1-[(*E*)-2-Arylethenyl]-2,2-diphenylcyclopropanes: Kinetics and Mechanism of Rearrangement to Cyclopentenes

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Dedicated to *Paul von Ragué Schleyer*, friend and mentor, on the occasion of his 80th birthday

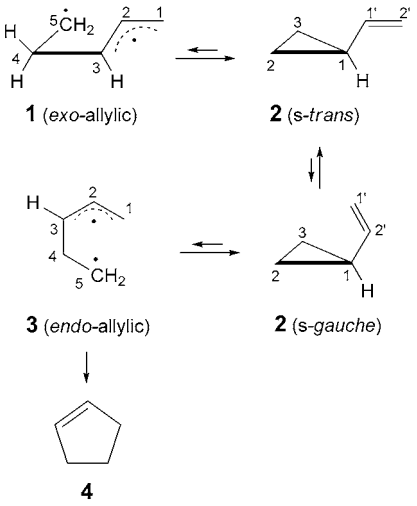
Kinetic measurements for the thermal rearrangement of 2,2-diphenyl-1-[(*E*)-styryl]cyclopropane (**22a**) to 3,4,4-triphenylcyclopent-1-ene (**23a**) in decalin furnished $\Delta H^{\neq}_{isom} = 31.0 \pm 1.2$ kcal mol^{-1} and $\Delta S^{\neq}_{isom} = -6.0 \pm 2.6$ e.u. The lowering of $\Delta H^{\neq}$ by 20 kcal mol^{-1}, compared with the rearrangement of the vinylcyclopropane parent, is ascribed to the stabilization of a transition structure (TS) with allylic diradical character. The racemization of (+)-(*S*)-**22a** proceeds with $\Delta H^{\neq}_{rac} = 28.2 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\neq}_{rac} = -5 \pm 2$ e.u., and is at 150° 106 times faster than the rearrangement. Seven further 1-(2-arylethenyl)-2,2-diphenylcyclopropanes **22**, (*E*)- and (*Z*)-isomers, were synthesized and characterized. The (*E*)-compounds showed only modest substituent influence in their k_{rac} (at 119.4°) and k_{isom} (at 159.3°) values. The lack of solvent dependence of rate opposes charge separation in the TS, but a linear relation of log k_{rac} with log p.r.f., *i.e.*, partial rate factors of radical phenylations of ArH, agrees with a diradical TS. The ring-opening of the preponderant s-*trans*-conformation of **22** gives rise to the 1-*exo*-phenylallyl radical **26** that bears the diphenylethyl radical in 3-*exo*-position, and is responsible for racemization. The 1-*exo*-3-*endo*-substituted allylic diradical **27** arises from the minor s-*gauche*-conformation of **22** and is capable of closing the three- or the five-membered ring, **22** or **23**, respectively. The discussion centers on the question whether the allylic diradical is an intermediate or merely a TS. Quantum-chemical calculations by *Houk et al.* (1997) for the parent vinylcyclopropane reveal the lack of an intermediate. Can the conjugation of the allylic diradical with three Ph groups carve the well of an intermediate?

1. Introduction. – 1.1. *Facts and Interpretations.* Rearrangements of the C-backbone of organic compounds have aroused the chemist's interest early on. The thermal rearrangement of vinylcyclopropane to cyclopentene, observed by two groups in 1960 [1][2], was a late-comer in a noble old family. For one of the discoverers, *E. Vogel*, it was worth only a footnote in a review. Soon, the formal simplicity of this conversion initiated a multitude of studies on scope and mechanism.

The first assumption of a diradical intermediate with allylic stabilization found solid ground in kinetics and thermochemistry. *Flowers* and *Frey* independently observed the rearrangement and, in 1961, published a gas kinetic study, which furnished an activation energy $E_A = 49.6$ kcal mol^{-1} [3]. Decades later, this value was rectified to 51.7 ± 0.5 kcal mol^{-1} [4]. The thermal breakup of the cyclopropane ring

requires $E_A = 63.0$ kcal mol^{-1}, as measured *via* the *cis* $\rightleftharpoons$ *trans* equilibration of [1,2-$^2H_2$]cyclopropane and reported in a classic paper by *Schlag* and *Rabinovitch* [5]. The difference of *ca.* 12 kcal mol^{-1} could well be accounted for by the allylic stabilization of an intermediate **3** (*Scheme 1*); 14.0 – 14.5 kcal mol^{-1} for the conjugation energy of the parent allyl radical resulted from a recent determination [6].

Scheme 1



Two conformations of **2**, s-*trans* > s-*gauche*, produce different diradicals on ring-opening. They bear the side chain on the *exo*-position (in **1**) or on the *endo*-side (in **3**) of the allylic system; only **3** is expected to yield cyclopentene (**4**) by radical recombination.

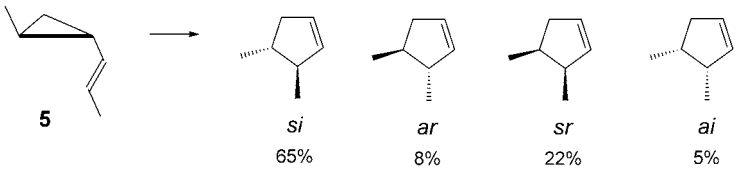
With the orbital-symmetry rules for concerted processes, *Woodward* and *Hoffmann* opened a new epoch of organic chemistry in 1965 (for a review, see [7]). In their systematics of sigmatropic reactions, the rearrangement of vinylcyclopropane offered one of the rare examples of 1,3 alkyl migration. The obvious course, *suprafacial* with *retention* (*sr*), is 'forbidden', as is likewise *antarafacial* with *inversion* (*ai*), but two other pathways, *antarafacial* with *retention* (*ar*) and *suprafacial* with *inversion* (*si*), would obey the orbital symmetry rules, all this under the proviso of *concertedness.* The transition structures (TSs) of these processes look awkward to a varying degree. *Woodward* and *Hoffmann* mentioned the vinylcyclopropane rearrangement only in passing; they did not refer to the question whether or not the rearrangement would in reality be concerted. However, *Woodward*'s authority may have played a role, when subsequently the orbital-symmetry-controlled, concerted courses dominated the discussion.

Willcott and *Cargle* observed in 1967 that *cis*-vinyl[2-$^2H_1$]cyclopropane equilibrates with the *trans*-isomer at 360°; the loss of stereospecificity was at least five times as fast as the irreversible rearrangement to cyclopentene [8]. *Doering* and *Sachdev* (1974/75) studied optically active *cis*-2-isopropenylcyclopropane-1-carbonitrile and the *trans*-

isomer. At 218°, the rearrangement competed with racemization and diastereomerization; the cyclopentene retained some enantiomeric excess (ee) making it possible to determine the whole set of rate constants [9]. The 'continuous diradical' enriched the vocabulary of interpretation.

Baldwin and co-workers gained valuable insight by investigating optically active *trans*-2,2′-disubstituted vinylcyclopropanes (for a review, see [10]). The 2,2′-dimethyl compound **5** at 296° furnished all four cyclopentenes, *i.e.*, two pairs of enantiomers [11] (*Scheme 2*). The kinetic data were expressed in partial rate constants of four concerted processes, in which the '*WH*-allowed' ones, *si* and *ar* (73%), dominated over the '*WH*-forbidden' *sr* and *ai* (27%). Compared with the high stereospecificities observed for electrocyclic reactions, the preference is meager. The inclination toward orbital-symmetry control is even smaller for [2,2′-$^2H_2$] labeling: *si* + *ar* reach only 53% [12].

Scheme 2



Tests with other 2,2′-substituents likewise showed a bias toward *si* + *ar* [10]. In a brilliant investigation, *Asuncion* and *Baldwin* in 1995 dealt with the rearrangement of optically active *trans*-2-phenyl-1-[(*E*)-styryl]cyclopropane and the *cis*-isomer; the rates of the competing enantiomerization and diastereomerization were likewise determined [13]. The deconvolution of the complex kinetics was highly demanding and disclosed a preference for the enantiomers of *trans*-3,4-diphenylcyclopent-1-ene over those of the *cis*-isomer. Thus, not the benefit of orbital symmetry, but sober thermodynamics appear to govern the steric course of the rearrangement. '*It seems rather more plausible to view these vinylcyclopropane to cyclopentene rearrangements as passing through alternative kinetically competitive diradical transition structures.*' [13].

1.2. *Computational Studies.* Concertedness of rearrangement, however, reentered through another door: computational chemistry. The experimental endeavors were accompanied by calculations, notably by *Houk et al.* (1992; [14]), who were interested in 1,3-sigmatropic shifts. In 1997, *Houk et al.* [15], as well as *Davidson* and *Gajewski* [16], reported on calculations of the vinylcyclopropane rearrangement by UB3LYP/6-31G*, confirmed by CAS-SCF(4,4) studies. A later extended version by *Houk* and co-workers included calculations of 2′-(*tert*-butyl)- and several methylated vinylcyclopropanes [17].

An intrinsic reaction coordinate, starting from the s-*gauche* conformation of **2** – without a TS for ring-opening – reached a slanting high plane at *ca.* 44 kcal mol^{-1} ascending to the TS of 1,5-cyclization at 46.9 kcal mol^{-1}. Structures on this plane return to s-*gauche*-**2** without a barrier. The mentioned TS is '*essentially pure diradical in character*' [17] and corresponds to the *endo*-allylic **3** in *Scheme 1*. Yet, the reaction is concerted, and the TS is located on the *si* pathway. In the TS, the two C,C bonds of the

allylic radical have similar bond lengths; the distance C(1)–C(3) is 2.489 Å and that of C(1)–C(5) 2.681 Å. The question arises whether these long bonds furnish enough energy for keeping the system on its concerted course. The *energy of concert* cannot be high.

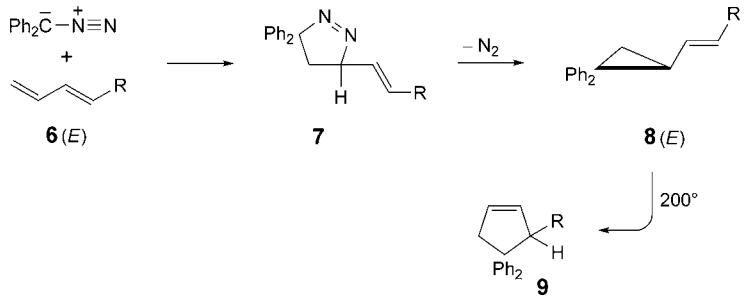
In the minimum-energy conformation of the *endo*-allylic diradical **3**, the allyl resonance keeps C(1) to C(4) in a common plane with only C(5) being mobile. Incipient bonding C(1)···C(3) requires less deformation than needed for C(1)···C(5). The molecular model shows that a certain strain must be overcome to achieve the conformation of *Houk*'s TS with its nearly equal distances for C(1)–C(3) and C(1)–C(5); this TS should be at a higher energy level than the *conformationally relaxed* diradical **3**. Why does the latter not occur as an *intermediate*?

In *Houk*'s splendid exposé [17], a closely related TS can lead to enantiomerized vinylcyclopropanes. That is achieved with less activation energy on another reaction coordinate, which converts s-*trans*-**2** into the *exo*-substituted allylic radicals; a C_s-symmetric TS (like **1** in *Scheme 1*), located at 43.5 kcal mol^{-1}, enters – with or without rotation – into the 1,3-cyclization. Should **1** not be an *intermediate*?

1.3. *New Contributions.* As described in a preceding paper, 1-(2-arylethenyl)-2,2-diphenylcyclopropanes became easily accessible [18]. It was shown that three Ph groups indeed stabilize the TS and bring down the temperature of the vinylcyclopropane rearrangement. It is not a far-fetched idea that electronic and steric effects of three Ph groups should cooperate in generating a deeper trough for the diradical intermediate and make it interceptible. It seemed rewarding to study the kinetics of racemization and rearrangement of oligophenylated vinylcyclopropanes and to examine the influence of substitutents and solvents on the rate. The pertinent computational study by *Sustmann et al.* reported in the following paper [19] is not free of surprises.

2. Results. – 2.1. *Preparation of 1-[2-Arylethenyl]-2,2-diphenylcyclopropanes*[1]). Recently, we described the preparation of vinylcyclopropane derivatives **8** by the interaction of diazo(diphenyl)methane with 1-substituted buta-1,3-dienes [18] (*Scheme 3*). The 1,3-cycloaddition to the unsubstituted C=C bond of **6** at room

Scheme 3

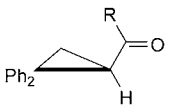


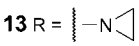
[1]) The IUPAC-conform systematic names of all compounds, mentioned in this work, are given in *Exper. Part* in parentheses.

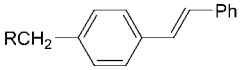
temperature is followed by a fast elimination of N_2 from the initially formed 4,5-dihydro-3*H*-pyrazole **7**; the (*E*)-configuration at the disubstituted C=C bond of **6** is retained. Although convenient and productive, the method leads only to racemic material.

Free of this disadvantage is a pathway *via* 2,2-diphenylcyclopropane-1-carboxylic acid (**11**), the optical resolution of which has been reported [20]. The reduction to aldehyde **14** and subsequent *Wittig* olefination should provide model compounds **22a**–**22h** for the study of racemization and rearrangement. Synthesis and reactions were first tested with racemic material.

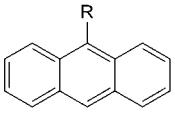
The ester **10** is easily available from methyl acrylate and diazo(diphenyl)methane [20]. For the reduction of **11** to the aldehyde **14**, the acid chloride **12** was converted to the aziridide **13**, which was treated with $LiAlH_4$, a known procedure [21]. We obtained 49% for the sequence **11** → **14**. The cycloaddition of diazo(diphenyl)methane to acrolein gave 70% of *rac*-**14**.



10 R = MeO
11 R = OH
12 R = Cl
13 R = 
14 R = H



15 R = Br
16 R = P^+Ph_3 Br^-



17 R = CHO
18 R = CH_2NMe_2
19 R = $CH_2N^+Me_3$ I^-
20 R = $CH_2N^+Ph_3$ I^-

The phosphonium salts for the *Wittig* reaction were prepared from benzyl-type halides and Ph_3P. Even the somewhat exotic 4-[(*E*)-styryl]benzyl bromide (**15**) [22] was reacted with Ph_3P in refluxing xylene to give **16**. Anthracene-9-aldehyde (**17**) was subjected to a modified *Leuckart–Wallach* reaction to give 9-[(dimethylamino)methyl]-anthracene (**18**). The quaternary ammonium salt **19**, obtained with MeI, was converted to the phosphonium iodide **20** with Ph_3P in refluxing BuOH (72% for **17** → **20**).

Various base systems were used for the deprotonation of the phosphonium salts and the *in situ* reactions of the (arylmethylidene)(triphenyl)phosphoranes **21** with the carbaldehyde **14** (*Scheme 4*). Our slight preference for EtONa in EtOH (*Variant B*; *cf. Exper. Part*) was based on a somewhat higher purity of the products. The problem – and failure – of a general stereocontrol of the *Wittig* reaction is as old as this valuable olefin synthesis. The 1-(2-arylethenyl)-2,2-diphenylcyclopropanes **22** were formed as mixtures of (*E*)- and (*Z*)-isomers of **22a**–**22h** in total yields of 69–89%, and the (*Z*)-content varied from 56 to 93% (*Table 1*). In organic synthesis, (*E*)-olefins are usually in higher demand than the (*Z*)-isomers. However, in our study the substantial amounts of (*Z*)-**22** were a fringe benefit, since their thermal reactions are noteworthy [23].

The rather laborious separation of (*E*)- and (*Z*)-**22** was performed by thick-layer chromatography (TLC) on 2-mm silica gel on glass plates with light petroleum as

Scheme 4

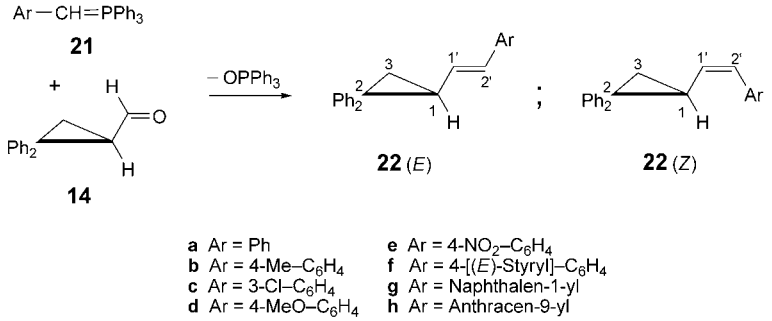


Table 1. *Properties of* rac-*1-(2-Arylethenyl)-2,2-diphenylcyclopropanes*

Formula No.	Ar	Yield [%]	M.p. [°]	δ(H–C(1′)) [ppm]	δ(H–C(2′)) [ppm]	^3J(1′,2′) [Hz]	C=C (str.) [cm^{-1}]
(*E*)-**22a**	Ph	31	60–61	5.46	6.55	15.8	1638
(*E*)-**22b**	4-Me–C_6H_4	22	88–89	5.47	6.58	15.8	1643
(*E*)-**22c**	3-Cl–C_6H_4	30	77–79	5.49	6.50	15.8	1639
(*E*)-**22d**	4-MeO–C_6H_4	28	61–63	5.34	6.52	15.8	1639
(*E*)-**22e**	4-NO_2–C_6H_4	18	98–100	5.68	6.62	15.8	1640
(*E*)-**22f**	4-[(*E*)-Styryl]–C_6H_4	32	144–145	5.48	6.68	16.0	1633
(*E*)-**22g**	Naphthalen-1-yl	20	108–110	5.17	[a])	15.5	1639
(*E*)-**22h**	Anthracen-9-yl	22	135–136	5.47	[a])	16.0	1642
(*Z*)-**22a**	Ph	39	88–89	4.94	6.39	11.5	1635
(*Z*)-**22b**	4-Me–C_6H_4	61	62–63	4.90	6.37	11.5	1640
(*Z*)-**22c**	3-Cl–C_6H_4	45	67–68	4.99	6.33	11.5	1627
(*Z*)-**22d**	4-MeO–C_6H_4	41	83–84	4.85	6.33	11.5	no signal
(*Z*)-**22e**	4-NO_2–C_6H_4	59	112–113	5.15	6.41	11.6	1629
(*Z*)-**22f**	4-[(*E*)-Styryl]–C_6H_4	57	125–127	4.96	6.39	11.5	1628
(*Z*)-**22g**	Naphthalen-1-yl	62	107–108	5.16	6.86	11.4	1635
(*Z*)-**22h**	Anthracen-9-yl	58	oil	5.47	[a])	11.0	no signal

[a]) Signal among those of aromatic H-atoms.

mobile phase and UV check on zone separation[2]). The (*Z*)-structures always showed higher R_f values than the (*E*) forms.

The vinylcyclopropanes **22** were crystalline compounds (with one exception), and the (*E*,*Z*)-assignment was infallibly based on the coupling constant of the vinylic H-atoms: $J(1',2') = 15.5–16.0$ for (*E*)-**22a**–**22h** and 11.0 to 11.6 Hz for (*Z*)-**22a**–**22h**. The chemical shifts, δ(H–C(1′)) and δ(H–C(2′)), are higher for (*E*)- than for (*Z*)-isomers (*Table 1*). The IR HC=CH stretching frequency at *ca.* 1640 cm^{-1} is regularly a bit higher for (*E*)- than for (*Z*)-**22**, but changes of intensity are considerable.

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[2]) The experimenter regarded his work as an orgy in TLC.

Furthermore, the out-of-plane (oop) deformation frequencies for (*E*)- and (*Z*)-HC=CH occur in different regions [24]. However, aromatic oop frequencies populate these regions also, sharply reducing the value of this criterion here.

2.2. *Optically Active 1-[2-(*E*)-Arylethenyl]-2,2-diphenylcyclopropanes and Their (Z)-Isomers. Walborsky* and *Hornyak* [20] achieved the optical resolution of the carboxylic acid **11** *via* the brucine salt in moderate yield. With the crystallization of the quinine salt of (+)-**11** from acetone, the same laboratory improved the procedure [25]. On treatment with HCl, the quinine salt produced optically pure (+)-**11** with $[\alpha]_D^{25} = +226$ ($CHCl_3$). The quinine salt of (−)-**11** from the mother liquor was impure, but, on treatment with brucine in acetone, could be converted to diastereomerically pure brucine salt and with HCl to (−)-**11** with $[\alpha]_D^{25} = -231$. Based on *rac*-**11**, we obtained 36% of (+)-**11** and 22% of (−)-**11**. *Via* the menthyl acrylate of known absolute configuration and its reaction with diazo(diphenyl)methane, *Walborsky et al.* connected (+)-**11** with the (*R*)-configuration [26].

Due to the easier access of (+)-(*R*) acid **11**, this enantiomer was reduced by the method described above to the aldehyde (+)-(*R*)-**14** which showed $[\alpha]_D^{25} = +150.5$, and its melting point (52–54°) was lower than that of *rac*-**14** (74–76°).

The *Wittig* olefinations of (+)-(*R*)-2,2-diphenylcyclopropane-1-aldehyde (**14**) were carried out as described above for *rac*-**14**. According to the notation rules, the olefinic products have the (*S*)-configuration for (*E*)-**22** as well as for (*Z*)-**22**. The specific rotations, $[\alpha]_D^{25}$, in *Table 2* reveal a regularity for (+)-(*S*,*E*)-**22** and (−)-(*S*,*Z*)-**22**.

Table 2. *Optically Active (*S*)-1-(2-Arylethenyl)-2,2-diphenylcyclopropanes*

Formula No.	Aryl	*Wittig* reaction, base system	Yield [%]	M.p. [°]	$[\alpha]_D^{25}$ in Decalin
(*E*)-**22a**	Ph	PhLi/Et_2O	36	85–86	+340
(*E*)-**22b**	4-Me–C_6H_4	EtONa/EtOH	12	76–78	+268
(*E*)-**22c**	3-Cl–C_6H_4	PhLi/Et_2O	21	100–102	+334
(*E*)-**22d**	4-MeO–C_6H_4	PhLi/Et_2O	14	76.5–78.5	+290
(*E*)-**22e**	4-NO_2–C_6H_4	EtONa/EtOH	18	99–101	+191
(*E*)-**22f**	4-[(*E*)-Styryl]–C_6H_4	EtONa/EtOH	35	158–150	+304
(*E*)-**22g**	Naphthalen-1-yl	EtONa/EtOH	24	112–114	+215
(*E*)-**22h**	Anthracen-9-yl	PhLi/C_6H_6	23	oil	+71
(*Z*)-**22a**	Ph	PhLi/Et_2O	57	oil	−232
(*Z*)-**22b**	4-Me–C_6H_4	EtONa/EtOH	32	oil	−346
(*Z*)-**22c**	3-Cl–C_6H_4	PhLi/Et_2O	29	54.5–56.5	−324
(*Z*)-**22d**	4-MeO–C_6H_4	PhLi/Et_2O	26	oil	−323
(*Z*)-**22e**	4-NO_2–C_6H_4	EtONa/EtOH	60	91–93	−361
(*Z*)-**22f**	4-[(*E*)-Styryl]–C_6H_4	EtONa/EtOH	56	128–130	−543
(*Z*)-**22g**	Naphthalen-1-yl	EtONa/EtOH	48	86–88	−224
(*Z*)-**22h**	Anthracen-9-yl	PhLi/C_6H_6	56	oil	−87

2.3. *Racemization Rates of (+)-(*S*)-1-[2-(*E*)-Arylethenyl]-2,2-diphenylcyclopropanes.* When (+)-(*E*)-**22a** was heated in decalin at 120°, the optical rotation continuously decreased. After 9 h, the rotation was close to zero, but the ^{1}H-NMR spectrum ($CDCl_3$) of the isolated product showed no change, and crystalline *rac*-(*E*)-

22a was isolated in high yield. Thus, the racemization can be studied without noticeable disturbance by the isomerisation to 3,4,4-triphenylcyclopent-1-ene (**23a**; *cf. Scheme 5*).

$$\ln(\alpha_o/\alpha_t) = k_{rac}\, t = 2\, k_{inv}\, t \quad (1)$$

The rate constants of racemization were measured polarimetrically and evaluated by the simple first-order law (*Eqn. 1*). For at least three half-reaction times (87.5%), the plots of ln (α_o/α_t) *vs.* time were linear. Rate constants k_{rac} for (+)-(*E*)-**22a** were measured at four temperatures over a range of 29° (*Table 3*), and double runs were reproducible within ±1%. The half-reaction time decreases from 246 (99.5°) to 15.6 min (128.7°). The activation parameters listed in *Table 3* will be compared with those of ring enlargement in *Sect. 2.4.2*.

Table 3. *Kinetics for the Racemization of (+)-(*S*)-2,2-Diphenyl-1-[(*E*)-2-phenylethenyl]cyclopropane* (**22a**; 20–30 mM) *in Decalin* (Polarimetry)

T [°]	k_{rac} [$\cdot 10^4$ s^{-1}]	Activation parameters	
99.5	0.469, 0.469	*Arrhenius*	$E_A = 28.2 \pm 0.8$ kcal mol^{-1}
109.6	1.32, 1.30		log $A = 12.2 \pm 0.4$
119.4	3.33, 3.33	*Eyring*	$\Delta H^{\neq} = 27.4 \pm 0.8$ kcal mol^{-1}
128.7	7.44, 7.35		$\Delta S^{\neq} = -5.2 \pm 2.1$ e.u.
			$\Delta G^{\neq}$ (100°) $= 29.3 \pm 1.6$ kcal mol^{-1}

Table 4 contains k_{rac} values for (+)-(*E*)-**22a** at 109.6° in 12 solvents which are ordered by increasing polarity; the E_T values of *Reichardt* [27] stretch over a wide range. The numerical response in k_{rac} is minimal and does not show any correlation with solvent polarity.

Table 4. *Rate Constants for Racemization of (+)-(*S,E*)-***22a** (20–30 mM) *and Ring Enlargement of* rac-*(*E*)-***22a** (0.15–0.20 mM): *Variation of Solvent*

Solvent	k_{rac} [$\cdot 10^4$ s^{-1}] at (109.6 ± 0.2)°	k_{rac} (rel.)	E_T(30)	k_{isom} [$\cdot 10^4$ s^{-1}] at (159.3 ± 0.2)°	k_{isom} (rel.)
Decalin	1.31	≡1.00	31.2	0.932	≡1.00
Cyclohexane	1.45	1.11	30.9	1.07	1.15
Bu_2O	1.41	1.08	33.4	0.994	1.07
Benzene	1.74	1.33	34.5	1.18	1.26
Dioxan	1.12	0.86	36.0	0.888	0.95
PhCl	1.53	1.17	37.5	1.04	1.12
$ClCH_2CH_2Cl$	1.18	0.90	41.9	0.900	0.97
DMF	1.20	0.92	43.8	0.907	0.97
DMSO	1.00	0.76	45.0	[a])	
MeCN	1.13	0.86	46.0	0.964	1.03
BuOH	1.22	0.93	50.2	0.941	1.01
EtOH	1.24	0.95	51.9	1.08	1.16
$HOCH_2CH_2OH$	[a])		56.3	0.821	0.88

[a]) No measurements.

Although the arylethenyl groups of (+)-(*E*)-**22a**–**22h** harbor electron-attracting and electron-releasing substituents, the data for k_{rac} (119.4° in decalin) in *Table 5* reveal an astonishingly small influence of aryl variation. We conclude that the activation process is not connected with a notable change of charge distribution. The highest rate increase – still modest – is shown by Ar = anthracen-9-yl (k_{rac} (rel.) = 2.38) which may indicate radical stabilization.

Table 5. *Kinetics of Racemization of (+)-(*S*)-1-[(*E*)-2-Arylethenyl]-2,2-diphenylcyclopropanes* (**22**; 20–30 mM) *and Ring Enlargement of* rac-**22** (0.15–0.20 mM) *in Decalin*

Formula No.	Ar	k_{rac} [$\cdot 10^4$ s^{-1}] at 119.4°	k_{rac} (rel.)	λ [nm]	k_{isom} [$\cdot 10^4$ s^{-1}] at 159.3°	k_{isom} (rel.)
22a	Ph	3.33	≡ 1.00	269	0.932	≡ 1.00
22b	4-Me–C_6H_4	3.34	1.00	269	1.01	1.09
22c	3-Cl–C_6H_4	2.73	0.82	269	0.863	0.93
22d	4-MeO–C_6H_4	3.52	1.06	274	1.12	1.20
22e	4-NO_2–C_6H_4	4.66	1.40	329	4.45	4.80
22f	4-[(*E*)-Styryl]–C_6H_4	6.57	1.97	350	2.13	2.28
22g	Naphthalen-1-yl	4.64	1.39	320	2.12	2.28
22h	Anthracen-9-yl	7.93	2.38	259	2.11	2.26

2.4. *3-Aryl-4,4-diphenylcyclopent-1-enes* (**23a**–**23h**; *cf. Scheme 5*). 2.4.1. *Thermal Isomerization of* (*E*)-**22a**–**22h**. Without solvent, samples of (*E*)-**22** were heated at 200° under N_2 for 1.5 h, usually followed by high-vacuum distillation and recrystallization, to furnish the cyclopentenes **23a**–**23h** (*Table 6*) in isolated yields of 90–96%. The ring enlargement of the parent compound (*E*)-**22a** was described in the preceding paper, and **23a** was characterized by epoxidation to give **25** and by catalytic hydrogenation [18].

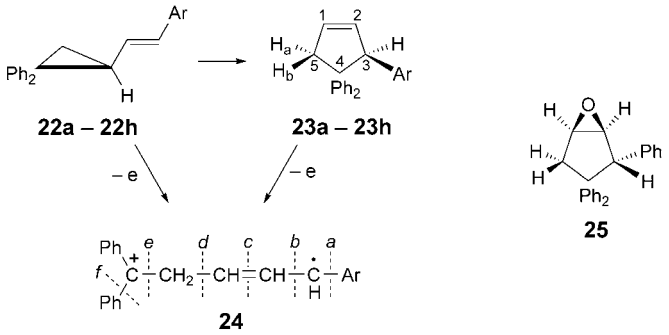
A striking phenomenon is the identity of the mass spectra of styryl-cyclopropanes **22** and the cyclopentenes **23**. It was suggested in the preceding paper [18] that the radical cations of **22** and **23** furnish one and the same open-chain **24** (*Scheme 5*). This

Table 6. *Properties of 3-Aryl-4,4-diphenylcyclopent-1-enes* (**23**)

Formula No.	Aryl	M.p. [°]	δ(H) [ppm]					^2J(5a,5b) [Hz]
			H–C(1)	H–C(2)	H–C(3)	H_a–C(5)	H_b–C(5)	
23a	Ph	68–70	6.00	6.02	4.78	2.78	3.62	16.3
23b	4-Me–C_6H_4	59–61	5.97	5.99	4.75	2.79	3.61	16.2
23c	3-Cl–C_6H_4	oil		5.98[a])	4.73	2.69	3.60	16[a])
23d	4-MeO–C_6H_4	99–101	5.96	5.99	4.74	2.77	3.59	16.3
23e	4-NO_2–C_6H_4	84–86	5.97	6.10	4.85	2.81	3.63	16.5
23f	4-Styryl–C_6H_4	115–117	5.98	6.03	4.78	2.80	3.63	16.0
23g	Naphthalen-1-yl	135–136	6.04	6.10	5.62	2.83	3.78	17.1
23h	Anthracen-9-yl	135–137	6.14	6.14	6.41	3.09	4.25	17.1

[a]) Not sufficiently resolved.

Scheme 5



more favorable structure is a distonic radical ion in which charge and electron spin are formally separated [28]. All the fragmentation pathways *a*–*f* were observed.

The ^{1}H-NMR spectra of **23a**–**23h** (*Table 6*) disclose a high aptitude for H,H coupling: each of the five aliphatic H-atoms couples with the other four. Apart from $^3J(1,2) = 5.9$ and $^2J(5a,5b) = -16.3$ Hz, the three vicinal, three allylic, and two homoallylic couplings were shown to be in the range of 1.7–2.4 Hz by the computer simulation of the complex spectrum of **23a**; the homoallylic $^5J(3,5) = 1.7$ Hz is even the same for *cis*- and *trans*-relation [18][29].

The cyclopentenes **23** are expected to be in an envelope conformation with C(4) as the flap. The paramagnetic influence of 3-aryl shifts the *cis*-located H_b–C(5) by 0.8–0.9 ppm to lower field, compared with H_a–C(5) in *trans*-position. The two H–C(5) appear as *doublet*s of *quadruplet*s. These are *pseudo-quadruplet*s generated by the similarity of $^3J(1,5)$, $^4J(2,5)$, and $^5J(3,5)$ (*cis* and *trans*).

The chemical shifts of the aliphatic H-atoms – the vinylic H–C(1) and H–C(2) with $^3J(1,2) = 5.8–5.9$ Hz included – do not change much, as long as 3-aryl is a monosubstituted phenyl group (*i.e.*, **23a**–**23f**), but the δ(H–C(3)) shoots up for Ar = naphthalen-1-yl and anthracen-9-yl, and that of **23h** passes the signal of the vinylic H-atoms. One side-ring of anthracenyl is located above the *cis*-4-phenyl in parallel planes. A mutual shielding spreads the signals of *cis*-4-Ph (2 H : 1 H : 2 H) and one anthracenyl-H upfield to 6.53–7.08 ppm, whereas three anthracenyl-H (out of H–C(1′) to H–C(4′)) are shifted up into the region of the 'unaffected' H-atoms of *trans*-4-phenyl. Another set of anthracenyl H-atoms, five 1-H signals for H–C(5′) to H–C(8′) and the *s* of H–C(10′) remain in the low-field region (7.74–8.31), as expected for anthracene derivatives. Thus, the anthracenyl residue has lost the magnetic equivalence of the two benzo rings in **23h**. A hindrance to rotation about the bond RC_6H_4–C(3) in **23a**–**23f** is not discernible by ^{1}H- and ^{13}C-NMR.

2.4.2. *Rate Constants of Ring Enlargement.* The styrene-type conjugation in (*E*)-**22a** is lost in the cyclopentene **23a**. As a consequence, the UV absorption coefficient in decalin at 269 nm is diminished by a factor of 40 in the rearrangement. Thus, UV spectrophotometry was chosen to determine the rate of conversion. The first-order *Eqn. 2* takes the experimentally determined A_∞ into account; A_∞ is usually somewhat larger than the precalculated absorbance of product **23**.

$$\ln \frac{A_o - A_\infty}{A_t - A_\infty} = k_{isom} t \quad (2)$$

The absorbance A_t was measured up to conversions of 85–90%, and the rate followed the first-order law. The values of k_{isom} of **22a** were measured over a temperature range of 25°, and linear regression provided the activation parameters (*Table 7*). The barrier to ring enlargement, $\Delta H^{\neq}_{isom} = 31.0$ kcal mol^{-1}, is by 3.6 kcal mol^{-1} higher than that of racemization. At 150°, a temperature between the ranges of measurement, (+)-**22a** racemizes with $t_{1/2} = 2.7$ min and rearranges with $t_{1/2} = 4.7$ h, *i.e.*, slower by a factor of 106.

Table 7. *Kinetics for the Ring Enlargement of* rac-*2,2-Diphenyl-1-[(*E*)-2-phenylethenyl]cyclopropane* (**22a**; 0.15–0.20 mM) *in Decalin* (UV Spectrophotometry)

T [°]	k_{isom} [$\cdot 10^4$ s^{-1}]	Activation parameters	
159.3	0.937, 0.925	*Arrhenius*	$E_A = 31.9 \pm 1.2$ kcal mol^{-1}
169.1	2.12, 2.12		log $A = 12.1 \pm 0.6$
177.5	4.29, 4.35	*Eyring*	$\Delta H^{\neq} = 31.0 \pm 1.2$ kcal mol^{-1}
184.0	6.76, 6.85		$\Delta S^{\neq} = -6.0 \pm 2.6$ e.u.
			$\Delta G^{\neq}$ (100°) $= 33.2 \pm 2.2$ kcal mol^{-1}

The influence of the solvent on the rate of rearrangement is as small as that on the racemization. On comparing the rate constants k_{rac} and k_{isom} in *Table 4*, the different temperatures, 109.6° *vs.* 159.3°, should be kept in mind. Columns *3* and *6* with the relative values of k_{rac} and k_{isom}, based on those of **22a**, reveal a certain parallelism, but none whatsoever with E_T, the parameter of solvent polarity. A noteworthy observation: racemization and ring enlargement smoothly proceed in alcohols. No interaction at 160° was observed in a preparative experiment with **22a** in ethane-1,2-diol, in which **23a** was isolated in high yield.

Somewhat larger, but still unimpressive, is the influence of the aryl substituent on the rate constant in (*E*)-**22a**–**22h**. For the photometric rate measurements, a wavelength was used which offers a great difference of absorbance in (*E*)-**22** and **23** (decalin), not necessarily λ_{max}. The values and the rate constants k_{isom} are listed in *Table 5*; the relative rate constants (columns *4* and *7*) on the basis of **22a** disclose the same small magnitude of substituent effects for racemization and rearrangement; with k_{isom} (rel.) = 4.80, **22e** (Ar = 4-NO_2–C_6H_4) is at the top. Further discussion is presented in *Sect. 3.3*.

2.5. *X-Ray Analyses.* The X-ray diffraction pattern reveals the s-*trans* conformation of 2,2-diphenyl-1-[(*E*)-styryl]cyclopropane (**22a**; *Fig. 1*). A precise 'bisectic' attachment of the styryl residue to the cyclopropane would require orthogonality of the plane C(1)–C(4)–C(5) and the three-membered ring; the deviation amounts to 5.8°. Even the planarity of the styryl residue is not perfect; the Ph group is twisted *vs.* the ethylenic plane by 6.5°. Presumably, lattice forces are responsible for these deviations. The bond lengths of C(1)–C(4) (1.473 Å) and C(4)–C(5) (1.336 Å) differ only on the third

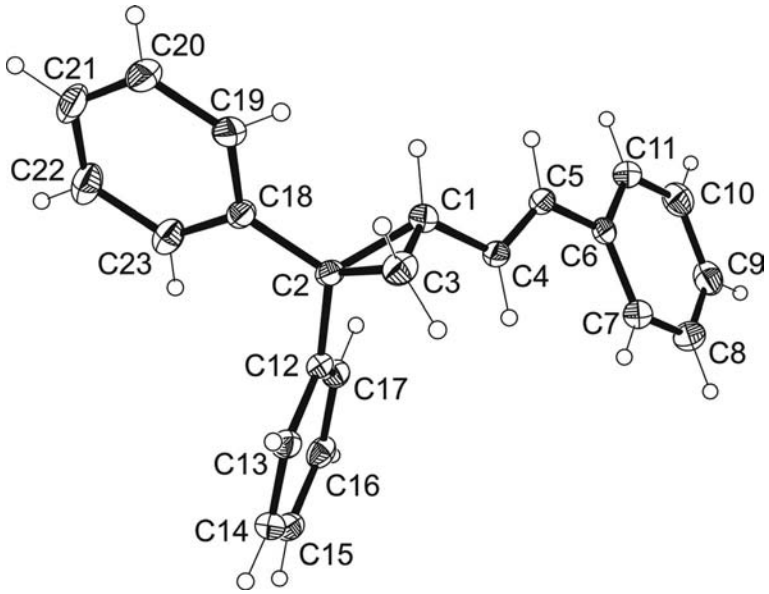


Fig. 1. *ORTEP View of* **22a** *with thermal ellipsoids drawn at 50% probability level*

decimal from those of the parent vinylcyclopropane (electron diffraction in gas [30]). Further features of the X-ray structure will be discussed in connection with calculations (*cf.* [19]).

The X-ray diffraction discloses for the 3,4,4-triphenylcyclopent-1-ene (**23a**) a rigidly frozen envelope conformation in two crystallographically independent molecules with very close geometrical parameters; *Fig. 2* shows the molecular structure of the first. In accord with the dihedral angle for C(3)C(2)=C(1)C(5) of 0.83°, the planarity of the ethylenic *bond* system is nearly perfect in the crystal. The two edges of the flap, C(3)–C(4) and C(4)–C(5), show almost identical dihedral angles, −32.59(10)° and 32.65(10)°, undisturbed by 3-Ph group. The flap, C(4), rises from the mentioned ethylenic plane by 0.56 Å.

3. Discussion. – 3.1. *Conformational Control of Racemization and Ring Enlargement.* We have anticipated *exo*,*endo*-isomeric open-chain allylic structures **1** and **3**. Both have the capacity to close the three-membered ring, but only the *endo*-substituted allylic diradical **3** is capable of 1,5-cyclization. 1,5-Radical recombination of **1** should lead to a highly strained (unknown) *trans*-cyclopentene; on the other hand, a rotation about the C=C bond should increase the energy balance of activation by an additional 14 kcal mol^{-1} for the transient loss of allylic resonance. These considerations are consistent with diradicals **1** and **3** as true *intermediates* or as '*intermediate phases*'. We discussed the latter term to describe significant conformations that are neither TS nor bottom of the energy trough. However, we learned that *Northrop* and *Houk* [31] in 2005 had proposed '*paraintermediates*' for such species occurring on flat hypersurfaces; we gladly adopt this designation.

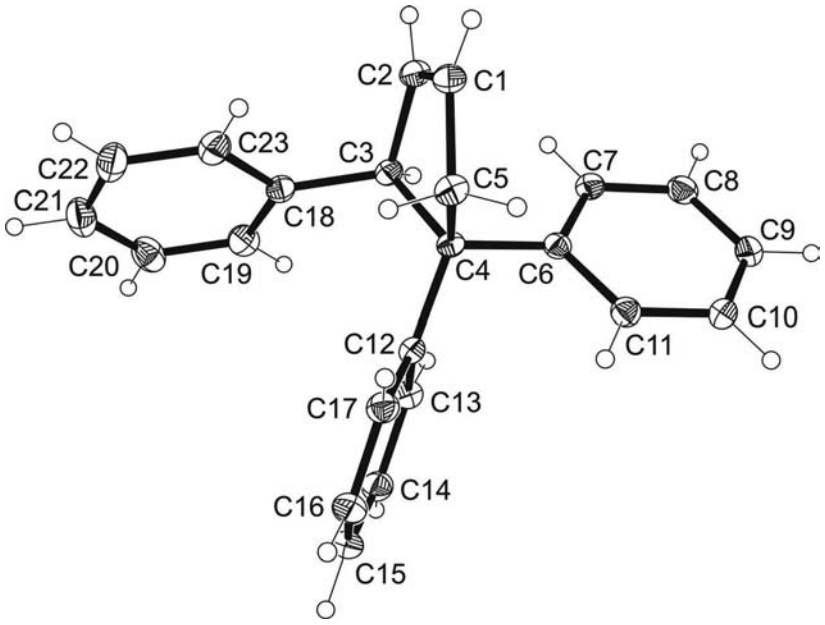


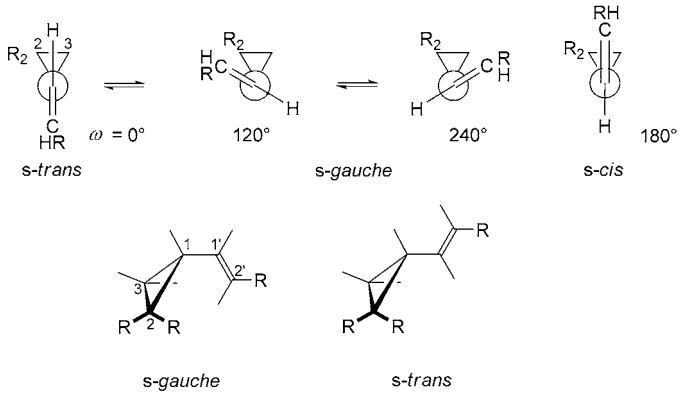
Fig. 2. *ORTEP View of* **23a** *with thermal ellipsoids drawn at 50% probability level*

Rotation about the 1,1′-bond of vinylcyclopropane allows several favored conformations. The bisectic s-*trans* as the most stable form has found general consent. The s-*cis*-conformation may suffer from front-side strain. In 1966, two groups proposed a mixture of s-*trans* and s-*gauche* in a three-well torsional potential with respect to the 1,1′-bond, based on ^{1}H-NMR phenomena [32]. *de Meijere* and *Lüttke* reported in 1969 on the electron diffraction of gaseous vinylcyclopropane and established an equilibrium of $75 \pm 6\%$ s-*trans* and $25 \pm 6\%$ s-*gauche* conformation, corresponding to $\Delta G_{293} = -1.06$ kcal mol^{-1} [30]. With the 1,1′-bond as a vertical axis, the *Newman* projection in *Scheme 6*, with R = H, shows the three conformations on the first line; there was no evidence for a s-*cis*-conformation. Our quantum-chemical calculations confirmed the relative stabilities [19].

The s-*trans* conformation of **2** appears to be predestined to generate the *exo*-substituted diradical **1** on ring-opening. Highly probable as well, the s-*gauche*-conformation of **2** is the precursor of the *endo*-allylic diradical **3**. The projections on the lower line of *Scheme 6* serve as illustrations.

On changing from vinylcyclopropane (**2**) to its triphenyl derivative **22a**, the steric interaction of the (*E*)-styryl group with the cyclopropane ring remains unaltered (*Scheme 6*; R = Ph). The *cis*-2-Ph group, however, generates strain in one s-*gauche* conformation (120°). Whether a true intermediate or a paraintermediate, a conformation of this kind must be passed in the 1,2-ring opening leading to the *endo*-substituted diradical, which yields the cyclopentene **23a** on 1,5-recombination. The Ph group of the (*E*)-styryl group winds up in the allylic *exo*-1-position of diradical **27**.

Scheme 6



A flow-sheet combines enantiomerization and ring enlargement (*Scheme 7*). It begins in the upper left with the reversible ring-opening of s-*trans*-(*R*)-**22a**. In the racemization, the rotational barrier for (*Re*)-*exo*,*exo*-**26** to the (*Si*)-enantiomer is overcome. It remains hidden, how often (*Re*)-**26** recyclizes, before it undergoes rotation about the C(3)–C(4) bond.

The 1-*exo*-Ph group contributes 8.8 kcal mol^{-1} to the allyllic stabilization of *exo*,*exo*-**26**. According to calculations (B3LYP/6-31G*) of the planar 3-*exo*-methyl-1-*exo*-phenylallyl radical as a model, + 8.8 kcal mol^{-1} must be invested for twisting the Ph group to the orthogonal position. In contrast, a 1-*endo*-Ph group in the isomeric structure would add only 4.2 kcal mol^{-1} to the conjugation energy of the allylic radical; the collision with the 3-*endo*-H requires a 19° rotation about the C(1)–Ph bond in the ground state[3]).

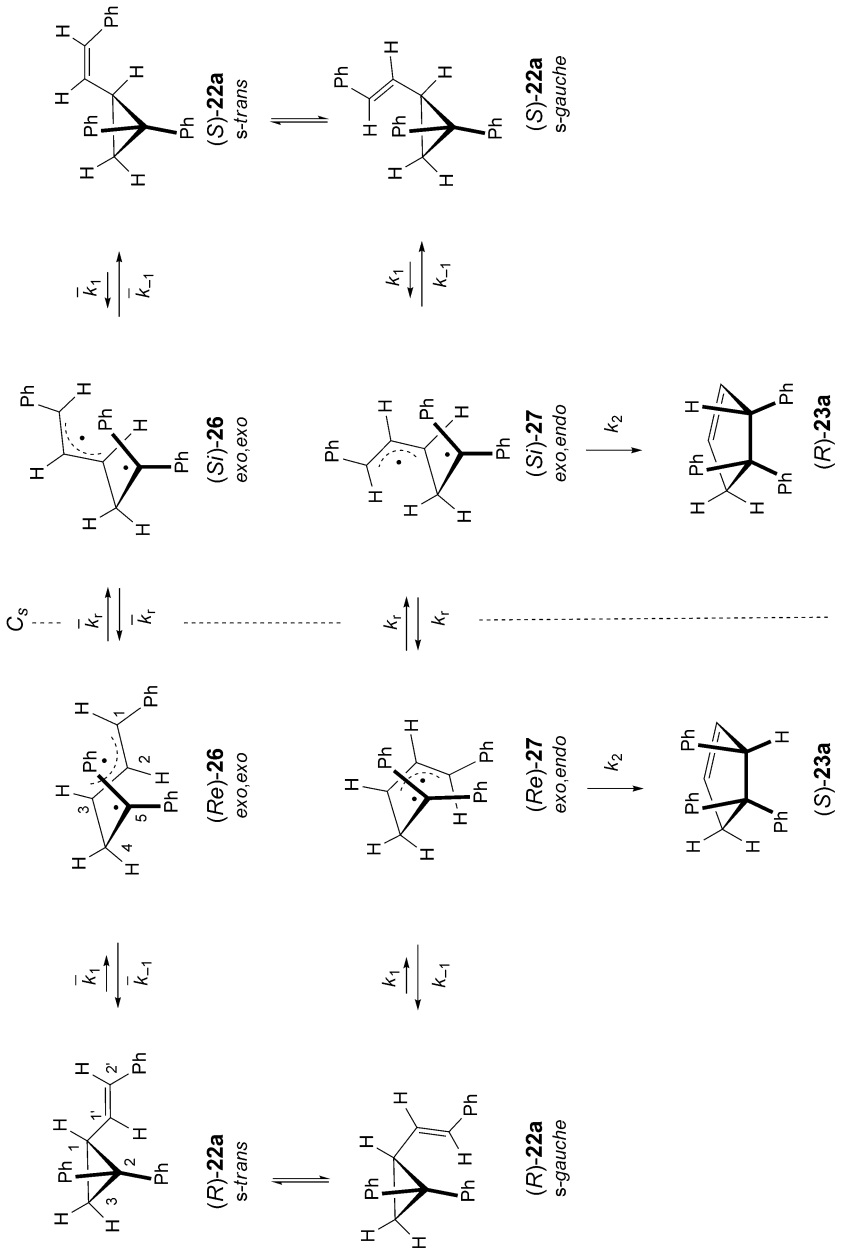
The less-populated s-*gauche* conformation of (*R*)-**22a** at the lower left of *Scheme 7* generates the more favored open-chain structure, (*Re*)-*exo*,*endo*-diradical **27**, on homolysis of the 1,2-bond. Here, rotation to (*Si*)-*exo*,*endo*-**27** competes with the 1,5-ring closure to give cyclopentene (*S*)-**23a**, in addition to the continued 3,5-recombination.

3.2. *Rate Increase on Substitution by Three Phenyl Groups.* The best activation data for the thermal rearrangement of the parent vinylcyclopropane are based on the gas kinetic measurements by *Lewis et al.* [4]: $E_A = 51.7 \pm 0.5$ kcal mol^{-1} and $\log A = 14.3 \pm 0.1$ s^{-1}. Our measurements (*Table 7*) with **22a** in decalin as solvent furnished $E_A =$ 31.9 kcal mol^{-1} and $\log A = 12.1$ s^{-1}. The lowering of E_A by 19.8 kcal mol^{-1} reflects the effect of three Ph groups on the TS of 1,5-cyclization minus their influence in the ground-state of **22a**. Several phenomena are contributing:

1) The diphenyl*methyl* radical is stabilized by − 20.4 kcal mol^{-1}. *Zipse* and co-workers calculated by (G3(MP2)-RAD//UB3LYP/6-31G(d)) an isodesmic H-abstraction by the CH_3 radical [33]; the energy includes the gain by relieving the steric

[3]) We thank *W. Sicking*, University of Duisburg-Essen, for the calculations.

Scheme 7


(S)-22a
s-trans
(S)-22a
s-gauche
(Si)-26
exo,exo
(Si)-27
exo,endo
(R)-23a
Cs
(Re)-26
exo,exo
(Re)-27
exo,endo
(S)-23a
(R)-22a
s-trans
(R)-22a
s-gauche

crowding in the ground-state of Ph_2CH–. A slightly higher stabilization is expected for the diphenyl*ethyl* in diradical **27**.

2) The conjugation energy of the Ph in the styryl group of **22a** may be worth -3 kcal mol^{-1}, but the stabilization of this Ph in the diradical *exo*,*endo*-**27** is higher. From the model calculations above, we derived $+8.8$ kcal mol^{-1} for twisting such an *exo*-Ph out of coplanarity. The stabilization may account for *ca.* -6 kcal mol^{-1}.

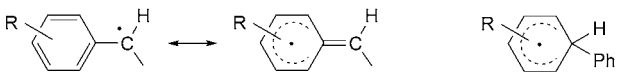
3) In the conformational equilibrium of **22a**, s-*gauche* is less populated than s-*trans*, and, on the energy level of the ring-opened diradicals, *exo*,*endo*-**27** is less favored than *exo*,*exo*-**26**. In model calculations (UB3LYP/6-31G*) with the 3-methyl-1-*exo*-phenyl-allyl radical, a 3-*exo*-Me group is by 1.1 kcal mol^{-1} better than a 3-*endo*-Me[3]). Admittedly, the steric interference of a 2,2-diphenylethyl group on the *endo*-side of the allyl radical in **27** exceeds that of Me. A partial cancellation of effects is expected.

4) A certain energy-demanding bending of the planar *exo*,*endo*-**27** is required to reach the TS of 1,5-cyclization. This last contribution recalls that we are still dealing with a TS which does not fully profit from the stabilization of a planar allyl radical.

3.3. *Variation of Aryl in the 2-Arylethenyl System.* The small influence of aryl variation on k_{rac} and k_{isom} of (*E*)-**22** was described above (*Sect. 2.3* and *2.4.2*, and *Table 5*). Substituents in the phenyl group change k_{rac} within a range of 2.4, and the exchange of phenyl by naphthalen-1-yl and anthracen-9-yl is rewarded by a 1.4- and 2.4-fold increase of k_{rac} (rel.), respectively.

The minor resonance structure **28** for a segment of (*E*)-**22** resembles the intermediate **29**, which occurs in the radical phenylation of aromatic compounds (*Scheme 8*) and furnishes Ph–Ar on H-abstraction. Phenyl radicals have been reacted *in situ* with binary mixtures of ArH/benzene, and the product analysis provides '*partial rate factors*' (p.r.f.), based on the phenylation of one benzene-CH (*cf.* the review of *Hey* [34]). Despite the small range of k_{rac}, a fairly straight line resulted, when log k_{rac} was plotted *vs.* log p.r.f. of radical phenylation (*Fig. 3*). The slope leaves no doubt that aromatic phenylation responds stronger to the variation of substituent R than the racemization of (+)-**22**. Reliable values of p.r.f. were chosen which are based on ^{14}C isotope dilution technique [35][36] or on GLC analysis [37].

Scheme 8



28 **29**

The substituent effects on k_{rac} and k_{isom} of **22a**–**22f** are 'diluted' by the benzene ring. Generally, carbon radicals are stabilized by electron-donating *and* -withdrawing substituents [33]: on introduction of a MeO group, the methyl radical is stabilized by 7.4 kcal mol^{-1}. The stabilization of the radical H_2C–CN is likewise 7.4 kcal mol^{-1}. 2-Donor-substituted vinylcyclopropanes rearrange faster than the parent, as shown by kinetic measurements. When we accept $E_A = 51.7$ kcal mol^{-1} for the ring enlargement of the parent, then a 2-methoxy or 2-dimethylamino group diminish E_A by 13.0 and 20.6 kcal mol^{-1}, respectively [38][39].

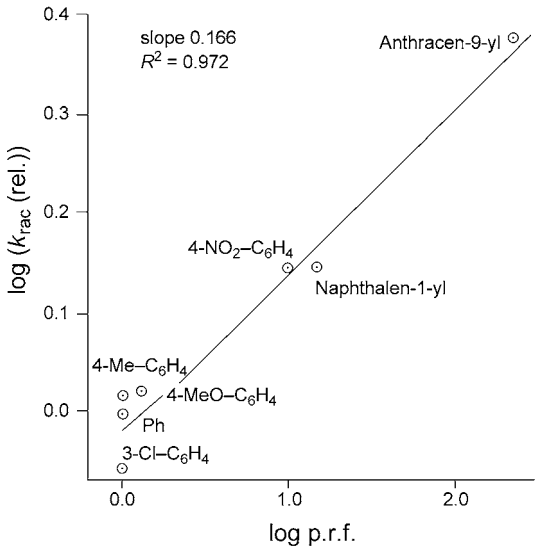
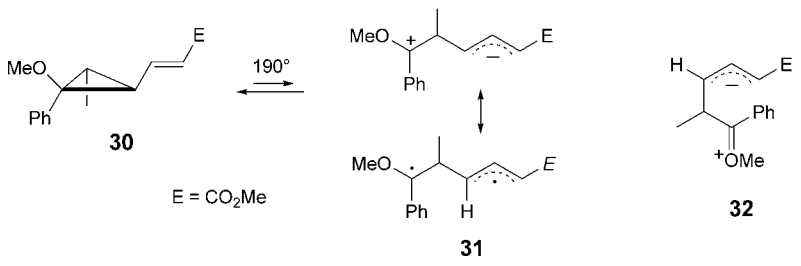


Fig. 3. *Relation of log* k_{rac} *(rel.) in decalin at 119.4° with the log of the partial rate factors of aromatic phenylation*

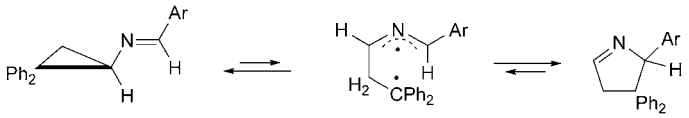
Donor- and acceptor-substituted vinylcyclopropanes of type **30** were studied by *Buchert* and *Reissig* (*Scheme 9*) [40]. The equilibration of the four conceivable (and identified) stereoisomers of **30** proceeded at 190° in PhCN much faster than in decalin. An *exo*,*exo*-substituted allylic *zwitterion* **31** evidences the solvent influence. The authors recognized the description as zwitterion or diradical as semantic; trimethylene zwitterions and diradicals are regarded as extremes on a continuous scale. At longer reaction times, **30** was converted to the four diastereomeric cyclopentenes, likewise identified, now formed *via* the *exo*,*endo*-allylic intermediate **32**.

Scheme 9



3.4. *A Heteroanalog of Vinylcyclopropane* (E)-**22**. The rearrangement of vinylcyclopropane is a prototype. Nearly each C-atom can be formally replaced by a heteroatom, and still the rearrangement works. Formal exchange of H–C(1′) of **22** by a N-atom gives rise to azomethines **33** (*Scheme 10*). These have been obtained optically active; their enantiomerization and rearrangement to 4,5-dihydro-3*H*-pyrroles **35** have

Scheme 10



33 **34** **35**

been investigated in scope, kinetics, and mechanism in the Munich laboratory [41]. The corresponding aza-allyl-diradicals **34** in *exo*,*exo*- and *exo*,*endo*-configuration were postulated as intermediates.

A surprise: the rate constants of racemization and ring enlargement of the azomethines **33** and the all-C-systems **22** are numerically fairly similar (*Table 8*). Even different solvents and the availability of activation parameters only for **33**, Ar = 4-MeO–C_6H_4, did not destroy the close analogy with **22a**. The rate constants for both systems were extrapolated to 150° and expressed in the same dimension: for the azomethine, the racemization is 41 times faster than the formation of the 4,5-dihydro-3*H*-pyrrole, whereas $k_{rac}/k_{isom} = 106$ was observed for **22a**.

Table 8. *Kinetic Data for* N-*(4-Methoxybenzylidene)-2,2-diphenylcyclopropylamine* (**33**; Ar = 4-MeO–C_6H_4) *in PhCN and 2,2-Diphenyl-1-[(*E*)-styryl]cyclopropane* (**22a**) *in Decalin*

	33 (Ar = 4-MeO–C_6H_4)	**22a**
Racemization		
k_{rac} [$\cdot 10^5$ s^{-1}] at 150°	390	440
$\Delta H^{\neq}$ [kcal mol^{-1}]	26.8 ± 0.8	27.4 ± 0.8
$\Delta S^{\neq}$ [e.u.]	−7 ± 2	−5.2 ± 2.1
Ring expansion		
k_{isom} [$\cdot 10^5$ s^{-1}] at 150°	9.46	4.14
$\Delta H^{\neq}$ [kcal mol^{-1}]	33.2 ± 0.9	31.0 ± 1.2
$\Delta S^{\neq}$ [e.u.]	1 ± 2	−6.0 ± 2.6

In the *Hückel* treatment of the allylic π-system, the SOMO (ψ_2) harbors the single electron, and the wavefunction has a node in the middle, *i.e.*, the introduction of the N-atom does not perturb the allylic system.

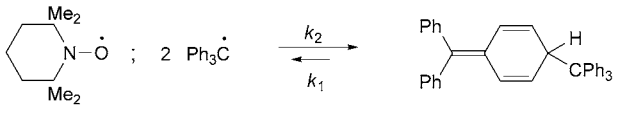
3.5. *Do Radical Recombinations Require Activation?* The combination of two H-atoms to give H_2 does not require an activation energy; part of the bond energy must be transferred to a 'third body'. When the recombination of polyatomic radicals involves drastic conformational changes, the occurrence of an entropic and/or enthalpic barrier cannot be ruled out *a priori*. However, the dimerization of primary, *sec*-, or *tert*-alkyl radicals appears to be diffusion-controlled. The capturing of the oct-1-yl radical by the persistent radical TEMPO (**36**) at 20° is slower by one order than diffusion rate and shows $E_A = 1.8 \pm 0.9$ kcal mol^{-1} [42]. When sterically demanding substituents are introduced in ethane, the central bond is widened and loses energy, as systematic studies by *Rüchardt et al.* revealed [43]. Whether the recombination of the strained radicals has to overcome an activation barrier could not be established with certainty.

With increase of steric strain, radicals lose the capacity of dimerization and find other outlets [44][45].

How does resonance stabilization influence the combination of alkyls radicals? *Sustmann* and co-workers found $E_A = 2.8$ kcal mol^{-1} for the combination of two allyl radicals in time-resolved measurements ($-38°$ to $119°$) in solution. However, the rate constants ($0.43 - 9.3 \cdot 10^9$ M^{-1} s^{-1}) still suggest diffusion control [6]. The meaning of modest activation barriers in diffusion-ruled reactions is unclear.

Beyond all doubts is the dimerization of triphenylmethyl (**37**), the veteran of radical chemistry [46], to give 1-(diphenylmethylidene)-4-(triphenylmethyl)cyclohexa-2,5-diene (**38**). This structure for the dimer resulted from re-examination in 1968 [47], but the older measurements of dissociation rates of 'hexaphenylethane' pertain as well to **38** (*Scheme 11*). The rate constants, k_1, were obtained from the uptake of NO by triphenylmethyl at temperatures between $-20°$ to $+10°$; *Ziegler et al.* observed $E_A =$ 20.0 kcal mol^{-1} in toluene as solvent [48]. Supplementary measurements at 35° to 60° by *Krístjánsdottir et al.* [49] were carried out with a stopped-flow dilution technique and provided the *Eyring* parameters, $\Delta H_1^{\neq} = 20.5 \pm 0.2$ kcal mol^{-1} and $\Delta S_1^{\neq} = 4.7 \pm 0.6$, *i.e.*, corresponding to a dissociation free energy of $\Delta G_1^{\neq}(20°) = +19.1$ kcal mol^{-1}. The early spectrophotometric measurements of the equilibrium constant by *Ziegler* and *Ewald* [50] likewise agreed well with later data collected by *Lewis* and co-workers [51], and furnished $\Delta H_{rxn} = -10.5$ kcal mol^{-1} and $\Delta S_{rxn} = -12.0$ e.u. in toluene. The dimerization free energy amounts to -14.0 kcal mol^{-1} at 20° and leaves $\Delta G_2^{\neq} = +5.1$ kcal mol^{-1} for the activation free energy of the radical recombination; $k_2 = 1.4 \cdot 10^3$ M^{-1} s^{-1} (toluene, 20°) results for the rate constant of dimerization.

Scheme 11



36 **37** **38**

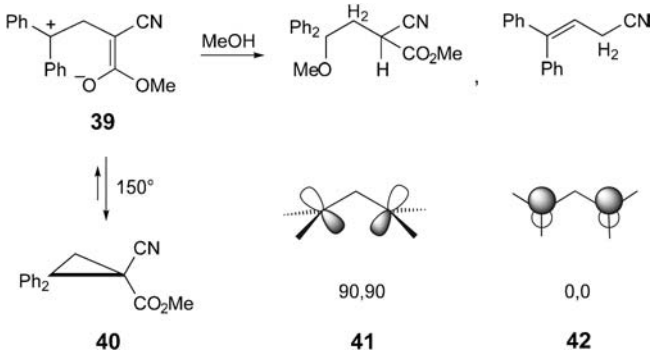
In the dimerization of triphenylmethyl, the resonance stabilization has to be relinquished, and the pyramidalization increases the steric strain. Probably, entropic and enthalpic factors contribute to the activation barrier. The 3,3′,5,5′-tetra(*tert*-butyl) derivative of 'hexaphenylethane' is colorless, and the establishing of the dissociation equilibrium with the yellow monomer requires weeks [52]; a much higher activation barrier is expected for the dimerization.

3.6. *Concerted or Stepwise?* All evidence for concertedness is indirect, whereas two-step processes can be established by interception of intermediates. The diradicals **26** and **27**, discussed as possible intermediates, are related to the trimethylene diradical, *i.e.*, the ring-opened cyclopropane. The failure of intercepting trimethylene diradicals is usually ascribed to the close vicinity of the internal trap: it is the second radical which waits for recombination.

The stabilization energy of trimethylenes can be increased by push-pull substitution. *Cram* and co-workers observed that the optically active cyclopropane derivative

40 racemizes with a half-life of 133 min in MeOH at 125° [53]. The further reaction at 150° corresponds to a carbocationic S_N1-type behavior, indicating an equilibrium with the zwitterion **39** (*Scheme 12*). The energy well of this intermediate is deep enough for interception by MeOH [54].

Scheme 12



When the ring-opening of cyclopropane involves only one stretching and one deformation mode, a 90,90-conformation **41** (*Scheme 12*) will be formed, as defined by *Roald Hoffmann* (1968) in a classic paper on trimethylene [55]. The energy of **41** will rise with increasing angle C–C–C, and an intermediate is not involved. By two 90° rotations about the C–C bonds, the 0,0-conformation **42** is reached; *EH*-calculations revealed an intermediate which has to overcome a barrier of 1 kcal mol^{-1} for ring closure. In later *ab initio* calculations, this barrier disappeared. Numerous theoretical studies of the electronic configurations of trimethylene, including reaction dynamics, are of appalling complexity and diversity.

The corresponding ring-opening of vinylcyclopropane reaches a 90,90-conformation that would energetically not profit from the allyl resonance. Two C–C rotations must accompany the cleavage of the C(1)–C(2) bond to reach the 0,0-conformation, *i.e.*, the planar allylic system in the diradicals **1** and **3**. It is relevant that a 0,90-trimethylene occurs in diastereomerization, and a 90,90-trimethylene is passed in a one-step enantiomerization. The substantial stabilization, which the allylic diradicals **26** and **27** experience by conjugation with three Ph groups, may well promote the formation of a trough in the energy profile. Concerning *intermediates* or *paraintermediates*, our calculations promote a noteworthy dual answer [19].

The *Fonds der Chemischen Industrie*, Frankfurt, supported our work; we express our thanks. *R. H.* is highly indebted to Prof. *Ken Houk*, UCLA, for an inspiring discussion, and to Prof. *Rudolf Knorr*, Munich, for NMR advice. We thank *Helmut Schulz* for carrying out numerous elemental analyses.

Experimental Part

1. *General.* See [18].

2. *Racemic 1-[2-Arylethenyl]-2,2-diphenylcyclopropanes* (*= 1,1′-[2-(2-Arylethenyl)cyclopropane-1,1-diyl]dibenzenes*; **22**). 2.1. *2,2-Diphenylcyclopropanecarboxylic Acid* (*rac*-**11**). Benzophenone hydrazone (130 g, 0.67 mol) was oxidized to diazo(diphenyl)methane with HgO, carefully washed alkali-free,

in Et_2O [56]. After removal of the solvent, the residue was dissolved in light petroleum (40–80°; 1 l) and added to ethyl acrylate (180 g, 1.80 mol) with stirring. After 14 h at r.t., the solvent and the excess of acrylate were distilled at normal pressure, and *rac*-**10** (146 g, 88%) was obtained at 158°/0.5 Torr as a yellow viscous oil. Ester hydrolysis with KOH (60 g) in MeOH (1200 ml) afforded *rac*-**11** (118.0 g, 90%). Colorless prisms. M.p. 169–171° ([20]: 169–171°).

2.2. *2,2-Diphenylcyclopropane-1-carbaldehyde* (*rac*-**14**). 2.2.1. *Path a.* Some drops of DMF were added to **11** (10.0 g, 42.0 mmol) in $SOCl_2$ (50 ml; *Merck*, zur Synthese) and kept overnight at r.t. Evaporation left **12** as crystalline residue. The soln. in abs. Et_2O (decanting from undissolved acid anhydride) was dropwise added with stirring to dry aziridine (1.81 g, 42.0 mmol) and Et_3N (4.24 g, 41.9 mmol) in abs. Et_2O (100 ml), precooled to −25°. After 2 h at −10°, Et_3NHCl was filtered, and the Et_2O soln. of **13** quickly stirred with 0.55M $LiAlH_4$ in Et_2O (23 ml, 12.6 mmol), kept at 0°. Stirring at 0° for 2 h and workup with 2N H_2SO_4/Et_2O and distillation at 140–160°/0.001 Torr gave crude product; *rac*-**14** (3.10 g), m.p. 72–74°, crystallized from Et_2O, and a further fraction (1.45 g, together 49%) was obtained by TLC (silica gel *Merck*, $PF_{254+366}$; cyclohexane/Et_2O 7:1). Analytically pure *rac*-**14** came from Et_2O at low temp. Colorless prisms. M.p. 74–76°. IR (KBr): 694v*s*, 704v*s*, 753v*s*, 765*s* (arom. oop (= out-of-plane)); 1440*s*, 1489*s* (arom. ring vibr.), 1695v*s* (C=O). ^{1}H-NMR (CCl_4): 1.52–2.62 (*m*, H–C(1), CH_2(3)); 6.95–7.45 (*m*, 10 arom. H); 8.57 (*d*, ^2J = 6.5, CHO). Anal. calc. for $C_{16}H_{14}O$ (222.27): C 86.45, H 6.35; found: C 86.56, H 6.40.

2,4-Dinitrophenylhydrazone of rac-**14**. Yellow-orange prisms (EtOH/AcOEt). M.p. 186–187° (dec.). Anal. calc. for $C_{22}H_{18}N_4O_4$ (402.40): C 65.66, H 4.51, N 13.92; found: C 65.92, H 4.56, N 14.28.

2.2.2. *Path b.* Benzophenone hydrazone (39.2 g, 200 mmol) was converted, as described above, to diazo(diphenyl)methane, which was reacted in benzene (200 ml) with freshly distilled acrolein (12.0 g, 214 mmol). After keeping at r.t. overnight, the N_2 evolution ceased, and the dark violet color turned to yellow. Filtering, removal of solvent, and distillation at 150°/10^{-3} Torr gave *rac*-**14** (31.2 g, 70%), which solidified as wax; from EtOH at low temp., transparent prisms, m.p. 72–74°, were obtained, in mixed m.p., IR und ^{1}H-NMR identical with those of the specimen of *Path a*.

2.3. Wittig *Olefinations.* 2.3.1. *With (Benzylidene)(triphenyl)phosphorane* (**21a**). *Variant A.* (Benzyl)(triphenyl)phosphonium chloride, m.p. 316–318° (317–318° [57]; 7.10 g, 18.2 mmol), suspended in abs. Et_2O (50 ml), was stirred with 1.38M ethereal PhLi (13.2 ml, 18.2 mmol) for 30 min at r.t., and a yellow-orange soln. of **21a** was obtained. The soln. of **14** (1.00g, 4.50 mmol) in Et_2O (20 ml) was added, and the mixture was kept at r.t. overnight. On treatment with H_2O, the excess of phosphonium salt precipitated and was filtered. After workup with 2N H_2SO_4/Et_2O, from Et_2O/light petroleum 1:1 triphenylphosphine oxide crystallized. M.p. 147–150° (pure 153°). The residue of the mother liquor was subjected to prep. thick-layer chromatography (TLC) on 20 glass plates (20 × 20 cm) on a 2-mm layer of silica gel *Merck* $PF_{254+366}$; ascending development, usually with light petroleum (40–80°); after evaporation of the solvent, the development was repeated four times, until the UV fluorescence showed a satisfactory separation. The scratched-off material was eluted with Et_2O and crystallized from EtOH. The faster-moving zone (R_f((*Z*)-**22**) is always > R_f((*E*)-**22**)) provided (*Z*)-**22a** (560 mg, 45%) from EtOH, m.p. 82–86°. Compound (*E*)-**22a** (402 mg, 32%) was isolated from the second zone; m.p. 54–57° (60–61.5° [18]).

Variant B. EtONa (18 mmol; from 415 mg Na) in abs. EtOH (100 ml) was reacted under N_2 with the phosphonium salt (7.10 g, 18.2 mmol). After addition of **14** (1.00 g, 4.50 mmol) in abs. EtOH (50 ml) and reaction at r.t. for 14 h, workup with H_2O/benzene (isolation of Ph_3PO from small volume of ether), separation by TLC provided (*Z*)-**22a** (655 mg, 49%) and (*E*)-**22a** (475 mg, 36%). UV (decalin) of (*E*)-**22a**: λ_{max} 269 nm (log ε 4.35).

1-[(Z)-2-Phenylethenyl]-2,2-diphenylcyclopropane (= *1,1′-{2-[(Z)-2-Phenylethenyl]cyclopropane-1,1-diyl}dibenzene*; (*Z*)-**22a**). Colorless prisms. M.p. 88–89° (EtOH). UV (decalin): λ_{max} 259 (log ε 4.23). IR (ATR (= attenuated total reflexion)): 689v*s*, 692v*s*, 753v*s*, 762*s*, 773*s* (arom. H, oop); 1442*s*, 1449*s*, 1491*s*, 1595*m* (arom. ring vibr.), 1575*w* (arom. conjug.), 1635*w* ((*Z*)-vinylic str.). ^{1}H-NMR (400 MHz): 1.59 (*dd*, H_a–C(3)); 1.69 (*dd*, H_b–C(3)); 2.76 (*m*, higher order, 14 signals resolved, H–C(1)); 4.94 (*dd*, H–C(1′)); 6.39 (*d*, H–C(2′)); 7.15–7.50 (*m*, 15 arom. H); ^2J(3a,3b) = 4.8, ^3J(1,3a) = 5.9 (*trans*), ^3J(1,3b) = 8.7 (*cis*), ^3J(1,1′) = 9.8, ^3J(1′,2′) = 11.5. ^{13}C-NMR (100 MHz): 24.0, 26.9, 37.8 (C(3), C(1), C(2)); 125.9, 126.57, 126.64, 128.7, 132.8 (C(1′), C(2′), 3 arom. *p*-CH); 127.2, 128.27, 128.31, 128.4, 128.8 130.8

(double signal height, as expected for free Ph rotation, 12 arom. *o*- and *m*-CH); 137.7, 141.2, 146.2 (3 arom. C_q). MS: 296 (37, M^+), 219 (9, $[M - Ph]^+$), 218 (28, $C_{17}H_{14}^+$), 205 (100, $C_{16}H_{13}^+$), 204 (95), 178 (24, $C_{14}H_{10}^+$, phenanthrene$^+$), 165 (40, $C_{13}H_9^+$, fluorenyl$^+$), 115 (36, $C_9H_7^+$, indenyl$^+$), 91 (41, $C_7H_7^+$, tropylium$^+$), 77 (9, Ph^+). Anal. calc. for $C_{23}H_{20}$ (296.39): C 93.20, H 6.80; found C 93.23, H 6.91.

2.3.2. *With (4-Methylbenzylidene)(triphenyl)phosphorane* (**21b**). 4-Methylbenzyl bromide (21.2 g, 115 mmol) and Ph_3P (73.0 g, 0.28 mol) were refluxed in xylene for 14 h; from little EtOH crystallized (4-methylbenzyl)(triphenyl)phosphonium bromide (48.3 g, 93%). M.p. 270–272°.

Variant B: Deprotonation of the phosphonium salt (4.1 g, 9.2 mmol) with EtONa/EtOH, reaction with **14** (500 mg, 2.25 mmol) as described above, and TLC afforded (*Z*)-**22b** (423 mg, 61%) and (*E*)-**22b** (157 mg, 22%) from EtOH.

Variant C used EtOLi (0.28M) in EtOH for deprotonation; the total yield was 60%, and the (*Z*)/(*E*) ratio was similar to the one before.

*1-[(*E*)-2-*p*-Tolylethenyl]-2,2-diphenylcyclopropane* (=*1-[(*E*)-2-(2,2-Diphenylcyclopropyl)ethenyl]-4-methylbenzene*; (*E*)-**22b**). M.p. 88–89° (EtOH). UV (decalin): λ_{max} 269 (log ε 4.41). IR (ATR): 697v*s*, 750v*s*, 762*s*, 768v*s*, 803*s* (Ph, oop); 823, 841 (*p*-disubst. arom. H, oop), 954*s*, 963*s* ((*E*)-ethylenic oop); 1443*s*, 1490*m*, 1596*m* (arom. breath. modes), 1643*w* ((*E*)–HC=CH, str.). ^{1}H-NMR (400 MHz): 1.63 (*t*, H_a–C(3)); 1.78 (*dd*, H_b–C(3)); 2.44 (*ddd*, H–C(1)); 2.33 (*s*, Me); 5.47 (*dd*, H–C(1′)); 6.58 (*d*, H–C(2′)); 7.05–7.48 (*m*, 14 arom. H); ^2J(3a,3b) = 4.9, ^3J(1,3a) = 5.9 (*trans*), ^3J(1,3b) = 8.7 (*cis*), ^3J(1,1′) = 9.6, ^3J(1′,2′) = 15.8; the signals of H_a–C(3) and H–C(1) are pseudo *t*s, due to similar coupling constants, here and in many spectra of **22**. ^{13}C-NMR (100 MHz): 21.5 (Me); 23.3, 31.6, 37.9 (C(3), C(1), C(2)); 126.3, 127.0, 129.5, 131.0 (C(1′), C(2′), 2 arom. *p*-CH); 126.1, 127.6, 128.7, 128.8, 129.6, 131.5 (double intensity, 12 arom. *o*- and *m*-CH); 135.4, 136.9, 141.8, 147.0 (4 arom. C_q). MS (program MASS): 310 (47, M^+; HR-MS: 310.1713; calc. 310.1716), 295 (9, $[M - Me]^+$, HR 295.148/295.148), 219 (100, $C_{17}H_{15}^+$, $[M - p$-tolyl$]^+$), 204 (69, $C_{16}H_{12}^+$), 165 (23, fluoren-9-yl$^+$), 115 (25, [indenyl]$^+$), 105 (13, xylyl$^+$). Anal. calc. for $C_{24}H_{22}$ (310.42): C 92.86, H 7.14; found: C 92.59, H 7.11.

*1-[(*Z*)-2-*p*-Tolylethenyl]-2,2-diphenylcyclopropane* (=*1-[(*Z*)-2-(2,2-Diphenylcyclopropyl)ethenyl]-4-methylbenzene*; (*Z*)-**22b**). M.p. 62–63° (EtOH). IR (ATR): 688*s*, 697v*s*, 711*m*, 727*m*, 761v*s* (Ph, oop), 827*s*, 839*s* (*p*-disubst. arom. oop); 1443*m*, 1449*m*, 1495*s*, 1512*m*, 1597*m* (br; arom. breath. modes); 1640v*w* ((*Z*)-CH=CH, str.). ^{1}H-NMR (400 MHz): 1.59 (*t*, H_a–C(3)); 1.70 (*dd*, H_b–C(3)); 2.37 (*s*, Me); 2.76 (*ddd*, H–C(1)); 4.90 (*dd*, H–C(1′)); 6.37 (*d*, H–C(2′)); 7.13–7.50 (4*m*, 14 arom. H); ^2J(3a,3b) = 4.8, ^3J(1,3a) = 5.6 (*trans*), ^3J(1,3b) = 8.7 (*cis*), ^3J(1,1′) = 9.9, ^3J(1′,2′) = 11.5. ^{13}C-NMR (100 MHz): 23.3 (Me); 24.5, 27.5, 38.1 (C(3), C(1), C(2)); 126.2, 127.0, 129.0, 132.5 (C(1′), C(2′), 2 arom. *p*-CH); 127.6, 128.8, 129.1, 129.4, 129.6, 131.3 (12 arom. *o*- and *m*-CH); 135.2, 136.7, 141.7, 146.7 (4 arom. C_q). Anal. calc. for $C_{24}H_{22}$ (310.42): C 92.86, H 7.14; found: C 93.02, H 7.13.

2.3.3. *With (3-Chlorobenzylidene)(triphenyl)phosphorane* (**21c**). The phosphonium bromide (90%, m.p. 304–306°), prepared from 3-chlorobenzyl bromide and Ph_3P by 14-h refluxing in benzene, was deprotonated as described in *Variant A* and reacted with **14** (4.50 mmol) as described above. The separation by TLC gave rise to (*Z*)-**22c** (670 mg, 45%) from the faster-moving zone and (*E*)-**22c** (441 mg, 30%) from the slower-moving zone.

*1-[(*E*)-2-(3-Chlorophenyl)ethenyl]-2,2-diphenylcyclopropane* (=*1-Chloro-3-[(*E*)-2-(2,2-diphenylcyclopropyl)ethenyl]benzene*; (*E*)-**22c**). M.p. 77–79° (EtOH). UV (decalin): λ_{max} 269 nm (log ε 4.20). IR (ATR): 853*m*, 878*m*, 896*m* (*m*-ClC_6H_4, oop), 958v*s*, 968*m* ((*E*)-CH=CH, oop); 1493*s*, 1560*m*, 1591*s* (arom. ring vibr.); 1639*m* ((*E*)-CH=CH, str.). ^{1}H-NMR (400 MHz): 1.62 (*dd*, H_a–C(3)); 1.77 (*dd*, H_b–C(3)); 2.41 (*dt*, H–C(1)); 5.49 (*dd*, H–C(1′)); 6.50 (*d*, H–C(2′)); 7.00–7.44 (*m*, 14 arom. H); ^2J(3a,3b) = 5.1, ^3J(1,3a) = 5.6 (*trans*), ^3J(1,3b) = 8.6 (*cis*), ^3J(1,1′) = 9.7, ^3J(1′,2′) = 15.8. ^{13}C-NMR (100 MHz): 23.4, 31.4, 38.3 (C(3), C(1), C(2)); 127.9 (C(2′)); 133.4 (C(1′)); 127.1, 128.36, 128.45, 130.9 (double intensity, 8 *o*- and *m*-CH of 2 Ph); 134.4, 139.6, 141.2, 146.3 (4 arom. C_q); 123.9, 125.7, 126.0, 126.6, 126.8, 129.6 (2 *p*-CH of Ph_2, 4 CH of C_6H_4Cl); the assignment of the olefinic C-atoms was based on a 2D GHSQC experiment. MS: 330 (24, M^+; HR-MS: 330.1173; calc. for $C_{23}H_{19}{}^{35}Cl^+$, 330.1171), 332 (8.7; HR-MS: 332.1143; calc. for $C_{23}H_{19}{}^{37}Cl$, 332.1141; intensity 7.8/8.7), 239 (31; HR-MS: 239.0630; calc. for $C_{16}H_{12}{}^{35}Cl^+$, 239.0625; intensity of $C_{16}H_{12}$ ^{37}Cl 9.9/11.0), 205 (100, $C_{16}H_{13}^+$, $[M - CH_2C_6H_4Cl]^+$), 191 (14; HR-MS: 191.0844; calc. for $C_{15}H_{11}^+$, 191.0858), 165 (22, Fluorenyl$^+$; HR-MS: 165.0701; calc. for $C_{13}H_9^+$,

165.0702), 91 (18; HR-MS: 91.0547; calc. for $C_7H_7^+$, 91.0546). Anal. calc. for $C_{23}H_{19}Cl$ (330.48): C 83.49, H 5.79; found: C 83.72, H 5.70.

1-[(Z)-2-(3-Chlorophenyl)ethenyl]-2,2-diphenylcyclopropane (=*1-Chloro-3-[(Z)-2-(2,2-diphenylcyclopropyl)ethenyl]benzene*; (*Z*)-**22c**). M.p. 67–68° (EtOH). IR (ATR): 820*m*, 844*m*, 893*s* (3-ClC_6H_4, oop); 1627*w* ((*Z*)-CH=CH, str.). ^{1}H-NMR (400 MHz): 1.60 (*t*, H_a–C(3)); 1.71 (*dd*, H_b–C(3)); 2.68 (*dt*, H–C(1)); 4.99 (*dd*, H–C(1′)); 6.33 (*d*, H–C(2′)); 7.12–7.49 (*m*, 14 arom. H); ^2J(3a,3b) = 4.9, ^3J(3a,1) = 6.0 (*trans*), ^3J(3b,1) = 8.7 (*cis*), ^3J(1,1′) = 10.0, ^3J(1′,2′) = 11.5. ^{13}C-NMR (100 MHz, DEPT): 24.2, 27.0, 38.5 (C(3), C(1), C(2)); 126.5–134.7 (14 arom. CH + 2 vinyl-C); 134.6, 139.9, 141.5, 146.3 (4 arom. C_q). Anal. calc. for $C_{23}H_{19}Cl$ (330.48): C 83.49, H 5.79; found: C 83.86, H 5.77.

2.3.4. *With (4-Methoxybenzylidene)(triphenyl)phosphorane* (**21d**). By *Variant A* (PhLi), the wine-red phosphorane **21d** was set free from (4-methoxybenzyl)(triphenyl)phosphonium bromide (m.p. 235–236° (dec.)) and reacted with **14** (1.00 g, 4.50 mmol). Workup by TLC (20 plates; light petroleum/Et_2O 96:4) gave (*Z*)-**22d** (604 mg, 41%) and (*E*)-**22d** (410 mg, 28%).

*1-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-2,2-diphenylcyclopropane* (=*1-[(*E*)-2-(2,2-Diphenylcyclopropyl)ethenyl]-4-methoxybenzene*; (*E*)-**22d**). M.p. 61–63° (EtOH). UV (decalin): λ_{max} 274.5 (log ε 4.56). IR (ATR): 807*s*, 823*s*, 829*s*, 879*m* (C_6H_4, oop); 956v*s*, 958*s* ((*E*)-CH=CH, oop); 1024*s* (C–O–C, sym. str.); 1239v*s*, 1247*s* (C–O–C, asym. str.); 1575*w* (arom. conj.), 1639*w* ((*E*)-vinylic str.). ^{1}H-NMR (400 MHz): 1.59 (*t*, H_a–C(3)); 1.73 (*dd*, H_b–C(3)); 2.40 (*dt*, H–C(1)); 3.78 (*s*, MeO); 5.34 (*dd*, H–C(1′)); 6.52 (*d*, H–C(2′)); 6.78 (*d*, H–C(3/5) of 4-$MeOC_6H_4$), 7.1–7.43 (*m*, 12 arom. H); ^2J(3a,3b) = 5.0, ^3J(3a,1) = 5.9 (*trans*), ^3J(3b,1) = 8.6 (*cis*), ^3J(1,1′) = 9.5, ^3J(1′,2′) = 15.8. ^{13}C-NMR (100 MHz, DEPT): 23.2, 31.5, 37.8 (C(3), C(1), C(2)); 55.7 (MeO); 114.3 (C(3/5) of $MeOC_6H_4$); 126.2–131.5 (9 lines for arom. CH); 131.0, 141.9, 147.0, 159.0 (4 arom. C_q). MS: 326 (86, M^+; HR-MS: 326.1657; calc., 326.1665; ^{13}C: 22.3; calc., 23.0), 295 (6, $[M - MeO]^+$), 235 (71, $C_{17}H_{15}O^+$, ^{13}C: 12.8; calc., 13.3), 205 (100, $C_{16}H_{13}^+$, $[M - CH_2C_6H_4OMe]^+$, 191 (21, $C_{15}H_{11}^+$, [1-phenylindenyl]$^+$), 165 (28, fluoren-9-yl$^+$), 121 (47, $[CH_2C_6H_4OMe]^+$), 91 (31, $C_7H_7^+$). Anal. calc. for $C_{24}H_{22}O$ (326.42): C 88.30, H 6.79; found: C 88.07, H 6.64.

1-[(Z)-2-(4-Methoxyphenyl)ethenyl]-2,2-diphenylcyclopropane (=*1-[(Z)-2-(2,2-Diphenylcyclopropyl)ethenyl]-4-methoxybenzene*; (*Z*)-**22d**). Colorless prisms. M.p. 83–84° (EtOH). IR (ATR): 813*m*, 834*m*, 845v*s* (*p*-disubst. C_6H_4, oop), 1029v*s* (br., C–O–C, sym. str.); 1176*s*, 1246*s*, 1258*s* (C–O–C, asym. str.); 1569*w* (arom. conj.). ^{1}H-NMR (400 MHz): 1.57 (*t*, H_a–C(3)); 1.69 (*dd*, H_b–C(3)); 2.72 (*dt*, H–C(1)); 3.82 (*s*, MeO), 4.85 (*dd*, H–C(1′)); 6.33 (*d*, H–C(2′)); 6.89 (*d*, H–C(3/5) of $MeOC_6H_4$); 7.2–7.45 (m, 12 arom. H); ^2J(3a,3b) = 4.8, ^3J(3a,1) = 6.0 (*trans*), ^3J(3b,1) = 8.7 (*cis*), ^3J(1,1′) = 9.8, ^3J(1′,2′) = 11.5. ^{13}C-NMR (100 MHz, DEPT): 24.5, 27.5, 38.07 (C(3), C(1), C(2)); 55.7 (MeO); 114.1 (C(3/5) of 4-$MeOC_6H_4$); 126.2, 127.0, 128.65, 131.53 (2 arom. *p*-CH, 2 vinyl C); 127.5, 128.72, 130.4, 131.3 (double intensity, 8 arom. *o*- and *m*-CH); 130.7, 141.7, 146.7, 158.7 (4 arom. C_q). Anal. calc. for $C_{24}H_{22}O$ (326.42): C 88.30, H 6.79; found: C 88.34, H 6.97.

2.3.5. *With (4-Nitrobenzylidene)(triphenyl)phosphorane* (**21e**). The phosphonium bromide, m.p. 261–262° (dec.) (260° [57]), prepared as usual, was converted to the cherry-red **21e** by *Variant B* and reacted with **14** (1.13 g, 5.1 mmol). PLC (5 × development, light petroleum/ether 96:4) provided (*Z*)-**22e** (1.03 g, 59%) and (*E*)-**22e** (315 mg, 18%).

*1-[(*E*)-2-(4-Nitrophenyl)ethenyl]-2,2-diphenylcyclopropane* (=*1-[(*E*)-2-(2,2-Diphenylcyclopropyl)-ethenyl]-4-nitrobenzene*; (*E*)-**22e**). Pale-yellow needles. M.p. 98–100° (EtOH). UV (decalin): λ_{max} 329 (log ε 4.23). IR (ATR): 861*m* ($C_6H_4NO_2$, oop); 953*s*, 967*m* ((*E*)-CH=CH, oop); 1335v*s*, 1507*s* (NO_2, sym. and asym. str.); 1640*m* ((*E*)-CH=CH, str.). ^{1}H-NMR (400 MHz): 1.69 (*t*, H–C(3a)); 1.82 (*dd*, H–C(3b)); 2.46 (*dt*, H–C(1)); 5.68 (*dd*, H–C(1′)); 6.62 (*d*, H–C(2′)); 7.14–7.43 (*m*, 12 arom. H, 2 vinyl H); 8.09 (*d*, 2 *m*-H of $NO_2C_6H_4$); ^2J(3a,3b) = 5.1, ^3J(3a,1) = 5.5 (*trans*), ^3J(3b,1) = 8.6 (*cis*), ^3J(1,1′) = 9.8, ^3J(1′,2′) = 15.8. ^{13}C-NMR (100 MHz): 23.6, 31.6, 39.0 (C(3), C(1), C(2)); 124.1–131.2 (16 arom. CH, C(1′), C(2′)); 141.4, 144.5, 146.3, 146.7 (4 arom. C_q). Anal. calc. for $C_{23}H_{19}NO_2$ (341.39): C 80.91, H 5.61, N 4.10; found: C 80.71, H 5.52, N 4.27.

1-[(Z)-2-(4-Nitrophenyl)ethenyl]-2,2-diphenylcyclopropane (=*1-[(Z)-2-(2,2-Diphenylcyclopropyl)-ethenyl]-4-nitrobenzene*; (*Z*)-**22e**). M.p. 112–113° (EtOH). IR (ATR): 855*s*, 866*s* ($O_2NC_6H_4$, oop), 960m ((*Z*)-CH=CH, oop); 1333v*s*, 1591*s* (NO_2, sym. and asym. str.); 1629*m* ((*Z*)-CH=CH, str.). ^{1}H-NMR (300 MHz): 1.66 (*t*, H–C(3a)); 1.78 (*dd*, H–C(3b)); 2.66 (*dt*, H–C(1)); 5.15 (*dd*, H–C(1′)); 6.41

(*d*, H–C(2′)); 7.12–7.42 (*m*, 10 arom. H, Ph_2); 7.57 (*d*, further split, 2 *o*-H of $NO_2C_6H_4$); 8.20 (*d*, further split, 2 *m*-H of $NO_2C_6H_4$); ^2J(3a,3b) = 4.8, ^3J(3a,1) = 5.6 (*trans*), ^3J(3b,1) = 8.8 (*cis*), ^3J(1,1′) = 10.2, ^3J(1′,2′) = 11.6. ^{13}C-NMR (75 MHz): 24.1, 27.1, 38.5 (C(3), C(1), C(2)); 126.7 (C(2′)); 137.1 (C(1′)); 123.7 (C(3/5) of $NO_2C_6H_4$); 129.3 (C(2/6) of $NO_2C_6H_4$); the assignments are based on an HSQCAD experiment. Anal. calc. for $C_{23}H_{19}NO_2$ (341.39): C 80.91, H 5.61, N 4.10; found: C 80.84, H 5.58, N 3.94.

2.3.6. *With (Triphenyl){4-[(*E*)-styryl]benzylidene}phosphorane* (**22f**). *{4-[(*E*)-2-Phenylethenyl]-benzyl}(triphenyl)phosphonium Bromide* (**16**). (*E*)-4-Bromomethylstilbene [22] (**15**; 3.84 g, 14.1 mmol) and Ph_3P (3.66 g, 14.0 mmol) in xylene (100 ml) were refluxed for 14 h. The product crystallized from EtOH. M.p. 297–299° (dec.). Anal. calc. for $C_{33}H_{28}BrP$ (535.45): C 74.02, H 5.27; found: C 73.95, H 5.38.

Wittig *Reaction by* Variant B. Compound **16** (9.65 g, 18.0 mmol) was deprotonated by EtONa/EtOH and reacted with **14** (1.00 g, 4.5 mmol). From the soln. of the crystalline crude product in hot benzene/EtOH, (*Z*)-**22f** (840 mg) was obtained. M.p. 115–123°. PLC (light petroleum/benzene 95:5; 3 × development) furnished further (*Z*)-**22f** (182 mg, together 57%) and (*E*)-**22f** (580 mg, 32%).

*2,2-Diphenyl-1-{2-[(*E*)-4-styrylphenyl]ethenyl}cyclopropane* (*=1-[(*E*)-2-(2,2-Diphenylcyclopropyl)-ethenyl]-4-[(*E*)-2-phenylethenyl]benzene*; (*E*)-**22f**). M.p. 144–145° (EtOH). UV (decalin): λ_{max} 337.5 (log ε 4.40). IR (ATR): 690*vs*, 718*m*, 748*vs* (Ph, oop), 800*s* (*p*-disubst. C_6H_4, oop), 960*vs*, 953*s* ((*E*)-CH=CH, oop), 1444*m*, 1492*s*, 1594*m* (arom. ring vibr.), 1633 ((*E*)-CH=CH, str., broadened). ^{1}H-NMR (60 MHz): 1.51–2.70 (*m*, $H_2C(3)$, H–C(1)); 5.48 (*dd*, ^3J(1,1′) = 9.2); 6.68 (*d*, ^3J(1′,2′) = 16.0); 6.93–7.19 (*m*, 19 arom. H + 2 vinyl H of stilbene group). Anal. calc. for $C_{31}H_{26}$ (398.51): C 93.42, H 6.58; found: C 93.47, H 6.61.

*2,2-Diphenyl-1-{(*Z*)-2-[(*E*)-4-styrylphenyl]ethenyl}cyclopropane* (*=1-[(*Z*)-2-(2,2-Diphenylcyclopropyl)ethenyl]-4-[(*E*)-2-phenylethenyl]benzene*; (*Z*)-**22f**). M.p. 125–127° (EtOH). IR (KBr): 818*vs*, 828*m* (*p*-disubst. C_6H_4, oop); 1446*s*, 1492*s*, 1596*w* (arom. ring vibr); 1628*w* and 1636 (sh, (*Z*)-CH=CH, str.). ^{1}H-NMR (400 MHz): 1.61 (*t*, H–C(3a)); 1.74 (*dd*, H–C(3b)); 2.79 (*m*, H–C(1)); 4.96 (*dd*, H–C(1′)); 6.39 (*d*, H–C(2′)); 7.12 (*s*, 2 vinyl H); 7.06–7.60 (*m*, 19 arom. H); ^2J(3a,3b) = 4.8, ^3J(3a,1) = 5.6 (*trans*), ^3J(3b,1) = 8.7 (*cis*), ^3J(1,1′) = 10.0, ^3J(1′,2′) = 11.5. ^{13}C-NMR (DEPT): 24.6, 27.7, 38.3 (C(3), C(1), C(2)); 136.1, 137.5, 137.8, 141.6, 146.6 (5 arom. C_q); 126.3–132.2 (21 lines printed, 19 arom. CH, 4 vinyl H). Anal. calc. for $C_{31}H_{26}$ (398.51): C 93.42, H 6.58; found: C 93.25, H 6.41.

2.3.7. *With [(Naphthalen-1-yl)methylidene](triphenyl)phosphorane* (**21g**). The phosphonium chloride, m.p. 294–295° (dec.), prepared from 1-(chloromethyl)naphthalene and Ph_3P in refluxing xylene, was deprotonated by EtONa/EtOH (*Variant B*) and reacted with **14** (1.00 g, 4.50 mmol). The workup by PLC (light petroleum/benzene 95:5, 3 × development) yielded (*Z*)-**22g** (974 mg, 62%) and (*E*)-**22g** (306 mg, 20%).

*1-[(*E*)-2-(Naphthalen-1-yl)ethenyl]-2,2-diphenylcyclopropane* (*=1-[(*E*)-2-(2,2-Diphenylcyclopropyl)-ethenyl]naphthalene*; (*E*)-**22g**). M.p. 108–110° (EtOH). UV (decalin): λ_{max} 230 (log ε 3.82). IR (ATR): 950*vs*, 962*m* ((*E*)-CH=CH, oop), 1444*m*, 1493*s*, 1590*m*, 1595*m* (arom. ring vibr.); 1639*w* ((*E*)-CH=CH, str.). ^{1}H-NMR (60 MHz): 1.53–1.90 (*m*, 2 H, H–C(3a) and H–C(3b) not fully separated); 2.56 (*dt*, H–C(1)); 5.17 (*dd*, ^3J(1,1′) = 9.3, ^3J(1′,2′) = 15.3, H–C(1′)); H–C(2′) signal not separated from arom. H. MS (program MASS): 346 (62, M^+; HR-MS: 346.1717; calc., 346.1716; ^{13}C: 19.7; calc., 18.8), 268 (8, $[M - C_6H_6]^+$, HR-MS: 268.1238; calc. 268.1248), 255 (97, $C_{20}H_{15}^+$, $[M - PhCH_2]^+$; HR-MS: 255.1160; calc., 255.1170), 205 (100, $C_{16}H_{13}^+$, $[M$ – naphthyl-$CH_2]^+$; HR-MS: 205.1001; calc., 205.1014), 179 (50, $C_{14}H_{11}^+$, perhaps 9-methylfluoren-9-yl$^+$), 167 (20, Ph_2CH^+), 165 (69, fluoren-9-yl$^+$), 115 (25, $C_9H_7^+$, indenyl$^+$), 91 (24, $C_7H_7^+$). Anal. calc. for $C_{27}H_{22}$ (346.45): C 93.60, H 6.40; found: C 93.35, H 6.51.

*1-[(*Z*)-2-(Naphthalen-1-yl)ethenyl]-2,2-diphenylcyclopropane* (*=1-[(*Z*)-2-(2,2-Diphenylcyclopropyl)ethenyl]naphthalene*; (*Z*)-**22g**). M.p. 107–108° (EtOH). IR (ATR): 1443*m*, 1491*m*, 1497*m*, 1589*w*, 1596*w* (arom. ring vibr.), 1635*w* ((*Z*)-CH=CH, str.). ^{1}H-NMR (400 MHz): 1.57 (*dd*, H–C(3b)); 1.61 (*t*, H–C(3a)); 2.55 (*dt*, H–C(1)); 5.16 (*dd*, H–C(1′)); 6.86 (*d*, H–C(2′)); 7.05–8.12 (*m* in 9 groups, 17 arom. H); ^2J(3a,3b) = 4.7, ^3J(3a,1) = 5.8 (*trans*), ^3J(3b,1) = 8.7 (*cis*), ^3J(1,1′) = 10.3, ^3J(1′,2′) = 11.4. ^{13}C-NMR (DEPT): 23.7, 26.9, 38.2 (C(3), C(1), C(2)); 127.8, 128.62, 128.82, 131.1 (lines of double intensity, 8 arom. *o*- and *m*-CH of Ph_2); 132.4, 134.1, 135.2, 142.0, 146.6 (5 arom. C_q); 10 more lines for 11 further arom. CH. Anal. calc. for $C_{27}H_{22}$ (346.45): C 93.60, H 6.40; found: C 93.78, H 6.51.

2.3.8. *With (Anthracen-9-ylmethylidene)(triphenyl)phosphorane* (**21h**). *9-[(Dimethylamino)methyl]-anthracene* (**18**): *Anthracene-9-carbaldehyd* (**17**; 5.00 g, 24.2 mmol), HCOOH (10 g), and DMF (8.0 ml)

were heated at 150–160° for 5 h, whereby H_2O formed was distilled off. On workup with 20% aq. NaOH, an oil separated, which was solidified, washed, dried, and distilled at 170–175°/10^{-3} Torr: **18** (5.10 g, 88%). M.p. 63.5–65° (light petroleum). ^{1}H-NMR (80 MHz): 2.14 (*s*, Me_2N); 4.05 (*s*, NCH_2). Anal. calc. for $C_{17}H_{17}N$ (235.31): C 86.76, H 7.28, N 5.95; found: C 86.69, H 7.17, N 6.31.

9-(Trimethylammoniomethyl)anthracene Iodide (**19**). MeI (20 mmol) was added to **18** (4.50, 19.1 mmol) in Et_2O (50 ml), and the mixture was kept at r.t. for a week. Filtering and air-drying gave **19** (6.63 g, 92%). Yellow crystal powder. M.p. 185–187° (dec.).

(Anthracen-9-ylmethyl)(triphenyl)phosphonium Iodide (**20**). Ph_3P (40 mmol) was added to the suspension of **19** (5.00 g, 13.2 mmol) in BuOH (300 ml). The stirred mixture was heated for 4 d at 135–140°; Me_3N was eliminated by N_2, and the salt **20** precipitated on cooling. Washing with EtOH and drying gave **20** (7.06 g, 92%). Yellow prisms (from EtOH). M.p. 265–267° (dec.). ^{1}H-NMR (60 MHz, (D_6)DMSO): 6.13 (*d*, J(P,H) = 15.0, CH_2). Anal. calc. for $C_{33}H_{26}IP$ (580.42): C 68.28, H 4.52; found: C 68.62, H 4.46.

The *Wittig* reaction by *Variant B* with **14** (4.50 mmol) furnished a crude product, which by digestion with light petroleum left triphenylphosphane oxide (1.11 g, 89%) and (*E*)-**22h** (143 mg); the latter, m.p. 130–133°, remained undissolved, when the solid was treated with cold EtOH. Slow evaporation of the light petroleum soln. afforded a second crystalline fraction of (*E*)-**22h** (151 mg). The residue of the mother liquor was subjected to PLC to provide (*E*)-**22h** (106 mg; together 22%) and (*Z*)-**22h** (1.04 g, 58%). A second experiment by *Variant C* (PhLi in benzene) produced 65% yield with (*Z*)/(*E*) 2.8.

*1-[(*E*)-2-(Anthracen-9-yl)ethenyl]-2,2-diphenylcyclopropane* (= *9-[(*E*)-2-(2,2-Diphenylcyclopropyl)-ethenyl]anthracene*; (*E*)-**22h**). Yellow glistening crystals. M.p. 135–136° (EtOH). UV (decalin): λ_{max} 259 (log ε 4.89), 385 (3.54). IR (ATR): 966*s* ((*E*)-CH=CH, oop), 1445*s*, 1493*s*, 1597*w* (arom. ring vibr.), 1642 ((*E*)-CH=CH, str.). ^{1}H-NMR (400 MHz): 1.77 (*dd*, H_b–C(3)), 1.85 (*t*, H_a–C(3)); 2.82 (*dt*, H–C(1)); 5.47 (*dd*, H–C(1′)); 7.21–7.40 (*m*, 10 arom. H of Ph_2, H–C(2′)); anthracenyl part (9 H): 7.43, 7.54 (2*d*, 2 × 2 H, H–C(3′/8′) and H–C(4′/7′)); 7.94, 8.08 (2*d*, further split, 2 × 2 H, H–C(5′/6′) and H–C(2′/9′); 8.30 (*s*, H–C(10′)); ^2J(3a,3b) = 5.1, ^3J(3a,1) = 5.8 (*trans*), ^3J(3b,1) = 8.6 (*cis*), ^3J(1,1′) = 8.7, ^3J(1′,2′) = 16.0. ^{13}C-NMR (DEPT): 22.5, 31.7, 38.2 (C(3), C(1), C(1), C(2)); 5 arom. C_q (3 for rotating anthracenyl + 2 for two Ph); eight lines of 'double intensity' would be expected for arom. CH, but only 6 can be distinguished; coincidence may play a role. Anal. calc. for $C_{31}H_{24}$ (396.50): C 93.90, H 6.10; found: C 93.80, H 6.02.

*1-[(*Z*)-2-(Anthracen-9-yl)ethenyl]-2,2-diphenylcyclopropane* (= *9-[(*Z*)-2-(2,2-Diphenylcyclopropyl)-ethenyl]anthracene*; (*Z*)-**22h**). Yellow oil. ^{1}H-NMR (60 MHz): 2.0–3.0 (*m*, H_a–C(3), H_b–C(3), H–C(1)); 5.47 (*dd*, ^3J(1,1′) = 9.5, ^3J(1′,2′) = 11.0, H–C(1′)); 6.7–8.5 (*m*, 19 arom. H, H–C(2′)).

3. *Optically Active 1-(2-Arylethenyl)-2,2-diphenylcyclopropanes* (= *1,1′-[2-(2-Arylethenyl)cyclopropane-1,1-diyl]dibenzenes*). 3.1. *Resolution of 2,2-Diphenylcyclopropane-1-carboxylic Acid* (**11**). According to [25], *rac*-**11** (57.0 g, 0.24 mol) was dissolved in acetone (1 l) and added to a boiling soln. of quinine (*Merck*; for resolution; 77.4 g, 0.24 mol) in acetone (3.5 l). Crystallization of the quinine salt from the cooled soln. required inoculation; a small sample, diluted with light petroleum, provided crystals on scratching. Within 2 d in the refrigerator, the acetone soln. furnished the quinine salt of (+)-(*R*)-**11** (57.6 g, 43%). M.p. 185–189°. Recrystallization from acetone gave fine colorless needles (47.2 g, 35%) with m.p. of 189.5–191° and $[\alpha]_D^{25}$ = 25.1 ($CHCl_3$, 5 mg/ml). The stirred suspension of the salt in acetone (150 ml) just dissolved, when conc. aq. HCl (25 ml) was added. After stirring for 15 min at r.t., mixing with H_2O (1 l), and keeping for 8 h in the refrigerator, the free acid (+)-(*R*)-**11** precipitated; 20.7 g. M.p. 149–151° ([20]: 150–151°). $[\alpha]_D^{25}$ = +226 ($CHCl_3$). Recrystallization from light petroleum (80–120°) changed neither m.p. nor $[\alpha]_D^{25}$ notably. The combined acetone mother liquors were evaporated to half of the volume; the crystalline salt, on treating with aq. HCl, furnished impure (−)-(*S*)-**11** (26.1 g, 0.105 mol). $[\alpha]_D^{25}$ = −165. Its soln. in acetone (130 ml) was combined with dry brucine (*Fluka*; 47.8 g, 0.105 mol) in acetone (200 ml) and refluxed for 1 h; after filtering and inoculating, the brucine salt of (−)-(*S*)-**11** (34.5 g) crystallized within several weeks at 8°. Colorless prisms, $[\alpha]_D^{25}$ = −78 ($CHCl_3$). Treatment with aq. HCl yielded (−)-(*S*)-**11** (12.3 g, 22%). M.p. 150–152°. $[\alpha]_D^{25}$ = −231 ($CHCl_3$).

3.2. *(+)-(*R*)-2,2-Diphenylcyclopropane-1-carbaldehyde* (**14**). The procedure described for *rac*-**11** was repeated with (+)-(*R*)-**11** (42.0 mmol). The crude aldehyde was not distilled, but immediately subjected to TLC (25 plates, silica gel, 2 mm; light petroleum/Et_2O 85:15). The major zone afforded

(+)-(*R*)-**11** (4.05 g, 43%), which crystallized. M.p. 45–50°. From Et_2O at low temp., small colorless prisms were obtained. M.p. 52–54°. $[\alpha]_D^{25} = +150.5$ ($CHCl_3$). ^{1}H-NMR and R_f were identical with those of *rac*-**14**, but the m.p. is lower.

3.3. Wittig *Olefinations with (+)-(*R*)-***14***. The experiments with *rac*-**14**, described in *Sect. 2.3*, were repeated with (+)-(*R*)-**14** on the same scale (4.5 mmol). The procedure was not optimized; usually, one experiment was carried out with each methylidenephosphorane. The identity of *rac*- and (*S*)-**22** in R_f and ^{1}H-NMR spectrum was in each case demonstrated. Melting points are different; when a compound (*S*)-**22** remained oily, a second TLC confirmed the purity. The specific rotations, $[\alpha]_D^{25}$, in decalin were measured for specimens which were recrystallized from EtOH, whenever possible. Data are compiled in *Table 2*.

3.4. *Measurements of Racemization Rates of (+)-(*S,E*)-***22***. The technique may be described with an example. About 60 mg of (+)-(*E*)-**22a** (29 mM) was dissolved in decalin (8 ml), filtered, and filled with an injection syringe in 0.6-ml portions into 12 ampoules (1 ml), which were carefully cleaned and dried before.

After sealing, the ampoules were fixed in a frame and immersed into the preheated polyglycol bath (119.4°) of an ultrathermostat (*Colora*, *HT 13*). After 15 min, temp. constancy (±0.3°) was reached, the first ampoule was taken out, cooled with ice water, and filled into the polarimeter tube (5 cm, 0.5-ml volume) of a light-electric precision polarimeter (LEP; *C. Zeiss*). Since first-order reactions can be cut off from the start side, the first value, $\alpha = +5.72°$, was defined as α_o. The withdrawal times of ten further ampoules were so chosen that three half-reaction times were covered; in our example, $\alpha_t = 0.51°$ (91% reaction) was measured after 120 min. The last ampoule served as control for $\alpha_e = 0.00°$ after 10 half-times (here 500 min).

The plot of ln (α_o/α_t) *vs. t* furnished the first-order rate constant k_{rac} from the slope of the straight line or – more elegantly – by linear regression; the correlation coefficient *R* is a measure of quality. In the experiment described for **22a**, $R = 0.999$ was found up to 91% reaction. The activation parameters were evaluated from measurements at different temperatures (*Table 3*) by linear regression: the activation energy E_A and the action constant *A* from k_{rac} as a function of $1/T$ by the *Arrhenius* equation, and activation enthalpy and entropy, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, resp., from k_{rac}/T as a function of $1/T$ by the *Eyring* equation. Here, too, $R = 0.999$ was observed. Generous estimates for the errors in the rate constants (±5%) and the temp. (±0.3°) led to the tolerances given in *Table 3*.

3.6. *Thermal Isomerization of Vinylcyclopropanes (*E*)-***22*** to 3-Aryl-4,4-diphenylcyclopent-1-enes* **23**. 3.6.1. *3,4,4-Triphenylcyclopent-1-ene* (*=1,1′,1″-Cyclopent-3-ene-1,1,2-triyltribenzene*; **23a**). The description in the preceding article [18] is supplemented: *a*) *rac*-(*E*)-**22a** (2.02 g, 6.82 mmol) was heated in a sealed ampoule under N_2 at 200° for 90 min; distillation at 170° (bath)/10^{-3} Torr gave **23a** (1.83 g, 91%), m.p. 64–67°; the ^{1}H-NMR spectrum [18] showed no additional signals. Recrystallization from EtOH furnished fine leaflets, m.p. 68–69° (68–70° [18]). *b*) A sample of (+)-(*E*)-**22a** was subjected to thermolysis (1.5 h, 200°) and showed $\alpha = 0.01°$ (decalin; 25 mg/ml); the mixed m.p. established the identity with *rac*-**23a**. *c*) The soln. of *rac*-(*E*)-**22a** (160 mg) in decalin (0.6 ml) was sealed in an NMR tube and heated at 180° (thermostat). In intervals of *ca.* 5 min, the region of olefinic H-atoms was checked; at sweep width of 100 Hz, only the signals of (*E*)-**22a** and **23a** were observed.

3.6.2. *3-(4-Methylphenyl)-4,4-diphenylcyclopent-1-ene* (*=1-(5,5-Diphenylcyclopent-2-en-1-yl)-4-methylbenzene*; **23b**). After treatment of (*E*)-**22b** (123 mg, 0.40 mmol) for 1.5 h at 200°, distillation from a microflask at 140°/10^{-3} Torr yielded **23b** (114 mg, 93%), which crystallized from EtOH in colorless prisms. M.p. 59–61°. UV (decalin): λ_{max} 261 (log ε 2.91), 265 (2.92). IR (KBr): 1441*m*, 1489*s*, 1507*s*, 1592*m* (arom. ring vibr.); 1617*w* (CH=CH, str.). ^{1}H-NMR (400 MHz): 2.16 (*s*, Me); 2.79, 3.61 (2 *dq*, H_a–C(5), H_b–C(5), ^2J(a,b) = 16.2; each of the two H-atoms shows similar couplings for $^3J(5,1)$, $^4J(5,2)$, $^4J(5,3) = 1.5–1.8$, resulting in *pseudo-q*); 4.75 (*s*, broadened, H–C(3)); 5.97, 5.99 (2*m*, $^3J(1,2) = 5.9$, H–C(1), H–C(2)); 6.70–7.40 (7*m*, 14 arom. H). ^{13}C-NMR (100 MHz, DEPT): 21.3 (Me); 46.7 (C(5)); 59.7 (C(3)); 51.3 (C(4)); 125.7, 126.0, 128.3, 136.0 (2 *p*-CH of Ph_2, C(1), C(2)); 127.4, 128.15, 128.65, 129.58, 129.60, 129.76 (double intensity, 4 *o*- and *m*-CH of Ph_2, 2 *o*- and *m*-CH of *p*-tolyl); 135.8, 138.1, 145.9, 151.7 (4 arom. C_q). Anal. calc. for $C_{24}H_{22}$ (310.42): C 92.86, H 7.14; found: C 92.84, H 6.99.

3.6.3. *3-(3-Chlorophenyl)-4,4-diphenylcyclopent-1-ene* (*=1-Chloro-3-(5,5-diphenylcyclopent-2-en-1-yl)benzene*; **23c**). Thermolysis (200°, 1.5 h) of (*E*)-**22c** (212 mg, 0.64 mmol) and distillation (160°/10^{-3}

Torr) furnished **23c** (194 mg, 92%). Pale-yellow oil. UV (decalin): λ_{max} 261 (log ε 3.40). ^{1}H-NMR (60 MHz): 2.69, 3.60 (*AB* spectrum, br., $J_{gem} = 16$, H_a–C(5), H_b–C(5)); 4.73 (br. *s*, H–C(3)); 5.98 (br. *s*, H–C(1), H–C(2)). Anal. calc. for $C_{23}H_{19}Cl$ (330.84): C 83.49, H 5.79; found: C 83.86, H 5.76.

3.6.4. *3-(4-Methoxyphenyl)-4,4-diphenylcyclopent-1-ene* (=*1-(5,5-Diphenylcyclopent-2-en-1-yl)-4-methoxybenzene*; **23d**). Compound (*E*)-**22d** was subjected to the usual thermolysis and distillation (150°/10^{-3} Torr) and afforded **23d** (90%). M.p. 99–101° (EtOH). UV (decalin): λ_{max} 279 (log ε 3.23). IR (KBr): 1020v*s* (C–O–C, sym. str.); 836*s*, 863*s* (C–O–C, asym. str.); 1440*s*, 1506v*s*, 1580*m*, 1610*s* (arom. breath. modes). ^{1}H-NMR (400 MHz): 2.77, 3.59 (2 *dq*, ^2J(5a,5b) = 16.2, three further small couplings, H_a–C(5), H_b–C(5)); 3.68 (*s*, MeO); 4.74 (*pseudo-s*, H–C(3)); 5.96, 5.99 (2*m*, 14 lines visible, ^3J(1,2) = 5.9, H–C(1), H–C(2)); 6.55 (*dt*, ^3J(2′,3′) = 6.7, 2 H–C(3′/5′) of $MeOC_6H_4$); 6.75 (*dt*, ^3J(2′,3′) = 6.7, 2 H–C(2′/6′) of $MeOC_6H_4$); 6.85–7.40 (5*m*, 10 arom. H). ^{13}C-NMR (100 MHz, DEPT): 46.6 (C(5)); 55.5 (MeO); 59.2 (C(3)); 61.4 (C(4)); 113.4 (C(3′/5′) of $MeOC_6H_4$); 133.3, 145.9, 151.6, 158.2 (4 arom. C_q). Anal. calc. for $C_{24}H_{22}O$ (326.42): C 88.30, H 6.79; found: C 88.57, H 6.86.

3.6.5. *3-(4-Nitrophenyl)-4,4-diphenylcyclopent-1-ene* (=*1-(5,5-Diphenylcyclopent-2-en-1-yl)-4-nitrobenzene*; **23e**). The thermolyzed (1.5 h, 200°) product was distilled at 190°/10^{-3} Torr; 92%, m.p. 80–85°; yellow-brown prisms from EtOH, m.p. 84–86°. UV (decalin): λ_{max} 274 (log ε 3.76). IR (ATR): 833*m*, 849*m* (*p*-disubst. C_6H_4, oop); 1335*s*, 1509*vs* (NO_2, sym. and asym. str.); 1442*m*, 1492*s*, 1595*m* (arom. ring vibr). ^{1}H-NMR (400 MHz): 2.81, 3.63 (2*dq*, ^2J(5a,5b) = 16.5, H_a–C(5), H_b–C(5)); 4.85 (*pseudo-s*, H–C(3)); 5.97, 6.10 (2*dq*, ^3J(1,2) = 5.9, H–C(1), H–C(2)); 6.80–7.36 (12 arom. CH); 7.85 (*d*, further split, H–C(3′,5′) of $NO_2C_6H_4$). ^{13}C-NMR (100 MHz, DEPT): 46.8 (C(5)); 59.8 (C(3)); 61.9 (C(4)); 150.8, 149.5, 145.0 (3 arom. C_q). Anal. calc. for $C_{23}H_{19}NO_2$ (341.39): C 80.91, H 5.61, N 4.10; found: C 81.20, H 5.65, N 4.15.

3.6.6. *4,4-Diphenyl-3-{4-[(*E*)-styryl]phenyl}cyclopentene* (=*1-(5,5-Diphenylcyclopent-2-en-1-yl)-4-[(*E*)-2-phenylethenyl]benzene*; **23f**). Thermolysis of **22f** at 200° for 1.5 h gave **23f** (96%). M.p. 115–117° (EtOH). UV (decalin): λ_{max} 302 (log ε 4.20), 316 (4.23), 330 (sh). IR (KBr): 695v*s*, 748*s*, 756*m* (Ph, oop); 820 (*p*-disubst. C_6H_4, oop); 960*s* (CH=CH, oop). ^{1}H-NMR (400 MHz): 2.80, 3.63 (2*dq*, ^2J(5a,5b) = 16.0, H_a–C(5), H_b–C(5)); 4.78 (*pseudo-s*, H–C(3)); 5.98, 6.03 (2*dq*, ^3J(1,2) = 5.8, H–C(1), H–C(2)); 6.80–7.50 (*m*, 19 arom. H, 2 olefin. H). ^{13}C-NMR (100 MHz, DEPT): 46.8 (C(5)); 59.9 (C(3)); 61.5 (C(4)); 8 double-intensity signals for pairs of *o*- and *m*-CH; 5 arom. C_q. Anal. calc. for $C_{31}H_{26}$ (398.52): C 93.42, H 6.58; found: C 93.49, H 6.47.

3.6.7. *3-(Naphthalen-1-yl)-4,4-diphenylcyclopentene* (=*1-(5,5-Diphenylcyclopent-2-en-1-yl)naphthalene*; **23g**). The usual rearrangement of (*E*)-**22g** yielded **23g** (94%). Glistening leaflets. M.p. 135–136° (EtOH). UV (decalin): λ_{max} 2.87 (log ε 3.45), sh at 276 and 299 nm. IR (KBr): 1492*s*, 1445*s*, 1490*s*, 1595*m* (arom. ring vibr.). ^{1}H-NMR (400 MHz): 2.83, 3.78 (2*dq*, ^2J(5a,5b) = 17.1, further split, H_a–C(5), H_b–C(5)); 5.62 (*s*, broadened, H–C(3)); 6.04, 6.10 (2*m*, ^3J(1,2) = 5.8, H–C(1), H–C(2)); 6.66–8.18 (8*m*, 17 arom. H). ^{13}C-NMR (100 MHz, DEPT): 46.8 (C(5)); 54.6 (C(3)); 61.2 (C(4)); 132.6, 134.0, 137.8, 145.0, 152.3 (5 arom. C_q). Anal. calc. for $C_{27}H_{22}$ (346.45): C 93.60, H 6.40; found: C 93.76, H 6.32.

3.6.8. *3-(Anthracen-9-yl)-4,4-diphenylcyclopentene* (=*9-(5,5-Diphenylcyclopent-2-en-1-yl)anthracene*; **23h**). Compound (*E*)-**22h** (112 mg, 0.28 mmol) in dioxan (2 ml) was sealed in a thick-walled ampoule and heated 14 h at 160°; from EtOH pale-yellow leaflets (103 mg, 93%) of **23h**. M.p. 135–137° (recryst. EtOH). UV (decalin): λ_{max} 261 (log ε 4.60), 352 (3.34), 370 (3.60), 391 (3.57). IR (KBr): 1621*w* ((*E*)-CH=CH, str.). ^{1}H-NMR (400 MHz): 3.09 (br. *d*, ^2J(5a,5b) = 17.1, H_a–C(5)); 4.25 (*dd*, ^2J(5a,5b) = 17.6, J = 3.4, H_b–C(5)); 6.14 (*s*, H–C(1/2)); 6.41 (br. *s*, H–C(3)); 6.55 (*t*, 2 H), 6.64 (*t*, 1 H), and 6.83 (*t*, 2 H) are tentatively assigned to *m*-H, *p*-H, and *o*-H of *cis*-4-Ph, shifted upfield by the ring current of one side-ring of anthracen-9-yl; the *m*s at 7.05–7.43 (9 H) are attributed to *trans*-4-Ph and the anthracen-9-yl H-atoms H–C(1′) to H–C(4′), the latter being shielded by the neighboring *cis*-4-Ph; five ^{1}H signals come from the 'undisturbed' second side-ring of anthracen-9-yl: 7.74 (*d*, ^3J = 8.00, H–C(5′)), 8.05 (*d*, ^3J = 9.08, H–C(8′)), 7.94, 8.31 (2*m*, H–C(6′/7′), 8.21 (*s*, H–C(10′)). ^{13}C-NMR (100 MHz, DEPT): 49.3 (C(5)); 59.8 (C(3)); 60.0 (C(4)); 4 double-intensity signals of arom. CH are consistent with *o*- and *m*-CH of 2 Ph. Anal. calc. for $C_{31}H_{24}$ (396.50): C 93.90, H 6.10; found: C 93.84, H 6.10.

3.6.9. *Rate Measurements of Ring Enlargement.* The ampoule technique was the same as described for the racemization, but the spectrophotometry required smaller concentrations. In a typical run, **22a** (1.30 mg, $4.39 \cdot 10^{-3}$ mmol) was dissolved in decalin (25 ml). The soln. (0.176 mM) was clarified by

filtering and filled in 2-ml portions into 12 ampoules which were sealed under N_2. After defined reaction times in the thermostat at 159.3°, the ampoules were cooled, opened, and the absorbance was measured in a 0.5-cm quartz cuvette, using the UV spectrometer *RPQ 20C* (*Zeiss*). From $A_o = 1.02$, the absorbance A_t at 269 nm decreased to 0.201 (80% reaction) within 360 min. $A_\infty = 0.076$ was observed after 25 h, in 10.7 half-times. The evaluation of ten measurements of A_t by *Eqn. 2* gave $k_{isom} = 9.36 \cdot 10^{-5}\ s^{-1}$ with $R = 0.999$.

The final A value deviated by a factor of 2.9 from $A_\infty = 0.026$, precalculated from the absorbance coefficients of 22,500 (for **22a**) and 450 (for **23a**) at 269 nm. This deviation amounts to factor 2.0–3.3 in the eight measurements listed in *Table 7*, and is caused by a small percentage of side reactions, which are not detectable in the ^{1}H-NMR spectrum. The neglect of the side reaction may bring a small systematic error into the numerical results, due to the seeming acceleration of the rate by parallel reactions. The k_{isom} values of double runs agree within 1.5%.

The activation parameters (*Table 7*) were calculated from measurements at 159.3–184.0° with $R = 0.995–0.999$. With an estimated uncertainty of ±5% in k_{isom} and ±0.3° in the temp., the tolerances given in *Table 7* resulted.

3.6.10. *^{1}H-NMR-Spectroscopic Measurement of Concentration.* The parent compound (*E*)-**22a** (100 mg, 0.34 mmol) was dissolved in decalin (0.5 ml), sealed under N_2 in a NMR tube, and brought into

Table 9. *X-Ray Crystallographic Data of Compounds* **22a** *and* **23a**

	22a (Jomu 002)	**23a** (Jomu 001)
Empirical formula	$C_{23}H_{20}$	$C_{23}H_{20}$
Formula weight	296.39	296.39
Temp. [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1$	triclinic, $P\bar{1}$
Unit cell dimensions:		
a [Å]	9.8543(2)	11.4326(4)
b [Å]	7.7983(2)	11.7904(4)
c [Å]	10.8859(2)	12.8679(4)
α [°]		81.153(2)
β [°]	94.2810(10)	89.214(2)
γ [°]		71.542(2)
V [Å^3], Z	834.21(4), 2	1624.59(9), 4
Calc. density [mg/mm^3]	1.180	1.212
Absorption coefficient [mm^{-1}]	0.066	0.068
$F(000)$	316	632
Crystal size [mm]	0.30 × 0.29 × 0.28	0.30 × 0.30 × 0.20
Θ Range [°]	2.07–30.05	1.60–30.07
Index ranges	$-13 \le h \le 13$	$-16 \le h \le 16$
	$-10 \le k \le 10$	$-16 \le k \le 16$
	$-15 \le l \le 15$	$-18 \le l \le 18$
Reflections collected	33412	105925
Reflections unique	2608	9501
R(int)	0.0459	0.0550
Completeness to $2\Theta = 30.05$	100.0%	99.6%
Data/restraints/parameters	2608/1/208	9501/0/415
Goodness-of-fit on F^2	1.037	1.027
Final R [$I > 2\sigma(I)$], $wR2$	0.0351, 0.0876	0.0446, 0.1088
Largest diff. peak/hole [e Å^{-3}]	0.239/−0.190	0.362/−0.219
CCDC Deposition No.	785107	785106

a preheated bath of polyethyleneglycol (177.5°). In suitable intervals, the 100-MHz spectra were taken, and the signals at 5.46 ppm for the H–C(1′) of **22a** and at 6.00 for the two vinyl H-atoms of **23a** were isolated from the printed spectra and weighed (F_{22} and F_{23}). The percentage of F_{22} in $F_{22}+F_{23}$ was introduced in the first-order *Eqn. 1*; 12 measurements up to 77% rearrangement furnished $k_{isom}=3.85\cdot 10^{-4}\,s^{-1}$. That is 11% less than $4.32\cdot 10^{-4}\,s^{-1}$, measured by spectrophotometry, but the very different concentrations of **22a** in the decalin soln. ($6.2\cdot 10^{-5}$% *vs. ca.* 20%) changed the medium.

3.6.11. *Solvent Dependence* (*Table 4*). It is noteworthy that no interaction with alcohols took place during the isomerization. In a prep. experiment, **22a** (117 mg) in ethane-1,2-diol (100 ml) was heated for 10 h at 170°. Workup with H_2O/Et_2O gave **23a** (108 mg, 92%). For the kinetic runs in low-boiling solvents, thick-walled ampoules were used. The gap between the exper. and the precalculated absorbance A_∞ appears to depend on the purity of the solvents; in benzene, PhCl, dioxan *etc.*, there was hardly a difference noticeable.

4. *Crystallographic Structure Determination.* X-Ray diffraction measurements were performed on a *Bruker X8 APEX II CCD*-diffractometer. Single crystals of compounds **22a** and **23a** were mounted on glass fibers, coated with *Parathone N* oil and positioned at 40 mm from the detector. 2271 and 3470 frames were measured, each for 20 s over 1° scan width for **22a** and **23a**, resp. The data were processed using SAINT software [58]. Crystal data, data collection parameters, and structure refinement details for **22a** and **23a** are given in *Table 9*. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-H-atoms were refined with anisotropic displacement parameters, while the H-atoms were placed at geometrically calculated positions and refined as riding atoms in the subsequent least-squares model refinements. The isotropic thermal parameters were estimated to be 1.2 times the values of the equivalent isotropic thermal parameters of the atoms to which H-atoms were bonded. The following computer programs and computer were used: structure solution, SHELXS-97 [59]; refinement, SHELXL-97 [60]; molecular diagrams, ORTEP [61]; computer: Pentium IV.

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