineral oil; 150 mmol) was added portionwise over 30 min at 0° which maintains a steady evolution of H_2. The mixture was stirred for 1 h at r.t., followed by dropwise addition of allyl bromide (16.3 ml; 188 mmol) over 1 h at 0°. It was stirred for 16 h at r.t. and 4 h under reflux. After usual workup, the resulting residue was purified by FC (500 g of silica gel; hexane through hexane/AcOEt 20:1) and bulb-to-bulb distillation (180°/0.2 Torr) and afforded 34.4 g (96%) of *(2*RS*)-2-(ethoxycarbonyl)-2-(prop-2-enyl)cyclotridecanone* (= *ethyl (*RS*)-2-oxo-1-(prop-2-enyl)cyclotridecanoate*; *rac*-**80**): TLC (hexane/AcOEt 8:1): R_f 0.70. IR (film): 3078*m* (unsat. C–H); 2930*s*, 2861*s* (sat. C–H); 1741*s* (ester); 1710*s* (ketone); 1639*m*, 1480*m*, 1444*m*, 1365*m*, 1208*m*, 1137*m*, 1030*m*, 917*m*. ^{1}H-NMR: 1.00–1.98 (*m*, 2 H–C(3) to 2 H–C(12)); 1.26 (*t*, *J*(OCH$_2$*Me*,OC*H*$_2$Me) = 7.2, *Me*CH$_2$O); 2.41 (*ddd*, *J*(H–C(13),H′–C(13)) = 18.1, *J*(H–C(13),H–C(12)) = 6.5, *J*(H–C(13),H′–C(12)) = 3.6, H–C(13)); 2.56–2.69 (*m*, 2 H–C(1′)); 2.62 (*ddd*, *J*(H′–C(13),H–C(13)) = 18.1, *J*(H′–C(13),H–C(12)) = 9.5, *J*(H′–C(13),H′–C(12)) = 3.4, H′–C(13)); 4.18 (*q*, *J*(OC*H*$_2$Me,OCH$_2$*Me*) = 7.2, MeC*H*$_2$O); 5.04–5.12 (*m*, 2 H–C(3′)); 5.52–5.68 (*m*, H–C(2′)). Anal. calc. for $C_{19}H_{32}O_3$ (308.46): C 73.98, H 1045; found: C 74.22, H 10.36.

A 2-l, double-necked, round-bottomed flask, equipped with a gas inlet and a gas exit tube, the former reaching within 5mm of the bottom, was charged with *rac*-**80** (34.4 g; 112 mmol), hexane (1 l), and dibenzoyl peroxide (250 mg; 1.0 mmol). Dry HBr [63] was bubbled into the mixture through the gas inlet for 3 h, while it was cooled to 0°. After usual workup, the obtained residue was purified by FC (300 g of silica gel; hexane through hexane/AcOEt 20:1) to give *rac*-**81** (41.0 g; 94%) as a colorless solid. A sample of *(2*RS*)-2-(3-bromopropyl)-2-(ethoxycarbonyl)cyclotridecanone* (= *ethyl (*RS*)-1-(3-bromopropyl)-2-oxocyclotridecaneoate*; *rac*-**81**) after semi-prep. HPLC (hexane/AcOEt 50:1; 10 ml/min; refract.) and crystallization (MeOH at −25°) had the following properties: M.p. 37° (MeOH). TLC (hexane/AcOEt 8:1): R_f 0.70. IR (film): 2931*s*, 2861*s* (sat. C–H); 1741*s* (ester); 1711*s* (ketone); 1462*m*, 1446*m*, 1409*w*, 1366*m*, 1284*m*, 1257*m*, 1209*s*, 1139*m*, 1032*m*, 997*m*, 918*m*. ^{1}H-NMR: 0.88–2.04 (*m*, 2 H–C(3) to 2 H–C(12), 2 H–C(1′), 2H–C(2′)); 1.27 (*t*, *J*(OCH$_2$*Me*, OC*H*$_2$Me) = 7.2, *Me*CH$_2$O); 2.43 (*ddd*, *J*(H–C(13),H′–C(13)) = 18.1, *J*(H–C(13),H–C(12)) = 7.0, *J*(H–C(13),H′–C(12)) = 3.8, H–C(13)); 2.61 (*ddd*, *J*(H′–C(13),H–C(13)) = 18.1, *J*(H′–C(13),H–C(12)) = 9.3, *J*(H′–C(13),H′–C(12)) = 3.5, H′–C(13)); 3.37 (ψdt, $J_1 \approx 6.9$, $J_2 \approx 1.5$, 2 H–C(3′)); 4.19 (*q*, *J*(OC*H*$_2$Me,OCH$_2$*Me*) = 7.2, MeC*H*$_2$O). Anal. calc. for $C_{19}H_{33}BrO_3$ (389.37): C 58.61, H 8.54, Br 20.52; found: C 58.47, H 8.40, Br 20.70.

A flame-dried, 250-ml, round-bottomed flask, equipped with a pressure-equalizing device and a magnetic stirring bar, was purged with dry Ar and charged at 0° with *rac*-**81** (8.9 g; 22.9 mmol) and dry DMF (25 ml). NaH (1.18 g of a 60% dispersion in oil; 29.5 mmol) was added portionwise within 15 min and the mixture stirred for 1 h at 0°. Usual workup afforded *(1*RS*,12*SR*)-1-(ethoxycarbonyl)bicyclo[10.3.1]hexadecan-16-one* (= *ethyl (1*RS*,12*SR*)-16-oxobicyclo[10.3.1]hexadecaneoate*; *rac*-**82**) as a colorless oil (6.90 g; 98%). A sample, after semi-prep. HPLC (hexane/AcOEt 40:1; 10 ml/min; refract.), showed the following properties: TLC (hexane/AcOEt 8:1): R_f 0.63. IR (film): 2926*s*, 2859*s* (sat. C–H); 1732*s* (ester); 1711*s* (ketone); 1462*m*, 1366*m*, 1255*s* (C–O); 1226*m*, 1164*m*, 1112*m*, 1028*m*. ^{1}H-NMR: 0.93 (*dddd*, $J_1 \approx 13.7$, $J_2 \approx 10.9$, $J_3 \approx 4.9$, $J_4 \approx 1.8$, H–C(11));

Scheme 29





1.05–1.17 (*m*, 2 H–C(3), 2 H–C(9)); 1.23–1.31 (*m*, 2 H–C(4) to 2 H–C(7), H–C(10)); 1.28 (*t*, *J*(OCH$_2$*Me*, OC*H*$_2$Me) = 7.1, *MeCH*$_2$O); 1.43 (*m*, H′–C(10)); 1.47–1.57 (*m*, 2 H–C(8)); 1.48 (*m*, H$_{ax}$–C(13)); 1.70 (*m*, H–C(2)); 1.76–1.99 (*m*, H′–C(2), 2 H–C(14), H$_{eq}$–C(13), H$_{ax}$–C(15); 2.06 (*m*, H′–C(11)); 2.35 (*m*, H$_{eq}$–C(15)); 2.60 (*dddd*, $J_1 \approx 3.5$, $J_2 \approx 5.0$, $J_3 \approx 9.2$, $J_4 \approx 12.5$, H–C(12)); 4.20 (*q*, *J*(OC*H*$_2$Me,OCH$_2$*Me*) = 7.1, MeC*H*$_2$O). The signals were assigned using a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 2.60/2.06, 2.60/1.76–1.99, 2.60/1.48, 2.60/0.93, 2.35/1.76–1.99, 2.06/1.23–1.31, 2.06/0.93, 1.70/1.76–1.99, 1.70/1.05–1.17, 0.93–1.43, 0.93/1.23–1.31. The relative configuration follows from a ^{1}H,^{1}H-NOESY spectrum. Further cross peaks: 2.60/1.23–1.31 and 2.60/1.05–1.17. The latter shows *trans*-annular interaction and reveals the indicated ring junction. Anal. calc. for $C_{19}H_{32}O_3$ (308.46): C 73.98, H 10.45; found: C 74.01, H 10.43.

A 100-ml, round-bottomed flask, equipped with a reflux condenser, was charged with *rac*-**82** (3.11 g; 10.1 mmol), AcOH (25 ml), H_2O (9 ml) and conc. H_2SO_4 (7 ml). The mixture was heated under reflux for 20 h. After usual workup, a solid product was obtained which was separated by prep HPLC (hexane/Et_2O 20:1; 2 ml/min; refract.) to give *(1*RS,*12*RS*)-bicyclo[10.3.1]hexadecan-16-one* (*rac*-**83**) and *(1*RS,*12*SR*)-bicyclo[10.3.1]hexadecan-16-one* (**84**) in a ratio of 77:23 (total yield: 60%).

Data of rac-**83**: M.p. 64–65° (MeOH). TLC (hexane/AcOEt 8:1): R_f 0.70. IR (KBr): 2927*s*, 2857*s* (sat. C–H); 1710*m*, 1670*s* (ketone); 1460*s*, 1375*s*, 1350*m*, 1255*m*, 1190*m*, 1165*m*, 1085*m*. ^{1}H-NMR: 0.86–1.52, 1.58–2.10 (2*m*, 2 H–C(2) to 2 H–C(11), 2 H–C(13) to 2 H–C(15)); 2.38–2.44 (*m*, H–C(1)); 2.79 (*dddd*, $J_1 \approx 10.2$, $J_2 \approx 9.8$, $J_3 \approx 5.2$, $J_4 \approx 2.6$, H–C(12)). Anal. calc. for $C_{16}H_{28}O$ (236.40): C 81.29, H 11.94; found: C 81.22, H 11.98.

Data of **84**: M.p. 77–78° (MeOH). TLC (hexane/AcOEt 8:1): R_f 0.78. IR (KBr): 2930*s*, 2850*s* (sat. C–H); 1700*s* (ketone); 1460*m*, 1445*m*, 1430*m*, 900*m*, 860*m*, 735*m*. ^{1}H-NMR: 1.06–1.84, 1.91–2.04 (2*m*, 2 H–C(2) to 2 H–C(11), 2 H–C(13) to 2 H–C(15)); 2.63 (br. ψt, $J \approx 10.4$, H–C(1), H–C(12)). Anal. calc. for $C_{16}H_{28}O$ (236.40): C 81.29, H 11.94; found: C 81.35, H 11.91.

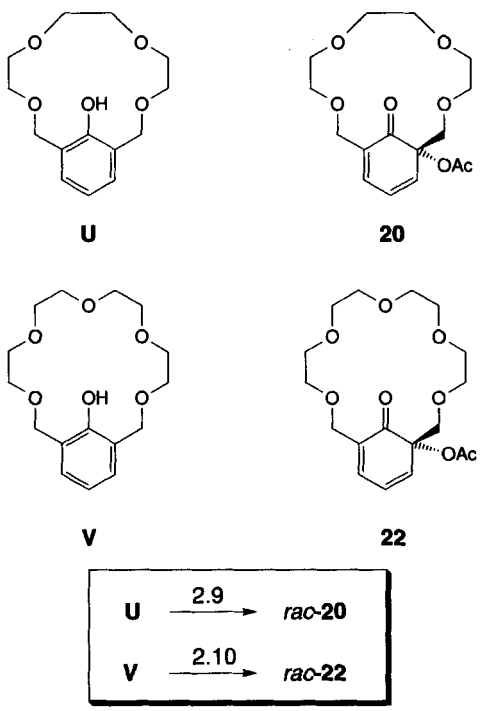
An oven-dried, 100-ml, two-necked, round-bottomed flask, equipped with a magnetic stirring bar, Ar-inlet, and rubber septum, was charged with freshly distilled $(i\text{-Pr})_2NH$ in THF (25 ml), followed by dropwise addition of BuLi (3.13 ml of a 1.6N soln. in hexane; 5.28 mmol) at −80°. After warming up to 0°, addition of HMPT (250 µl; 1.44 mmol), and cooling again to −80°, *rac*-**83** (295 mg; 1.25 mmol) in THF (5 ml) was added dropwise. To this soln., which was stirred for 1 h at −80°, PhSeCl (973 mg; 5.08 mmol) in anh. THF (2 ml) was added and the mixture allowed to warm up to 0° during 1 h. After H_2O (2.5 ml), AcOH (0.5 ml), and H_2O_2 (2.3 ml of a 30% aq. soln.) successively had been added, the mixture was stirred over 30 min. After usual workup, the obtained residue was purified by FC (15 g of silica gel; hexane/AcOEt 100:1) and bulb-to-bulb distillation (170°/0.1 Torr) to give 182 mg (61%) of *(12*RS*)-bicyclo[10.3.1]hexadec-1(15)-en-16-one* (*rac*-**85**): M.p. 49–50° (Et_2O). TLC (hexane/AcOEt 8:1): R_f 0.65. IR (KBr): 3020*w* (unsat. C–H); 2930*s*, 2860*s* (sat. C–H); 1672*s* (unsat. ketone); 1628*m* (C=C); 1460*m*, 1374*m*, 1255*m*, 1170*m*, 1083*m*, 995*m*. ^{1}H-NMR: 1.04–2.57 (*m*, 2 H–C(2) to 2 H–C(11), 2 H–C(13), 2 H–C(14)); 2.71–2.78 (*m*, H–C(12)); 6.53–6.55 (*m*, H–C(15)). Anal. calc. for $C_{16}H_{26}O$ (234.38): C 81.99, H 11.18; found: C 81.78, H 11.27.

A 250-ml, round bottomed flask was charged with *rac*-**85** (20.05 g; 85.5 mmol), 1-isopropyl-4-methylbenzene (100 ml), mesityl oxide (10.1 ml; 88.3 mmol), and Pd/C (10%; 6.70 g). The mixture was refluxed for 12 h, cooled down to r.t., and filtered through *Celite*. After usual workup, the resulting red residue was chromatographed (300 g of silica gel; hexane) and distilled (bulb-to-bulb; 170°/0.15 Torr) to furnish 16.21 g (82%) of *16-hydroxy[10]metacyclophane* (= *bicyclo[10.3.1]hexadeca-1(16),12,14-trien-16-ol*; **86**) as a colorless solid. Prep. HPLC (hexane/Et_2O 40:1; 254 nm and refract.) and recrystallization from pentane gave a sample with the following properties: M.p. 36–37°. TLC (hexane/AcOEt 8:1): R_f 0.63. IR (KBr): 3560*s* (br., OH); 3042*w*, 3023*w* (unsat. C–H); 2925*s*, 2855*s* (sat. C–H); 1591*m* (C=C); 1460*s*, 1345*m*, 1310*m*, 1260*m*, 1185*s*, 1085*m*, 780*m*, 765*m*, 845*m*, 655*m*. ^{1}H-NMR: 0.60–0.68, 0.82–0.97, 1.11–1.55 (3*m*, H–C(3), 2 H–C(4) to 2 H–C(9), H–C(10)); 1.94–2.07 (*m*, H′–C(3), H′–C(10)); 2.51 (*ddd*, J(H–C(2),H′–C(2)) = J(H–C(11),H′–C(11)) = 13.8, J(H–C(2),H–C(3)) = J(H–C(11),H–C(10)) = 7.0, J(H–C(2),H′–C(3)) = J(H–C(11),H′–C(10)) = 4.1, H–C(2),H–C(11)); 2.90 (*ddd*, J(H′–C(2),H–C(2)) = J(H′–C(11),H–C(11)) = 13.8, J(H′–C(2),H–C(3)) = J(H′–C(11),10)) = 9.6, J(H′–C(2),H′–C(3)) = J(H′–C(11),H′–C(10)) = 4.1, H′–C(2), H′–C(11); 4.81 (*s*, exchangeable by D_2O, OH); 6.80 (m_c, H–C(14)); 6.95 (m_c, H–C(13), H–C(15)). The signals were assigned using a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 0.60–0.68/0.82–0.97; 0.82–0.97/1.11–1.55; 1.94–2.07/2.51, 1.94–2.07/2.90 and at 2.51/2.90. Anal. calc. for $C_{16}H_{24}O$ (232.37): C 82.70, H 10.41; found: C 82.75, H 10.36.

Phenol **86** (5.74 g; 24.7 mmol) in anh. $CHCl_3$ (50 ml) was added slowly to a stirred slurry of $Pb(OAc)_4$ (95%; 17.5 g; 37 mmol) in $CHCl_3$ (25 ml) with the temp. kept below 30°. Following the workup procedure of *Exper. 2.13*, the obtained residue was purified by chromatography (200 g of silica gel; hexane through hexane/AcOEt 20:1) to afford 5.55 g (77%) of *(*RS*)-1-acetoxybicyclo[10.3.1]hexadeca-12,14-dien-16-one* (= *(*RS*)-16-oxobicyclo[10.3.1]hexadeca-2,4-dienyl acetate*; *rac*-**18**) as a slightly yellow solid. A sample, purified by prep. HPLC (first run hexane/AcOEt 10:1; second run hexane/AcOEt 5:1; 254 nm and refract.) and crystallization (Et_2O at −25°) showed the following properties: M.p. 59–60° (Et_2O). TLC (hexane/AcOEt 8:1): R_f 0.30. UV (hexane): λ_{max} 307 (4690). UV (MeOH): λ_{max} 311 (4260). UV(TFE): λ_{max} 313.5 (3910). IR (KBr): 3050*w* (unsat. C–H); 2935*s*, 2865*s*, 2450*m* (sat. C–H); 1735*s* (acetate); 1665*s*, 1644*s* (unsat. ketone); 1465*m*; 1440*m*; 1405*m*; 1370*m* (CH_3); 1240*s* (acetate); 1115*w*; 1055*m*; 1020*s*; 975*w*; 940*w*; 895*w*; 870*w*; 760*s*. ^{1}H-NMR: 1.15–1.59 (*m*, 2 H–C(3) to 2 H–C(10)); 1.70–1.97 (*m*, 2 H–C(11), H–C(2)); 2.06 (*s*, $MeCO_2$); 2.95 (ψdd, J(H′–C(2),H–C(2)) ≈ 12.6, J(H′–C(2),H–C(3)) ≈ 6.1, H′–C(2));)); 6.05 (*dd*, J(H–C(15),H–C(14)) = 9.7, J(H–C(15),H–C(13)) = 1.6, H–C(15)); 6.26 (*dd*, J(H–C(14),H–C(15)) = 9.7, J(H–C(14),H–C(13)) = 6.0, H–C(14)); 6.69 (*d* with f.s., J(H–C(13), H–C(14)) = 6.0, H–C(13)). ^{13}C-NMR: 20.59 ($MeCO_2$); 17.60, 22.13, 23.68, 24.16, 25.18, 25.51, 25.81, 26.61 (C(3) to C(10)); 29.79 (C(2)); 38.23 (C(11)); 81.76 (C(1)); 123.52 (C(14)); 137.84 (C(13)); 138.79 (C(15)); 139.22 (C(12)); 169.40 ($MeCO_2$); 199.63 (C(16)). The signals were assigned using ^{1}H,^{13}C-COSY and DEPT spectra. Cross peaks at 138.79/6.05, 137.84/6.69, 123.52/6.26, 38.23/1.70–1.97, 29.79/2.95, 29.79/1.70–1.97, and at 20.59/2.06. Anal. calc. for $C_{16}H_{26}O_3$ (290.40): C 74.45, H 9.02; found: C 74.65, H 8.87.

2.9. *(RS)-1-Acetoxy-3,6,9,12-tetraoxobicyclo[12.3.1]octadeca-14,16-dien-18-one* (= *(RS)-18-Oxo-7,10,13,16-tetraoxabicyclo[12.3.1]octadeca-2,4-dienyl Acetate*; *rac*-**20**; see *Scheme 30*). 2-Hydroxy-1,3-xylyl[15]crown-4 (**U**) [64] (2.0 g; 7.4 mmol) in anh. $CHCl_3$ (50 ml) was added slowly within 15 min to a vigorously stirred slurry of $Pb(OAc)_4$ (96%; 9.9 g; 22 mmol), [18]crown-6 (5.9 g; 22 mmol), and $CHCl_3$ (80 ml). Stirring was continued and reaction progress controlled by TLC (hexane/AcOEt 1:4) for another 15 min. Excessive oxidant was removed by addition of ethylene glycol (2 ml) over a 5-min period to the stirred mixture. After $NaHCO_3$ (100 ml of a sat. aq. soln.) had been cautiously added, usual workup afforded a crude product which was purified by FC (200 mg of silica gel; hexane/AcOEt 1:1), prep. HPLC (hexane/AcOEt 2:3; 254 nm), and crystallization (Et_2O/pentane) to give *rac*-**20** (1.8 g; 75%): M.p. 68–70°. UV (hexane): λ_{max} 303 (4420). UV (MeOH): λ_{max} 303.5 (4200). UV (TFE): λ_{max} 302.5 (4090). IR (KBr): 2956*m* (unsat. C–H); 2864*m* (sat. C–H); 1736*s* (acetate); 1685*s* (unsat. ketone); 1640*m* (C=C); 1240*s* (acetate); 1112*s* (C–O ether). ^{1}H-NMR: 2.11 (*s*, $MeCO_2$); 3.50–3.65 (*m*, 3 OCH_2CH_2O); 3.66–3.69 (*d*, *J*(H–C(2),H′–C(2)) = 10, H–C(2)); 3.97 (*s*, *J*(H′–C(2),H–C(2)) = 10, H′–C(2)); 4.01 (*dd*, *J*(H–C(13),H′–C(13) = 13, *J*(H–C(13),H–C(15)) = 1.0, H–C(13)); 4.62–4.67 (*d*, *J*(H′–C(13),H–C(13)) = 13.0, H′–C(13)); 6.20–6.24 (*dd*, *J*(H–C(17),H–C(16)) = 11, *J*(H–C(17),H–C(15)) = 1.4, H–C(17)); 6.35–6.40 (*dd*, *J*(H–C(16),H–C(15)) = 5.9, *J*(H–C(16),H–C(17)) = 8.6, H–C(16)); 6.96–6.98 (*ψddd*, *J*(H–C(15), H–C(16)) ≈ 5.8, *J*(H–C(15),H–C(17)) ≈ 1.4, *J*(H–C(15),H–C(13)) ≈ 1.3, H–C(15)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. ^{13}C-NMR: 20.52 ($MeCO_2$); 67.1 (C(13)); 69.9–71.3 (C(4) to C(11)); 75.47 (C(2)); 80.92 C(1)); 124.17 (C(16)); 135.38 (C(14)); 138.20 (C(15)); 138.3 (C(17)); 169.19 ($MeCO_2$); 196.79 (C(18)). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Anal. calc. for $C_{16}H_{22}O_7$ (326.35): C 58.88, H 6.79; found: C 58.92, H 6.81.

Scheme 30



2.10. *(RS)-1-Acetoxy-3,6,9,12,15-pentaoxabicyclo[15.3.1]henicosa-17,19-dien-21-one* (= *(RS)-21-Oxo-3,6,9,12,15-pentaoxa[15.3.1]henicosa-17,19-dienyl Acetate*; *rac*-**22**; see *Scheme 30*). A 250-ml, three-necked, round-bottomed flask, equipped with a thermometer, a mechanical stirrer, and a pressure-equalizing dropping funnel, was charged with [18]crown-6 (2.6 g; 9.8 mmol), $Pb(OAc)_4$ (95%; 4.5 g; 9.6 mmol), and anh. $CHCl_3$ (80 ml). To the suspension, under vigorous stirring at r.t., a soln. of phenol **V** [64] (1.0 g; 3.2 mmol) in $CHCl_3$

(20 ml) and, 10 min later, ethylene glycol (1 ml) was added. Basic workup gave a residue, which was purified by chromatography (first run: 80 g of silica gel; CH_2Cl_2/MeOH/NH_3 100:10:3; second run: 60 g of silica gel, H_2O/MeOH 1:1). Product-containing fractions were extracted with CH_2Cl_2 to give, after concentration of the dried ($MgSO_4$) soln. an oily residue (768 mg; 65%). An anal. sample was purified by prep. HPLC (H_2O/MeCN 4:1 or H_2O/MeOH 2:1): TLC (CH_2Cl_2/MeOH/NH_3 100:10:3): R_f 0.55. UV (hexane): λ_{max} 304 (4040). UV (MeOH): λ_{max} 305.5 (3935). UV (TFE): λ_{max} 304 (3600). IR (film): 3005*w* (unsat. C–H); 2865*s* (sat. C–H); 1745*s* (acetate); 1670*s* (unsat. ketone); 1595*s*, 1469*s* (C=C); 1245*s* (acetate); 1115*s* (C–O, ether). ^{1}H-NMR: 2.11 (*s*, $MeCO_2$); 3.56–3.68 (*m*, 4 OCH_2CH_2O); 3.74 (*d*, *J*(H–C(2),H′–C(2)) = 9.8, H–C(2)); 3.88 (*d*, *J*(H′–C(2),H–C(2)) = 9.8, H′–C(2)); 4.06 (*ddd*, *J*(H–C(16),H′–C(16)) = 13.5, *J*(H–C(16),H–C(18)) = 1.2, H–C(16)); 4.59 (*d*, *J*(H′–C(16),H–C(16)) = 13.5, H′–C(16)); 6.24 (*dd*, *J*(H–C(20),H–C(19)) = 9.7, *J*(H–C(20),H–C(18)) = 1.6, H–C(20)); 6.39 (*dd*, *J*(H–C(19),H–C(20)) = 9.7, *J*(H–C(19),H–C(18)) = 6.0, H–C(19)); 7.03 (*ψddd*, *J*(H–C(18),H–C(19)) = 6.0, *J*(H–C(18),H–C(20)) = 1.5, *J*(H–C(18),H–C(16)) = 1.4, H–C(18)). The signals were assigned using a ^{1}H,^{1}H-COSY spectrum. Cross peaks at 7.03/6.39; 7.03/6.24; 7.03/4.59; 7.03/4.06; 6.39/6.24; 4.59/4.06. ^{13}C-NMR: 20.48 (*Me*CO_2); 66.84 (C(16)); 70.09–71.99 (C(4) to C(14)); 75.83 (C(2)); 80.94 (C(1)); 124.15 (C(19)); 135.00 (C(17)); 137.62 (C(18)); 138.11 (C(20)); 169.15 (*Me*CO_2); 196.49 (C(21)). The signals were assigned using a ^{1}H,^{13}C-COSY spectrum. Cross peaks at 20.48/2.22; 66.84/4.06, 4.59; 70.08–71.99/3.56–3.68; 75.83/3.74, 3.88; 124.15/6.39; 137.62/7.03; 138.11/6.24. Anal. calc. for $C_{18}H_{26}O_8$ (370.40): C 58.37, H 7.08; found: C 58.39, H 7.12.

2.11. *(RS)-6-Acetoxy-2,6-di(*tert*-butyl)cyclohexa-2,4-dien-1-one* (= *(RS)-(1,5-Di(*tert*-butyl)-6-oxocyclohexa-2,4-dienyl Acetate*; *rac*-**24a**; see *Scheme 31*). *2,6-Di(*tert*-butyl)phenol* (**W**) (12.4 g; 59 mmol) in anh. benzene (50 ml) was added slowly, with stirring at 0°, within 30 min to a slurry of $Pb(OAc)_4$ (96%: 36.04 g, 78 mmol) in benzene (30 ml), while the temp. was kept below 30°. After stirring for an additional 30 min, ethylene glycol (2 ml) was added to remove excessive oxidant. Stirring was continued for 5 min, and $NaHCO_3$ (250 ml sat. aq. soln.) was added. After further stirring for 10 min, the mixture was filtered through *Celite*. Usual workup afforded an oily residue which was chromatographed (500 g of silica gel; hexane/AcOEt 10:1) to give *rac*-**24a** (7.3 g; 46%) and **27** (3.9 g; 24%; for characteristic data, see *Exper. 1.11.3.1*).

Data of rac-**24a**: M.p. 49–50° (pentane). TLC (hexane/AcOEt 10:1): R_f 0.24. UV (hexane): λ_{max} 307 (4450); 380 (150). UV (MeOH): λ_{max} 311 (4040); 375 (230). UV (TFE): λ_{max} 313 (3690), 365 (340). IR (KBr): 2995*s* (sat. C–H); 1744*s* (acetate); 1673*s* (unsat. ketone); 1369*s* (CH_3); 1252*s* (acetate). ^{1}H-NMR: 0.98 (*s*, Me_3C–C(6)); 1.22 (*s*, Me_3C–C(2)); 2.09 (*s*, $MeCO_2$); 6.12 (*dd*, *J*(H–C(5),H–C(4)) = 9.8, *J*(H–C(5),H–C(3)) = 1.7, H–C(5)); 6.30 (*dd*, *J*(H–C(4),H–C(5)) = 9.8, *J*(H–C(4),H–C(3)) = 6.2, H–C(4)); 6.70 (*dd*, *J*(H–C(3),H–C(4)) = 6.2, *J*(H–C(3),H–C(5)) = 1.7, H–C(3)). Anal. calc. for $C_{16}H_{24}O_3$ (264.37): C 72.69, H 9.15; found: C 72.78, H 9.01.

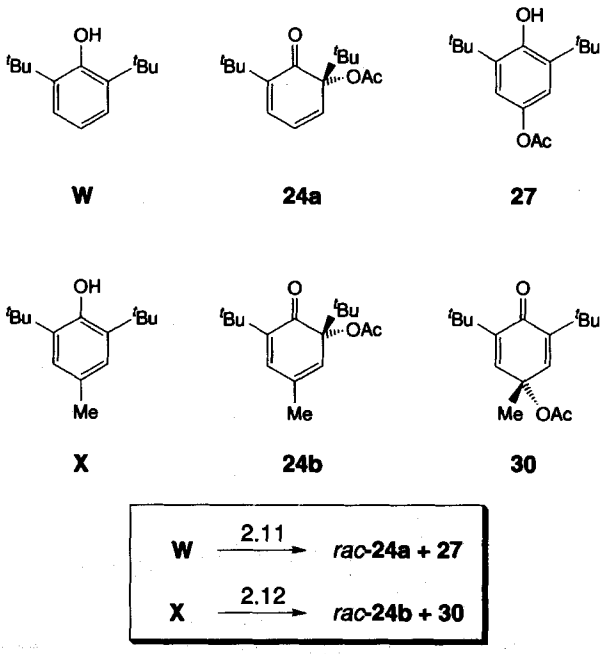
2.12. *(RS)-6-Acetoxy-2,6-di(*tert*-butyl)-4-methylcyclohexa-2,4-dien-1-one* (= *(RS)-1,5-Di(*tert*-butyl)-4-methyl-6-oxocyclohexa-2,4-dienyl Acetate*; *rac*-**24b**; see *Scheme 31*). *2,6-Di(*tert*-butyl)-4-methylphenol* (**X**) (22.0 g; 0.1 mol) in anh. C_6H_6 (400 ml) was added slowly, with stirring at 0°, over 30 min to a slurry of $Pb(OAc)_4$ (96%; 50.82 g, 0.11 mmol) in benzene (200 ml), while the temp. was kept below 30°. Following the procedure of *Exper. 2.11*, *rac*-**24b** (13.4 g; 48%) and **30** (8.9 g; 32%; for data see *Exper. 1.12.2*) were isolated.

Data of rac-**24b**: M.p. 55–56° (pentane). TLC (hexane/AcOEt 10:1): R_f 0.35. UV (hexane): λ_{max} 313 (3830); 380 (180). UV (MeOH): λ_{max} 317 (3410); 375 (290). UV (TFE): λ_{max} 321 (3130); 367 (450). IR (KBr): 2958*s*, 2918*s* (sat. C–H); 1743*s* (acetate); 1678*s*, 1665*s* (unsat. ketone); 1369*s* (CH_3); 1250*s* (acetate). ^{1}H-NMR: 0.96 (*s*, Me_3C–C(6)); 1.22 (*s*, Me_3C–C(2)); 1.95 (*d* with f.s., Me–C(4)); 2.06 (*s*, $MeCO_2$); 5.81 (*s* with f.s., H–C(5)); 6.52 (*s* with f.s., H–C(3)). Anal. calc. for $C_{17}H_{26}O_3$ (278.39): C 73.35, H 9.41; found: C 73.34, H 9.40.

2.13. *(RS)-6-Acetoxy-6-(2-oxopropyl)cyclohexa-2,4-dien-1-one* (= *(RS)-6-Oxo-1-(2-oxopropyl)cyclohexa-2,4-dienyl Acetate*; *rac*-**33a**; see *Scheme 32*). A 1-l, three-necked, round-bottomed flask, equipped with a mechanical stirrer, a thermometer, and a pressure-equalizing dropping funnel, was charged with $Pb(OAc)_4$ (93%; 33.4 g; 70.0 mmol) and anh. AcOEt (300 ml). To the vigorously stirred slurry, MeOH (60 ml) and $BF_3 \cdot OEt_2$ (15.4 ml; 125 mmol) were added at −20°. Within 10 min, a soln. of **Y** [65] (7.51 g; 50.0 mmol) in AcOEt/MeOH 5:1 (80 ml) were dropwise added; 10 min later **Y** had disappeared (TLC control). To the mixture, ethylene glycol (5 ml) was added under stirring. The workup procedure began with careful addition of $NaHCO_3$ (250 ml sat. aq. soln.) under stirring, filtration of the mixture through *Celite* to give a product (8.28 g) which was purified by chromatography (600 g of silica gel; CH_2Cl_2/AcOEt 5:1) and prep. HPLC (first run: hexane/MeOAc 2:1; second run: hexane/Et_2O 1:1; 2 ml/min; 254 nm and refract.) to afford *rac*-**33a** (4.02 g; 39%), **87** (1.58 g; 12%), and **88** (0.88 g; 8%). Control by anal. HPLC showed *rac*-**33a**, **87**, and **88** had been formed in 58, 19, and 9% yield.

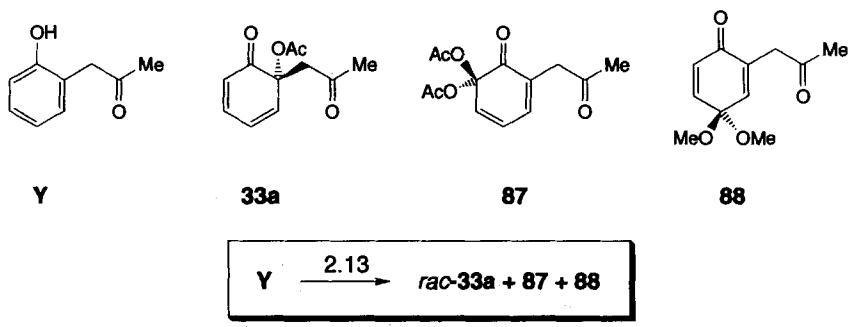
Data of rac-**33a**: M.p. 46° (Et_2O/pentane). TLC (hexane/AcOEt 1:1): R_f 0.34. UV (hexane): λ_{max} 295 (3720). UV (MeOH): λ_{max} 301 (3410). UV (TFE): λ_{max} 304 (3390). IR (film): 3050*w* (unsat. C–H); 1745*s* (acetate); 1710*s* (ketone); 1680*s* (unsat. ketone); 1635*m* (C=C); 1240*m* (acetate). ^{1}H-NMR: 2.08 (*s*, $MeCO_2$); 2.21 (*s*, 3 H–C(3′));

Scheme 31



2.78 (*d*, *J*(H′–C(1′),H–C(1′)) = 15.7, H′–C(1′)); 2.96 (*d*, *J*(H–C(1′),H′–C(1′)) = 15.7, H–C(1′)); 6.22 (*dψt*, *J*(H–C(2),H–C(3)) = 9.9, *J*(H–C(2),H–C(4)) = *J*(H–C(2),H–C(5)) = 0.9, H–C(2)); 6.34 (*ddd*, *J*(H–C(4), H–C(5)) = 9.7, *J*(H–C(4),H–C(3)) = 5.9, *J*(H–C(4),H–C(2)) = 1.0, H–C(4)); 6.51 (*ddd*, *J*(H–C(5),H–C(4)) = 9.7, *J*(H–C(5),H–C(3)) = 1.8, *J*(H–C(5),H–C(2)) = 0.9, H–C(5)); 7.03 (*ddd*, *J*(H–C(3),H–C(2)) = 9.9, *J*(H–C(3),H–C(4)) = 5.9, *J*(H–C(3),H–C(5)) = 1.8, H–C(3)). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks at 7.03/6.51; 7.03/6.34; 7.03/6.22; 6.51/6.34; 6.34/6.22. ^{13}C-NMR: 20.27 ($MeCO_2$); 31.34 (C(3′)); 50.82 (C(1′)); 78.30 (C(6)); 123.22 (C(4)); 126.48 (C(2)); 139.32 (C(5)); 140.44 (C(3)); 168.86 ($MeCO_2$); 197.09 (C(1)); 202.87 (C(2′)). The signals were assigned by DEPT and ^{1}H,^{13}C-COSY spectra. Cross peaks at 140.44/7.03; 139.32/6.51; 126.48/6.22; 123.22/6.34; 31.34/2.21 and 20.27/2.08; 50.82/2.78 and 50.82/2.96. Anal. calc. for $C_{11}H_{12}O_4$ (208.21): C 63.45, H 5.81; found: C 63.36, H 5.93.

Scheme 32



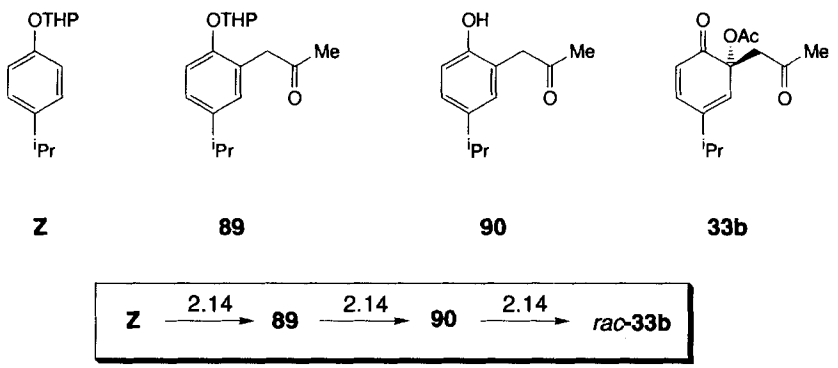
6,6-Diacetoxy-2-(2-oxopropyl)cyclohexa-2,4-dien-1-one (= *1-Acetoxy-6-oxo-5-(2-oxopropyl)cyclohexa-2,4-dienyl Acetate*; **87**): M.p. 90–92° (Et_2O). TLC (hexane/AcOEt 1:1): R_f 0.34. UV (hexane): λ_{max} 319 (4140). UV (MeOH): λ_{max} 320 (3960). UV (TFE): λ_{max} 320 (3690). IR (KBr): 1755*s* (acetate); 1715*s* (ketone); 1690*s* (unsat.

ketone); 1650*s* (C=C); 1225*s* (acetate). ^{1}H-NMR: 2.11 (*s*, 2 $MeCO_2$); 2.19 (*s*, 3 H–C(3')); 3.44 (*s*, 2 H–C(1')); 6.21 (*dd*, *J*(H–C(5),H–C(4)) = 9.8, *J*(H–C(5),H–C(3)) = 1.2, H–C(5)); 6.47 (*dd*, *J*(H–C(4),H–C(3)) = 6.2, *J*(H–C(4),H–C(5)) = 9.8, H–C(4)); 6.81 (*dd*, *J*(H–C(3),H–C(4)) = 6.2, *J*(H–C(3),H–C(5)) = 1.2, H–C(3)). Anal. calc. for $C_{13}H_{14}O_6$ (266.25): C 58.65, H 5.30; found: C 58.37, H 5.51.

4,4-Dimethoxy-2-(2-oxopropyl)cyclohexa-2,5-dien-1-one (**88**): M.p. 42° (Et_2O/pentane). TLC (hexane/AcOEt 1:1): R_f 0.36. UV (hexane): λ_{max} 218 (10280). IR (KBr): 2830*m* (CH_3O); 1720*s* (sat. ketone); 1680*s* (unsat. ketone); 1650*s* (C=C). ^{1}H-NMR: 2.24 (*s*, 3 H–C(3')); 3.39 (*s*, 2 MeO); 3.42 (*d*, *J*(H–C(1'),H–C(3)) = 0.5, 2 H–C(1')); 6.30 (*d*, *J*(H–C(6),H–C(5)) = 10.3, H–C(6)); 6.65 (*dt*, *J*(H–C(3),H–C(5)) = 3.2, *J*(H–C(3),H–C(1')) = 1.0, H–C(3)); 6.82 (*dd*, *J*(H–C(5),H–C(6)) = 10.3, *J*(H–C(5),H–C(3)) = 3.2, H–C(5)). ^{13}C-NMR: 30.00 (C(3')); 43.33 (C(1')); 50.50 (2 MeO); 93.06 (C(4)); 129.76 (C(6)); 134.74 (C(2)); 141.83 (C(3)); 143.55 (C(5)); 184.34 (C(1)); 204.21 (C(2')). The signals were assigned by a DEPT spectrum. Anal. calc. for $C_{11}H_{14}O_4$ (210.23): C 62.85, H 6.71; found: C 62.61, H 6.97.

2.14. *(RS)-6-Acetoxy-4-isopropyl-6-(2-oxopropyl)cyclohexa-2,4-dien-1-one* (= *(RS)-3-Isopropyl-6-oxo-1-(2-oxopropyl)cyclohexa-2,4-dienyl Acetate*; *rac*-**33b**; see *Scheme 33*)[31]. A 250-ml, three-necked, round-bottomed flask, containing a magnetic stirring bar and equipped with a thermometer, a pressure-equalizing N_2 inlet, and a septum, was charged with **Z** [66] (5.51 g; 25 mmol), dry THF (75 ml), and cooled to 0°. TMEDA (4.12 ml; 27.5 mmol) and BuLi (22.5 ml of a 1.22M soln. in hexane; 27.5 mmol) were successively injected with syringes through the septum, taking care that the temp. did not rise above 5°. The reaction vessel was immersed in an ice-water bath, and, after 1 h stirring, CuBr (3.94 g; 27.5 mmol) was added with such a rate that the temp. was kept below 5°. After 1 h stirring, the mixture was cooled to −78°. 3-Bromo-2-methoxypropene[32] [67] (10.9 g; 37.5 mmol) was added and the mixture left overnight to warm up to r.t. Usual workup gave a crude product which was purified by FC (180 g of silica gel; hexane/AcOEt 10:1) to furnish 6.00 g (87%) of *1-{5-isopropyl-2-[(2RS)-tetrahydro-2H-pyran-2-yloxy]phenyl}propan-2-one* (**89**). An anal. sample, after semi-prep. HPLC (hexane/AcOEt 10:1; 254 nm), showed the following properties: M.p. 53°. TLC (hexane/AcOEt 10:1): R_f 0.14. IR (KBr): 2957*s*, 2871*s* (sat. C–H); 1712*s* (ketone); 1610*w*, 1503*s* (C=C); 1246*s*, 1124*s*, 1037*s* (C–O). ^{1}H-NMR: 1.22 (*d*, *J*((*H*–CH_2)$_2$CH, Me_2CH) = 6.9, Me_2CH); 1.55–2.00 (*m*, 2 H–C(3''), 2 H–C(4''), 2 H–C(5'')); 2.14 (*s*, 3 H–C(3)); 2.84 (*sept.*, *J*(Me_2CH,(H–CH_2)$_2$CH) = 6.9, Me_2CH); 3.56–3.64, 3.80–3.89 (2*m*, H–C(6''), H'–C(6'')); 3.67 (m_c, H–C(1), H'–C(1)); 5.38 (*m*, H–C(2'')); 6.98–6.99, 7.07–7.08 (2*m*, 3 arom. H). Anal. calc. for $C_{17}H_{24}O_3$ (276.37): C 73.88, H 8.75; found: C 73.88, H 8.74.

Scheme 33



PPTS (1.49 g; 5.92 mmol) was added to a stirred soln. of **89** (8.18 g; 29.6 mmol) in MeOH/H_2O 4:1 (120 ml). Stirring was continued until **89** had disappeared (TLC control). The mixture was partitioned between CH_2Cl_2 (240 ml) and H_2O (120 ml), and acidified (some drops of HCl were added). After usual workup, the resulting

[31]) We escape the necessity for graphically describing an ephemeral compound's formula by abbreviating the acetal fragment as THP and stop then using the stereodescriptor *rac* attached to the arabic formula number.

[32]) Actually, the soln. of the acetonyl alkylating reagent contains a mixture of 3-bromo-2-methoxyprop-1-ene, the 3-bromo-2-methoxyprop-2-enes, and 1-bromo-2,2-dimethoxypropane [67].

residue was purified by FC (200 g of silica gel; hexane/AcOEt 10:1) and crystallization (Et_2O/hexane) to give 4.88 g (86%) of *1-(2-hydroxy-5-isopropylphenyl)propan-2-one* (**90**): M.p. 53°. TLC (hexane/AcOEt 10:1): R_f 0.20. IR (KBr): 3430*s* (O–H); 2956*s*, 2867*s* (sat. C–H); 1707*s* (ketone); 1614*m*, 1512*s* (C=C). ^{1}H-NMR: 1.20 (*d*, *J*((*H*–CH_2)$_2$CH,Me_2C–H) = 6.9, *Me*$_2$CH); 2.26 (*s*, 3 H–C(3)); 2.81 (*sept.*, *J*(Me_2CH,(*H*–CH_2)$_2$CH) = 6.9, Me_2CH); 3.71 (*s*, 2 H–C(1)); 6.81 (*d*, *J*(H–C(3′),H–C(4′)) = 8.2, H–C(3′)); 6.91 (*d*, *J*(H–C(6′),H–C(4′)) = 2.2, H–C(6′)); 6.91 (*s*, in D_2O, exchangeable, OH); 7.01 (*dd*, *J*(H–C(4′),H–C(3′)) = 8.2, *J*(H–C(4′),H–C(6′)) = 2.2, H–C(4′)). Anal. calc. for $C_{13}H_{16}O_2$ (192.26): C 74.95, H 8.39; found: C 74.77, H 8.38.

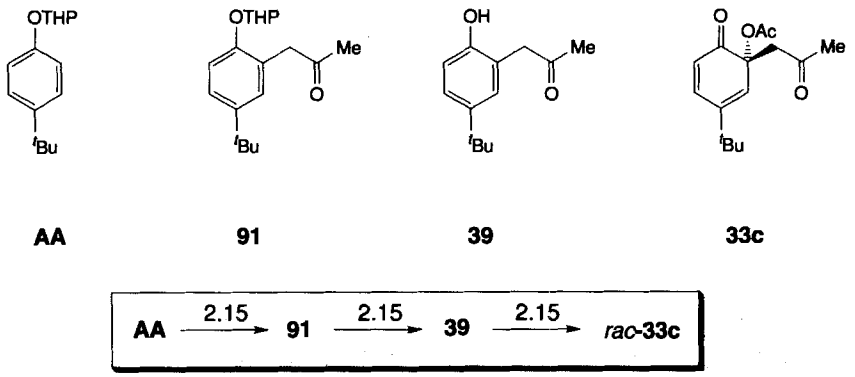
A 500-ml, three-necked, round-bottomed flask, equipped with a mechanical stirrer, a thermometer, and a pressure-equalizing dropping funnel, was charged with $Pb(OAc)_4$ (96%; 5.11 g; 11.1 mmol) and dry AcOEt (120 ml). To the vigorously stirred slurry, cooled to 0°, a soln. of **90** (1.42 g; 7.38 mmol) was added dropwise over 10 min. Stirring was continued for 30 min and excessive oxidant removed by added ethylene glycol (4 ml). After 3 min, a sat. aq. soln. of $NaHCO_3$ (100 ml) was carefully added and stirring continued until no more CO_2 was evolved. Usual workup afforded a crude product (2.34 g) which was purified by FC (175 g of silica gel; hexane/AcOEt 4:1) to give *rac*-**33b** (1.24 g; 67%) (anal. HPLC (hexane/AcOEt 30:13; 313 nm): no impurities detectable): TLC (hexane/AcOEt 4:1): R_f 0.13. UV (hexane): λ_{max} 304.4 (3280). UV (MeOH): λ_{max} 309.6 (3033). UV (TFE): λ_{max} 313.0 (2899). IR (film): 2963*s*, 2932*m*, 2874*w* (sat. C–H); 1748*s* (acetate); 1714*s* (sat. ketone); 1682*s* (unsat. ketone); 1651*m* (C=C); 1238*s* (C–O). ^{1}H-NMR: 1.10 (*d*, *J*((*H*–CH_2)$_2$CH, Me_2CH) = 6.8, *Me*$_2$CH); 2.07 (*s*, $MeCO_2$); 2.19 (*s*, 3 H–C(3′)); 2.47 (*sept.*, *J*(Me_2CH, (*H*–CH_2)$_2$CH) = 6.8, Me_2CH); 2.75, 2.92 (*AB* system, *J*(H–C(1′),H′–C(1′)) = 15.3, H–C(1′),H′–C(1′)); 6.07 (*d*, *J*(H–C(5),H–C(3)) = 2.3, H–C(5)); 6.21 (*d*, *J*(H–C(2),H–C(3)) = 10.0, H–C(2)); 6.97 (*dd*, *J*(H–C(3),H–C(2)) = 10.0, *J*(H–C(3),H–C(5)) = 2.3, H–C(3)). ^{13}C-NMR: 20.2 ($MeCO_2$); 20.9, 21.2 (*Me*$_2$CH); 31.3 (C(3′)); 32.7 (Me_2CH); 51.0 (C(1′)); 77.7 (C(6)); 126.1 (C(2)); 130.3 (C(5)); 141.3 (C(4)); 142.8 (C(3)); 168.4 ($MeCO_2$); 197.1 (C(1)); 202.8 (C(2′)). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross signals between: 2.07/20.2; 1.10/20.9, 21.2; 31.3/2.19; 2.47/32.7; 2.75, 2.92/51.0; 6.21/126.1; 6.07/130.3; 6.97/142.8. Anal. calc. for $C_{14}H_{18}O_4$ (250.29): C 67.18, H 7.25; found: C 67.11, H 7.15.

2.15. *(*RS*)-6-Acetoxy-4-(*tert*-butyl)-6-(2-oxopropyl)cyclohexa-2,4-dien-1-one* (= *(*RS*)-3-(*tert*-Butyl)-6-oxo-1-(2-oxopropyl)cyclohexa-2,4-dienyl Acetate*; *rac*-**33c**; see *Scheme 34*)[31]. A 250-ml, three-necked, round-bottomed flask, containing a magnetic stirring bar and equipped with a thermometer, a pressure-equalizing N_2 inlet, and a septum, was charged with **AA** [68] (11.7 g; 50.0 mmol), dry THF (150 ml), and cooled to 0°. TMEDA (8.24 ml; 55.0 mmol) and BuLi (45 ml of a 1.22M soln. in hexane; 55.0 mmol) were successively injected with syringes through the septum, taking care that the temp. did not rise above 5°. The reaction vessel was immersed in an ice-water bath and, after 1 h stirring, CuBr (7.88 g; 55 mmol) was added with such a rate that the temp. was kept below 5°. After 1 h stirring, the mixture was cooled to −78°. 3-Bromo-2-methoxyprop-1-ene[32]) [67] (21.8 g; 750 mmol) was added and the mixture left overnight to warm up to r.t. before being partitioned between CH_2Cl_2 and sat. aq. NH_4Cl (150 ml each). After usual workup, a residue was obtained which was purified by FC (150 g of silica gel; hexane/AcOEt 10:1) to give 12.6 g (87%) of crystalline *1-{5-(*tert*-butyl)-2-[(2*RS*)-tetrahydro-2H-pyran-2-yloxy]phenyl}propan-2-one* (**91**): M.p. 41–42° (AcOEt/hexane). TLC (hexane/AcOEt 10:1): R_f 0.22. IR (KBr): 2953*s*, 2871*s* (sat. C–H); 1715*s* (ketone); 1607*m* (C=C); 1365*m* (*t*-Bu); 1125*m*, 1040*m* (C–O). ^{1}H-NMR: 1.29 (*s*, *t*-Bu); 1.54–1.94 (*m*, 2 H–C(3″), 2 H–C(4″), 2 H–C(5″)); 2.14 (*s*, 3 H–C(3)); 3.56–3.65, 3.74–3.89 (2*m*, H–C(6″), H′–C(6″)); 3.68 (m_c, H–C(1), H′–C(1)); 5.40 (ψt, *J*(H–C(2″),H–C(3″)) ≈ 3.0, H–C(2″)); 7.07 (*d*, *J*(H–C(3′),H–C(4′)) = 8.6, H–C(3′)); 7.13 (*d*, *J*(H–C(6′),H–C(4′)) = 2.4, H–C(6′)); 7.23 (*dd*, *J*(H–C(4′), H–C(3′)) = 8.6, *J*(H–C(4′),H–C(6′)) = 2.4, H–C(4′)). Anal. calc. for $C_{18}H_{26}O_3$ (290.40): C 74.45, H 9.03; found: C 74.56, H 8.97.

To a soln. of **91** (2.05 g; 7.06 mmol) in MeOH/H_2O 4:1 (28 ml), PPTS (710 mg; 2.82 mmol) was added and the mixture stirred at r.t. until **91** had disappeared (TLC control). After usual workup the residue was purified by FC (50 g of silica gel; hexane/AcOEt 4:1) and crystallization (Et_2O/pentane) to give 1.19 g (82%) of *1-[5-(*tert*-butyl)-2-hydroxyphenyl]propan-2-one* **39** (for data, see *Exper. 1.15.2.2*).

A 100-ml, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, a thermometer, and a pressure-equalizing dropping funnel, was charged with $Pb(OAc)_4$ (96%; 2.10 g; 4.50 mmol) and anh. AcOEt (20 ml). To the vigorously stirred slurry, anh. MeOH (5 ml) and $BF_3 \cdot OEt_2$ (1.14 ml; 9.25 mmol) were added at −20°. After 10 min stirring at this temp., **39** (516 mg; 2.50 mmol) in AcOEt/MeOH 4:1 (10 ml) was added dropwise. The mixture was allowed to warm up to r.t. and excessive oxidant quenched by ethylene glycol (1 ml). The workup procedure began with a careful addition of $NaHCO_3$ (10 ml sat. aq. soln.) under stirring and filtration of the mixture through *Celite*. The resulting crude product was purified by chromatography (30 g of silica gel; hexane/AcOEt 2:1) and prep. HPLC (hexane/Et_2O-AcOEt 10:5:2; 2 ml/min; 254 nm) to give *rac*-**33c** (245 mg; 37%): TLC (hexane/AcOEt 1:1): R_f 0.48. UV (hexane): λ_{max} 302.5 (3460). UV (MeOH): λ_{max} 308.0 (3250). UV

Scheme 34



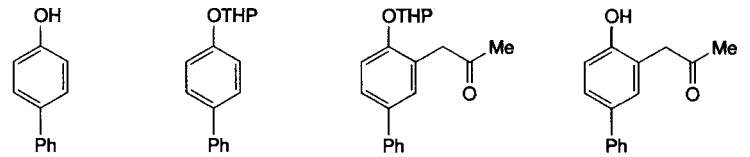
(TFE): λ_{max} 312.0 (3100). IR (film): 2966*s*, 2873*m* (sat. C–H); 1744*s* (acetate); 1724*s* (sat. ketone); 1686*s* (unsat. ketone); 1644*s* (C=C); 1369*s* (*t*-Bu); 1237*s*, 1128*s*, 1097*s*, 1048*s*, 1019*s* (C–O). ^{1}H-NMR: 1.14 (*s*, *t*-Bu); 2.07 (*s*, $MeCO_2$); 2.20 (*s*, 3 H–C(3')); 2.69, 2.89 (*AB* system, *J*(H–C(1'),H'–C(1')) = 15.1, H–C(1'), H'–C(1')); 6.14 (*d* with f.s., *J*(H–C(5),H–C(3)) = 2.2, H–C(5)); 6.22 (*d*, *J*(H–C(2),H–C(3)) = 10.2, H–C(2)); 7.18 (*dd*, *J*(H–C(3),H–C(2)) = 10.2, *J*(H–C(3),H–C(5)) = 2.2, H–C(3)). ^{13}C-NMR: 20.45 ($MeCO_2$); 28.57 (Me_3C); 31.64 (C(3')); 34.15 (Me_3C); 51.11 (C(1')); 78.00 (C(6)); 125.90 (C(2)); 130.09 (C(5)); 141.89 (C(3)); 143.46 (C(4)); 168.68 ($MeCO_2$); 197.30 (C(1)); 203.07 (C(2')). Anal. calc. for $C_{15}H_{20}O_4$ (264.32): C 68.16, H 7.63; found: C 68.14, H 7.62.

2.16. *(RS)-6-Acetoxy-2-(2-oxopropyl)-4-phenylcyclohexa-2,4-dien-1-one* (= *(RS)-6-Oxo-1-(2-oxopropyl)-3-phenylcyclohexa-2,4-dienyl Acetate*; *rac*-**33d**; see *Scheme 35*)[31]. A soln. of **AB** (20.52 g; 121 mmol) and dihydropyran (22 ml; 242 mmol) in dry toluene/CH_2Cl_2 1:1 (400 ml) containing PPTS (250 mg; 1 mmol) was stirred for 3 h at r.t. The mixture was poured under stirring into a sat. aq. $NaHCO_3$ soln. (300 ml). The org. layer was separated, washed twice with sat. aq. NaCl soln. (100 ml each), and concentrated at a rotary evaporator at *ca.* 5 Torr. The residue was crystallized from Et_2O/hexane to give 23.81 g (77%) of *(RS)-2-(1,1'-biphenyl-4-oxy)tetrahydro-2H-pyran* (**92**): M.p. 65°. TLC (hexane/AcOEt 1:1): R_f 0.69. IR (KBr): 3031*m* (unsat. C–H); 2942*s*, 2869*m* (sat. C–H); 1608*s*; 1515*s*; 1483*s*; 1240*s*; 1106*s*; 832*s*; 959*s*; 760*s*; 695*s*. ^{1}H-NMR: 1.55–1.72, 1.85–1.88, 1.97–2.05 (3 *m*, 2 H–C(3), 2 H–C(4), 2 H–C(5)); 3.58–3.63, 3.89–3.95 (2*m*, H–C(6'), H'–C(6')); 5.45 (ψt, *J*(H–C(2),H–C(3)) = 3.3, H–C(2)); 7.10–7.19, 7.26–7.30, 7.36–7.42, 7.48–7.55 (4*m*, 9 arom. H). Anal. calc. for $C_{17}H_{18}O_2$ (254.33): C 80.29, H 7.13; found: C 80.45, H 7.41.

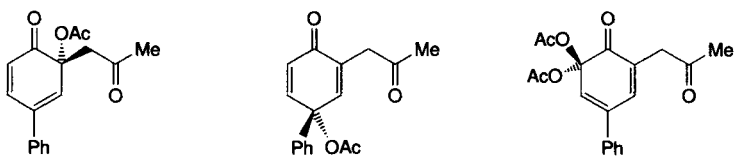
A 250-ml, three-necked, round-bottomed flask, containing a magnetic stirring bar and equipped with a thermometer, a pressure-equalizing N_2 inlet, and a septum, was charged with **92** (5.09 g; 20 mmol), dry THF (60 ml), and cooled to 0°. TMEDA (3.30 ml; 22 mmol) and BuLi (18 ml of a 1.22M soln. in hexane; 22 mmol) were successively injected with syringes through the septum, taking care that the temp. did not rise above 5°. The reaction vessel was immersed in an ice-water bath, and, after 1 h stirring, CuBr (3.16 g; 22 mmol) was added with such a rate that the temp. was kept below 5°. After 1 h stirring, the mixture was cooled to –78°. 3-Bromo-2-methoxypropene[32] [67] (8.71 g; 22 mmol) was added and the mixture left overnight to warm up to r.t. before being partitioned between CH_2Cl_2 and sat. aq. NH_4Cl (60 ml each). After usual workup, a residue was obtained which was purified by FC (250 g of silica gel; hexane/AcOEt 10:1) to give 5.16 g (83%) of crystalline *1-{4-[(2RS)-tetrahydro-2H-pyran-2-yloxy]-1,1'-biphenyl-3-yl}propan-2-one* (**93**): M.p. 61° (Et_2O/hexane at –30°). TLC (hexane/AcOEt 20:1): R_f 0.17. IR (KBr): 3058*w* (unsat. C–H); 2944*s*, 2873*m* (sat. C–H); 1714*s* (ketone); 1609*m*, 1510*s* (C=C); 1243*s*, 1122*s*, 1036*s* (C–O); 763*s*, 699*s* (monosubst. benzene). ^{1}H-NMR: 1.59–2.01 (*m*, 2 H–C(3''), 2 H–C(4''), 2 H–C(5'')); 2.20 (*s*, 3 H–C(3)); 3.61–3.70, 3.83–3.92 (2*m*, H–C(6''), H'–C(6'')); 3.77 (m_c, H–C(1), H'–C(1)); 5.48 (ψt, *J*(H–C(2''),H–C(3'')) ≈ 2.4, H–C(2'')); 7.23–7.59 (*m*, 8 arom. H). Anal. calc. for $C_{20}H_{22}O_3$ (310.39): C 77.39, H 7.14; found: C 77.11, H 7.23.

To a soln. of **93** (12.5 g; 40.3 mmol) in MeOH/H_2O 4:1 (160 ml), PPTS (4.05 g; 16.1 mmol) was added and the mixture stirred at r.t. until **93** had disappeared (TLC control). After usual workup, the residue was extracted by boiling hexane to give, after evaporation, 8.05 g (88%) of crystalline *1-(4-hydroxy-1,1'-biphenyl-3-yl)propan-2-one* (**94**): M.p. 136° (Et_2O/hexane). TLC (hexane/AcOEt 4:1): R_f 0.18. IR (KBr): 3399*s* (O–H); 3032*w*, 3007*w* (unsat. C–H); 1707*s* (ketone); 1610*m*, 1520*m* (C=C); 759*s*, 688*s* (monosubst. benzene). ^{1}H-NMR: 2.30

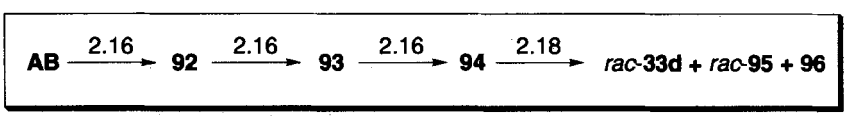
Scheme 35



AB **92** **93** **94**



33d **95** **96**



(*s*, 3 H–C(3)); 3.78 (*s*, 2 H–C(1)); 7.16 (*s*, in D_2O exchangeable, OH); 6.93–6.96, 7.23–7.52 (2*m*, 8 arom. H). Anal. calc. for $C_{15}H_{14}O_2$ (226.27): C 79.62, H 6.24; found: C 79.57, H 6.23.

A 500-ml, three-necked, round-bottomed flask, equipped with a mechanical stirrer, a thermometer, and a pressure-equalizing dropping funnel, was charged with $Pb(OAc)_4$ (96%; 10.4 g; 22.5 mmol) and anh. AcOEt (140 ml). To the vigorously stirred slurry, cooled to 0°, a soln. of **94** (3.39 g; 15 mmol) in AcOEt (60 ml) was added dropwise over 10 min. Stirring was continued for 30 min and excessive oxidant removed by added ethylene glycol (4 ml). Careful addition of a sat. aq. soln. of $NaHCO_3$ (75 ml) was followed by the usual workup procedure as soon as the gas production has ceased to afford a residue (4.37 g) which was purified by FC (160 g of silica gel; hexane/AcOEt 2:1) and prep. HPLC (hexane/AcOMe 20:7; 2 ml/min; 313 nm): *rac*-**33d** (1.38 g; 32%), *rac*-**95** (316 mg; 8%), and **96** (205 mg; 4%).

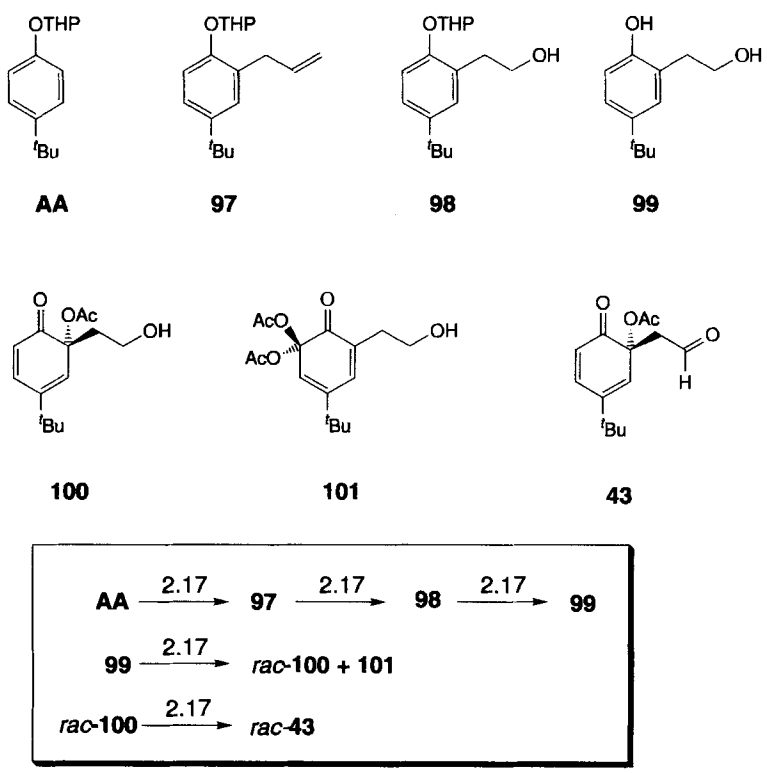
Data of rac-**33d**: M.p. 137° (CH_2Cl_2/hexane). TLC (hexane/AcOEt 4:1): R_f 0.13. UV (hexane): λ_{max} 317.0 (1795). UV (MeOH): λ_{max} 319.5 (1464). UV (TFE): λ_{max} 321.5 (1296). IR (KBr): 3963*w*, 3007*w* (unsat. C–H); 2966*w*, 2908*w* (sat. C–H); 1742*s* (acetate); 1711*s* (sat. ketone); 1688*s* (unsat. ketone); 1676*s*, 1640*m* (C=C); 1232*s* (C–O); 773*s*, 701*s* (monosubst. benzene). ^{1}H-NMR: 2.09 (*s*, $MeCO_2$); 2.23 (*s*, 3 H–C(3')); 2.85, 3.04 (*AB* system, *J*(H–C(1'),H'–C(1')) = 15.6, H–C(1'), H'–C(1')); 6.35 (*d*, *J*(H–C(2),H–C(3)) = 9.7, H–C(2)); 6.64 (*d*, *J*(H–C(5),H–C(3)) = 1.8, H–C(5)); 7.31–7.46 (*m*, H–C(3), Ph). ^{13}C-NMR: 20.3 ($MeCO_2$); 31.5 (C(3')); 51.1 (C(1')); 78.1 (C(6)); 126.0, 128.3, 128.7 (5 arom. C); 126.6 (C(2)); 134.5 (C(5)); 135.2, 137.8 (C(4), C_{ipso}); 142.5 (C(3)); 168.8 ($MeCO_2$); 196.7 (C(1)); 209.9 (C(2')). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross signals at 2.09/20.3; 2.23/31.5; 2.85, 3.04/51.1; 6.35/126.6; 6.64/134.5; 7.31–7.46/142.5. Anal. calc. for $C_{17}H_{16}O_4$ (284.31): C 71.82, H 5.67; found: C 71.58, H 5.77.

(RS)-4-Acetoxy-2-(2-oxopropyl)-4-phenylcyclohexa-2,5-dien-1-one (= *(RS)-4-Oxo-3-(2-oxopropyl)-1-phenylcyclohexa-2,5-dienyl Acetate*; *rac*-**95**): M.p. 99° (CH_2Cl_2/hexane). TLC (hexane/AcOEt 2:1): R_f 0.45. HPLC: hexane/AcOEt 30:13 + 30% CH_2Cl_2; 254 nm. UV (hexane): λ 231.0 (sh, 11493). UV (MeOH): λ_{max} 218.0 (13535), λ_{max} 238.0 (10763). IR (KBr): 3077*w* (unsat. C–H); 2901*w* (sat. C–H); 1764*s* (acetate); 1716*s* (sat. ketone); 1673*s* (unsat. ketone); 1644*s*, 1615*w* (C=C); 1230*s*, 1168*s*, 1098*s*, 1033*s* (C–O); 757*s*, 700*s* (monosubst. benzene). ^{1}H-NMR: 2.18 (*s*, $MeCO_2$); 2.22 (*s*, 3 H–C(3')); 3.29, 3.60 (*AB* system, *J*((H–C(1'),H'–C(1')) = 16.5, H–C(1'),H'–C(1')); 6.29 (*d*, *J*(H–C(6),H–C(5)) = 10.0, H–C(5)); 6.85 (*d*, *J*(H–C(3),H–C(5)) = 3.1, H–C(3)); 6.93 (*dd*, *J*(H–C(5),H–C(6)) = 10.0, *J*(H–C(5),H–C(3)) = 3.1, H–C(5)); 7.29–7.43, 7.49–7.54 (2*m*, 5 arom. H). Anal. calc. for $C_{17}H_{16}O_4$ (284.31): C 71.82, H 5.67; found: C 71.68, H 5.70.

6,6-Diacetoxy-2-(2-oxopropyl)-4-phenylcyclohexa-2,4-dien-1-one (= *1-Acetoxy-6-oxo-5-(2-oxopropyl)-3-phenylcyclohexa-2,4-dienyl Acetate*; **96**): M.p. 70°. TLC (hexane/AcOEt 4:1): R_f 0.14. UV (hexane): λ_{max} 237.6 (12864), λ 276.2 (sh, 5570). UV (MeOH): λ_{max} 236.4 (12911), λ_{max} 279.4 (6541). UV (TFE): λ_{max} 232.0 (11848), λ_{max} 283.3 (6809). IR (KBr): 3082*w*, 3024*w* (unsat. C–H); 2934*m*, 2851*w* (sat. C–H); 1756*s* (acetate); 1719*s* (sat. ketone); 1694*s* (unsat. ketone); 1652*m*, 1628*w* (C=C); 1226*s*, 1197*s*, 1010*s* (C–O); 765*s*, 698*s* (monosubst. benzene). ^{1}H-NMR: 2.12 (*s*, 2 $MeCO_2$); 2.22 (*s*, 3 H–C(3′)); 3.52 (ψs, 2 H–C(1′)); 6.36 (*d*, *J*(H–C(5), H–C(3)) = 2.2, H–C(5)); 7.20 (*dt*, *J*(H–C(3),H–C(5)) = 2.2, *J*(H–C(3),H–C(1′)) = 1.1, H–C(3)); 7.36–7.48 (*m*, 5 arom. H). Anal. calc. for $C_{19}H_{18}O_6$ (342.35): C 66.66, H 5.30; found: C 66.56, H 5.11.

2.17. *(RS)-6-Acetoxy-4-(*tert*-butyl)-2-(2-oxoethyl)cyclohexa-2,4-dien-1-one* (= *(RS)-3-(*tert*-Butyl)-6-oxo-1-(2-oxoethyl)cyclohexa-2,4-dienyl Acetate*; *rac*-**43**; *Scheme 36*)[31]. A 100-ml three-necked, round-bottomed flask, equipped with a thermometer, a magnetic stirring bar, a pressure-equalizing N_2 inlet, and a serum cap, was charged with a soln. of **AA** [68] (5.85 g; 25.0 mmol) and TMEDA (3.20 ml; 27.5 mmol) in anh. THF (50 ml) and cooled down to 0°. A soln. of BuLi (183 ml, 1.5M in hexane; 27.5 mmol) was transferred into the flask by cannulation techniques, taking care that the temp. did not rise above 5°. After 1 h stirring at 0°, CuBr (3.95 g; 27.5 mmol) was added portionwise, again keeping the temp. below 5°. After stirring for 1 h at 0°, the mixture was cooled down to −78° and, after allyl bromide (4.23 ml; 50 mmol) had been added, it was slowly warmed up to r.t. Usual workup afforded a liquid (7.22 g) which was purified by bulb-to-bulb distillation (160°/0.2 Torr) giving 6.72 g (98%) of *(RS)-2-[2-allyl-4-(*tert*-butyl)phenoxy]tetrahydro-2H-pyran* (**97**): TLC (hexane/AcOEt 100:1): R_f 0.17. IR (film): 3076*w* (unsat. C–H); 2951*s*, 2871*s* (sat. C–H); 1638*m* (C=C); 1607*w*, 1508*s* (C=C); 1362*m* (*t*-Bu); 1241*s*, 1111*s*, 1021*s* (C–O). ^{1}H-NMR: 1.29 (*s*, *t*-Bu); 1.52–2.05 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5)); 3.42 (ψd, *J*(H–C(1″),H–C(2″)) ≈ 6.6, 2 H–C(1″)); 3.57–3.63, 3.85–3.95 (2*m*, H–C(6), H′–C(6)); 5.00–5.11 (*m*, H–C(3″), H′–C(3″)); 5.40 (ψt, *J*(H–C(2),H–C(3)) ≈ 3.0, H–C(2)); 5.94–6.09 (*m*, H–C(2″)); 7.01–7.05, 7.15–7.30 (2*m*, H–C(3′), H–C(5′), H–C(6′)). Anal. calc. for $C_{18}H_{26}O_2$ (274.41): C 78.79, H 9.55; found: C 78.69, H 9.68.

Scheme 36



O_3 was passed into a soln. of **97** (2.74 g; 10.0 mmol) in abs. MeOH (20 ml) contained in a 100-ml, three-necked, round-bottomed flask fitted with a straight gas inlet tube, a $CaCl_2$ drying tube, and a glass stopper. The soln. was cooled in a MeOH/dry-ice bath and magnetically stirred, while O_3 was added until educt had disappeared (TLC control). After dry N_2 had been bubbled through the soln., followed by warming up to $-10°$, $NaBH_4$ (579 mg; 15.0 mmol) was added portionwise. After stirring overnight at r.t. and usual workup, a yellowish oil (2.51 g) was isolated which was submitted to FC (100 g of silica gel; hexane/AcOEt 4:1) yielding 1.81 g (65%) of crystalline *(RS)-2-{5-(*tert*-butyl)-2-[(2RS)-tetrahydro-2H-pyran-2-yloxy]phenyl}ethanol* (**98**): M.p. 45°. TLC (hexane/AcOEt 4:1): R_f 0.18. IR (KBr): 3416*m* (br., O–H); 3034*w* (unsat. C–H); 2951*s*, 2871*s* (sat. C–H); 1608*w*, 1503*s* (C=C); 1362*m* (*t*-Bu); 1241*s*, 1039*s* (C–O). ^{1}H-NMR: 1.30 (*s*, *t*-Bu); 1.61–2.04 (*m*, 2 H–C(3''), 2 H–C(4''), 2 H–C(5'')); 2.95 (*t*, *J*(H–C(2),H–C(1)) = 6.7, 2 H–C(2)); 3.59–3.64, 3.85–3.93 (2*m*, 2 H–C(1), H–C(6''), H'–C(6'')); 5.40 (ψt, *J*(H–C(2''),H–C(3'')) ≈ 3.3, H–C(2'')); 7.05 (*d*, *J*(H–C(3'),H–C(4')) = 8.9, H–C(3')); 7.18–7.22 (*d*, *dd*, overlaid, H–C(4'), H–C(6')). The proton signal of the OH group cannot be detected. On addition of D_2O, the signal due to 2 H–C(1) becomes a *t* (*J*(H–C(1),H–C(2)) = 6.7). Anal. calc. for $C_{17}H_{26}O_3$ (278.39): C 73.34, H 9.41; found: C 73.36, H 9.41.

To a soln. of **98** (2.50 g; 8.98 mmol) in MeOH/H_2O 4:1 (40 ml), contained in a 50-ml, round-bottomed flask, PTS · H_2O (428 mg; 2.25 mmol) was given. After stirring for 2 d at r.t. and usual workup, an orange oil (2.18 g) remained which crystallized overnight. Recrystallization from hexane yielded 1.31 g (75%) of *4-(*tert*-butyl)-2-(2-hydroxyethyl)phenol* (**99**): M.p. 91°. TLC (hexane/AcOEt 4:1): R_f 0.29. IR (KBr): 3402*s*, 3139*s* (br., OH); 2960*s*, 2897*s*, 2865*s* (sat. C–H); 1612*m*, 1512*m* (C=C); 1361*m* (*t*-Bu). ^{1}H-NMR: 1.27 (*s*, *t*-Bu); 2.85 (*t*, *J*(H–C(1'), H–C(2')) = 5.5, 2 H–C(1')); 3.17 (br. *s*, disappears on addition of D_2O, HO–C(2')); 3.91 (*t*, *J*(H–C(2'), H–C(1')) = 5.5, 2 H–C(2')); 6.80 (*d*, *J*(H–C(3),H–C(4)) = 8.4, H–C(3)); 7.05 (*d*, *J*(H–C(6),H–C(4)) = 2.5, H–C(6)); 7.14 (*dd*, *J*(H–C(4),H–C(3)) = 8.4, *J*(H–C(4),H–C(6)) = 2.5, H–C(4)); 7.99 (br. *s*, exchangeable with D_2O, HO–C(2)). Anal. calc. for $C_{12}H_{18}O_2$ (194.27): C 74.18, H 9.34; found: C 74.30, H 9.34.

A 500-ml, three-necked, round-bottomed flask, fitted with a mechanical stirrer, a thermometer, and a pressure-equalizing dropping funnel, was charged with $Pb(OAc)_4$ (96%; 9.75 g; 21.1 mmol) in anh. AcOEt (150 ml). To the mixture, cooled down to 0°, a soln. of **99** (2.57 g; 13.2 mmol) in AcOEt (50 ml) was dropwise added. After stirring for 30 min, ethylene glycol (4 ml) was added, stirring continued and vigorously extended following the addition of sat. aq. $NaHCO_3$ soln. (75 ml), until gas development had ceased. Usual workup furnished a dark oil (3.73 g) which was purified by FC (160 g of silica gel; hexane/AcOEt 2:1) giving *rac*-**100** (2.15 g; 65%) and **101** (698 mg; 17%) which, according to HPLC (hexane/AcOEt 2:3 + 30% CH_2Cl_2; 313 nm) did not show any impurities.

*(RS)-6-Acetoxy-4-(*tert*-butyl)-6-(2-hydroxyethyl)cyclohexa-2,4-dien-1-one* (= *(RS)-3-(*tert*-Butyl)-1-(2-hydroxyethyl)cyclohexa-2,4-dienyl Acetate*; *rac*-**100**): M.p. 79–80°. TLC (hexane/AcOEt 2:1): R_f 0.12. UV (hexane): λ_{max} 302.1 (3425). UV (MeOH): λ_{max} 306.8 (3417). UV (TFE): : λ_{max} 309.1 (3268). IR (KBr): 3463*m* (br., O–H); 3049*w* (unsat. C–H); 2964*s*, 2874*m* (sat. C–H); 1742*s* (acetate; 1681*s* (unsat. ketone); 1643*m* (C=C); 1370*s* (*t*-Bu); 1241*s*, 1047*s* (C–O). ^{1}H-NMR: 1.15 (*s*, *t*-Bu); 1.83–2.12 (*m*, 2 H–C(1')); 2.09 (*s*, $MeCO_2$); 2.22 (br. *s*, OH); 3.61–3.70 (*m*, 2 H–C(2')); 5.95 (*dd*, *J*(H–C(5),H–C(3)) = 2.5, *J*(H–C(5),H–C(2)) = 0.6, H–C(5)); 6.19 (*dd*, *J*(H–C(2),H–C(3)) = 10.2, *J*(H–C(2),H–C(5)) = 0.6, H–C(2)); 7.16 (*dd*, *J*(H–C(3), H–C(2)) = 10.2, *J*(H–C(3),H–C(5)) = 2.5, H–C(3)). ^{13}C-NMR: 20.4 ($MeCO_2$); 28.5 (Me_3C); 34.0 (Me_3C); 40.8 (C(1')); 57.3 (C(2')); 80.2 (C(6)); 126.0 (C(2)); 131.8 (C(5)); 141.8 (C(3)); 142.8 (C(4)); 168.9 (MeCOO); 198.9 (C(1)). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross peaks between 1.15/28.5; 1.83–2.12/40.8; 2.09/20.4; 3.61–3.80/57.3; 5.95/131.8; 6.19/126.0; 7.16/141.8. Anal. calc. for $C_{14}H_{20}O_4$ (252.31): C 66.65, H 7.99; found: C 66.35, H 8.01.

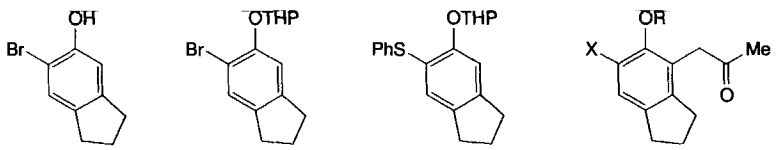
*6,6-Diacetoxy-4-(*tert*-butyl)-2-(2-hydroxyethyl)cyclohexa-2,4-dien-1-one* (= *1-Acetoxy-3-(*tert*-butyl)-5-(2-hydroxyethyl)-6-oxocyclohexa-2,4-dienyl Acetate*, **101**): M.p. 99° (Et_2O/hexane). TLC (hexane/AcOEt 2:1): R_f 0.20. UV (hexane): λ_{max} 317.5 (3497). UV (MeOH): λ_{max} 322.6 (3234). UV (TFE): λ_{max} 327.9 (2889). IR (KBr): 3540*m* (O–H); 2972*m*, 2887*m* (sat. C–H); 1756*s*, 1735*s* (acetate); 1693*s* (unsat. ketone); 1655*m* (C=C); 1368*s* (*t*-Bu); 1225*s*, 1037*s*, 1004*s* (C–O). ^{1}H-NMR: 1.15 (*s*, *t*-Bu); 2.09 (*s*, 2 $MeCO_2$); 2.23 (*t*, *J*(OH,H–C(2')) = 7.0, OH); 2.64 (*t* with f.s., *J*(H–C(1'),H–C(2')) = 5.4, 2 H–C(1')); 3.71 (m_c, 2 H–C(2')); 5.77 (*d*, *J*(H–C(5), H–C(3)) = 2.3, H–C(5)); 6.87 (*d* with f.s., *J*(H–C(3), H–C(5)) = 2.3, H–C(3)). Anal. calc. for $C_{16}H_{22}O_6$ (310.35): C 61.92, H 7.14; found: C 62.04, H 7.10.

Into a soln. of the *Dess-Martin-Periodinane* [69] (1.18 g; 2.40 mmol) in anh. CH_2Cl_2 (3 ml), contained in a 25-ml, round-bottomed flask, fitted with a magnetic stirring bar, a soln. of *rac*-**100** (252 mg; 1.00 mmol) in CH_2Cl_2(1 ml) was slowly introduced. After 20 min stirring at r.t., Et_2O (6 ml) and a soln. of $Na_2S_2O_3$ (1.50 g) in a sat. aq. soln. of $NaHCO_3$ (6 ml) were aded. The mixture was stirred for another 5 min, before Et_2O (6 ml) was added and the org. phase washed at first with sat. aq. $NaHCO_3$ soln. (6 ml) and then with H_2O (6 ml). Further

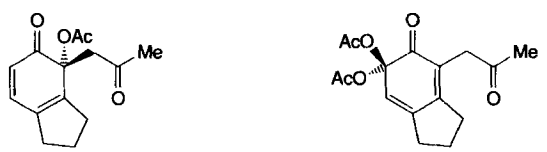
workup afforded an orange oil which was purified by semi-prep. HPLC (hexane/AcOEt 10:3; 313 nm) to give *rac*-**43** (130 mg; 52%) as a pale yellow oil: TLC (hexane/AcOEt 4:1): R_f 0.20. UV (hexane): λ_{max} 299.0 (3280). UV (MeOH): λ_{max} 306.8 (3135). UV (TFE): λ_{max} 310.1 (2914). IR (film): 2965*s*, 2909*m*, 2872*m* (sat. C–H); 1746*s* (acetate); 1725*s* (aldehyde); 1682*s* (unsat. ketone); 1645*m* (C=C); 1369*s* (*t*-Bu); 1238*s*, 1105*m*, 1020*m* (C–O). ^{1}H-NMR: 1.15 (*s*, *t*-Bu); 2.11 (*s*, $MeCO_2$); 2.66 (*d*, *J*(H–C(1'),H–C(2')) = 2.5, 2 H–C(1')); 6.02 (*dd*, *J*(H–C(5),H–C(3)) = 2.5, *J*(H–C(5),H–C(2)) = 0.5, H–C(5)); 6.24 (*dd*, *J*(H–C(2),H–C(3)) = 10.2, *J*(H–C(2),H–C(5)) = 0.5, H–C(2)); 7.21 (*dd*, *J*(H–C(3),H–C(2)) = 10.2, *J*(H–C(3),H–C(5)) = 2.5, H–C(3)); 9.76 (*t*, *J*(H–C(2'),H–C(1')) = 2.5, H–C(2')). ^{13}C-NMR: 20.3 ($MeCO_2$); 28.5 (Me_3C); 34.1 (Me_3C); 49.7 (C(1')); 77.9 (C(6)); 125.9 (C(2)); 129.6 (C(5)); 142.1 (C(3)); 144.0 (C(4)); 168.7 (MeCOO); 196.7 (C(1)); 197.2 (C(2')). Anal. calc. for $C_{14}H_{18}O_4$ (250.29): C 67.18, H 7.25; found: C 67.16, H 7.01.

2.18. *(RS)-4-Acetoxy-4,5-dihydro-4-(2-oxopropyl)indan-5-one (= (RS)-4,5-Dihydro-5-oxo-4-(2-oxopropyl)-indan-4-yl Acetate*; *rac*-**46**; *Scheme 37*)[31]. *6-Bromo-5-hydroxyindane* (**AC**) [70] (22.3 g; 104 mmol) was dissolved in CH_2Cl_2 (100 ml) containing dihydropyran (18.1 ml; 208 mmol) and PPTS (500 mg; 2 mmol). The soln. was stirred at r.t. until no more **AC** could be detected (TLC control). The mixture was poured under stirring into H_2O (100 ml). The org. layer was washed with 2N NaOH and brine (100 ml each). The aq. layers were extracted twice with CH_2Cl_2 (100 ml each), and finally the combined org. layers were dried ($MgSO_4$). After removement of solvent, the crude product was chromatographed (300 g of silica gel; hexane/AcOEt 20:1) and recrystallized from Et_2O/BuOH to afford 29.4 g (95%) of *(RS)-2-(6-bromoindan-5-oxy)tetrahydro-2H-pyrane* (**102**) as colorless crystals: M.p. 67°. TLC (hexane/AcOEt 20:1): R_f 0.40. IR (KBr): 2944*s*, 2870*s*, 2847*s* (sat. C–H); 1604*m*, 1571*w* (C=C); 1477*s* ($\delta(CH_2)$); 1259*s*, 1108*s* (C–O). ^{1}H-NMR: 1.56–2.15 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5), 2 H–C(2')); 2.82 (*t*, *J*(H–C(1'),H–C(2')) = *J*(H–C(3'),H–C(2')) = 7.3, 2 H–C(1'), 2 H–C(3')); 3.55–3.63, 3.88–3.98 (2*m*, H–C(6), H'–C(6)); 5.43 (ψt, *J*(H–C(2),H–C(3)) ≈ 2.9, H–C(2)); 7.01 (*s*, H–C(4')); 7.34 (*s*, H–C(7')). Anal. calc. for $C_{14}H_{17}BrO_2$ (297.19): C 56.58, H 5.77; found: C 56.41, H 5.91.

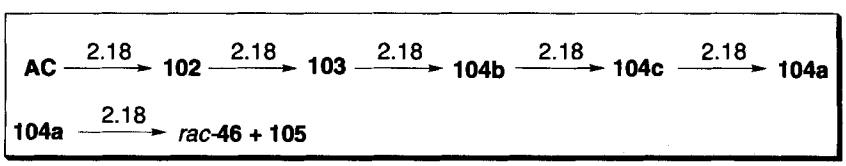
Scheme 37



AC **102** **103** **104 a** R=X=H
b R=THP; X=PhS
c R=THP; X=H



46 **105**



In a 250-ml, three-necked, round-bottomed flask equipped with a magnetic stirring bar, a thermometer, a rubber septum with an 18-gauge needle connected to a dry N_2-cource, and a pressure-reducing outlet, a soln. of **102** in abs. THF (60 ml) was placed and cooled down to −78°. A soln. of BuLi (18.3 ml, 1.2M in hexane;

22.0 mmol) was added *via* syringe. The soln. turned yellow at first and afterwards into a white suspension. After stirring for 30 min at −78° and warming up to 0°, a soln. of Ph_2S_2 (5.28 g; 24.0 mmol) in THF (40 ml) was added during 40 min. The mixture was stirred overnight at r.t. Usual workup yielded an orange oil which was purified by FC (250 g of silica gel; hexane/AcOEt 50:1) and crystallization from Et_2O/MeOH to furnish 4.90 g (75%) of *(RS)-2-[6-(phenylthio)indan-5-yloxy]tetrahydro-2H-pyran* (**103**): M.p. 69°. TLC (hexane/AcOEt 50:1): R_f 0.14. IR (KBr): 3046*w* (unsat. C–H); 2944*s*, 2846*m* (sat. C–H); 1604*m*, 1582*m* (C=C); 1475*s* ($\delta(CH_2)$); 1255*s*, 1107*s* 1022*s* (C–O); 744*s*, 690*s* (Ph). ^{1}H-NMR: 1.41–1.86 (*m*, 2 H–C(3), 2 H–C(4), 2 H–C(5)); 2.05 (*quint.*, *J*(H–C(2'),H–C(1')) = *J*(H–C(2'),H–C(3')) = 7.4, 2 H–C(2')); 2.79, 2.88 (*t*, with f.s., *J*(H–C(1'), H–C(2')) = *J*(H–C(3'),H–C(2')) = 7.4, 2 H–C(1'), 2 H–C(3')); 3.48–3.55 (*m*, H–C(6)); 3.77 (*td*, *J*(H'–C(6), H–C(6)) = *J*(H'–C(6),H–C(5)) = 11.0, *J*(H'–C(6),H'–C(5)) = 2.7, H'–C(6)); 5.39 (ψt, *J*(H–C(2),H–C(3)) ≈ 2.9, H–C(2)); 7.05–7.31 (*m*, H–C(4'), H–C(7'), Ph). Anal. calc. for $C_{20}H_{22}O_2S$ (326.46): C 73.58, H 6.79; found: C 73.46, H 6.80.

Compound **103** (2.73 g; 8.3 mmol) was converted into **104b** following the analogous procedure described under *Exper. 2.14*. The crude product after FC (200 g of silica gel; hexane/AcOEt 4:1) gave a colorless solid (3.18 g) which was recrystallized from hexane affording 2.83 g (89%) of *1-{6-(phenylthio)-5-[(2RS)-tetrahydro-2H-pyran-2-yloxy]indan-4-yl}propan-2-one* (**104b**): M.p. 77°. TLC (hexane/AcOEt 10:1): R_f 0.09. IR (KBr): 3057*w* (unsat. C–H); 2944*s*, 2848*m* (sat. C–H); 1724*s* (ketone); 1582*m* (C=C); 1201*s*, 1070*s*, 1932*s* (C–O). ^{1}H-NMR: 1.44–1.89 (*m*, 2 H–C(3''), 2 H–C(4''), 2 H–C(5'')); 2.02–2.10 (*m*, 2 H–C(2')); 2.17 (*s*, 3 H–C(3)); 2.68–2.84 (*m*, 2 H–C(1'), 2 H–C(3')); 3.29–3.38, hidden at 3.88–3.95 (2*m*, H–C(6''), H'–C(6'')); 3.89 (m_c, H–C(1), H'–C(1)); 4.89 (*dd*, *J*(H–C(2''),H–C(3'') = 7.6, *J*(H–C(2''),H'–C(3'')) = 2.5, H–C(2'')); 6.99 (*s*, H–C(7')); 7.19–7.26 (*m*, 5 arom. H). Anal. calc. for $C_{23}H_{26}O_3S$ (382.52): C 72.22, H 6.85; found: C 72.26, H 6.88.

To a suspension of freshly prepared *Raney*-Ni (15 g) in anh. acetone (50 ml) was added a soln. of **104b** (1.30 g) in acetone (25 ml). The mixture was vigorously stirred for 3 d at r.t. and filtered through *Celite*. After concentration under reduced pressure, the obtained residue was purified by FC (20 g of silica gel; hexane/AcOEt 10:1) to afford 864 mg (93%) of *1-{5-[(2RS)-tetrahydro-2H-pyran-2-yloxy]indan-4-yl}propan-2-one* (**104c**). An anal. sample of the solid material was recrystallized from Et_2O/MeOH at −30°: M.p. 52°. TLC (hexane/AcOEt 10:1): R_f 0.22. IR (KBr): 2945*s*, 2876*s*, 2845*m* (sat. C–H); 1712*s* (ketone); 1605*m*, 1593*m* (C=C); 1253*s*, 1114*s*, 1025*s* (C–O). ^{1}H-NMR: 1.55–1.98 (*m*, 2 H–C(3''), 2 H–C(4''), 2 H–C(5'')); 2.07 (m_c, 2 H–C(2')); 2.13 (*s*, 3 H–C(3)); 2.78–2.91 (*m*, 2 H–C(1'), 2 H–C(3')); 3.55–3.63, 3.80–3.90 (2*m*, H–C(6''), H'–C(6'')); 3.70 (m_c, 2 H–C(1)); 5.35 (m_c, H–C(2'')); 6.97 (*d*, *J*(H–C(6'),H–C(7')) = 8.2, H–C(6')); 7.07 (*d*, *J*(H–C(7'),H–C(6')) = 8.2, H–C(7')). Anal. calc. for $C_{17}H_{22}O_3$ (274.36): C 74.41, H 8.08; found: C 74.60, H 8.07.

To a soln. of **104c** (4.10 g; 14.9 mmol) in MeOH/H_2O 4:1 (60 ml), PPTS (0.87 g; 3 mmol) was added and the mixture stirred at r.t. until **104c** had disappeared (TLC control). After usual workup, the residue (3.65 g) was crystallized from Et_2O/hexane to give 2.36 g (83%) *1-(5-hydroxyindan-4-yl)propan-2-one* (**104a**): M.p. 109°. TLC (hexane/AcOEt 4:1): R_f 0.20. IR (KBr): 3424*s* (OH); 3016*w* (unsat. C–H); 2951*m*, 2904*m*, 2845*m* (sat. C–H); 1710*s* (ketone); 1605*m* (C=C). ^{1}H-NMR: 2.09 (m_c, 2 H–C(2')); 2.26 (*s*, 3 H–C(3)); 2.83–2.90 (*m*, 2 H–C(1'), 2 H–C(3')); 3.74 (*s*, 2 H–C(1)); 6.64 (*s*, disappears on addition of D_2O, OH); 6.69 (*d*, *J*(H–C(6'),H–C(7')) = 8.0, H–C(6')); 7.00 (*d*, *J*(H–C(7'),H–C(6')) = 8.0, H–C(7')). Anal. calc. for $C_{12}H_{14}O_2$ (190.24): C 75.78, H 7.42; found: C 75.78, H 7.34.

A 250-ml, three-necked, round-bottomed flask, equipped with a mechanical stirrer, a thermometer, and a pressure-equalizing dropping funnel, was charged with $Pb(OAc)_4$ (96%; 7.20 g; 15.6 mmol) in anh. AcOEt (80 ml). To the vigorously stirred mixture, a soln. of **104a** (1.48 g; 7.78 mmol) in AcOEt (30 ml) was dropwise added at 0°. Stirring was continued before and after ethylene glycol (2 ml) had been added. After usual workup, a dark oil (2.26 g) was obtained which was separated by FC (150 g of silica gel; hexane/AcOEt 3:1) to yield *rac*-**46** (490 mg; 25%) and **105** (28%) as solid materials. In both fractions, no impurities were to be detected by HPLC (hexane/AcOEt 4:1; 313 nm). Anal. samples after recrystallization (from CH_2Cl_2/hexane) showed properties as follows: *rac*-**46**: M.p. 84°. TLC (hexane/AcOEt 4:1): R_f 0.10. UV (hexane): λ_{max} 326.3 (3626). UV (MeOH): λ_{max} 331.7 (3289). UV (TFE): λ_{max} 340.2 (3004). IR (KBr): 3043*w* (unsat. C–H); 2984*m*, 2924*m*, 2851*s* (sat. C–H); 1736*s* (acetate); 1715*s* (sat. ketone); 1674*s* (unsat. ketone); 1639*s* (C=C); 1240*s*, 1165*s*, 1011*s* (C–O). ^{1}H-NMR: 1.94–2.09 (*m*, 2 H–C(2)); 2.07 (*s*, $MeCO_2$); 2.16 (*s*, 3 H–C(3')); 2.36–2.48, 2.53–2.61 (2*m*, 2 H–C(1), 2 H–C(3)); 2.91, 3.04 (*AB* system, *J*(H–C(1'),H'–C(1')) = 14.4, H–C(1'),H'–C(1')); 6.13 (*d*, *J*(H–C(6), H–C(7)) = 9.8, H–C(6)); 6.96 (*d*, *J*(H–C(7),H–C(6)) = 9.8, H–C(7)). ^{13}C-NMR: 20.2 ($MeCO_2$); 22.8 (C(2)); 31.2 (C(3')); 31.7, 33.2 (C(1), C(3)); 51.2 (C(1')); 78.6 (C(4)); 125.5 (C(6)); 135.9 (C(9)); 146.4 (C(8)); 139.5 (C(7)); 168.3 ($MeCO_2$); 198.4 (C(5)); 203.2 (C(2')). The signals were assigned by a ^{1}H,^{13}C-COSY spectrum. Cross peaks between 1.94–2.09/22.8; 2.07/20.2; 2.16/31.2; 2.36–2.48, 2.53–2.61/31.7, 33.2; 2.91, 3.04/51.2; 6.13/125.5; 6.96/139.5. Anal. calc. for $C_{14}H_{16}O_4$ (248.28): C 67.73, H 6.50; found: C 67.72, H 6.56.

6,6-Diacetoxy-5,6-dihydro-4-(2-oxopropyl)indan-5-one (= *5-Acetoxy-5,6-dihydro-6-oxo-7-(2-oxopropyl)-indan-5-yl Acetate*; **105**): M.p. 134–135°. TLC (hexane/AcOEt 4:1): R_f 0.05. UV (hexane): λ_{max} 326.8 (4282). (UV (MeOH): λ_{max} 327.9 (3887). UV (TFE): λ_{max} 332.3 (3523). IR (KBr): 3000*w* (unsat. C–H); 2964*m*, 2949*m*, 2938*m* (sat. C–H); 1754*s* (acetate); 1713*s* (sat. ketone); 1677*s* (unsat. ketone); 1621*m* (C=C); 1227*s*, 1173*s*, 1003*s* (C–O). ^{1}H-NMR: 1.90 (*quint.*, *J*(H–C(2),H–C(1)) = *J*(H–C(2),H–C(3)) = 7.3, 2 H–C(2)); 2.09 (*s*, $MeCO_2$); 2.14 (*s*, 3 H–C(3')); 2.56–2.68 (*m*, 2 H–C(1), 2 H–C(3)); 3.46 (*s*, 2 H–C(1')); 6.13 (*t*, *J*H–C(7),H–C(1)) = 2.3, H–C(7)). Anal. calc. for $C_{16}H_{18}O_6$ (306.31): C 62.74, H 5.92; found: C 62.77, H 6.03.

2.19. *(6RS)-2-Acetyl-6-acetoxy-4,6-dimethylcyclohexa-2,4-dien-1-one* (= *(RS)-5-Acetyl-1,3-dimethyl-6-oxocyclohexa-2,4-dienyl Acetate*; *rac*-**62**; *Scheme 20*). A soln. of 6-acetyl-2,4-dimethylphenol [71] (3.3 g; 20 mmol) in anh. $CHCl_3$ (50 ml) was added at r.t. to a vigorously stirred suspension of Pb $(OAc)_4$ (12.4 g, 96%; 30 mmol) in anh. $CHCl_3$ (50 ml) following a modification of a known procedure [72]. After 4 h, ethylene glycol (2 ml) was added, and usual workup led to 2.9 g (66%) of *rac*-**62**. M.p. 80–81° (Et_2O/pentane). TLC (hexane/AcOEt 4:1): R_f 0.2. UV (MeOH): λ_{max} 227.5 (6152), 319.5 (5762). UV (hexane): λ_{max} 223.5 (6070), 314.5 (5898). UV (TFE): λ_{max} 230 (6432), 322 (5655). IR (KBr): 1740*s* (acetate); 1695*s* (acetyl and unsat. ketone); 1650*w* (C=C); 1370*m*, 1240*s* (acetate). ^{1}H-NMR: 1.41 (*s*, Me–C(2)); 2.02 (*d*, *J* = 1.6, Me–C(4)); 2.11 (*s*, $MeCO_2$); 2.52 (*s*, MeCO); 6.16–6.19 (*m*, H–C(3)); 7.59 (*d*, *J* = 2.5, H–C(5)). ^{13}C-NMR: 20.35 (*Me*CO_2); 20.70 (*Me*CO); 23.96 (Me–C(2)); 30.92 (Me–C(4)); 79.60 (C(4)); 129.56 (C(2)); 133.24 (C(6)); 142.14 (C(5)); 149.64 (C(3)); 169.59 ($MeCO_2$); 195.89 (C(1)); 197.42 (MeCO). Anal. calc. for $C_{12}H_{14}O_4$ (222.24): C 64.85, H 6.34; found: C 64.75, H 6.34.

3. Preparation of Imines. – 3.1. *N-[(Methylsulfanyl)methylidene]benzylamine* (**53**). A 250-ml, round-bottomed, three-necked flask, equipped with a magnetic stirring bar, a pressure-equalizing dropping funnel fitted with a NaOH-filled drying tube, a thermometer, and a septum, was charged under an Ar atmosphere with a soln. of *N*-benzylthioformamide [73] (2 g; 33 mmol) in anh. Et_2O (60 ml). To the soln., cooled down to 0°, within 30 min, a soln. of BuLi (11 ml of a 1.6M hexane soln.; 18 mmol) was added dropwise. 10 min later a soln. of MeI (1.1 ml; 18 mmol) in Et_2O (5 ml) was added by syringe. After 4 h at r.t. usual workup furnished **53** which, without further purification, was immediately used for β-lactam formation (see *Exper. 1.19.3*).

3.2. *(2RS)-N-(Phenylmethylidene)bicyclo[2.1.1]heptan-2-amine* (*rac*-**56**). Following a general procedure [45] (*RS*)-*exo*-nornornan-2-amine (1.66 g; 15 mmol) and PhCHO (1.54 g; 15 mmol) was added at r.t. to a vigorously agitated suspension of basic alumina (4 g) in anh. hexane (10 ml). After 3 h stirring and usual workup, the obtained residue was purified by bulb-to-bulb distillation (130°/0.2 Torr) to give 5.4 g (90%) of *rac*-**56**: TLC (hexane/AcOEt 2:1): R_f 0.7. UV (MeOH): λ_{max} 247.5 (18623). IR (film): 3026*w* (unsat. C–H); 2952*s* (sat. C–H); 2868*s*, 1642*s* (C=N); 1450*m*. ^{1}H-NMR: 1.14–1.27 (*m*, H–C(6), H–C(3), H–C(4)); 1.42–1.65 (*m*, H'–C(6), H'–C(3) H'–C(4), H–C(7)); 1.94 (*dt*, *J*(H'–C(7),H–C(7)) = 9.5, *J*(H'–C(7),H–C(2)) = *J*(H'–C(7),H–C(5)) = 1.7, H'–C(7)); 2.14 (ψ*d*, *J*(H–C(5),H–C(1)) = 2.3, H–C(5)); 2.32 (ψ*s*, H–C(2)); 3.30 (*dd*, *J*(H–C(1),H–C(2)) = 2.3, *J*(H–C(1),H'–C(6)) = 7.5, H–C(1)); 7.32–7.39, 7.66–7.73 (2*m*, 5 arom. H); 8.18 (*s*, H–C(1')). The signals were assigned by a ^{1}H,^{1}H-COSY spectrum. Cross peaks between 1.14–1.27/1.42–1.65 and 1.94; 1.42–1.65/2.14, 2.23, and 3.30. Anal. calc. for $C_{14}H_{17}N$ (199.30): C 84.37, H 8.60, N 7.03; found: C 84.48, H 8.50, N 6.83.

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