Diazodiphenylmethane and Monosubstituted Butadienes: Kinetics and a New Chapter of Vinylcyclopropane Chemistry[1])

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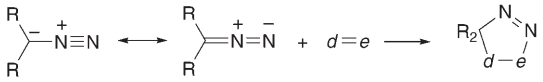
Dedicated to *Emanuel Vogel,* the discoverer of the vinylcyclopropane rearrangement, on the occasion of his 80th birthday

Diazodiphenylmethane (**DDM**) undergoes cycloadditions to 1-substituted buta-1,3-dienes exclusively at the C(3)=C(4) bond. At room temperature, the N_2 loss from the initially formed 4,5-dihydro-3*H*-pyrazoles **2** is faster than the cycloaddition and furnishes the vinylcyclopropane derivatives **7** and **9** with structural retention at the C(1)=C(2) bond. 2-Substituted butadienes react with **DDM** at the C(3)=C(4) bond to give **12**; isoprene, however, affords 3,4/1,2 products in the ratio of 86:14. **DDM** is a nucleophilic 1,3-dipole: 1-Cyanobutadiene reacts 400 times faster than 1-methoxybuta-1,3-diene (DMF, 40°). The $\log k_2$ for the additions to six 1-substituted butadienes show a linear correlation with σ_p (*Hammett*) and $\varrho = +2.9$; the $\log k_2$ of five 2-substituted butadienes are linearly related to *Taft*'s σ_I ($\varrho = +1.7$). The structures of the vinylcyclopropanes **7**, **9**, and **12** are established by NMR spectra and oxidation. A cyclopropyl carbinyl cation is made responsible for the isomerization of **12**, R = Ph, Me, by acetic acid to 4-substituted 1,1-diphenylpenta-1,3-dienes **25** and **29**; TsOH at 200° converts **25** further to 9,10-dihydro-9-methyl-10-phenyl-9,10-ethanoanthracene (**27**). Thermal rearrangement of **7**, **9**, and **12** at 200–300° produces the 3- or 1-substituted 4,4-diphenylcyclopentenes **30** and **31**. These give the same mass spectra as the vinylcyclopropanes, and an open-chain distonic radical cation is suggested as common intermediate. Besides spectroscopic evidence for the cyclopentene structures, hydrogenation and epoxidation are described; NMR data support the *trans*-attack by perbenzoic acid.

1. Introduction. – Diazomethane and diazodiphenylmethane are nucleophilic 1,3-dipoles and preferably react with electrophilic C=C bonds (*Scheme 1*). The rate constant k_2 (DMF, 25°) for the 1,3-cycloadditions of diazomethane (**DM**) to ethyl acrylate exceeds that of styrene 2500-fold, and that of butyl vinyl ether by a factor of 10^7 [2]; enamines are inert to **DM**.

Scheme 1



DM R = H
DDM R = Ph

[1]) 1,3-Dipolar Cycloadditions, Part 137; for Part 136, see [1].

The corresponding cycloadditions of diazodiphenylmethane (**DDM**) in DMF at 40° are slower than those of **DM** at 25°, and cover a smaller range: ethyl acrylate is only 660 times faster than styrene and 10^4-fold ahead of hex-1-ene; vinyl ethers no longer react [2]. Whereas the cycloadditions of **DM** usually allow the isolation of dihydropyrazoles, those of **DDM** are accompanied by N_2 loss and afford vinylcyclopropane derivatives.

In the 1970s, MO perturbation theory (PMO) offered the clue to a successful description of reactivity and regiochemistry in concerted cycloadditions (for reviews, see [3–5a]). Among the two frontier orbital (FMO) interactions, HO(diazomethane)–LU(dipolarophile) controls the energy of the transition structure (TS) to a higher extent than the second HO–LU pair. In a simplified version of the perturbation equation, $\log k_2$ should be linearly related to the reciprocal energy distance of the controlling HO–LU pair [3]. Using the *IP* of **DM** for HO(diazomethane) and ($IP - E_{\pi\rightarrow\pi^*}$) for LU(dipolarophile), the $\log k_2$ for the cycloadditions to numerous ethylene and butadiene derivatives fulfilled such a linear relationship [6]. In an orthodox PMO calculation, however, the interaction of all π-MOs of both cycloaddition partners must be included [7][8].

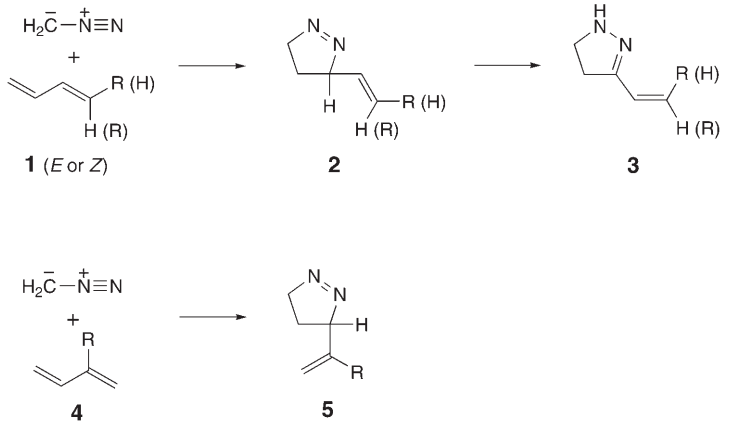
The present state of the art is an *ab initio* calculation of TSs; its increasing sophistication reflects the progress of quantum-chemical methods as well as that of computer efficiency. As early as 1975, *Leroy* and *Sana* calculated cycloadditions of **DM** at the STO-3G level [9]. In 1998, RHF and B3LYP calculations by *Rastelli, Gandolfi et al.* [10] confirmed the concertedness; the calculated activation energies for the additions of **DM** to substituted ethylenes showed an '*impressive agreement both in trend and absolute values*' with measured data. Recently, *Ess* and *Houk* demonstrated by B3LYP calculations that the distortion energies of 1,3-dipoles (diazonium and nitrilium betaines) constitute a substantial part of the activation energies for the concerted 1,3-cycloadditions to ethylene and acetylene [11].

An experimental argument for concertedness rests on the high stereospecificity observed for the cycloadditions of **DM** to methyl tiglate and methyl angelate. The configurational retention of $> 99.997\%$ would burden the C–C bond of a hypothetical intermediate in a two-step process with a rotational barrier of > 7.2 kcal mol^{-1} [12].

2. Results and Discussion. – 2.1. *Site Selectivity, Regiochemistry, and Products.* Diazodiphenylmethane (**DDM**) resembles diazomethane (**DM**) in its preference for electrophilic cycloaddition partners, as mentioned above. However, the steric demands of **DDM** exceed those of the parent **DM**. Monosubstituted buta-1,3-dienes offer a model for separating, to some extent, steric and electronic effects on the cycloaddition rate. Fortunately, 1-substituted butadienes accepted **DM** and **DDM** exclusively at the C(3)=C(4) bond.

In a previous contribution from our laboratory, the cycloadditions of **DM** to 1-substituted buta-1,3-dienes **1** were studied [13]. The 4,5-dihydro-3-vinyl-3*H*-pyrazoles **2** were isolated in experiments with **1**, R = H, Me, MeO, whereas tautomerization to dihydro-1*H*-pyrazoles **3** took place on workup after reactions of **1**, R = Ph, CO_2Me, CN (*Scheme 2*). In the HOMO and LUMO, **DM** has the larger atomic-orbital coefficient at the C-atom, thus directing the addition to **1** which possesses in the LUMO the larger coefficients at C(1) and C(4) [14]. The consistent site selectivity is more problematic [15] and speaks for participating steric effects.

Scheme 2

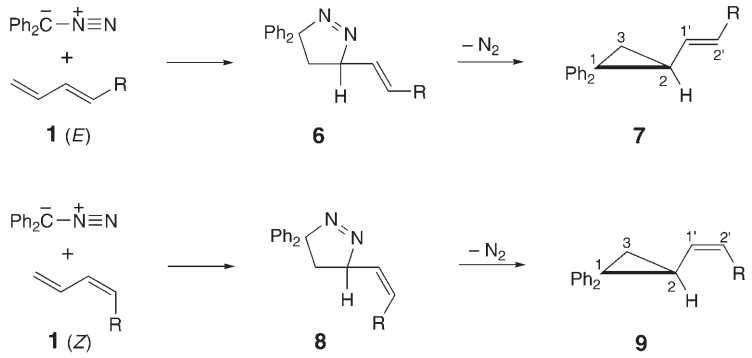


As an example of 2-substituted buta-1,3-dienes, **4**, R = Ph, was reacted with **DM** to give the 3,4-cycloadduct **5**, R = Ph [13].

The cycloadditions of **DDM** to 1- and 2-substituted butadienes were attended by elimination of N_2. Most of the butadienes **1** were available as (*E*)-forms, the cyano compound was **1**(*Z*), and **1**, R = MeO, consisted of an (*E*)/(*Z*) mixture with a ratio of 60 : 40. Products of N_2 extrusion from the 4,5-dihydro-3*H*-pyrazoles **6** and **8** were the 1,1-diphenyl-2-vinylcyclopropanes **7** and **9**, which, according to the NMR spectra, occurred with retention of configuration at the former C(1)=C(2) bond (*Scheme 3*). The C(3)=C(4) bond of **1** is definitely the reaction site, but, due to the rapid N_2 loss, there is no experimental evidence for the regiochemistry of cycloaddition. The assumption of structures **6** and **8** rests on the analogy with the isolated **DM** cycloadducts **2** and **3**.

The reactions of **DDM** with **1** were run at room temperature, and the butadienes **1**, R = H, Me, Ph, MeO, served as solvent for the slow additions. These cycloadditions

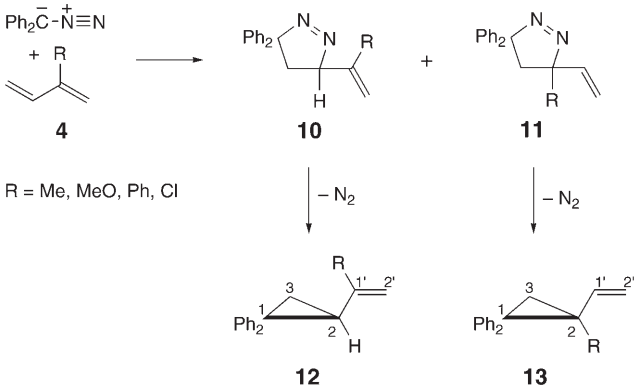
Scheme 3



competed with the self-decomposition of **DDM** which proceeds in DMF at 25° with a half-life of 72 days. 1,3-Dipolar cycloadditions usually have large negative $\Delta S^{\#}$ values, and, therefore, a lower temperature dependence of rate than the first-order decomposition of **DDM**. We accepted reaction times of weeks and months to promote the cycloaddition. The faster reactions with **1**, R = CO_2Me, CN, were carried out with 1:1 stoichiometry in benzene.

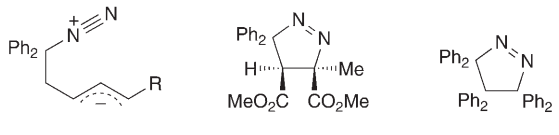
Correspondingly, several 2-substituted buta-1,3-dienes **4** were reacted with **DDM**. Isoprene (**4**, R = Me) accepted the 1,3-dipole both at the C(3)=C(4) and the C(1)=C(2) bond, and **12**/**13** 86:14 was observed. The cycloadditions with **4**, R = Ph, Cl, MeO, took place only at the C(3)=C(4) bond and provided **12** (*Scheme 4*).

Scheme 4



The yields of the vinylcyclopropane derivatives (see *Table 2* below) amounted to 33–91%. Limiting factors were the decomposition of **DDM** in the reactions with the 'slow' dienes **1**, R = Me, MeO, and the oligomerization of **4**, R = Ph. The spectra and the chemistry of the products will be dealt with in *Sect. 2.3*.

The intermediacy of the 4,5-dihydro-3*H*-pyrazoles of type **6** and **10** requires brief consideration. An alternative to the concerted cycloaddition of **DDM** would be the formation of a diazonium zwitterion **14** (or biradical) and ring closure after loss of N_2; the cycloadduct would be bypassed. However, the N_2 extrusion from 4,5-dihydro-3*H*-pyrazoles (1-pyrazolines) is known as '*Buchner–Curtius* Cyclopropane Synthesis'; the first examples dealt with cycloadducts of diazoacetate (1888) [16]. According to *van Alphen* [17], **DDM** and methyl citraconate afford **15**, which cannot tautomerize to the more stable dihydro-1*H*-pyrazole (2-pyrazoline), and N_2 is eliminated above 100°.



What determines the rate of N_2 evolution from 4,5-dihydro-3*H*-pyrazoles? Various kinetic studies of the thermolysis [18] suggest that conjugating substituents are already effective in the TS of N_2 loss. The initially formed trimethylene species, often described as biradical, is stabilized by Ph, vinyl, or CO_2Me groups. That makes the **DDM** cycloadducts **6**, **8**, **10**, and **11** prone to N_2 extrusion; whether the loss of N_2 is a one-step or two-step process will not be discussed here. Interestingly, the perphenylated compound **16** requires 48 h at 240° for N_2 elimination [19]; here, TS and product suffer from steric hindrance of resonance.

2.2. *Rate Constants of Diazodiphenylmethane Cycloadditions.* The rates were measured as pseudo-first-order reactions in the presence of *ca.* 10 equiv. of dipolarophile in DMF at 40°. The concentration of **DDM** was determined volumetrically in withdrawn samples (N_2 evolution with Cl_3CCOOH). The high solubility of **DM** in DMF was originally responsible for the choice of DMF as solvent. The $k_{1\psi}$ values were corrected for k_1 of self-decomposition. The rate constants of **DDM** additions at 40° are compared with those of **DM** at 25° in *Table 1*.

Table 1. *Rate Constants* k_2 [$\cdot 10^5$ M^{-1} s^{-1}] *for the 1,3-Cycloadditions of Diazomethane* [13] *and Diazodiphenylmethane to Butadiene and Its Monosubstituted Derivatives in DMF*

Substituent R	$H_2C{=}CH{-}CH{=}CHR$ + CH_2N_2 at 25°	$H_2C{=}CH{-}CH{=}CHR$ + Ph_2CN_2 at 40°	$H_2C{=}CH{-}CR{=}CH_2$ + Ph_2CN_2 at 40°
CN[a])		33.0	
Cl			2.22
CO_2Me	2570	11.4	
H	21.4	0.78[b])	0.78[b])
Ph	21.0	0.58	0.71
Me	2.43	0.10	0.25
MeO[c])	1.34	0.08	0.76
ϱ(*Hammett*)	+4.3	+2.2	ϱ(*Taft*) +1.7

[a]) 98% (*Z*) and 2% (*E*). [b]) Statistical value ½ used for the plots of *Figs. 1* and *2*. [c]) 60% (*E*) and 40% (*Z*).

In the reaction with (*E*)-1-phenylbuta-1,3-diene in DMF at 40°, **DM** is 108 times faster than **DDM**. The rate constants were measured at different temperatures, and the *Eyring* parameters suggest that mainly the higher activation enthalpy is responsible for the lower rate of **DDM**: $\Delta H^{\#} = 16.1 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\#} = -31 \pm 3$ e.u. for **DDM**, compared with $\Delta H^{\#} = 13.8 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\#} = -29 \pm 3$ e.u. for **DM**. Remarkably, the entropies at 40° contribute 38% (**DDM**) and 40% (**DM**) to the activation free energy. The data confirm an earlier experience that the dramatic differences in the rates of diazoalkane cycloadditions (methyl diazoacetate and dimethyl diazomalonate were also included) are controlled by variation of $\Delta H^{\#}$ [20].

The k_2 values for the cycloadditions of **DDM** to the C(3)=C(4) bond of 1-substituted butadienes reveal a diminished substituent influence, compared with the k_2 of **DM** reported in [13]. **DM** reacts with methyl buta-1,3-diene-1-carboxylate (**1**, R = CO_2Me) 1900 times faster than with 1-methoxybuta-1,3-diene (R = MeO); this ratio shrinks to 143 for **DDM**. Nevertheless, the k_2 values of **DDM** stretch over a range of

> 400. The log k_2 for **DDM**, like those for **DM**, fit linear free energy correlations fairly well, when plotted *vs.* σ_p (*Hammett*) (*Fig. 1*). This is reasonable, since both resonance and inductive effects of substituents R are conducted through the butadiene system as in *p*-substituted benzenes, virtually without steric impairment. The ϱ values, 4.3 for **DM** [13] and 2.9 for **DDM**, reflect the lower sensitivity of the latter. The configuration at the C(1)=C(2) bond of **1**, (*E*) or (*Z*), appears to be of minor importance.

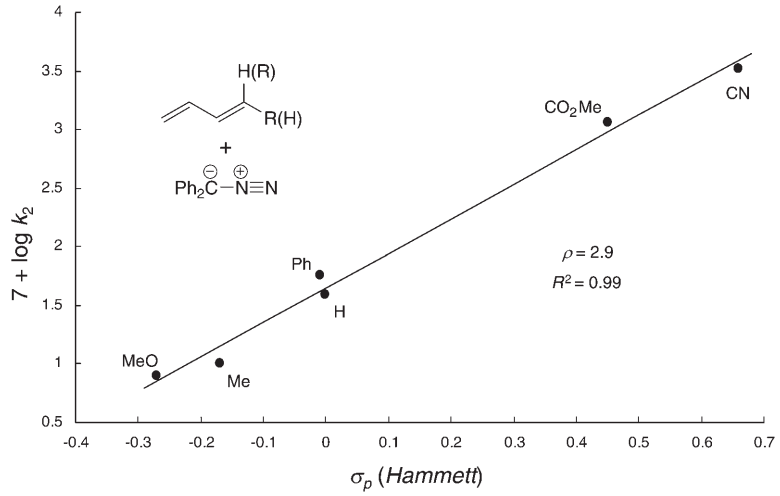


Fig. 1. *Rate Constants* k_2 *for the Cycloadditions of* **DDM** *to 1-Substituted Buta-2,3-dienes* (DMF, 40°). Plot of log k_2 *vs.* σ_p (*Hammett*).

In 2-substituted butadienes **4**, the C(1)=C(2) bond profits from resonance and inductive contributions of R, whereas only the *I*-effect reaches the C(3)=C(4) bond. As mentioned above, **DDM** cycloadditions take place at the C(3)=C(4) bond of **4** with the exception of isoprene, which furnishes 3,4- and 1,2-adduct in a ratio of 86:14. The five rate constants given in *Table 1* cover the modest range of factor 9. The log k_2 values fit *Taft*'s inductive substituent constants σ_I [21][22] slightly better (*Fig. 2*) than *Hammett*'s σ_m; coincidence may play a role, since steric effects of R are no longer negligible.

We regard the analogy of **DM** and **DDM** in the rate phenomena as further confirmation for assuming dihydro-3*H*-pyrazoles to be initial products of **DDM** reactions (see *Sect. 2.1*).

As a 1,3-dipole, **DDM** is less nucleophilic than **DM**. Benzylic resonance distributes the charge, and, in the language of MO theory, the phenyl conjugation decreases the HOMO energy. Superimposed is the retardation of **DDM** reactions by steric hindrance.

In the framework of a highly successful concept of electrophile–nucleophile combinations (recent review: [23]), *Mayr* and co-workers [24] determined the kinetics for the C–C bond formation of aliphatic diazo compounds with benzhydryl-type cations (CH_2Cl_2, 20°) and assigned *nucleophilicity parameters N:* 10.48 (**DM**) and 5.29 (**DDM**) correspond to a decrease of 5 logarithmic units caused by the two Ph groups.

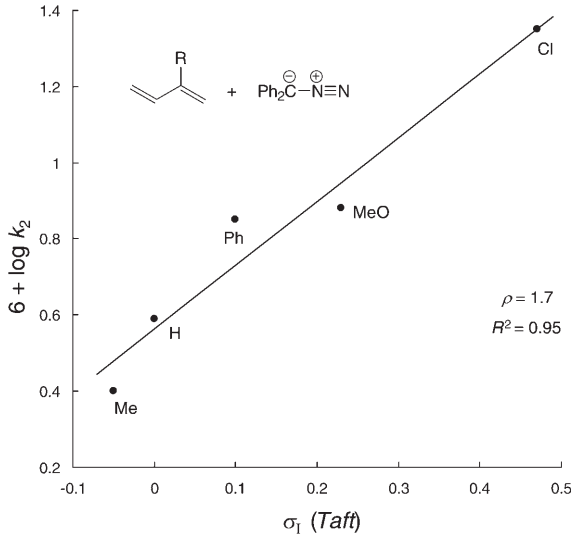


Fig. 2. *Cycloadditions of* **DDM** *with 2-Substituted Buta-1,3-dienes.* Plot of log k_2 (DMF, 40°) *vs. Taft*'s inductive substituent constants σ_I.

Since both reactants, **DDM** and carbocation, are sterically demanding, steric shielding participates in the effect.

In the cycloadditions of **DM** and **DDM** with (*E*)-1-phenylbuta-1,3-diene (DMF, 40°, $k_{DM}/k_{DDM} = 108$), $\Delta\Delta G^{\#}$ amounts to 2.9 kcal mol^{-1}, *i.e.*, the retardation is smaller. 1,3-Dipoles are ambiphilic, *i.e.*, both termini are nucleophilic and electrophilic [5b]; it is the preponderance of nucleophilic character that is disclosed in the rate ratio k_{DM}/k_{DDM} as well as in the substituent effects observed in cycloadditions to substituted butadienes.

2.3. *Properties and Some Reactions of 1,1-Diphenyl-2-vinylcyclopropanes.* The structures of the vinylcyclopropanes were elucidated by NMR spectroscopy. The high-field shifts of $\delta(^1H)$ and $\delta(^{13}C)$ are in accordance with a cyclopropane ring. The ^{1}H-NMR parameters of **7**, R = Ph, given in formula **17** (see below) serve as an example. They were confirmed by computer simulation (DAVINX [25]); the coupling constants $J_{gem} = -5.0$, $J_{cis} = 8.6$, and $J_{trans} = 5.8$ Hz, are within the range of literature data for cyclopropanes [26]. The chemical shifts of the olefinic H-atoms change more with variation of R, and J_{vic} establishes the assignments of (*E*)- and (*Z*)-configurations (*Table 2*).

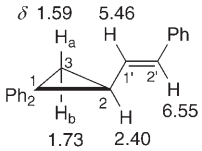
Chemical confirmation came from oxidation with $KMnO_4$, which, in the example of **7**, R = Ph, furnished 2,2-diphenylcyclopropane-1-carboxylic acid (**18**; 73%) and PhCOOH (68%). The $KMnO_4$ oxidation of **12**, R = Ph, stopped at the glycol **20**, which was cleaved by $Pb(OAc)_4$ to give the cyclopropyl ketone **19**.

Noteworthy is the sensitivity of **12**, R = Ph, to acid. In boiling AcOH, a conversion to 1,1,4-triphenylpenta-1,3-diene (**25**) took place with 95% yield (*Scheme 5*). Besides the spectroscopic characterization, the oxidation of **25** furnished benzophenone and acetophenone. Catalytic hydrogenation converted **25** to 1,1,4-triphenylpentane (**28**). Supposedly, **25** has the (*E*)-configuration at the C(3)=C(4) bond. Compound **25** has

Table 2. *2-Ethenyl-1,1-diphenylcyclopropanes as Products of Cycloadditions of* **DDM** *with Monosubstituted Buta-1,3-dienes*

	R	Yield [%]	M.p. (B.p. at 10^{-3} Torr)	^{1}H-NMR Chemical shifts [ppm] and coupling constants [Hz]		
				H–C(1′)	H–C(2′)	^3J(1′,2′)
7	H	79	(93–95°)	5.24	5.32	17.0 (*E*)
					5.04	9.6 (*Z*)
7	Me	33	(95–100°)	4.73	5.60	15.2 (*E*)
7	Ph	76	60–61.5°	5.46	6.55	15.8 (*E*)
7	MeO	31[a])	(120–130°)	4.25	6.60	12.6 (*E*)
9	MeO	16[a])	(120–130°)	3.83	6.05	6.3 (*Z*)
7	CO_2Me	90	66.5–67.5°	6.28	6.00	15.5 (*E*)
9	CN	91	66–67°	5.23	5.69	11.0 (*Z*)
13	Me	11[b])	(100–102°)	5.41	5.18	17.2 (*E*)
					5.01	10.7 (*Z*)
				H_a–C(2′)	H_b–C(2′)	$^2J_{gem}$
12	Me	70[b])	(100–102°)	4.58	4.79	1.4
12	Ph	48	149.5–150.5°	4.63	5.16	0.77
12	MeO	81	52.0–52.5°	3.74	3.83	2.0
12	Cl	74	(118–121°)	4.81	4.96	1.5

[a]) Mixture **7**/**9** 74 : 26. [b]) Mixture **12**/**13** 84 : 16.



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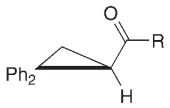
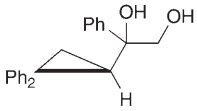


18 R = OH
19 R = Ph



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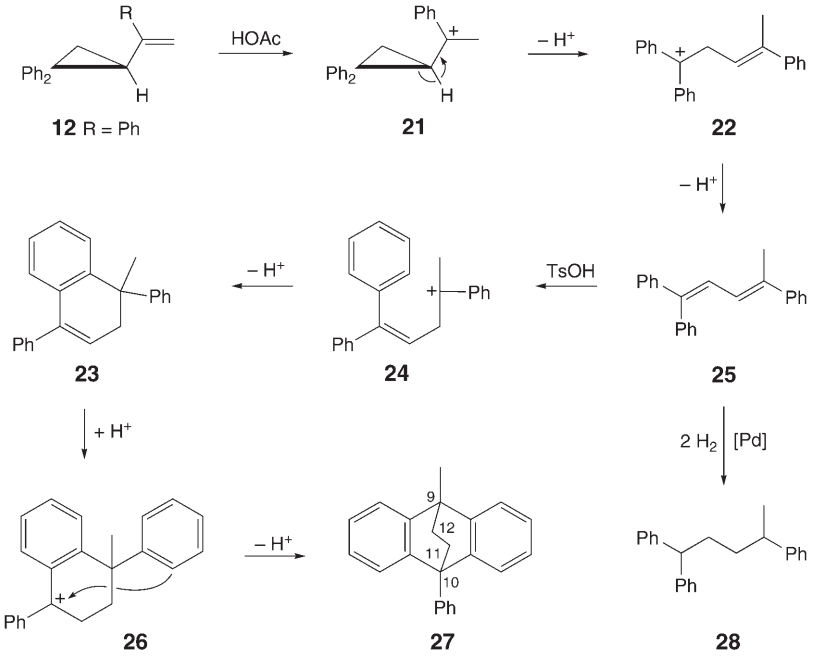
been described twice, likewise with uncertain configuration [27][28], but with the same melting point (122–124°).

Protonation at the terminal methylidene group of **12**, R = Ph, affords a carbocation **21**, which profits from benzyl and cyclopropylcarbinyl resonance: '*the cyclopropyl group is equal to or better than a phenyl in stabilizing an adjacent carbocationic center*' [29]. The rearrangement of [cyclopropylcarbinyl]$^+$ to [cyclobutyl]$^+$ and [but-3-enyl]$^+$ has long been known [30]. Ring opening of **21** provides the diphenylmethyl cation **22**, which forms **25** by proton loss.

When diene **25** (or **12**, R = Ph) was treated with toluene-4-sulfonic acid at 200°, another isomerization generated a hydrocarbon (55%), with a melting point 181–182°, stable to peracid or H_2/Pd. It turned out to be the bridgehead-substituted 9,10-dihydro-9,10-ethanoanthracene **27**. The ^{13}C-NMR spectrum shows signals of two CH_2 groups, four signals for Ph, and six signals for two equivalent benzo rings, thus revealing a plane of symmetry. The ^{1}H-NMR spectrum displays an *AA′BB′* pattern for the CH_2 groups,

Scheme 5

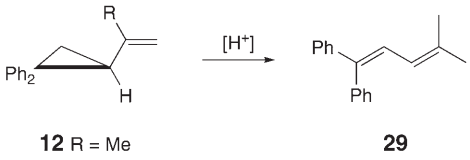


which was solved by calculation: the coupling constants, $J_{cis} = 10.6$ and $J_{trans} = 4.2$, are in accordance with other dibenzobicyclo[2.2.2]octadienes [31]. The base peak in the mass spectrum of **27** is $[M - CH_2CH_2]^+$, *i.e.*, the radical cation of methyl-phenyl-anthracene.

The interpretation in *Scheme 5* foresees a sequence of two acid-induced cationic cyclizations. The first leads to the 1,2-dihydronaphthalene derivative **23**, which, in turn, is protonated to give a new diphenyl-methyl-type cation **26**. The latter undergoes a second aromatic alkylation, which yields the 9,10-dihydroanthracene derivative **27** after proton loss. It is noteworthy that all the acid-catalyzed conversions take place in the manifold $C_{23}H_{20}$.

The major product obtained from **DDM** and isoprene (**12**, R = Me) is likewise sensitive to acid. Hot AcOH (even adsorption on silica gel was sufficient) effected the analogous formation of **29** (*Scheme 6*).

Scheme 6



2.4. *Thermal Rearrangements of the Vinylcyclopropanes to Cyclopentene Derivatives.* Compared to the classic rearrangements of organic chemistry, the thermal isomerization of vinylcyclopropane and its derivatives to yield cyclopentenes is a late discovery: it was observed by three groups in 1959/60 [32–34], but, 25 years later, a review with 228 references [35] collected the publications on all-carbon systems, neglecting, however, the rich harvest on hetero analogues. This flaring up of interest was fanned by *Woodward* and *Hoffmann* who discussed the rearrangement as a [1.3]-sigmatropic alkyl shift, but avoided a clear mechanistic conclusion [36]. In 2003, *Baldwin* competently summarized the mechanistic contributions [37] (237 references).

Most of the substituted vinylcyclopropanes of *Table 2* were subjected to the rearrangement by heating to 310° for 5 min. After high-vacuum distillation, the cyclopentenes of type **30** and **31** were isolated in good yield (*Table 3* and *Scheme 7*). In many cases, milder conditions were sufficient, as shown by 91% yield of **30**, R = Ph, after heating of **7**, R = Ph, for 10 min at 200°.

Scheme 7

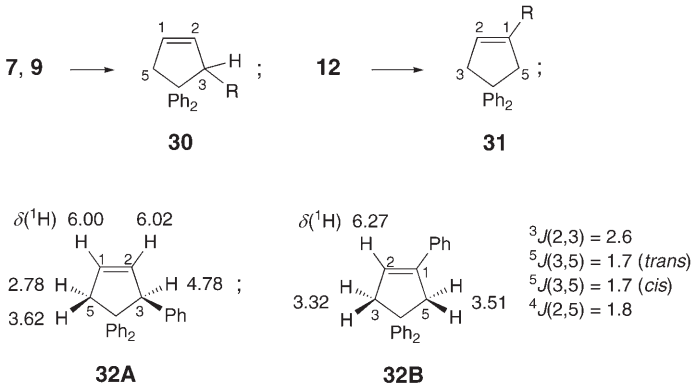


Table 3. *4,4-Diphenylcyclopent-1-enes* **30** *and* **31** *by Thermal Isomerization of 2-Ethenyl-1,1-diphenylcyclopropanes* **7**, **9**, *and* **12** *at 310°*

	R	Yield [%]	M.p. (B.p. at 10^{-3} Torr)	^{1}H-NMR Chemical shifts [ppm] and coupling constants [Hz]			
3-Substituted cyclopentenes				H–C(1)	H–C(2)	*J*(1,2)	H–C(3)
30	H	77	(100–105°)	5.74	5.74		3.02
30	Me	98	(100–105°)	6.01	6.07	5.9	3.87
30	Ph	91	68–70°	6.00	6.02	5.9	4.78
30	CO_2Me	90	52.5–53.0°	5.89	6.06	5.8	4.50
30	CN	[a])	96.0–96.5°	6.01	5.69	5.8	4.37
1-Substituted cyclopentenes				H–C(2)	H–C(3)	H–C(5)	
31	Me	87	(100–105°)	5.51	3.09	3.16	
31	Ph	59	93.5–94.0°	6.27	3.32	3.51	

[a]) Not determined.

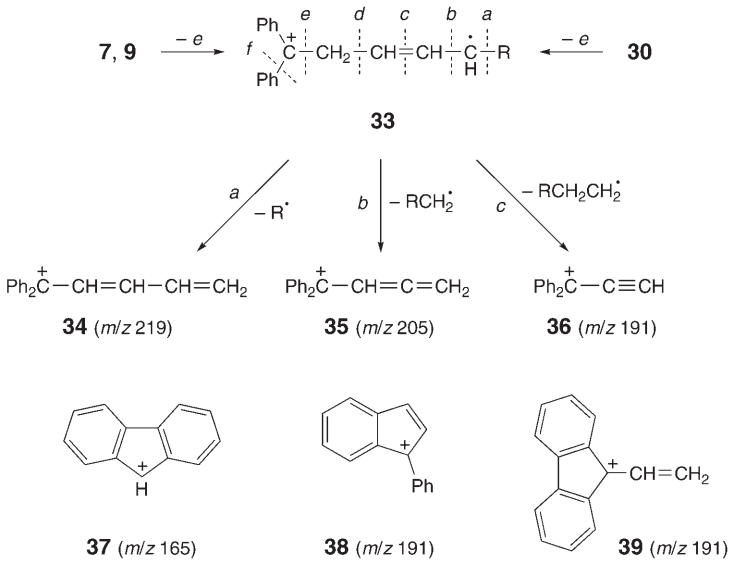
The ^{1}H-NMR spectra of the cyclopentenes **30** reveal a high propensity for H,H-coupling, like cyclopentene itself [38][39]; the latter still enjoys the bonus of symmetry. The computer simulation [25] of the 600-MHz spectrum of **30**, R = Ph, showed, that each of the five aliphatic H-atoms couples with the other four; the assignments in formula **32A** (*Scheme 7*) are based on several assumptions. The (*Z*)-ethylenic *J*(1,2) is 5.9 Hz, and the geminal *J*(5a,5b) is −16.8 Hz. The three vicinal, three allylic, and two homoallylic couplings are in the range of 1.7–2.3 Hz. With ten *J* values as variables, the simulation becomes problematic.

The 1-substituted cyclopentenes **31** are blessed with a symmetry plane, as shown in **32B** for the ^{1}H-NMR parameters of **31**, R = Ph. Double-resonance experiments disclosed that both homoallylic couplings, *trans* and *cis*, are identical ($^5J = 1.7$); for cyclopentene, the parent compound, different homoallylic couplings, $^5J_{trans} = 3.0$ and $^5J_{cis} = 2.1$, were reported [38][39].

Remarkably, the mass spectra of corresponding pairs of vinylcyclopropanes and cyclopentenes are the same. Thus, the mass spectra of, *e.g.*, **7**, **9**, and **30**, R = Ph, recorded at room temperature, are virtually indistinguishable. We doubt that the rearrangement is so fast on the level of the radical cation, but we rather tend to assume that both initial radical ions rapidly afford one and the same open-chain species **33** (*Scheme 8*). This species is a *distonic radical cation* [40], in which charge and electron spin are formally separated. With a carbocation of the diphenylmethyl type and an allylic radical, **33** should be more stable than the initial cyclic radical cations. The rapid move of one electron allows a certain distribution of cationic charge and spin density between the termini.

The dashed lines in **33** denote fragmentation pathways *a*–*f*, and all of these were observed. In the mass spectrum of **7**, R = Ph, the radicals phenyl$^\bullet$ and benzyl$^\bullet$ are lost

Scheme 8



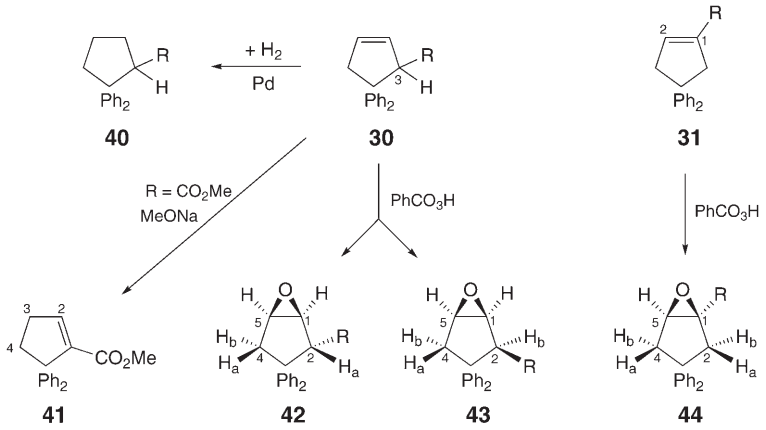
from the benzylic terminus of **33**, R = Ph, as shown by **33**, R = *p*-tolyl. With the cleavage of type *a* in **33**, *i.e.*, the ion $[M-R]^+$, all the fragmentation sequences converge, regardless of the nature of R. The bond rupture *b* reaches in $[M-CH_2R]^+$, *m*/*z* 205, one of the most populous fragments. It represents loss of Me (77%) in the case of **33**, R = H, whereas **33**, R = MeO, loses $MeOCH_2^{\cdot}$, and in the mass spectrum of **33**, R = Ph or *p*-tolyl, *m*/*z* 205 constitutes the base peak.

The speculative formulae **34**–**36** contain conjugated diphenylmethyl cations and may help to visualize the fragmentations *a*–*c*. The dehydrocyclization of diphenylmethyl to fluorenyl cations is well-known in mass spectrometry [41]. As the result of cleavage *e*, more [fluorenyl]$^+$ (*m*/*z* 165, **37**) than [benzhydryl]$^+$ (*m*/*z* 167) was observed, *e.g.*, 49% of **37** and 8% of Ph_2CH^+ from **33**, R = H. Thus, **39** appears more probable than **36** for *m*/*z* 191, and [9-phenylindenyl]$^+$ (**38**) is another alternative. The peak at *m*/*z* 115 ([indenyl]$^+$) occurs in all mass spectra of **7**, **9**, and **30**, and so does *m*/*z* 178 (diphenylacetylene, phenanthrene) as product of cleavage *d*.

Chemical evidence for the cyclopentene structures came from the catalytic hydrogenation of **30**, R = Me, Ph, and CO_2Me, which provided the cyclopentanes **40** (*Scheme 9*). During the thermolysis of **7**, R = CO_2Me, no shift of the C=C bond into conjugation occurred; the conversion of **30**, R = CO_2Me, to **41** required catalysis by MeONa. Perbenzoic acid converted **30** and **31** to the crystalline epoxides **42**–**44**. Their IR spectra show the strong *as*-stretching frequency C–O–C near 845 cm^{-1}, characteristic for oxiranes [26]. The ^{1}H-NMR spectra reveal that the epoxide H-atoms, H–C(1) and H–C(5) have a low propensity for coupling; $^3J(1,5) < 1$ Hz is not resolved, but only diagnosed from an increased line width.

An epoxidation *trans* to the 3-substituent R of **30** is the less-hindered pathway. There is ^{1}H-NMR evidence for the *exo*-position of R = Ph, CO_2Me, at the oxabicyclo system in compliance with **42**. Only in the epoxidation of **30**, R = Me, both steric paths were observed, as shown by **42**/**43** formed in the ratio of 74:26. It is H_b–C(4) of **42**, rather than H_a–C(2) of **43**, that couples with the oxirane H–C(5). This assignment rests on the reliability of $J_{vic,cis} > J_{vic,trans}$ in cyclopentanes.

Scheme 9



3. Conclusions. – The 1,3-dipolar cycloaddition of **DDM** to the C(3)=C(4) bond of 1- or 2-substituted buta-1,3-dienes at room temperature offers a convenient and general access to 1,1-diphenyl-2-vinylcyclopropanes substituted in 1′- or 2′-position (*i.e.*, **7**, **9**, and **10**). The rapid N_2 loss from the initially formed 4,5-dihydro-3*H*-pyrazoles exceeds the rate of cycloaddition. Electron-releasing substituents in the butadienes slow down the cycloaddition, and the first-order decomposition of **DDM** begins to compete.

DM cycloadditions are much faster; the dihydropyrazoles are isolable, and the N_2 elimination requires heating [13]. A disadvantage is the formation of **DM**-bisadducts, which are favored with butadienes bearing electron-attracting 1-substituents (CO_2R, CN). Diazophenylmethane stands in 1,3-dipolar activity in between, but closer to **DM** [20]; its reactions with butadienes have not been studied so far.

The thermal ring expansion of the 1,1-diphenyl-2-vinylcyclopropanes to 4,4-diphenylcyclopentenes **30** and **31** proceeds smoothly and appears to be free of major side reactions.

We express our thanks to the *Fonds der Chemischen Industrie*, Frankfurt, for support. Dr. *David S. Stephenson* deserves our gratitude for the computer simulation of ^{1}H-NMR spectra. We owe special thanks to *Claudia Dubler*, who competently dealt with the NMR spectra. Furthermore, we thank *Sonja Kosak* for recording the mass spectra, and to *Helmut Schulz* for carrying out the elemental analyses.

Experimental Part

1. *General.* PLC is prep. layer chromatography on 20 × 20 cm glass plates, often with 2-mm siliga gel *Merck 60 PF_{254}*. IR Spectra were either taken from KBr disks with a *Perkin-Elmer 125* instrument or recorded with *Perkin-Elmer BX II* as ATR spectra (without KBr, attenuated total reflection); *oop* is out-of-plane deformation, and *str* the stretching frequency. NMR spectra were recorded with *Varian Systems 300*, *400*, or *600*, some with *Varian A60*, and all ^{13}C-NMR spectra were ^{1}H-decoupled and used DEPT. Solvent was acid-free $CDCl_3$, if not otherwise stated. The MS are EI spectra at 70 eV, recorded on a *MAT 95Q* instrument. High resolutions (HR) were obtained with the program CMASS; small distortions of *m*/*z* can occur when ^{13}C or ^{37}Cl isotope peaks were not fully separated. Intensities of isotope peaks are given as, *e.g.*, ^{13}C % calc./% found, and HR as calc./found. Tentative assignments of frequently occurring *m*/*z* peaks are given for **7**, R = H, and are not repeated later. Molecular mass with vapor pressure osmometer in $CHCl_3$ (*Mechrolab*).

2. *Rate Measurements of Cycloadditions of Diazodiphenylmethane* (**DDM**). 2.1. *Anal. Method.* The solns. of **DDM** (50 ml) [42] and dipolarophile (20 ml) in carefully purified DMF [43] were thermostated at 40.0 ± 0.1°. After combination of the two, the soln. was *ca.* 90 mM in **DDM**, and the concentration of dipolarophile was nearly ten times larger. The soln. was briefly purged with N_2, and 2-anilinonaphthalene (0.4 g) was added as polymerization inhibitor [44]. After suitable reaction times, 5-ml samples were withdrawn with an *Inaltera* syringe and injected through a rubber septum into a long-necked 50-ml flask. The latter contained 2M Cl_3CCOOH in $MeOCH_2CH_2OH$ (15 ml) at 20.0 ± 0.1° and was connected to a double-walled gas buret (25 ml); water of 20.0° was pumped through the mantle. The N_2 evolution was completed by shaking the flask, until the gas volume remained constant (*ca.* 2 min). About 8–12 samples were drawn to reach 65–80% conversion.

The rate constants of pseudo-first order were graphically evaluated from the N_2 volumes, corrected to 720 Torr/25°; $8.1 \cdot 10^{-7}$ s^{-1}, *i.e.*, the k_1 of the **DDM** thermolysis at 40° (see below), was subtracted, an important correction for the less reactive butadienes. The second-order-rate constant k_2 resulted when $k_{1\psi}$(corr.) was divided by 0.95 [dipolarophile]$_o$, *i.e.*, the concentration at half-conversion. The k_2 of two independent runs rarely differed by more than 5%. The *Eyring* parameters for **DDM** + 1-phenylbuta-1,3-diene (*Sect. 2.2*) came from measurements at 25°, 35°, and 40° (k_2 = 0.15, 0.37, and 1.34×10^{-5} [$M^{-1}s^{-1}$]).

2.2. *Thermolysis of* **DDM** *in DMF.* By the same method, the decomposition rate was measured in 0.132M **DDM** in DMF at 40.0 ± 0.1°; the N_2 volumes fit the first-order law up to 65%. Two runs gave k_1 = 8.0 and $8.1 \cdot 10^{-7}$ s^{-1}, which corresponds to $t_{1/2}$ = 239 h. Experiments at different temp. ($k_1 = 1.11 \cdot 10^{-7}$ at 24.8° and $25.1 \cdot 10^{-7}$ at 50.0° [M^{-1} s^{-1}]) provided $\Delta H^{\#} = 23.1$ kcal mol^{-1} and $\Delta S^{\#} = -13$ e.u.

3. *2-Ethenyl-1,1-diphenylcyclopropane* (**7**, R = H). *Buta-1,3-diene* (12.5 g, 231 mmol) and **DDM** (9.70 g, 49.9 mmol) were reacted in a thick-walled sealed glass tube at r.t.; after 2 weeks, the deep-red color of the soln. was changed to orange. After cooling, the tube was opened, the N_2 pressure was relieved, and the excess of butadiene was removed. Distillation at 110–115°/10^{-3} Torr furnished **7**, R = H, as a colorless liquid (8.71 g, 79%); when the residue was triturated with Et_2O, *benzophenone azine* as product of decomposition of **DDM** was obtained. Redistillation of **7**, R = H, from a microflask (b.p. 93–95°/10^{-3} Torr) gave the anal. sample, n_D^{20} 1.5915. IR (film): 694v*s*, 751*s* (arom. *oop*), 898*s*, 988*m* (vinyl *oop*); 1445*m*, 1493*s*, 1600*m* (arom. breath. modes); 1631*m*, 1660*m* (C=C *str*). ^{1}H-NMR (300 MHz): 1.64 (*dd*, $^2J_{gem}$ = 5.1, $^3J_{trans}$ = 5.8, H_a–C(3)); 1.72 (*dd*, $^2J_{gem}$ = 5.1, $^3J_{cis}$ = 8.6, H_b–C(3)); 2.44 (*m*, 6 lines visible, H–C(2)); 5.04 (*ddd*, $^3J_{(Z)}$ = 9.6, $^2J_{gem}$ = 1.2, ^4J(2′a,2) = 2.4, H_a–C(2′)); 5.32 (*ddd*, $^3J_{(E)}$ = 17.0, $^2J_{gem}$ = 1.2, ^4J(2′b,2) = 2.4, H_b–C(2′)); 5.24 (*ddd*, $^3J_{(E)}$ = 17.0, $^3J_{(Z)}$ = 9.7, ^3J(1′,2) = 8.6, H–C(1′)); 7.2–7.5 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz): 22.3, 31.1, 37.2 (C(3), C(2), C(1)); 113.9, 139.3 (C(2′), C(1′)); 126.0, 126.6 (2 arom. *p*-CH); 127.4, 128.4 (2×), 131.0 (8 arom. *o*,*m*-CH); 141.4, 146.7 (2 arom. C_q). MS: 220 (82, M^+; HR 220.1248/220.1249; ^{13}C 15.4/13.2), 219 (24, **34**), 205 (47, [$M - CH_2 - H$]$^+$, ^{13}C 13.6/14.3, **35**), 204 (27, [$M - CH_2 - 2H$]$^+$, $C_{16}H_{12}^+$), 203 (22), 192 (12, [$M - CH_2CH_2$]$^+$, $C_{15}H_{12}^+$ perhaps $Ph_2C{=}C{=}CH_2^+$ or [methylphenanthrene]$^+$), 191 (27, $C_{15}H_{11}^+$, **38** or **39**), 182 (26, $C_{14}H_{14}^+$; ^{13}C 4.0/3.6, [diphenylethane]$^+$), 180 (11, $Ph_2C{=}CH_2^+$), 179 (17, $C_{14}H_{11}^+$, [9-methylfluorenyl]$^+$), 178 (27, $C_{14}H_{10}^+$, PhC≡CPh or phenanthrene), 167 (8, [benzhydryl]$^+$), 165 (49, [9-fluorenyl]$^+$, **37**; HR 165.0702/165.0697), 152 (11, $C_{12}H_8^+$, [biphenylene]$^+$), 142 (48, $C_{11}H_{10}^+$, possibly Ph–CH=CH–C≡C–CH_3^+ or [methylnaphthalene]$^+$), 141 (30, $C_{11}H_9^+$, [1-vinylinden-1-yl]$^+$ or [naphthylmethyl]$^+$), 129 (100, $C_{10}H_9^+$; ^{13}C 11.1/12.6, Ph–CH$^+$–CH=C=CH_2 or [methylindenyl]$^+$), 128 (43, $C_{10}H_8^+$, [naphthalene]$^+$), 115 (31, $C_9H_7^+$, PhCH$^+$–C≡CH or [1-indenyl]$^+$), 105 (42, $C_8H_9^+$, PhCH$^+$–CH=CH_2), 101 (16), 91 (42, $C_7H_7^+$, PhCH$_2^+$/[tropylium]$^+$), 77 (41, Ph$^+$), 43 (26, [isopropyl]$^+$). Anal. calc. for $C_{17}H_{16}$ (220.30): C 92.68, H 7.32; found: C 92.07, H 7.20.

4. *1,1-Diphenyl-2-[(*E*)-prop-1-enyl]cyclopropane* (**7**, R = Me). *(*E*)-Piperylene* (*Fluka*; 3.40 g, 49.9 mmol), **DDM** (10.7 g, 55 mmol), and 2-anilinonaphthalene (0.20 g) as polymerization [44] inhibitor were dissolved in benzene (10 ml) and kept at r.t. for 2 months; N_2 evolution and decolorization were observed. Workup gave *benzophenone azine* (2.16 g), identified by mixed m.p. and IR spectrum. Distillation at 95–100°/10^{-3} Torr afforded **7**, R = Me, (3.86 g, 33%); a redistilled colorless liquid showed n_D^{20} 1.5839. IR (film): 694v*s*, 743*s* (arom. *oop*), 950 + 957*s* (*trans*-CH=CH *oop*), 1440*s*, 1488*s*, 1574*w*, 1595*s* (arom. ring vibr.), 1657*w* (C=C *str*). ^{1}H-NMR (60 MHz): 1.55 (*dd*, ^3J = 6.4, ^4J = 1.5, Me; superimposed by *m* of CH_2(3)); 2.23 (*dt*, ^3J(2,3*cis*) = ^3J(2,1′) = 8.7, ^3J(2,3*trans*) = 6.8, H–C(2)); 4.73 (*ddq*, $^3J_{(E)}$ = 15.2, ^3J(2,1′) = 8.7, ^4J = 1.4, H–C(1′)); 5.60 (*dq*, ^3J = 15.2 and 6.4, H–C(2′)). Anal. calc. for $C_{18}H_{18}$ (234.32): C 92.26, H 7.74; found: C 91.85, H 7.48.

5. *1,1-Diphenyl-2-[(*E*)-2-phenylethenyl]cyclopropane* (**7**, R = Ph). 5.1. *Preparation.* The soln. of **DDM** (17.5 g, 90.0 mmol) and 2-anilinonaphthalene (0.20 g) in *(*E*)-1-phenylbuta-1,3-diene* (23.4 g, 180 mmol, [44]), were reacted at r.t., and the deep-red color vanished in 4 weeks. After distilling the excess of **1**, R = Ph, at 75°/10^{-3} Torr, the residue was subjected to column chromatography (CC; 100 g silica gel) with petroleum ether (b.p. 40–55°) and furnished **7**, R = Ph, as a colorless oil, which solidified. Recrystallization from EtOH gave needles (20.3 g, 76%). M.p. 60–61.5°. IR (ATR): 957*s*, 968*m*, 979*m* (*trans*-CH=CH *oop*); 1443*m*, 1493*s*, 1596*m* (arom. ring vibr.), 1638*w* (C=C str). ^{1}H-NMR (400 MHz): The non-aromatic 5-H system was simulated by DAVINX [25] and provided 1.59 (H_a–C(3)); 1.73 (H_b–C(3)); 2.40 (H–C(2)); 5.46 (H–C(1′)); 6.55 (H–C(2′)); ^3J(2,3a) = 5.84 (*trans*), ^3J(2,3b) = 8.64 (*cis*), ^3J(2,1′) = 9.61, ^4J(2,2′) = 0.70, ^2J(3a,3b) = –4.99, and $^3J_{(E)}$ = 15.8; 7.10–7.42 (*m*, 15 arom. H). ^{13}C-NMR (100 MHz): 22.9 (C(3)); 31.1 (C(2)); 37.6 (C(1)); 125.7, 127.1, 128.30, 128.34, 128.42, 131.0 (6 signals for 12 arom. *o*,*m*-CH, as expected for free Ph rotation); 125.85, 126.64, 126.68, 129.1, 131.6 (5 signals of lower intensity for C(1′), C(2′), and 3 arom. *p*-CH); 137.7, 141.3, 146.5 (3 arom. C_q). MS (25°): 296 (47, M^+; HR 296.1560/296.1563), 219 (9, [M – Ph]$^+$, $C_{17}H_{15}^+$), 218 (29, [M – Ph – H]$^+$, $C_{17}H_{14}^+$), 217 (15), 206 (38), 205 (100, [$M - PhCH_2$]$^+$, $C_{16}H_{13}^+$; HR 205.1014/205.1003, **35**), 204 (31, [M – toluene]$^+$, $C_{16}H_{12}^+$), 203 (35), 192 (24, [M – styrene]$^+$, $C_{15}H_{12}^+$), 191 (21, $C_{15}H_{11}^+$), 178 (24, $C_{14}H_{10}^+$), 167 (8, $C_{13}H_{11}^+$),

165 (37, $C_{13}H_9^+$, **37**), 115 (35, $C_9H_7^+$), 91 (41, $C_7H_7^+$), 77 (8, Ph^+). Anal. calc. for $C_{23}H_{20}$ (296.39): C 93.20, H 6.80; found: C 93.26, H 6.75.

5.2. *$KMnO_4$ Oxidation.* The soln. of **7**, R = Ph, (593 mg, 2.0 mmol) in pyridine (20 ml) was treated at 50–55° with $KMnO_4$ (4 mmol); the MnO_2 was filtered and washed with Na_2CO_3; workup with HCl/Et_2O gave 350 mg of colorless crystals. In boiling H_2O, 310 mg (73%) of *2,2-diphenylcyclopropane-1-carboxylic acid* (**18**), m.p. 167–169°, remained undissolved. After recrystallization from acetone/H_2O, m.p. 168–169.5°; the identity with authentic **18** [45] was established by mixed m.p., and IR spectrum. ^{1}H-NMR (60 MHz): 1.59 (*dd*, $^2J_{gem}$ = 4.8, $^3J_{cis}$ = 7.9, H_a–C(3)); 2.07 (*dd*, $^2J_{gem}$ = 4.8, $^3J_{trans}$ = 5.6, H_b–C(3)); 2.46 (*dd*, $^3J_{cis}$ = 7.9, $^3J_{trans}$ = 5.6, H–C(1)). Ether extracted from the aq. phase *benzoic acid* (165 mg, 68%) in colorless needles, m.p. 118–119° (mixed m.p.).

6. *2-[(*E*)-2-Methoxyethenyl]-1,1-diphenylcyclopropane* (**7**, R = MeO) *and the Corresponding (*Z*)-Isomer* **9**, *R = MeO.* 6.1. *Preparation.* The homogenous mixture of *1-methoxybuta-2,3-diene* [46] (12.60 g, 150 mmol; (*E*)/(*Z*) 60:40, based on δ(H) 3.51 and 3.47 for MeO), **DDM** (9.71 g, 50 mmol), and 2-anilinonaphthalene (200 mg) slowly developed N_2, but, even after 55 days at r.t. the red color of **DDM** had not completely disappeared. The excess of 1-methoxybuta-2,3-diene was distilled at 12 Torr, the brown residue digested with petroleum ether, polymeric material filtered, the soln. subjected to CC over alumina (neutral, 40 g), and eluted with petroleum ether/Et_2O 9:1. Distillation at 120–130° (bath)/10^{-3} Torr gave 5.85 g (47%) crude material. On renewed CC (silica gel, (100 g); eluant as before), the first fraction furnished, after distillation at 130°/10^{-3} Torr, the mixture of **7** and **9**, R = MeO ((*E*)/(*Z*) 74:26, 4.12 g, 33%). n_D^{20} 1.5853. IR (film): 928*s* (olefin. *oop*); 1101*s*, 1121*m*, 1206*s*, (C–O–C *str as* and *sy*), 1651*s* (C=C *str*). ^{1}H-NMR (300 MHz): 1.54, 1.71 (2*m*, H_a–C(3) and H_b–C(3) of (*E*) and (*Z*)); 2.32, 2.82 (2*m*, (*E*)/(*Z*) 73:27, H–C(2)); 3.45, 3.74 (2*s*, (*E*)/(*Z*) 74:26, Me); 3.83 (*dd*, $^3J_{(Z)}$ = 6.2, $^3J(1',2)$ = 9.6, H–C(1′) of (*Z*)); 4.25 (*dd*, $^3J_{(E)}$ = 12.6, $^3J(1',2)$ = 9.0, H–C (1′) of (*E*), (*E*)/(*Z*) 73:27); 6.05 (*d*, $^3J_{(Z)}$ = 6.3, H–C(2′) of (*Z*)); 6.60 (*d*, $^3J_{(E)}$ = 12.6, H–C(2′) of (*E*)); 7.33–7.56 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz, (*E*)/(*Z*) ratio from peak heights): 22.3, 22.8 (C(3) of (*E*) and (*Z*)); 26.4, 23.0 (C(2), (*E*)/(*Z*) 74:26); 35.8, 36.6 (C(1), (*E*)/(*Z*) 74:26); 56.0, 59.8 (MeO, (*E*)/(*Z*) 78:22); 104.2, 107.3 (C(1′), (*E*)/(*Z*) 73:27); 141.6, 141.9 (C(2′) of (*E*)/(*Z*)); arom. CH of (*E*) and (*Z*) assigned; 141.6, 147.02 (2 arom. C_q of (*E*)); 141.9, 147.03 (2 arom. C_q of (*Z*)). MS: 250 (19, M^+, $C_{18}H_{18}O^+$; HR 250.1353/250.1347, ^{13}C 3.8/3.9), 219 (18, $[M - MeO]^+$), 218 (33, $[M - MeOH]^+$), 217 (21), 205 (37, $[M - CH_2OMe]^+$, $C_{16}H_{13}^+$), 204 (16), 193 (32), 192 (58), 191 (31), 183 (25, $Ph_2C{=}OH^+$), 182 (52, $C_{13}H_{10}O^+$; HR 182.0729/182.0716, benzophenone), 180 (28), 178 (28), 167 (22), 165 (41), 115 (27), 105 (100, $C_6H_5{-}C{\equiv}O^+$, HR 105.0339/105.0313 (a shift of the O-function in the ring-opened M^+ is conceivable), 91 (50), 77 (55), 43 (16). Anal. calc. for $C_{18}H_{18}O$ (250.32): C 86.36, H 7.25; found: C 85.93, H 7.23.

6.2. *Oxidation of* **7**, *R = MeO.* The reaction with $KMnO_4$ in acetone afforded **18** (61%). Colorless crystals. M.p. 168–169.5°; mixed m.p. without depression.

7. *Methyl (*E*)-3-(2,2-Diphenylcyclopropyl)prop-2-enoate* (**7**, R = CO_2Me). 7.1. *Preparation. Methyl (*E*)-buta-1,3-diene-1-carboxylate* (5.60 g, 49.9 mmol) [47][48], **DDM** (10.68 g, 55 mmol), and 2-anilinonaphthalene (200 mg) were dissolved in benzene (30 ml). After 3 weeks, the N_2 evolution was finished, and the red color had faded. Distillation at 160–165° (bath)/10^{-3} Torr furnished **7**, R = CO_2Me, as a yellow oil (12.46 g, 90%), which solidified. M.p. 50–60°. Recrystallization from MeOH gave colorless prisms (11.60 g). M.p. 66.5–67.5°. IR (ATR): 951*s*, 984*s* (olefin. *oop*); 1146v*s*, 1243*s* (C–O); 1438*s*, 1493*m*, 1600*w* (arom. ring vibr.), 1644*s* (C=C), 1714*s* (C=O). ^{1}H-NMR (300 MHz)[2]): 1.74 (*t*-like, $J \approx 5.3$, H_a–C(3′)); 1.83 (*dd*, $^3J_{cis}$ = 8.5, $^2J_{gem}$ = 5.1, H_b–C(3′)); 2.41 (*ddd*, $^3J_{trans}$ = 5.6, $^3J_{cis}$ = 8.5, $^3J(2',3)$ = 10.5, H–C(2′)); 6.00 (*d*, $^3J_{(E)}$ = 15.5, H–C(2)); 6.28 (*dd*, $^3J(3,2')$ = 10.5, $^3J_{(E)}$ = 15.5, H–C(3)); the assignments of the non-aromatic H-atoms were confirmed by HSQCAD. ^{13}C-NMR (75.5 MHz)[2]): 23.3 (C(3′)); 30.2 (C(2′)); 39.7 (C(1′)); 51.3 (MeO), 119.6 (C(3)); 126.3, 127.1 (arom. *p*-CH); 127.8, 128.45, 128.65, 130.5 (8 arom. *o,m*-CH); 140.5, 145.5 (2 arom. C_q); 150.4 (C(2)); 166.8 (C=O). MS: 278 (45, M^+; HR 278.1302/278.1310; ^{13}C 9.5/8.6), 246 (15, $[M - MeO - H]^+$, $C_{18}H_{14}O^+$), 219 (36, $[M - CO_2Me]^+$, $C_{17}H_{15}^+$), 218 (38, $[M - HCO_2Me]^+$), 217 (41, $C_{17}H_{13}^+$), 205 (10), 204 (31), 203 (33), 202 (33), 192 (15), 191 (16), 187 (23), 180 (17), 178 (20), 165 (45), 141 (25), 115 (26), 111 (43, $C_6H_7O_2^+$; HR 111.0444/

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[2]) The nonsystematic C-atom numbering used for assignments corresponds to that indicated in the *Formulae.*

111.0404), 98 (100, $C_5H_6O_2^+$, HR 98.0366/98.0303, $MeC{\equiv}C-CO_2Me^+$ or $H_2C{=}C{=}CH-CO_2Me^+$), 91 (62), 77 (13). Anal. calc. for $C_{19}H_{18}O_2$ (278.33): C 81.98, H 6.52; found: C 82.05, H 6.57.

7.2. *Oxidation of* **7**, *R* = *CO*$_2$*Me*. The reaction with $KMnO_4$ in acetone produced **18** (88%). M.p. 167–169°; mixed m.p. without depression and ^{1}H-NMR spectrum confirmed the structure.

8. *(Z)-3-(2,2-Diphenylcyclopropyl)prop-2-enenitrile* (**9**, R = CN). 8.1. *Preparation*. *Buta-1,3-diene-1-carbonitrile* (*Knapsack-Griesheim AG*; (*Z*)/(*E*) 98 : 2, 1.98 g, 24.7 mmol), **DDM** (5.34 g, 27.5 mmol), and 2-anilinonaphthalene (100 mg) in benzene (15 ml) reacted at r.t. in 10 d. Distillation at 165° (bath)/10^{-3} Torr furnished a light-yellow oil (6.06 g) that solidified; recrystallization from MeOH gave **9**, R = CN (5.50 g, 91%). Colorless prisms. M.p. 66–67°. IR (ATR): 960*s* (C=C *oop*); 1485*s*, 1493*s*, 1597*m* (arom. breath. modes), 1613*s* (C=C conj. *str*), 2112*s* (C≡N conj. *str*). ^{1}H-NMR (300 MHz)^2): 1.79 (*t*, $^2J_{gem} \approx {}^3J_{trans} \approx 5.3$, $H_a-C(3')$); 1.88 (*dd*, $^3J_{cis} = 8.5$, $^2J_{gem} = 5.1$, $H_b-C(3')$); 2.88 (*ddd*, $^3J(2',3) = 10.7$, $^3J_{cis} = 8.6$, $^3J_{trans} = 5.4$, $H-C(2')$); 5.23 (*dd*, $^3J_{(Z)} = 11.0$, $^4J(2,2') = 0.5$, $H-C(2)$); 5.69 (*t*, $^3J_{(Z)} \approx {}^3J(3,2') \approx 10.7$, $H-C(3)$); 7.2–7.4 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz)^2): 23.4 (C(3′)); 28.9 (C(2′)); 40.4 (C(1′)); 97.2 (C(2)); 116.8 (C≡N); 126.7, 127.2 (2 arom. *p*-CH); 127.7, 128.61, 128.73, 130.2 (8 arom. *o*,*m*-CH); 140.4, 144.6 (2 arom. C_q); 155.8 (C(3)). MS: 245 (55, M^+), 244 (100, $[M-H]^+$; HR 244.1123/244.1104), 217 (15, $[M-CN-2H]^+$, $C_{17}H_{13}^+$), 205 (13, $[M-CH_2CN]^+$, $C_{16}H_{13}^+$), 203 (17), 202 (14), 192 (12, $[M-H_2C{=}CHCN]^+$, $C_{15}H_{12}^+$), 191 (13, $C_{15}H_{11}^+$), 178 (18, $C_{14}H_{10}^+$), 168 (87, $C_{12}H_{10}N^+$), 167 (41, $[M-Ph-2H]^+$, $C_{12}H_9N^+$; HR 167.0733/167.0714), 165 (40), 154 (15 $[M-CH_2Ph-H]^+$, $C_{11}H_8N^+$), 115 (15), 91 (18), 77 (6). Anal. calc. for $C_{18}H_{15}N$ (245.31). C 88.13, H 6.16, N 5.71; found: C 87.97, H 6.18, N 5.98.

8.2. *Oxidation of* **9**, *R* = *CN*. The reaction with $KMnO_4$ in aq. acetone afforded **18**, m.p. 169.5–170°, and showed the intact cyclopropane ring.

9. *2-(1-Methylethenyl)-1,1-diphenylcyclopropane* (**12**, R = Me) *and 1-Ethenyl-1-methyl-2,2-diphenylcyclopropane* (**13**, R = Me). 8.1. *Preparation*. *Isoprene* (20.4 g, 300 mmol), **DDM** (11.65 g, 60 mmol), and 2-anilinonaphthalene (0.2 g) were kept at r.t. for 50 d. A light-yellow liquid (11.36 g, 81%) was distilled at 100–102°/10^{-3} Torr, $n_D^{20} = 1.5829$. TLC showed two spots, and the NMR signals of Me established the two title compounds in the ratio 86 : 14. IR (film): 881*s*, 1026*m* (olefin. *oop*), 1445*s*, 1493*s*, 1579*w*, 1597*m* (arom. ring vibr.), 1629*w*, 1648*w* (C=C *str*). ^{1}H-NMR (300 MHz) of **12**, R = Me: 1.49 (*dd*, $^2J_{gem} = 5.3$, $^3J_{cis} = 8.7$, $H_a-C(3)$); 1.64 (*s*, broadened, Me); 1.88 (*dd*, $^2J_{gem} = 5.3$, $^3J_{trans} = 6.5$, $H_b-C(3)$); 2.38 (*t*-like, $H-C(2)$); 4.68, 4.79 (2*d*, $^2J_{gem} = 1.4$, $CH_2(2')$); 7.15–7.60 (*m*, 10 arom. H). ^{1}H-NMR of **13**, R = Me^2): 3 H of cyclopropane overlap with those of **12**, R = Me; 1.20 (*s*, Me); 5.01 (*dd*, $^3J_{(Z)} = 10.6$, $^2J_{gem} = 1.5$, $H_a-C(2')$); 5.18 (*dd*, $^3J_{(E)} = 17.2$, $^2J_{gem} = 1.5$, $H_b-C(2')$); 5.41 (*dd*, $^3J_{(Z)} = 10.7$, $^3J_{(E)} = 17.2$, $H-C(1')$); 7.15–7.60 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz; assignments of **12** and **13** by signal height) of **12**, R = Me: 18.8 (C(3)); 23.0 (Me); 33.6 (C(2)); 37.5 (C(1)); 111.7 (C(2′)); 125.97, 126.26 (2 arom. *p*-CH); 127.94, 128.12, 128.35, 130.11 (8 arom. *o*,*m*-CH); 141.0, 142.9, 147.1 (C(1′) and 2 arom. C_q). ^{13}C-NMR of **13**, R = Me^2): 19.3 (Me); 27.1 (C(3)); 28.6 (C(2)); 43.5 (C(1)); 110.8 (C(2′)); 126.15, 126.21 (2 arom. *p*-CH); 128.25, 128.37, 129.64, 130.26 (8 arom. *o*,*m*-CH); 144.0, 144.1, 144.7 (C(1′) and 2 arom. C_q). MS (**12**/**13** 86 : 14): 234 (66, M^+; HR 234.1404/234.1403), 219 (90, $[M-Me]^+$; ^{13}C 16.9/15.9), 205 (50, $[M-CH_2Me]^+$), 191 (36, $[M-CH_2CH_2Me]^+$), 165 (45), 156 (25, $[M-Ph-2H]^+$), 143 (100, $[M-CH_2Ph]^+$; HR 143.0858/143.0843), 128 (38), 115 (42), 105 (11), 91 (76), 77 (17). Anal. calc. for $C_{18}H_{18}$ (234.32): C 92.26, H 7.74; found: C 92.31, H 7.89.

9.2. *4-Methyl-1,1-diphenylpenta-1,3-diene* (**29**). *a*) The mixture of **12**, R = Me, and **13**, R = Me (86 : 14, 500 mg, 2.13 mmol) was refluxed in AcOH (10 ml) for 1 h; at 110–115°/10^{-3} Torr, a pale-yellow oil (495 mg) was distilled which contained **29** and **13**, R = Me, 85 : 15. ^{1}H-NMR of **29** (60 MHz): 1.86, 1.73 (2*s* broadened, 2 Me); 5.95 (*dq*, $^3J(2,3) = 11.4$, $^4J(2,Me) = 1.3$, $H-C(3)$); 6.92 (*d*, $^3J(2,3) = 11.6$, $H-C(2)$); 7.1–7.5 (*m*, 10 arom. H). Anal. calc. for $C_{18}H_{18}$ (234.32): C 92.26, H 7.74; found: C 92.44, H 7.74.

b) Cyclopropanes **12**, R = Me, and **13**, R = Me, (86 : 14) were subjected to CC (silica gel; petroleum ether) and furnished after distillation a mixture of **29**, **12**, R = Me, and **13**, R = Me, 69 : 18 : 13 (^{1}H-NMR analysis).

10. *1,1-Diphenyl-2-(1-phenylethenyl)cyclopropane* (**12**, R = Ph). 10.1. *Preparation*. The homogenous mixture of *2-phenylbuta-1,3-diene* [49] (19.53 g, 150 mmol), **DDM** (9.71 g, 50.0 mmol), and 2-anilinonaphthalene (200 mg) was reacted at r.t. without solvent for 37 d; after 20 d, the crystallization started. Trituration with a small amount of Et_2O gave **12**, R = Ph (7.10 g, 48%) as prisms, m.p. 136–147°;

after recrystallization from AcOEt, m.p. 149.5–150.5°. The mother liquor contained oligomers of the diene; only 1.58 g of 2-phenylbuta-1,3-diene was re-isolated by distillation. IR (ATR) of **12**, R = Ph: 895*s* (C=CH_2 *oop*), 1442*s*, 1450*m*, 1492*s*, 1552*w*, 1599*w* (arom. breath. modes), 1625*m* (C=CH_2 *str*). ^{1}H-NMR (400 MHz): simulation of the 5 non-arom. H by DAVINX [25] led to 1.59 (H_b–C(3)); 1.92 (H_a–C(3)); 2.72 (H–C(2)); 4.63 (H_a–C(2′)); 5.16 (H_b–C(2′)); ^2J(3a,3b) = –5.29, ^3J(2,3b) = 8.74 (*cis*), ^3J(2,3a) = 6.68 (*trans*), ^4J(2,2′a) = 1.20, ^4J(2,2′b) = 0.27, ^2J(2′a,2′b) = 0.77; 7.10–7.45 (*m*, 15 arom. H). ^{13}C-NMR (100 MHz): 19.7 (C(2)); 31.7 (C(3)); 38.8 (C(1)); 112.4 (C(2′)); 125.9, 126.23, 127.26 (3 arom. *p*-CH); 126.3, 127.43, 127.68, 128.16, 128.32, 130.7 (12 arom. *o*,*m*-CH); 140.2, 142.2, 144.6, 146.6 (C(1′) and 3 arom. C_q). MS: 296 (M^+, $C_{23}H_{20}^+$; HR 296.1560/296.1548; ^{13}C 5.6/5.9), 281 (14, $[M-CH_2-H]^+$, $C_{22}H_{17}^+$), 219 (10), 218 (26, $[M-Ph-H]^+$, $C_{17}H_{14}^+$), 205 (100, $[M-CH_2Ph]$, $C_{16}H_{13}^+$; HR 205.1014/205.0999), 204 (28), 193 (24), 192 (21), 191 (37), 178 (25), 167 (12), 165 (26), 115 (48), 105 (43), 91 (32), 77 (11). Anal. calc. for $C_{23}H_{20}$ (296.39): C 93.20, H 6.80; found: C 93.00, H 6.71.

10.2. *Oxidation.* 10.2.1. *1-(2,2-Diphenylcyclopropyl)-1-phenylethane-1,2-diol* (**20**). Compound **12**, R = Ph (1.19 g, 4.0 mmol), in pyridine (60 ml) was treated with $KMnO_4$ (0.79 g) in H_2O (30 ml) at 50–60° for 1 h. After reduction with $NaHSO_3$, the neutral product (1.22 g) was purified by PLC (silica gel, C_6H_6/MeOH 20:1), and **20** (930 mg, 71%) was obtained. M.p. 104–105°. IR (ATR): 3419*s* (OH, assoc.), 3495*s* (O–H, free). ^{1}H-NMR (300 MHz): 1.15 (*dd*, $^2J_{gem}$ = 5.0; $^3J_{cis}$ = 9.6, H_a–C(3′)), shielded by Ph–C(1)); 1.56 (*s*, *tert*-OH); 1.67 (br., *t*, ^3J(2,OH) = 6.1, *prim*-OH); 1.83 (*dd*, $^2J_{gem}$ = 5.1, $^3J_{trans}$ = 6.9, H_b–C(3′)); 2.26 (*dd*, $^3J_{cis}$ = 9.5, $^3J_{trans}$ = 6.8, H–C(1′)); 3.97, 4.08 (2 *dd*, $^2J_{gem}$ = 11.2, ^3J(2,OH) = 6.0, CH_2(2)); 7.15–7.45 (*m*, 15 arom. CH). ^{13}C-NMR (75.5 MHz): 14.1 (C(3′)); 32.8 (C(1′)); 37.0 (C(2′)); 70.8 (C(2)); 76.6 (C(1)); 126.3, 126.9, 127.0 (3 arom. *p*-CH); 6 peaks for 12 arom. *o*,*m*-CH); 140.5, 143.4, 147.3 (3 arom. C_q). Anal. calc. for $C_{23}H_{22}O_2$ (330.41): C 83.60, H 6.71; found: C 83.76, H 6.86.

10.2.2. *(2,2-Diphenylcyclopropyl)(phenyl)methanone* (**19**). Glycol **20** (330 mg, 1.0 mmol) and $Pb(OAc)_4$ (653 mg, 1.5 mmol) in benzene (25 ml) were heated at 60° for 4 h. Workup and recrystallization from EtOH gave **19** (265 mg, 89%). M.p. 133–134.5° (133–134° [50]). IR (KBr): 1665*s* (C=O). NMR (60 MHz): 1.71 (*dd*, H_b–C(3)); 2.55 (*dd*, H_a–C(3)); 3.48 (*dd*, H–C(1)) with ^3J(1,3b) = 7.5 (*cis*), ^3J(1,3a) = 5.8 (*trans*), $^2J_{gem}$ = 4.5. Anal. calc. for $C_{22}H_{18}O$ (298.36): C 88.56, H 6.08; found: C 89.02, H 6.37.

10.3. *1,1,4-Triphenylpenta-1,3-diene* (**25**). Cyclopropane **12**, R = Ph (300 mg, 1.01 mmol), was refluxed in AcOH (10 ml) for 3 h and distilled at 190° (bath)/10^{-3} Torr: **25** (285 mg, 95%), m.p. 115–120°; colorless prisms from EtOH, m.p. 122–124° ([27]: 121–122°; [28]: 122–123°). IR (ATR): 1440*m*, 1488*m*, 1596*w* (arom. ring vibr.), 1639*w* (C=C *str*). UV (EtOH): 329 nm (log ε = 4.58), 244 (4.21), 207 (4.54), similar to (*E*,*E*)-1,4-diphenylbuta-1,3-diene [51] (EtOH): 330 (4.78), 232 (4.12), 207 (4.27). ^{1}H-NMR (300 MHz): 2.34 (*d*, ^3J = 1.4, Me); 6.62 (*dq*, ^3J(2,3) = 11.5, ^4J(3,5) = 1.4, H–C(3)); 7.10 (*d*, ^3J = 11.5, H–C(2)); 7.16–7.59 (*m*, 15 arom. H). MS: 296 (100, M^+, $C_{23}H_{20}^+$; HR 296.1560/296.1548), 281 (42, $[M-Me]^+$), 268 (21), 205 (43), 203 (28), 202 (18), 167 (31), 165 (17), 115 (12), 105 (13), 91 (11), 77 (5). Anal. calc. for $C_{23}H_{20}$ (296.39): C 93.20, H 6.80; found: C 93.20, H 6.86.

10.4 *Oxidation of* **25**. Compound **25** (87 mg, 0.29 mmol) and $KMnO_4$ (326 mg) in acetone (10 ml) were refluxed for 30 min, filtered, made alkaline, and extracted with Et_2O. TLC (silica gel, petroleum ether/Et_2O 4:1) of the neutral fraction showed the presence of *benzophenone* and *acetophenone*. The *2,4-dinitrophenylhydrazones* were separated by PLC (silica gel; petroleum ether/AcOEt 95:5): that of *benzophenone* (45%, m.p. 238–239°, mixed m.p.), and that of *acetophenone* (36%, m.p. 248–249°, mixed m.p.).

10.5. *Hydrogenation* of **25**. The soln. of **25** (520 mg, 1.75 mmol) in EtOH consumed 80.2 ml H_2 in the presence of Pd (10% on C). Distillation at 140–150° (bath)/10^{-3} Torr furnished *1,1,4-Triphenylpentane* (**28**, 97%). Colorless oil. n_D^{20} 1.5811. IR (film): 698v*s*, 744*s*, 759*s* (arom. *oop*), 1456s, 1494*s*, 1601*m* (arom. ring vibr.). UV (EtOH): absorptions of Ph at 266.5 nm (log ε = 1.70), 264 (1.76), 259 (1.85), 248.5 (1.66), 241.5 (148). ^{1}H-NMR (60 MHz, CCl_4): 1.14 (*d*, ^3J = 7.0, Me); 1.70 (*m*, 2 CH_2); 2.63 (*sext.*, ^3J = 7.0, H–C(4)); 3.76 (*t*, ^3J = 7.1, H–C(1)); 7.07 (br. *s*, 15 arom. H). Anal. calc. for $C_{23}H_{24}$ (300.42): C 91.95, H 8.05; found: C 92.27, H 8.21.

10.6. *9,10-Dihydro-9-methyl-10-phenyl-9,10-ethanoanthracene* (**27**). Compound **12** (300 mg, 1.01 mmol) and TsOH (100 mg) were heated to 200–205° for 10 min, distilled at 180–200° (bath)/10^{-3} Torr, dissolved in Et_2O, and washed with aq. Na_2CO_3. Removal of the ether left **27** (165 mg, 55%). M.p. 178–180°. The anal. sample, colorless prisms, m.p. 181–182° crystallized from petroleum ether. The

same compound was obtained, when **25** was treated with TsOH at 200°. IR (ATR): 705v*s*, 740v*s*, 757v*s*, 781*m* (arom. *oop*); 1443*m*, 1453*s*, 1484*w*, 1498*m*, 1597*w*, br. (arom. breath. modes). UV (EtOH): fine structure of benzene at 271 nm (log $\varepsilon = 2.06$), 263.5 (2.06), 257 (1.97), 251.5 (1.86). ^{1}H-NMR (400 MHz): 1.68, 2.17 (*AA′BB′* spectrum, which – on computer simulation [25] – provided $^2J_{AA'} = -11.2$, $^2J_{BB'} = -11.0$, $^3J_{AB} = 4.22$ (*trans*), $^3J_{AB} = 10.6$ (*cis*), CH_2(11) and CH_2(12)); 2.04 (*s*, Me); 6.85–7.60 (*m*, 13 arom. H). ^{13}C-NMR (100.6 MHz): 18.4 (Me); 31.7 (C(12)); 35.8 (C(11)); 41.7 (C(9)); 52.1 (C(10)); 120.3, 123.3, 125.0, 125.6, 127.0, 128.1, 130.4 (13 arom. CH of C(1)–C(4), C(5)–C(8), and Ph, in accordance with C_s); 139.7, 145.6, 145.8 (5 arom. C_q). MS: 296 (1, M^+, $C_{23}H_{20}^+$), 281 (1, $[M - Me]^+$), 268 (100, $[M - CH_2CH_2]^+$, $C_{21}H_{16}^+$; HR 268.1248/268.1271; ^{13}C 23.4/22.2), 252 (17, $[268 - CH_4]^+$, $C_{20}H_{12}^+$; ^{13}C 2.6/2.5), 126 (16, $C_{10}H_6^+$). Anal. calc. for $C_{23}H_{20}$ (296.39): C 93.20, H 6.80; found: C 92.82, H 6.78. Hydrocarbon **27** does not react with H_2 or $PhCO_3H$.

11. *1,1-Diphenyl-2-[1-methoxyethenyl]cyclopropane* (**12**, R = MeO). *2-Methoxybuta-1,3-diene* (11.35 g, 135 mmol)) [52][53] and **DDM** (12.2 g, 62.8 mmol) reacted 90 h at 40° in the dark. Distillation at 121–123°/10^{-3} Torr afforded **12**, R = MeO, in colorless crystals (14.2 g, 81%). M.p. 49–51°. Recrystallization from petroleum ether at −15° gave anal. pure **12**, R = MeO. M.p. 52–52.5°. ^{1}H-NMR (60 MHz): 1.35 (*dd*, $^3J_{cis} = 9.0$, $^2J_{gem} = -4.8$, H_a–C(3)); 1.79 (*dd*, $^3J_{trans} = 6.2$, $^2J_{gem} = -4.8$, H_b–C(3)); 2.29 (*dd*, $^3J_{trans} = 6.2$, $^3J_{cis} = 9.0$, H–C(2)); 3.15 (*s*, MeO); 3.74, 3.83 (2*d*, $^2J_{gem} = 2.0$, CH_2(2′)). Anal. calc. for $C_{18}H_{18}O$ (250.32): C 86.36, H 7.25; found: C 86.46, H 7.29.

12. *2-(1-Chloroethenyl)-1,1-diphenylcyclopropane* (**12**, R = Cl). The soln. of **DDM** (13.55 g, 69.8 mmol) and 2-anilinonaphthalene (200 mg) in 2-chlorobuta-1,3-diene (33.6 g, 380 mmol) lost the red color in 4 d at r.t., and the excess of the diene was distilled at 12 Torr. At b.p. 110–120°/10^{-3} Torr, **12**, R = Cl (14.21 g, 74%), was obtained as a colorless oil. After fractional distillation at 118–121°/10^{-3} Torr, the product showed $n_D^{20} = 1.5939$. IR (film): 694v*s*, 743v*s*, 762*s* (arom. *oop*); 820*m*, 890*s*, br. (C–Cl *str* and olefinic *oop*); 1018*s*, 1090*s*, 1141*s* (skeletal vibr.); 1440*s*, 1488*s*, 1592*s* (arom. ring vibr.), 1628*s* (C=C *str*). ^{1}H-NMR (60 MHz): 1.43 (*dd*, $^3J_{cis} = 8.7$, $^2J_{gem} = 5.1$, H_a–C(3)); 1.78 (*t*-like, H_b–C(3)); 2.51 (*dd*, $^3J_{trans} = 6.5$, $^3J_{cis} = 8.7$, H–C(2)); 4.70, 4.80 (2*d*, $^2J_{gem} = 1.4$, CH_2(2′)); 7.0–7.8 (*m*, 10 arom. H). Anal. calc. for $C_{17}H_{15}Cl$ (254.75): C 80.15, H 5.94; found: C 80.31, H 5.92.

13. *Rearrangement of Ethenylcyclopropanes to Cyclopentenes.* 13.1. *4,4-Diphenylcyclopent-1-ene* (**30**, R = H). Compound **7**, R = H (1.37 g, 6.22 mmol), was heated in a sealed tube to 300–310° (metal bath) for 5 min. Distillation at 100–105° (bath)/10^{-3} Torr afforded **30**, R = H (1.27 g, 93%), as a pale-yellow oil; the TLC showed a small impurity at the starting line. After redistillation, **30**, R = H (1.06 g, 77%), was NMR-pure. n_D^{20} 1.5767. IR (film): 1449*s*, 1487*s*, 1591*s* (arom. ring vibr.). ^{1}H-NMR (60 MHz, CCl_4; in accordance with C_{2v} symmetry): 3.02 (*s*, 4 H); 5.74 (*s*, 2 H, vic. and allyl. coupling unresolved); 7.10 (br. *s*, 10 H). Anal. calc. for $C_{17}H_{16}$ (220.30): C 92.68, H 7.32; found: C 92.16, H 7.15.

13.1.1. *3,3-Diphenyl-6-oxabicyclo[3.1.0]hexane* (**42**, R = H). The reaction of **30**, R = H, with 1.2 equiv. of $PhCO_3H$ in $CHCl_3$ (see *Sect. 13.3.2*) furnished, after purification by CC, **42**, R = H (72%). Colorless crystals. M.p. 56–57°. IR (ATR): 696v*s*, 748*s*, 776s (arom. *oop*), 842*s* (C–O–C, oxirane [26]). ^{1}H-NMR (300 MHz): 2.53 (*d*, $^2J_{gem} = 14.6$, slightly broadened, $J(1,2b) = J(4b,5) \leq 0.6$ by comparison of line widths, H_b–C(2/4)); 3.16 (*d*, sharp, $^2J_{gem} = 14.5$, H_a–C(2/4)); 3.68 (*s*, $\Sigma J < 0.6$ from line width, H–C(1/5)); 7.10–7.35 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz): 40.8 (C(2/4)); 52.3 (C(3)); 56.8 (C(1/5)); 8 peaks for 12 arom. C, as expected for free rotation of both Ph. Anal. calc. for $C_{17}H_{16}O$ (236.30): C 86.40, H 6.83; found: C 86.15, H 6.69.

13.2. *3-Methyl-4,4-diphenylcyclopentene* (**30**, R = Me). Prepared from **7**, R = Me, as described in *Sect. 13.1*, the rearrangement product **30**, R = Me, was obtained as a colorless oil (98%) after distillation at 100–105° (bath)/10^{-3} Torr. n_D^{20} 1.5878. IR: 696v*s*, 727*s*, 745s, 759*m* (arom. and olefin. *oop*); 1443*s*, 1491*s*, 1578*w*, 1598*m* (arom. vibr.), 1661*w* (C=C *str.*). ^{1}H-NMR (300 MHz): 0.99 (*d*, $^3J_{vic} = 7.1$, Me); 3.04, 3.71 (2 *dq*, $^2J_{gem} = 16.0$, $^3J_{vic} \approx {}^4J_{allyl} \approx J_{homoallyl} = 1.9–2.0$, H_a–C(5), H_b–C(5)); 3.87 (*m*, 14 lines visible, $^3J(3,Me) = 7.1$, H–C(3)); 6.01, 6.07 (2*m*, $^3J(1,2) = 5.9$, H–C(1), H–C(2)); 7.34–7.60 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz): 17.0 (Me); 46.4 (C(5)); 47.0 (C(3)); 58.8 (C(4)); 128.0, 137.1 (C(1), C(2)); 6 peaks for 10 arom. CH; 147.1, 150.8 (2 arom. C_q). MS: 234 (100, M^+; HR 234.1404/234.1388), 219 (38, $[M - Me]^+$), 205 (72, $[M - Et]^+$, $C_{16}H_{13}^+$), 204 (19), 191 (12, $C_{15}H_{11}^+$), 178 (15), 165 (25), 143 (52), 128 (20), 115 (21), 91 (39), 77 (10). Anal. calc. for $C_{18}H_{18}$ (234.32): C 92.26, H 7.74; found: C 92.34, H 7.85.

13.2.1. *2(*exo*)- and 2(*endo*)-Methyl-3,3-diphenyl-6-oxabicyclo[3.1.0]hexane* (**42**, R = Me, and **43**, R = Me). The reaction of **7**, R = Me, with $PhCO_3H$ (1.2 equiv.) was carried out, as described in *Sect. 13.3.2,* and provided the crystalline **42**, R = Me, m.p. 107–108°, and the oily **43**, R = Me, in 74:26 ratio.

Data of **42***, R = Me (*exo*)*. IR (KBr): 844*s* (C–O–C, oxirane). ^{1}H-NMR (60 MHz): 0.61 (*d*, ^3J = 7.2, Me); 2.67, 2.69 (perhaps *AB*, H_a–C(4), H_b–C(4)); 3.22–3.60 (*m*, 3 H, poorly resolved); 6.78–7.33 (*m*, 10 arom. H). Anal. calc. for $C_{18}H_{18}O$ (250.32): C 86.36, H 7.25; found: C 86.29, H 7.23.

Data of endo*-isomer* **43***, R = Me.* IR (film): 842*s* (C–O–C, oxirane). ^{1}H-NMR (60 MHz): 0.84 (*d*, ^3J = 7.2, Me, deshielded by oxide function); 2.30 (*dd*, $^2J_{gem}$ = 15.2, ^3J(4b,5) = 1.7, H_b–C(4)); 2.98 (*dq*, ^3J(2b,1) = 1.7, ^3J(2b,Me) = 7.2, partial overlap, H_b–C(2)); 3.24 (*d*, ^2J = 15.2, H_a–C(4)); 3.30, 3.41 (2*dd*, ^3J = 1.7, ^3J(1,5) = 3.0, partial overlap, H–C(1), H–C(5)); 6.87–7.58 (*m*, 10 arom. H).

13.3. *3,4,4-Triphenylcyclopent-1-ene* (**30**, R = Ph). Compound **7**, R = Ph (7.00 g, 23.6 mmol), was heated without solvent to 200–210° for 10 min. Distillation at 190–200° (bath)/10^{-3} Torr gave a pale-yellow liquid, which solidified and was recrystallized from EtOH: **30**, R = Ph (6.38 g, 91%). Colorless prisms. M.p. 68–70°. IR (ATR): 1443*s*, 1451*m*, 1490*s*, 1577*m*, 1594*m* (arom. ring vibr.), 1630*m* (C=C *str*). ^{1}H-NMR (600 MHz): Simulation by DAVINX [25] afforded the chemical shifts for the 5 cycloaliphatic H; precondition for δ assignment in **32A** is the deshielding by Ph–C(3): H_b–C(3) > H_a–C(5) > H_b–C(5); coupling constants: ^3J(1,2) = 5.93, ^4J(1,3) = 1.66, ^3J(1,5a) = 1.72, ^3J(1,5b) = 2.22, ^3J(2,3) = 2.28, ^4J(2,5a) = 1.99, ^4J(2,5b) = 1.56, ^5J(3,5a) = 2.05, ^5J(3,5b) = 1.28, ^2J(5a,5b) = –16.31. ^{13}C-NMR (100 MHz): 46.3 (C(5)); 59.6 (C(3)); 61.1 (C(4)); 129.5 (C(1)); 135.2 (C(2)); 125.3, 125.7, 126.0 (3 arom. *p*-CH); 6 peaks of double height for 12 arom. *o*,*m*-CH; 140.8, 145.4, 151.2 (3 arom. C_q). MS: similar to **7**, R = Ph, *Sect. 5.1.*

13.3.1. *Oxidation.* Treatment of **30**, R = Ph, with $KMnO_4$ (4.2 mol-equiv.) in boiling pyridine furnished, after the usual workup, *benzophenone* (isolated as 2,4-dinitrophenylhydrazone) and PhCOOH, both in poor yield.

13.3.2. *2(*exo*),3,3-Triphenyl-6-oxabicyclo[3.1.0]hexane* (**42**, R = Ph). In $CHCl_3$ (20 ml), **30**, R = Ph (593 mg, 2.0 mmol), were reacted with $PhCO_3H$ (2.2 mmol) at r.t. for 48 h. After washing with Na_2CO_3 and H_2O, the solvent was evaporated, and the crystalline residue was subjected to CC (neutral alumina, 50 g). The first fraction eluted with petroleum ether/Et_2O was unchanged **30**, R = Ph (150 mg), followed (with Et_2O alone) by **42**, R = Ph (430 mg, 92% of consumed **30**). Colorless prisms (from MeOH). M.p. 87–89°. IR (ATR): 690v*s*, 703*s*, 740*s*, 751*m* (arom. *oop*), 848*s* (C–O–C *as str*, oxirane [26]). ^{1}H-NMR (600 MHz; best assignments, not free of doubt): 2.92 (*d*, $^2J_{gem}$ = 14.5, H_a–C(4)); 3.10 (*dd*, $^2J_{gem}$ = 14.5, ^3J(4b,5) = 1.7, H_b–C(4)); 3.72 (*d*, *J* = 2.8, signal width 3.7, H–C(1)); 3.88 (*t*, *J*(4b,5) ≈ *J*(1,5) ≈ 1.9, signal width 5.8, H–C(5)); 4.61 (*s*, line width 2.0 (0.8 for $CHCl_3$), H_a–C(2)); 6.80–7.38 (*m*, 15 arom. H). ^{13}C-NMR (75.5 MHz): 39.3 (C(4)); 52.8 (C(2)); 57.3 (C(5)); 58.3 (C(3)); 60.5 (C(1)); 12 peaks for 18 arom. C show free rotation of 3 Ph. MS: 312 (6, M^+; HR 312.1509/312.1513), 294 (5, [M – H_2O]$^+$), 207 (11, [M – C_8H_9]$^+$, $C_{15}H_{11}O^+$; HR 207.0807/207.0789); 192 (51, $C_{15}H_{12}^+$), 191 (15, **38**), 180 (100, $C_{14}H_{12}^+$, diphenylethene; HR 180.0936/180.0942; ^{13}C 15.6/14.1), 179 (33), 178 (31), 165 (48, **37**), 115 (33), 105 (14), 91(22), 82 (48, $C_5H_7O^+$), 77 (16, Ph). Anal. calc. for $C_{23}H_{20}O$ (312.39): C 88.42, H 6.45; found: C 88.28, H 6.55.

13.3.3. *1,1,2-Triphenylcyclopentane* (**40**, R = Ph). In the presence of Pd (10% on C), **30**, R = Ph (1.0 mmol), in EtOH (10 ml) consumed *ca.* 1 mmol of H_2. Recrystallization from MeOH afforded **40**, R = Ph. Needles. M.p. 81.5–82.5°. ^{1}H-NMR (100 MHz): 1.6–3.0 (*m*, 6 H); 4.00 (*t*, *J* = 6.8, further split, H–C(2)); 6.60–7.55 (*m*, 15 arom. H). MS: 298 (100, M^+; HR 298.1716/298.1729; ^{13}C 25.6/25.7), 207 (19), 193 (100, [M – CH_2CH_2Ph]$^+$, $C_{15}H_{13}^+$, possibly [9-ethylfluorenyl]$^+$), 180 (69), 179 (41), 167 (54), 165 (56), 129 (24), 115 (53), 91 (45), 82 (13), 77 (10). Anal. calc. for $C_{23}H_{22}$ (298.41): C 92.57, H 7.43; found: C 92.13, H 7.29.

13.4. *Methyl 5,5-Diphenylcyclopent-2-ene-1-carboxylate* (**30**, R = CO_2Me). After heating **7**, R = CO_2Me (7.64 g, 27.4 mmol), in N_2 atmosphere for 10 min at 310–320°, distillation at 175–185°/10^{-3} Torr gave a yellow oil, which crystallized after a while from MeOH/H_2O 9:1 and yielded **30**, R = CO_2Me (4.47 g). M.p. 50–52.5°. CC (silica gel; petroleum ether/Et_2O 95:5) of the mother liquor afforded another 2.39 g (together 90%). M.p. 52.5–53° (MeOH). IR (KBr): 701v*s*, 715*s*, 740*s*, 746*s* (arom. and olefin. *oop*), 1170*s* (C–O *str*), 1625*w*, 1644*w* (*cis*-CH=CH *str*), 1735v*s* (C=O). ^{1}H-NMR (60 MHz,

simulation of aliph. 5-H system): 3.18 (*s*, MeO); 2.82, 3.52 (2 *dq*-like, H_b–C(4), H_a–C(4)); 4.50 (*quint.*-like, H_b–C(1)); 5.89, 6.06 (*sym*, 14 lines, H–C(3), H–C(2)); coupling constants: ^3J(1b,2) = 2.10; ^4J(1b,3) = −2.13; ^5J(1b,4b) = 1.80; ^5J(1b,4a) = 1.77; ^3J(2,3) = 5.82; ^4J(2,4b) = −2.17; ^4J(2,4a) = −2.12; ^3J(3,4b) = 2.19; ^3J(3,4a) = 2.15; ^2J(4a,4b) = −16.05; 7.1–7.5 (*m*, 10 arom. H). Molecular mass (osmometr., $CHCl_3$): calc.: 278, found: 282. Anal. calc. for $C_{19}H_{18}O_2$ (278.33): C 81.98, H 6.52; found: C 82.33, H 6.38.

13.4.1. *Methyl 3,3-Diphenyl-6-oxabicyclo[3.1.0]hexane-2(*exo*)-carboxylate* (**42**, R = CO_2Me). Ester **30**, R = CO_2Me (3.53 mmol), and $PhCO_3H$ (4.30 mmol) in benzene (45 ml) were reacted at r.t. in the dark for 1 week. Workup (see *Sect. 13.3.2*) rendered back olefin (0.98 mmol) and yielded **42**, R = CO_2Me (2.43 mmol, 95% of consumed **30**). The oil crystallized after several weeks. M.p. 70–71° (MeOH/H_2O 9:1). IR (ATR): 694v*s*, 703v*s*, 748*s*, 767*m* (arom. *oop*); 830*m*, 846*s*, 851*s* (oxirane, *as str*); 1165*s*, 1188*s* (C–O *str*), 1730v*s* (C=O). ^{1}H-NMR (300 MHz): 2.86 (*d*, $^2J_{gem}$ = 14.1, H_a–C(4)); 3.19 (*dd*, $^2J_{gem}$ = 14.1, ^3J(4b,5) = 1.2, H_b–C(4)); 3.28 (*s*, MeO); 3.81 (*s*, broadened, some evidence of *AB*, H–C(1) + H–C(5)); 4.38 (*s*, H_a–C(2)); 7.1–7.3 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz): 39.7 (C(4)); 51.5, 53.9 (C(2), Me); 56.7 (C(3)); 57.3, 58.2 (C(1), C(5)); 8 peaks for 12 arom. C; 171.7 (C=O). MS: 294 (27, M^+; HR 294.0990/294.0999), 262 (26, $[M - MeOH]^+$), 234 (30, $[M - HCO_2Me]^+$, $C_{17}H_{14}O^+$; HR 234.1041/234.1047), 217 (17), 207 (21), 192 (100, $C_{15}H_{12}^+$), 191 (60, **38**), 181 (33), 179 (55), 165 (55), 115 (57), 91 (32), 77 (22). Anal. calc. for $C_{19}H_{18}O_3$ (294.33): C 77.53, H 6.16; found: C 77.58, H 6.16.

13.4.2. *Methyl 2,2-Diphenylcyclopentane-1-carboxylate* (**40**, R = CO_2Me). Catalytic hydrogenation (see *Sect. 13.3.3*) converted **30**, R = CO_2Me, into **40**, R = CO_2Me, which was purified by TLC (silica gel; petroleum ether/Et_2O 8:2) and distillation at 125–130° (bath)/10^{-3} Torr. Colorless oil (90%). n_D^{20} = 1.5715. IR (film): 1162*s* (br., C–O), 1725v*s* (C=O). ^{1}H-NMR (60 MHz): 1.30–2.56 (*m*, 5 H); 2.64–3.08 (*m*, 1 H), 3.20 (*s*, MeO); 3.79 (*t*-like, ^3J = 5.9, H–C(1)); 7.0–7.4 (*d*-like, 10 arom. H). Anal. calc. for $C_{19}H_{20}O_2$ (280.35): C 81.39, H 7.19; found: C 81.79, H 7.45.

13.4.3. *Methyl 5,5-Diphenylcyclopent-1-ene-1-carboxylate* (**41**). MeONa (6.7 mmol) and **30**, R = CO_2Me (2.12 mmol), in MeOH (30 ml) were refluxed for 1 h and worked up with 0.5N HCl and Et_2O. TLC (silica gel; petroleum ether/Et_2O) furnished **41** (76%). Colorless oil. B.p. 145–150° (bath)/10^{-3} Torr. n_D^{20} = 1.5928. IR (film): 1109*s* (C–O), 1620*w* (C=C *str*), 1719*s* (C=O). ^{1}H-NMR (600 MHz, C_s symmetry): 2.68 (*dt*, ^3J(2,3) = 2.7, ^3J(3,4) = 7.0; 2,3-coupling established by GDQCOSY, CH_2(3)); 2.80 (*t*-like, ^3J(3,4) = 6.9, broadened, CH_2(4)); 3.66 (*s*, MeO); 7.20 (*t*, ^3J(2,3) = 2.7, H–C(2)); 7.25–7.41 (*m*, 10 arom. H). ^{13}C-NMR: 31.4 (C(3)); 45.5 (C(4)); 51.3 (MeO); 62.1 (C(5)); 126.2 (2 arom. *p*-CH); 127.9, 128.3 (8 arom. *o,m*-CH); 141.9 (C(1)); 146.4 (C(2)); 146.8 (2 arom. C_q); 164.9 (C=O). MS: 278 (28, M^+; HR 278.1302/278.1289; ^{13}C 5.9/5.5), 246 (26, $[M - MeOH]^+$), 219 (100, $[M - CO_2Me]^+$), 218 (42), 204 (21), 141 (37), 91 (22). Anal. calc. for $C_{19}H_{18}O_2$ (278.33): C 81.98, H 6.52; found: C 82.13, H 6.95.

13.5. *5,5-Diphenylcyclopent-2-ene-1-carbonitrile* (**30**, R = CN). Prepared from **9**, R = CN, at 300–310°, b.p. 130–135°/10^{-3} Torr, m.p. 96–96.5°. IR (KBr): 1625*w* (C=C *str*), 2245*m* (C≡N). ^{1}H-NMR (60 MHz, simulation): 2.93 (H_b–C(4)); 3.36 (H_a–C(4)); 4.37 (H–C(1)); 5.69 (H–C(3)); 6.01 (H–C(2)); coupling constants: ^3J(1b,2) = 2.17; ^4J(1b,3) = −2.31; ^5J(1b,4b) = 2.16; ^5J(1b,4a) = 2.02; ^3J(2,3) = 5.83; ^4J(2,4b) = −2.34; ^4J(2,4a) = −2.03; ^3J(3,4b) = 2.41; ^3J(3,4a) = 2.57; ^2J(4a,4b) = −16.76. Anal. calc. for $C_{18}H_{15}N$ (245.31): C 88.13, H 6.16, N 5.71; found: C 87.92, H 6.05, N 5.75.

13.6. *1-Methyl-4,4-diphenylcyclopentene* (**31**, R = Me). For preparation from **12**, R = Me, see *Sect. 13.1*. Yield: 87%. Colorless liquid. B.p. 100–105° (bath)/10^{-3} Torr. n_D^{20} = 1.5852. IR (film): 1650*w* (C=C *str*). ^{1}H-NMR (300 MHz; σ-plane): 1.89 (*t*-like, ^4J(2,Me) ≈ ^5J(3,Me) = 0.8, Me); 3.09, 3.16 (2*m*, 6 and 5 peaks visible, CH_2(3) and CH_2(5)); 5.51 (*m*, H–C(2)); 7.2–7.4 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz): 16.8 (Me); 47.0, 50.8 (C(3), C(5)); 55.7 (C(4)); 123.2 (C(2)); 125.6 (2 arom. *p*-CH); 127.7, 128.1 (8 arom. *o,m*-CH); 139.2 (C(1)); 150.5 (2 arom. C_q). MS: 234 (100, M^+; HR 234.1404/234.1397), fragments similar to MS of **12**, R = Me. Anal. calc. for $C_{18}H_{18}$ (234.32): C 92.26, H 7.74; found: C 92.65, H 7.85.

13.6.1. *1-Methyl-3,3-diphenyl-6-oxabicyclo[3.1.0]hexane* (**44**, R = Me). Compound **44**, R = Me, was prepared as described in *Sect. 13.3.2*; yield after recrystallization: 72%. M.p. 86.5–87.5°. IR (ATR): 843*s* (C–O–C, oxirane), 1446*s*, 1491*s*, 1579*w*, 1591*w* (arom. ring vibr.). ^{1}H-NMR (300 MHz): 1.53 (*s*, Me); 2.50 (*d*, $^2J_{gem}$ = 14.4, H_b–C(2)); 2.53 (*dd*, $^2J_{gem}$ = 14.4, ^3J(4b,5) = 1.7 (*cis*), H_b–C(4)); 3.03, 3.12 (2 *d*, J_{gem} = 14.3, H_a–C(2), H_a–C(4)); 3.44 (*d*, ^3J(4b,5) = 1.4, H–C(5); 7.1–7.3 (*m*, 10 arom. H). ^{13}C-NMR

(75.5 MHz): 18.0 (Me); 41.2, 45.0 (C(2), C(4)); 53.0 (C(3)); 62.9 (C(5)); 64.0 (C(1)); 6 lines for 10 arom. CH; 149.7, 150.9 (2 arom. C_q). MS: 250 (19, M^+; HR 250.1353/250.1345; ^{13}C 3.8/3.3), 207 (46, $[M-MeCO]^+$), 192 (100, $C_{15}H_{12}^+$), 191 (25), 180 (56, [diphenylethene]$^+$), 179 (37, $C_{14}H_{11}^+$), 165 (54), 129 (45), 115 (42), 91 (37), 77 (19). Anal. calc. for $C_{18}H_{18}O$ (250.32): C 86.36, H 7.25; found: C 86.60, H 7.20.

13.7. *1,4,4-Triphenylcyclopent-1-ene* (**31**, R = Ph). 13.7.1. *Preparation*. Thermal polymerization of **12**, R = Ph (2.95 mmol), could be diminished by heating with 2-anilinonaphthalene (0.7 mmol) to give a homogenous melt. After 5 min at 310–320°, the material was purified by TLC (silica gel; petroleum ether/Et_2O 99:1) and furnished **31**, R = Ph, as the main product (0.70 g), which was recrystallized from EtOH: colorless needles (59%). M.p. 93.5–94°. IR (ATR): 1631*w* (C=C *str*). ^1H-NMR (400 MHz; δ and J values in **32B**): 3.30 (*q*-like, broadened, $J \approx 2.0$, $CH_2(3)$); 3.48 (*q*, sharp, $J = 1.8$, $CH_2(5)$; 6.84 (structured *sept.* by superposition of two *t*, $^3J + {}^4J = 4.35$, H–C(2)); irradiation at 6.24 generates 2*t* at 3.30 and 3.48 with $^5J(3,5)_{cis} = {}^5J(3,5)_{trans} = 1.79$; the signal at 6.24 is converted to *t*, $^3J(2,3) = 1.69$ when $CH_2(3)$ is decoupled whereas *t* with $^4J(2,5) = 2.64$ for H–C(2) results on decoupling of $CH_2(5)$; thus, $^3J_{vic} + {}^4J_{allyl} = 4.33$; 7.15–7.57 (*m*, 15 arom. H). ^{13}C-NMR (75.5 MHz): 46.96, 47.14 (C(3), C(5)); 55.2 (C(4)); 124.2 (C(2), established by comparison of line heights and confirmed by a HSQCAD experiment); 136.2 (C(1)); 125.6, 125.8, 127.21, 127.24, 128.1, 128.4 (15 arom. CH); 141.1, 149.0 (3 arom. C_q).

13.7.2. *1(*exo*),3,3-Triphenyl-6-oxabicyclo[3.1.0]hexane* (**44**, R = Ph). The reaction of **31**, R = Ph, with $PhCO_3H$ (1.3 equiv.), as described above, produced the epoxide **44**, R = Ph, as leaflets (67%) after recrystallization from EtOH. M.p. 129.5–131°. IR (ATR): 880*m* (C–O–C, oxirane), 1446*m*, 1492*m*, 1594*w* (arom. ring vibr.). ^1H-NMR (400 MHz): 2.70 (*dd*, $^2J_{gem} = 14.7$, $^3J(4b,5) = 1.5$, H_b–C(4)); 3.06 (*d*, $^2J_{gem} = 14.2$, H_b–C(2)); 3.21 (*d*, $^2J_{gem} = 14.7$, H_a–C(4)); 3.36 (*d*, $^2J_{gem} = 14.3$, H_a–C(2)); 3.69 (*t*, $^3J(4b,5) = 0.8$, H–C(5)); 7.02–7.38 (*m*, 15 arom. H); GDQ-COSY shows $^3J(4b,5)$ (calc. by simulation [25] to be 1.59) as the only vicinal coupling. ^{13}C-NMR (100 MHz): 41.2, 42.3 (C(2), C(4)); 52.2 (C(3)); 65.7 (C(5)); 66.1 (C(1)); 3 peaks for 3 arom. *p*-CH, 6 peaks for 12 *o*,*m*-CH, and 3 peaks for C_q. MS: 312 (36, M^+; HR 312.1509/312.1492; ^{13}C 9.2/10.3), 268 (14, $[M-MeCHO]^+$, $C_{21}H_{16}^+$), 234 (14, $[M-C_6H_6]^+$), 207 (48, $[M-PhC_2H_4]^+$, $C_{15}H_{11}O^+$; HR 207.0807/207.0802), 192 (78), 191 (53); 180 (100, [diphenylethylene]$^+$), 178 (53), 165 (55), 105 (41), 91 (36), 77 (31). Anal. calc. for $C_{23}H_{20}O$ (312.39): C 88.42, H 6.45; found: C 88.31, H 6.73.

REFERENCES

[1] R. Huisgen, P. Pöchlauer, G. Mloston, K. Polborn, *Helv. Chim. Acta* **2007**, *90*, 983.
[2] L. Fisera, J. Geittner, R. Huisgen, H.-U. Reissig, *Heterocycles* **1978**, *10*, 153.
[3] R. Sustmann, *Pure Appl. Chem.* **1974**, *40*, 569.
[4] K. N. Houk, K. Yamaguchi, 'Theory of 1,3-Dipolar Cycloadditions', in '1,3-Dipolar Cycloaddition Chemistry', Ed. A. Padwa, John Wiley & Sons, New York, 1984, Vol. II, Chapt. 13.
[5] R. Huisgen, 'Introduction, Survey, Mechanism', in '1,3-Dipolar Cycloaddition Chemistry', Ed A. Padwa, John Wiley & Sons, New York, 1984, Vol. I; a) p. 103–121; b) 31–35.
[6] J. Geittner, R. Huisgen, R. Sustmann, *Tetrahedron Lett.* **1977**, *18*, 881.
[7] R. Sustmann, W. Sicking, *Chem. Ber.* **1987**, *120*, 1653.
[8] M. Burdisso, R. Gandolfi, S. Quartieri, A. Rastelli, *Tetrahedron* **1987**, *43*, 159.
[9] G. Leroy, M. Sana, *Tetrahedron* **1975**, *31*, 2091; G. Leroy, M. Sana, *Tetrahedron* **1976**, *32*, 709.
[10] A. Rastelli, R. Gandolfi, M. S. Amadé, *J. Org. Chem.* **1998**, *63*, 7425.
[11] D. H. Ess, K. N. Houk, *J. Am. Chem. Soc.* **2007**, *129*, 10646.
[12] W. Bihlmaier, J. Geittner, R. Huisgen, H.-U. Reissig, *Heterocycles* **1978**, *10*, 147.
[13] R. Huisgen, A. Ohta, J. Geittner, *Chem. Pharm. Bull* **1975**, *23*, 2735.
[14] K. N. Houk, J. Sims, R. E. Duke, R. W. Strozier, J. K. George, *J. Am. Chem. Soc.* **1973**, *95*, 7287; K. N. Houk, J. Sims, C. R. Watts, L. J. Luskus, *J. Am. Chem. Soc.* **1973**, *95*, 7301.
[15] J. Martelli, F. Tonnard, R. Carrié, R. Sustmann, *Nouv. J. Chim.* **1978**, *2*, 609.
[16] E. Buchner, *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 2010.
[17] J. van Alphen, *Recl. Trav. Chim. Pays-Bas* **1943**, *62*, 210, 334.
[18] R. J. Crawford, R. J. Dummel, A. Mishra, *J. Am. Chem. Soc.* **1965**, *87*, 3023, 3768; R. J. Crawford, D. M. Cameron, *Can. J. Chem.* **1967**, *45*, 691; C. G. Overberger, N. Weinschenker, J. P. Anselme, *J.*

Am. Chem. Soc. **1965**, *87*, 4119; D. E. McGreer, N. W. K. Chiu, M. G. Vinje, K. C. K. Wong, *Can. J. Chem.* **1965**, *43*, 1407.
[19] B. S. Gorton, *J. Org. Chem.* **1965**, *30*, 648.
[20] J. Geittner, R. Huisgen, H.-U. Reissig, *Heterocycles* **1978**, *11*, 109.
[21] R. W. Taft, I. C. Lewis, *J. Am. Chem. Soc.* **1958**, *80*, 2436.
[22] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165.
[23] H. Mayr, A. R. Ofial, *Pure Appl. Chem.* **2005**, *77*, 1807.
[24] T. Bug, M. Hartnagel, C. Schlierf, H. Mayr, *Chem.—Eur. J.* **2003**, *9*, 4068.
[25] D. S. Stephenson, 'Encyclopedia of Nuclear Magnetic Resonance', Eds. T. M. Grant, R. K. Harris, John Wiley & Sons, New York, 1996, pp. 816–821.
[26] E. Pretsch, T. Clerc, J. Seibl, W. Simon, 'Tabellen zur Strukturaufklärung organischer Verbindungen', Springer-Verlag, Berlin, 1976.
[27] J. M. Edinger, S. F. Sisenwine, A. R. Day, *J. Org. Chem.* **1971**, *36*, 3614.
[28] R. Boyce, W. S. Murphy, E. A. O'Riordan, *J. Chem. Soc., Perkin Trans. 1* **1974**, 792.
[29] G. A. Olah, K. K. Laali, Q. Wang, G. K. S. Prakash, 'Onium Ions', John Wiley & Sons, New York, 1998, p. 359.
[30] W. J. Brittain, M. E. Squillacote, J. D. Roberts, *J. Am. Chem. Soc.* **1984**, *106*, 7280.
[31] S. J. Cristol, T. W. Russell, J. R. Mohrig, D. E. Plorde, *J. Am. Chem. Soc.* **1966**, *31*, 581.
[32] N. P. Neureiter, *J. Org. Chem.* **1959**, *24*, 2044.
[33] E. Vogel, *Angew. Chem.* **1960**, *72*, 4.
[34] C. G. Overberger, A. E. Borchert, *J. Am. Chem. Soc.* **1960**, *82*, 1007.
[35] T. Hudlicky, T. M. Kuchan, S. M. Naqvi, *Org. React.* **1985**, *33*, 247.
[36] R. B. Woodward, R. Hoffmann, *Angew. Chem., Int. Ed.* **1969**, *8*, 781.
[37] J. E. Baldwin, *Chem. Rev.* **2003**, *103*, 1197.
[38] B. Lemarié, R. Lozach, B. Braillon, *J. Chim. Phys.* **1975**, *72*, 1523.
[39] D. S. Stephenson, G. Binsch, *Mol. Phys.* **1981**, *43*, 697.
[40] B. F. Yates, W. J. Bouma, L. Radom, *Tetrahedron* **1986**, *42*, 6225.
[41] D. Schumann, E. Frese, A. Schönberg, *Chem. Ber.* **1969**, *102*, 3192.
[42] J. B. Miller, *J. Org. Chem.* **1959**, *24*, 560.
[43] W. Bunge in 'Methoden der Organischen Chemie (Houben-Weyl)', G. Thieme, Stuttgart, 1959, Vol. I/2, p. 831.
[44] O. Grummitt, E. J. Becker, *Org. Synth.* **1963**, *Coll. Vol. IV*, 771.
[45] W. M. Jones, T. H. Glenn, D. G. Baarda, *J. Org. Chem.* **1963**, *28*, 2887.
[46] W. Flaig, *Liebigs Ann. Chem.* **1950**, *568*, 1.
[47] O. Doebner, *Chem. Ber.* **1902**, *35*, 1136.
[48] H. O. House, G. H. Rasmussen, *J. Org. Chem.* **1961**, *26*, 4278.
[49] C. C. Price, F. L. Benton, C. J. Schmidle, *J. Am. Chem. Soc.* **1949**, *71*, 2860.
[50] F. J. Impastato, H. M. Walborsky, *J. Am. Chem. Soc.* **1962**, *84*, 4838.
[51] 'DMS UV Atlas of Organic Compounds', Butterworths/Verlag Chemie, London/Weinheim, 1966, spectr. D 10/36.
[52] A. A. Petrov, *Acta Univ. Voronegiensis* **1935**, *8*, 68; A. A. Petrov, *Chem. Zentralbl., I* **1937**, 1920.
[53] R. O. Norris, J. J. Verbanc, G. F. Hennion, *J. Am. Chem. Soc.* **1938**, *60*, 1159.

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