Facial Selectivities and Rate Effects in the Thermal [4+2] Dimerization of Arylated 1,3-Dienes. 1,5-H Shift versus Dimerization of (*Z*)-1,3-Dienes

Johann Mulzer*[a], Uwe Kühl[a], Gottfried Huttner[b], and Kaspar Evertz[b]

Institut für Organische Chemie der Freien Universität Berlin[a], Takustraße 3, D-1000 Berlin 33, FRG

Anorganisch-Chemisches Institut der Universität Heidelberg[b], Im Neuenheimer Feld 270, D-6900 Heidelberg 1, FRG

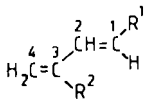
Received July 22, 1988

For the thermal [4+2] dimerization of the dienes **1** and **4** a parallel increase in facial selectivity and reaction rate is observed on going from the (*E*)-alkyl-aryl dienes **1h–m** and the (*Z*)-dienes **4a, b** to the (*E*)-aryl-aryl dienes **1a–f**. This phenomenon is interpreted in terms of the resonance stabilization of a diradical intermediate **8**. The (*Z*)-dienes **4c, d** show a sigmatropic 1,5-H shift instead of a dimerization on heating.

Faciale Selektivitäten und Geschwindigkeitseffekte bei der thermischen [4+2]-Dimerisierung arylierter 1,3-Diene. 1,5-Verschiebung versus Dimerisierung bei (*Z*)-1,3-Dienen.

Bei der thermischen [4+2]-Dimerisierung der Diene **1** und **4** beobachtet man eine parallele Zunahme der facialen Selektivität und der Geschwindigkeitskonstanten beim Übergang von den (*E*)-Aryl-alkyl-dienen **1h–m** bzw. den (*Z*)-Dienen **4a, b** zu den (*E*)-Aryl-aryl-dienen **1a–f**. Dieses Phänomen wird über die Resonanzstabilisierung einer diradikalischen Zwischenstufe **8** interpretiert. Die (*Z*)-Diene **4c, d** erleiden beim Erhitzen eine 1,5-H-Verschiebung zu den Isomeren **10a, b** statt zu dimerisieren.

The uncatalyzed thermal dimerization of 1,3-dienes has been regularly observed as a side reaction in Diels-Alder cycloadditions, particularly for unreactive dienophiles[1]. In great mechanistic detail, the dimerization has been studied for 1,3-butadiene[2] and piperylene[3], with the objective of using these systems as test cases for a distinction between diradical and concerted Diels-Alder reactions in general. However, the results obtained so far, do not allow a clear interpretation in terms of either alternative[4]. Recently, we described an efficient synthesis of the stereochemically pure (*E*)- and (*Z*)-1,3 dienes **1** and **4**[5]. We now report the regio- and stereochemical course of their thermal [4+2] dimerization. In an ensuing paragraph, some kinetic data are presented. The entire body of our experiments suggests a diradical mechanism for this Diels-Alder-type reaction.



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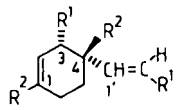

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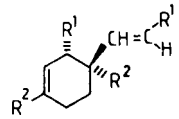

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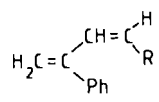
1, 2, 3	R^1	R^2
a	C_6H_5	C_6H_5
b	4-$H_3C-C_6H_4$	C_6H_5
c	4-$Cl-C_6H_4$	C_6H_5
d	4-$CH_3O-C_4H_4$	C_6H_5
e	2-thienyl	C_6H_5
f	2-furyl	C_6H_5
g	C_6H_5	(*E*)-$CH=CH-C_6H_5$
h	CH_3	C_6H_5
i	$C(CH_3)_3$	C_6H_5
j	C_6H_5	H
k	C_6H_5	CH_3
l	C_6H_5	$CH(CH_3)_2$
m	C_6H_5	$C(CH_3)_3$
n	CH_3	H



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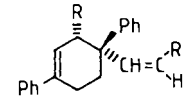

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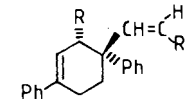

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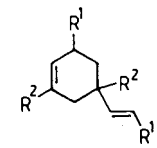
4	R	5, 6	R
a	C_6H_5	**a**	C_6H_5
b	$C(CH_3)_3$	**b**	$C(CH_3)_3$
c	C_2H_5		
d	$CH(CH_3)_2$		



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Regio- and Stereochemistry of the Dimerization

For the dimerization, the dienes **1a–g** were kept neat at 22°C for 14 h, whereas **1h–m** and **4a** had to be heated to 130°C in benzene for several days. The sterically hindered (*Z*)-diene **4b** required three weeks for complete dimerization. In all cases, the dimerization furnished quantitative yields of the 4-vinylcyclohexene derivatives, however, in strongly varying stereoisomeric ratios (Table 1). From the (*E*)-tetraaryl dienes **1a–f**, only the *r*-3,*t*-4 isomers **2a–f** were formed within the limit of detection (ca. 5% according to TLC and ^{1}H-NMR analysis), whereas the dimerization of the (*E*)-alkyl-aryl dienes **1h–m** and the (*Z*)-dienes **4a, b** furnished almost equimolar amounts of the isomers **2/3** and **5/6**. The

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isomeric mixtures were separated by preparative TLC; **2a–c**, **e** and **5/6a** were obtained as colorless crystals. The pure isomers, e.g. **2m** or **3m**, did not isomerize on further heating so that the isomeric distributions listed in Table 1 are the result of kinetically controlled reactions.

Table 1. Diastereomeric ratios and total yields in the dimerization of the dienes **1** and **4**

Diene	Diastereomeric ratio[a]	Yield (%)[b]
1a	**2a** : **3a** = >95:5	93
1b	**2b** : **3b** = >95:5	95
1c	**2c** : **3c** = >95:5	91
1d	**2d** : **3d** = >95:5	96
1e	**2e** : **3e** = >95:5	93
1f	**2f** : **3f** = >93:7	96
1g	—	92
1h	**2h** : **3h** = 1.3 : 1	89
1i	**2i** : **3i** = 1.1 : 1	95
1j	**2j** : **3j** = 1.4 : 1	91
1k	**2k** : **3k** = 1.4 : 1	96
1l	**2l** : **2l** = 1.3 : 1	92
1m	**2m** : **3m** = 1.6 : 1	92
4a	**5a** : **6a** = 1.1 : 1	97
4b	**5b** : **6b** = 1.3 : 1	91

[a] Determined by ^{1}H NMR. In the cases of **1a–1f** no second isomer could be detected. — [b] After chromatography.

The structural assignment of the dimers is based on ^{1}H-NMR comparison with the *trans*-tetraphenyl derivative **2a**, for which a crystal structure analysis was performed (Figure 1). The C-5,6,1,2,3 portion of the cyclohexene ring is essentially planar. C-4 points out of this plane, thus creating approximately a chair conformation at C-3,4,5. Presumably for the sake of maximum distance, the two phenyl rings in 3,4 position adopt *trans*-diaxial positions. The ^{1}H-NMR spectra of **2a** and the other tetra-aryl derivatives (**2b–f** and **5/6a**) are so similar that the structures follow from analogy.

The remaining dimers (**2/3h–m** and **5/6b**) required some additional consideration with respect to their regio- and stereostructure. Obviously, in dimer formation, the 1,2 or the 3,4 double bond of the diene could be used as the dienophile. The 3,4 bond is the less hindered and, hence, the more active one. So, in terms of regiochemistry, the only plausible alternative to the dimers **2/3** would be structure **7**, which, however, appears to be unlikely in the light of simple ^{1}H-NMR arguments. In particular, the chemical shifts of the α and β protons of 3-alkyl groups in **2/3h, i** and **5/6b** and of the 4-alkyl group in **2/3k–m** quite sensitively respond to the *cis* or *trans* position of the 4- and 3-phenyl substituent, respectively (Tables 2, 3). The same is true for the 1′-H signal and the 3-phenyl group in **2/3k–m** and **5/6a** (Table 4).

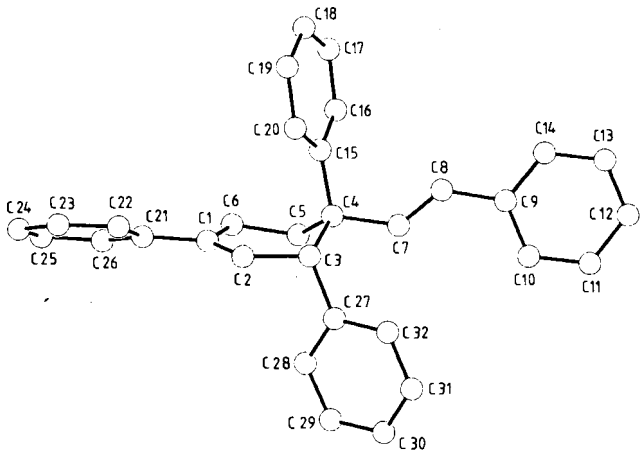

Fig. 1. Crystal structure of **2a**

Table 2. ^{1}H-NMR shift effects of the 3-phenyl group on 4-alkyl protons in the dimers **2,3k–m** ($CDCl_3$)

Dimer	4-Alkyl	δ(*H*) [ppm]
2k	CH_3	1.18
3k		0.78
2l	$CH(CH_3)_2$	0.96/1.11[a]
3l		0.70/0.91[a]
2m	$C(CH_3)_3$	0.94
3m		0.61

[a] Diastereotopic.

Table 3. ^{1}H-NMR shift effects of the 4-phenyl group on 3-alkyl protons in the dimers **2,3h,i** and **5,6b** ($CDCl_3$)

Dimer	3-Alkyl	δ(*H*) [ppm]
2h	CH_3	1.04
3h		0.63
2i	$C(CH_3)_3$	0.93
3i		0.66
5b	$C(CH_3)_3$	0.92
6b		0.66

Table 4. ^{1}H-NMR shift effects of the 3-phenyl group on the 4-styryl-1′-H in some dimers **2**, **3**, **5**, and **6** ($CDCl_3$)

Dimer	δ(1′-H) [ppm]
2g	6.20
	6.47
2k	6.10
3k	6.23
2l	5.90
3l	6.01
2m	6.10
3m	6.20
5a	5.82
6a	6.15

Thus, R^1 and R^2 are obviously in a vicinal position, which is in accord with the structures **2/3** and eliminates **7**. The same ^{1}H-NMR criterion may also be used for assigning the

relative stereochemistry at centers C-3/4 in **2/3** and **5/6**. Thus, in **2k–m** and **5a**, the shielding influence of the *cis*-vicinal 3-phenyl group induces an upfield shift of the 1′-H signal relative to the isomers **3k–m** and **6a**. Additionally, the δ- and β-H signals of the 3- and 4-alkyl substituents in **2/3h–m** and **5/6b** are subject to characteristic shift differences due to the *cis* or *trans* location of the vicinal phenyl group. In 4- and 5-membered rings, phenyl substituents exert a substantial upfield shift on the α and β protons of *cis*-vicinal alkyl groups, whereas those in *trans* substituents are hardly affected[6]. The data compiled in Tables 2 and 3 demonstrate the applicability of this criterion to our system, which is easy to understand, if we assume that the diaxial arrangement of R^1 and R^2, found in the crystal structure of **2a**, exists for **2h–m** as well. Thus, the phenyl residue cannot exert its anisotropic effect on the vicinal alkyl group, whereas this is easily possible in **3h–m**, where R^1 and R^2 adopt axial/equatorial positions. The stereochemical assignment thus achieved is congruent with the one obtained from the 1′-H signals. It is also noteworthy, that the (*Z*)-styryl unit of **4a** survives the dimerization without double-bond isomerization, as indicated by the coupling constant $J_{1',2'}$ = 12.5 Hz in **5/6a**, compared to 16 Hz for **2a**.

2a[7] and **2j**[8] have already been described, with correct regiochemistry, but without sterochemical assignment. Remarkably, **2a** has been obtained from the acid-catalyzed dehydration of 1,3-diphenyl-2-buten-1-ol and 1,3-diphenyl-1-buten-3-ol. The monomer **1a** could not be isolated under these conditions[7].

In order to test its tendency towards dimerization versus "normal" Diels-Alder addition, **1a** was treated with tetracyanoethylene and maleic anhydride in benzene solution and with a large excess of dimethylfumarate without a solvent. Only the first two very reactive dienophiles gave the normal adducts without concomitant dimerization; in dimethylfumarate, however, only the dimer and no cycloadduct was formed, though the fumarate ranks among the highly active dienophiles in "normal" Diels-Alder additions.

Discussion

How can our results contribute to the issue of diradical versus concerted mechanism in the Diels-Alder reaction? First of all, the regiochemistry of the dimerization does not provide any evidence on favor of either hypothesis. Both, the concerted mechanism which follows the "*ortho-para* rule"[1] and the diradical pathway which favors the diradical with the optimal stabilization of the radical centers, would predict the 4-vinylcyclohexene structure actually found. More conclusive are the stereochemical results (Table 1). Whereas the alkyl-aryl dienes **1g–m** and the (*Z*)-dienes **4a, b** dimerize almost stereorandomly, high enantioface-enantioface (= non-induced or "simple") stereoselectivity is observed for the (*E*)-tetra-aryl dienes **1a–f**. This so-called "endo" phenomenon[1] is common in Diels-Alder reactions, however, only for dienophiles with strongly electron-withdrawing substituents, (CO_2R,NO_2,CN, etc.) and can thus not be used as an explanation for the high selectivity towards **2a–f**. On the other hand, the stereochemical results can be rationalized by postulating a symmetrical diradical intermediate **8**[2]. Due to allylic resonance, C–C rotations should be strongly hindered in the two allyl moieties, whereas confomational freedom should be given to the 1,6, 5,6 and 4,5 axes. This leaves us with the possibility of (*E,E*), (*E,Z*) and (*Z,Z*) configurations around the 1,2 and 4,1′ bonds of **8**[2]. (*E,E*)-**8** would give only 1,2-divinylcyclobutanes on cyclization as in the dimerization of 1,3-butadiene itself[2,9]. As no such products nor the corresponding 1,5-cyclooctadienes have been discovered according to TLC and ^{1}H-NMR analysis in our case, (*E,E*)-**8** may be neglected, although its formation and consumption in rapid reversible processes[2] cannot be excluded. (*Z,Z*)-**8**, on the other hand, is sterically too congested to be formed, so that (*E,Z*)-**8** remains as the actual reactive species in the dimerization. The pivotal issue of stereoselectivity may be addressed in terms of a mobile equilibrium between the two rotamers **A** and **B**, the first one leading to **3** and the second one to **2**, respectively. During the formation of the 5,6 bond the resonance of both allylic subunits has to be destroyed.

Thus, the reactivity and, hence, the selectivity of the ring-forming step, will crucially depend on the resonance energy of **8**. Poorly stabilized species with R^1 or R^2 = alkyl can be expected to react unselectively forming **2/3** in comparable amounts, whereas well-stabilized diradicals with R^1 and R^2 = aryl will be able to select the more favorable pathway to the sterically less congested (R^1 and R^2 in *anti*-position!) diasteromer **2**.

Similar considerations also apply to the (*Z*)-dienes **4a, b**. Despite its tetra-phenyl substitution, **4a** dimerizes stereounselectively; apparently, the steric effect of the *cis*-located phenyl groups in the R^1 position causes a nonplanar and, hence, destabilized geometry of the allylic subunits.

Kinetic Results

To gain additional support for the diradical hypothesis, kinetic studies were performed in benzene solution at temperatures ranging from 50 to 170°C. Normally, ^{1}H-NMR spectroscopy was used for determining the relative concentrations of both the diene and the dimers, relative to dioxane as an internal standard. Independently, the dimerization of **1a** was followed by titrating the unreacted diene with a standardized solution of 4-phenyl-Δ^1-1,2,4-triazoline-3,5-dione (**9**) at given intervals[10]. The rate constants obtained from both methods were in good agreement. All dimerizations strictly obey a second-order rate law with respect to the concentration of the diene, and the rate constants *k* were calculated from equation (1), in which c_0 and c_t stand for the diene concentrations at 0 and *t* seconds, respectively. Tables 5 and 6 contain the absolute and relative rate constants of the dimerization of **1** and **4** at the indicated temperatures. The relative values are based on the gas-phase dimerization rates of 1,3-butadiene, which have been calculated from the activation parameters for the indicated temperatures[11]. This procedure appears acceptable as the rate constants for the dimerization of 1,3-butadiene are about the same in the condensed phase and the gas phase[12].

$$C_0/C_t = 1 + k \cdot t \cdot c_0 \qquad (1)$$

Table 5. Absolute and relative rate constants (1,3-butadiene: ≡ 1) of the dimerization of **1a–n** in C_6D_6 (^{1}H-NMR method)

1	Temp. [°C]	$k_D \cdot 10^4$ [lmol^{-1}s^{-1}]	k_{rel}[a]
a	50.0	1.4	$1.0 \cdot 10^6$
b	50.0	1.1	$7.9 \cdot 10^5$
c	50.0	2.4	$1.7 \cdot 10^6$
d	65.0	1.7	$4.5 \cdot 10^5$
e	50.0	2.5	$1.8 \cdot 10^6$
f	50.0	1.8	$1.3 \cdot 10^6$
g	25	–	$\approx 10^8$[b]
h	126.7	0.89	260
i	130.0	1.7	390
j	130.0	0.45	100
k	130.0	0.42	94
l	130.0	0.18	40
m	130.0	0.040	9.0
n[c]	190	0.13	3.5

[a] k_D(1,3-butadiene) = 1. – [b] Estimated value. – [c] Calculated from ref.[3].

Table 6. Absolute and relative rate Constants for the dimerization of **4a** and **4b** in C_6D_6

4	Temp. [°C]	$k_D \cdot 10^5$ [lmol^{-1}s^{-1}]	k_{rel}[a]	k_E/k_Z
a	100.0	1.6	220	141
b	170.1	0.40	0.59	47

[a] k_D(1,3-butadiene) = 1.

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The data thus obtained indeed support the diradical hypothesis. For instance, the introduction of 1- and 3-phenyl groups stabilizes the radical centers and drastically enhances the dimerization rate (rate factors of 100 for **1j** and 10^6 for **1a**!). Further replacement of the 1-phenyl group by an (*E*)-styryl moiety (**1g**) extends the conjugated system and accounts for an additional acceleration by a factor of at least 100. Alkyl substituents alone do not show significant effects, neither as a single 1-methyl group (**1n**) nor in combination with phenyl substituents (**1h** versus **1j**, factor 2.6). In concerted Diels-Alder reactions, phenyl groups in the diene component do not lead to such drastic rate enhancements. Moreover, the rate effect of a phenyl substituent does not differ so much from that of a methyl group. For instance, the addition rate of maleic anhydride, relative to 1,3-butadiene, is 3.4 for **1n**, 1.7 for **1j**, and 8.8 for 2-phenyl-1,3-butadiene[13].

Another peculiarity of our dimerization rates is the fact that for analogously substituted systems (**1h/k** and **1i/m**) the 1-alkyl-3-phenyl derivative reacts faster. This observation may be interpreted by assuming that the 5,6 bond is closed prior to the 3,4 bond (dimer notation), so that the incipient diradical is stabilized better by the phenyl groups at C-1/4. In the case of **1i/m** an additional steric effect may be operative. The (*Z*)-dienes **4a, b** dimerize at a significantly lower rate than their (*E*)-substituted counterparts (Table 6). In terms of activation enthalpies, this accounts for about 20 kJ/mol in favor of **1a** over **4a** (Table 7). The lower rate of the (*Z*)-dienes may be explained by assuming that (*Z*)-substituted allylic radicals cannot be expected to be entirely planar, due to steric hindrance, and thus lose resonance energy. In addition to this effect, in the diradical generated from **4a**, the terminal phenyl groups cannot adopt a coplanar arrangement with the allylic moiety and suffer an extra loss of resonance energy.

Table 7. Activation parameters for the dimerization of **1a** and **4a** in C_6D_6

Diene	$k_D \cdot 10^4$ [lmol^{-1}s^{-1}]	Temp. [K]	E_a [kJmol^{-1}]	log *A*	$\Delta H^{\neq}$ [kJmol^{-1}]	$\Delta S^{\neq}$ [Jmol^{-1}K^{-1}]
1a	1.44	325.15				
	2.62	335.15				
	3.31	338.15	53.9	4.9	51.8	–159
	4.70	345.15	±3	±0.5	±3	±10
4a	15.9	373.45				
	35.9	383.15				
	55.5	393.15	77.3	6.1	72.7	–142
	107	403.15	±3	±0.5	±3	±10

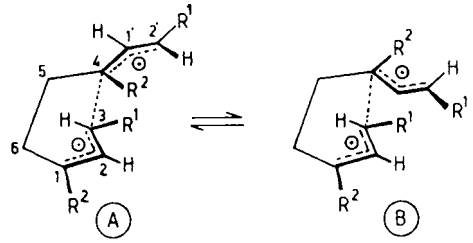
The $k_{E/Z}$ ratio for **1a/4a** is by far higher than that for **1i/4b**. Both ratios, however, are dwarfed by those found for concerted Diels-Alder reactions. Thus, (*E*)-1-methyl-1,3-butadiene reacts 45000 times faster with tetracyanoethylene than its (*Z*) isomer, and for the 1-phenyl-1,3-butadienes the (*E*)/(*Z*) ratio is no less than 170000[13]! These enormous effects are usually interpreted in terms of the *s-cis-s-trans*-conformational equilibrium of the dienes[1]. In our dimerizations, by contrast, we assume a terminal interaction, which eventually leads to 5,6-bond formation in the rate determining step. Clearly, this process allows a higher amount of *gauche* conformations in the diene component than the concerted mechanism does, where C-1 and C-4 of the diene have to form new C–C bonds almost simultaneously.

In conclusion, the substituent effects exerted both on the rates and the facial selectivities of the dimerization, strongly suggest a two-step mechanism. In the first, rate-determining step an intermediate **8** is formed, which, in the second, product-determining step collapses to generate the dimers **2/3/5/6**, via the rotamers **A** and **B** as cyclizable species. **8**, in principle, could be of zwitterionic or diradical character. The

Table 8. Solvent effects for the dimerization of **1d** (65.0°C)

Solvent	$k_D \cdot 10^4$ [lmol^{-1}s^{-1}]
C_6D_6	1.7
[D$_6$]DMSO	1.6
[D$_6$]DMSO/methan-[D]ol (1:4)	5.6

low solvent effect (Table 8), however, is an argument in favor of the diradical.



(E,Z)-8

1,5-H Shift versus Dimerization of the (Z)-Dienes 4c, d

The (Z)-dienes **4c, d** cleanly underwent a sigmatropic 1,5-H shift to form **10a, b** at temperatures around 150°C. No dimers were observed according to TLC and ^{1}H-NMR analysis. The structure of **10a, b** followed from elemental analysis and the mass and ^{1}H-NMR spectra. In particular, the configurations at both double bonds can be derived from the coupling constants.

The 1-CH_3 group in **10a, b** appears as a singlet without allylic coupling to 3-H, which indicates a *trans* arrangement of these substituents. Similarly, the value of $J_{4,5}$ = 16 Hz in **10a** is consistent with an (*E*) configuration at C-4,5. No (*Z*) isomer could be detected (ca. 5% according to ^{1}H-NMR analysis).

Both rearrangements exhibited clean first-order kinetics in [D_6]benzene. The rate constants were correlated with those of the 1,5-H shift of (*Z*)-1,3-pentadiene (**11**)[14] (Table 9). Both **4c** and **4d** rearrange far more rapidly than **11**, the rate factors being 4500 and 220, respectively.

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Table 9. Absolute and relative rates of the thermal 1,5-H shifts in **4c, d** → **10a, b** in C_6D_6

4	Temp. [°C]	$k \cdot 10^5$ [s^{-1}]	k_{rel}[a]
c	126.7	4.03	4600
d	161.7	4.86	220

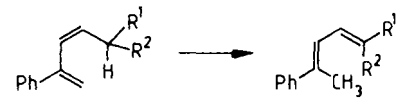
[a] k[(Z)-1,3-pentadiene] = 1. Calculated from the known activation parameters of (Z)-1,3-pentadiene ($\Delta H^{\neq}$ = 147 kJ, $\Delta S^{\neq}$ = −29 $Jmol^{-1}K^{-1}$)[14].

These results may be interpreted in terms of a concerted mechanism via the transition state **12**. To avoid steric congestion, the 5-methyl group in **4c** adopts the less hindered R^1 position and thus generates the (*E*)-4,5 configuration in **10a**. The R^2 position in **4d**, however, must be occupied by the second methyl group, which results in a considerable rate decrease (factor 20 compared to **4c**). In each case, the newly formed 1-methyl group is placed into the (*Z*) position.

The astounding rate increase relative to **11** must be attributed to the 2-phenyl group. This is unusual, since only substituent effects concerning the carbon atom which bears the migrating hydrogen have been studied so far[10,15].

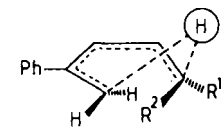
Two interpretations may be suggested. Either the known[16] increase of the HOMO coefficient at C-1, which is induced by the 2-phenyl group, facilitates the formation of the new C–H bond, or the rearrangement is not synchronous, though concerted, and some unsaturated character is imposed on C-2, finding stabilization by the phenyl substituent.

On considering the dichotomy between dimerization and 1,5-H shift in our (*Z*)-dienes, it is remarkable that, given the requisite hydrogen atom, only the 1,5-H shift and no dimerization takes place on comparable concentrations and reaction temperatures. In cyclopentadienes, the ratio of dimerization versus 1,5-H shift is strongly controlled by the nature of the substituent in position 5[10]. Possibly, such effects could also be obtained in our systems.



4 **10**

4, 10	R^1	R^2
4c, 10a	CH_3	H
4d, 10b	CH_3	CH_3



12

Experimental

^{1}H-NMR spectra ($CDCl_3$ unless stated otherwise, TMS): Bruker WP 80, WH 270, Varian EM 360. – IR: Perkin-Elmer IR 580 B. – MS: Varian MAT 711, AEI 902 (Associated Electronic Industries). – All reactions were performed in purified solvents under argon and monitored by TLC (Merck 5560). Preparative TLC on self-made plates (20 × 20 cm, 2 mm, silica gel Merck PF 254 + 366).

Dimerization of the Dienes **1** *and* **4**: **1a–g** (5 mmol) were kept at 22°C for 14 h, and analyzed by ^{1}H NMR. On trituration with ethanol, crystalline **2a, b, d** and **e** were obtained in 85–90% yield. The mother liquors were submitted to preparative TLC [hexane/ether (6:1)] to furnish additional 5–8% of dimers. No other regio- or stereoisomers could be detected in the chromatography fractions. **2c** and **2f** were isolated by TLC as colorless oils in isomerically pure form. **2g** was crystallized from ethanol.

1h–m and **4a–c** (5 mmol) in benzene (2 ml) were heated to 130.0°C in a sealed ampoule for 48 h. The solvent was removed under reduced pressure, and the dimers were separated by preparative TLC (hexane). **5a** and **6a** were crystallized from ethanol, the other dimers remained oily. In these cases, the determination of the molecular formula by elemental analysis or mass spectrometry was performed with the isomeric mixtures.

1,r-3,t-4-Triphenyl-c-4-[(E)-styryl]-1-cyclohexene (**2a**): Colorless prisms, mp. 135–138°C. – ^{1}H NMR (60 MHz): δ = 2.1–2.8 (m, 4H, 5, 6-H$_2$), 4.20 (br. d, J = 5 Hz, 1H, 3-H), 6.01 (br. s, 2H, styryl-H), 6.31 (br. d, J = 5 Hz, 1H, 2-H), 7.0–7.5 (m, 20 H, phenyl-H). – ^{1}H NMR (270 MHz): δ = 2.0–2.4 (m, 3H, 5, 6-H), 2.60 (dt, J = 17 Hz, J = 7 Hz, 1H, 5- or 6-H), 4.21 (d, J = 5 Hz, 1H, 3-H), AB system (δ$_A$ = 6.02, δ$_B$ = 6.13, J_{AB} = 16 Hz, (*E*)-styryl-H), 6.41 (d, J = 5 Hz, 1H, 2-H), 7.1–7.5 (m, 20 H, phenyl-H). – IR (KBr): ν = 3010 cm^{-1}, 1630, 1595, 1440, 980, 750, 690.

$C_{32}H_{28}$ (412.6) Calcd. C 93.16 H 6.84
Found C 93.33 H 6.99

r-3-(Methylphenyl)-c-4-[(E)-2-(4-methylphenyl)ethenyl]-1,t-4-diphenyl-1-cyclohexene (**2b**): Colorless prisms, mp. 130–131°C. – ^{1}H NMR (80 MHz): δ = 2.0–2.2 (m, 4H, 5, 6-H$_2$), 2.16 (s, 6H, CH$_3$), 4.20 (br. d, J = 4 Hz, 3-H), 6.01 (br., 2H, styryl-H), 6.30 (br. d, J = 4 Hz, 1H, 2-H), 7.0–7.5 (m, 18 H, aromat. H). – IR (KBr): ν = 1638 cm^{-1}, 1595, 1510, 1450, 1458, 1440, 1110, 1030, 975, 800, 760.

$C_{34}H_{32}$ (440.6) Calcd. C 92.68 H 7.32
Found C 92.36 H 7.29

r-3-(4-Chlorophenyl)-c-4-[(E)-2-(4-chlorophenyl)ethenyl)]-1,t-4-diphenyl-1-cyclohexene (**2c**): Colorless oil. – ^{1}H NMR (60 MHz): δ = 2.0–2.8 (m, 4H, 5, 6-H), 4.10 (d, J = 4 Hz, 1H, 3-H, 6.00 (br. s, 2H, styryl-H), 6.17 (d, J = 4 Hz, 2-H), 7.0–7.5 (m, 18 H, aromat. H).

$C_{32}H_{26}Cl_2$ (481.5) Calcd. C 79.82 H 5.44
Found C 79.51 H 5.30

r-3-(4-Methoxyphenyl)-c-4-[(E)-2-(4-methoxyphenyl)ethenyl]-1,t-4-diphenyl-1-cyclohexene (**2d**): Colorless crystals, mp. 141–142°C. – ^{1}H NMR (80 MHz): δ = 2.0–2.8 (m, 4H, 5, 6-H$_2$), 3.60 (s, 6H, OCH$_3$), 4.10 (br. d, J = 4 Hz, 1H, 3-H), 5.92 (s, 2H, styryl-H), 6.20 (br. d, J = 4 Hz, 1H, 2-H), 6.5–7.5 (m, 18 H, aromat. H). – IR (KBr): ν = 1640 cm^{-1}, 1605, 1245, 1150, 1030, 970, 805, 765.

$C_{34}H_{32}O_2$ (472.6) Calcd. C 86.40 H 6.83
Found C 86.18 H 6.87

1,t-4-Diphenyl-r-3-(2-thienyl)-c-4-[(E)-2-(2-thienyl)ethenyl]-1-cyclohexene (**2e**): Colorless crystals, m.p. 146–147°C. – ^{1}H NMR (60 MHz): δ = 1.8–2.8 (m, 4H, 5, 6-H$_2$) 4.42 (d, J = 4.5 Hz, 1H, 3-H), 6.17 (s, 2H, styryl-H), 6.38 (br. d, J = 4.5 Hz, 1H, 2-H), 6.6–7.6 (m, 16H, aromat. H). – IR (KBr): ν = 1630 cm^{-1} (br., C=C), 1595, 1490, 1440, 982, 925, 697.

$C_{28}H_{24}S_2$ (424.5) Calcd. C 79.22 H 5.70 S 15.08
Found C 79.38 H 5.72 S 15.20

r-3-(2-Furyl)-c-4-[(E)-2-(2-furyl)ethenyl]-1,t-4-diphenyl-1-cyclohexene (**2f**): Colorless oil. – ^{1}H NMR (60 MHz): δ = 1.8–2.8 (m, 4H, 5, 6-H), 4.18 (d, J = 5 Hz, 1H, 3-H), 5.66–6.41 (m, 7H, furyl-, vinyl-H), 6.95–7.5 (m, 12 H, aromat. H).

$C_{28}H_{24}O_2$ (392.5) Calcd. C 85.68 H 6.18
Found C 85.42 H 6.20

3-Phenyl-1,4,4-tri[(E)-styryl]-1-cyclohexene (**2g**): Colorless crystals, mp. 122–124°C. – ^{1}H NMR (80 MHz): δ = 2.10, 2.50 (2m$_c$, 4H, 5, 6-H), 3.75 (d, J = 4 Hz, 1H, 3-H), 5.99 (d, J = 4 Hz, 1H, 2-H), 6.20, 6.49 [2s, 4H, 4,4-(*E*)-distyryl-H], AB system [δ$_A$ = 6.53, δ$_B$ = 6.93, J_{AB} = 16.5 Hz, 1-(*E*)-styryl-H], 7.0–7.7 (m, 20H, phenyl-H). – IR (KBr): ν = 1620 cm^{-1}, 1560, 1490, 1070, 965, 745.

$C_{36}H_{32}$ (464.6) Calcd. C 93.06 H 6.94 Found C 92.82 H 7.11
Mol. mass 465 (osm. in C_6H_6)

r-3-Methyl-1,t-4-diphenyl-c-4-[(E)-propenyl]-1-cyclohexene (**2h**): ^{1}H NMR (80 MHz): δ = 1.04 (d, J = 7 Hz, 3H, C-CH$_3$), 1.65 (d, J = 5 Hz, 3H, propenyl-CH$_3$), 2.0–3.0 (m, 5H, 3-H, 5, 6-H$_2$), 5.32–5.62 (m, 2H, vinyl-H), 6.17 (d, J = 5 Hz, 1H, 2-H), 7.1–7.5 (m, 10H, phenyl-H).

r-3-Methyl-1,c-4-diphenyl-t-4-[(E)-propenyl]-1-cyclohexene (**3h**): ^{1}H NMR (80 MHz): δ = 0.63 (d, J = 6.5 Hz, 3H, 3-CH$_3$), 1.75 (d, J = 5 Hz, 3H, propenyl-CH$_3$), 2.0–3.0 (m, 5H, 3-H, 5, 6-H$_2$), 5.32–5.62 (m, 2H, vinyl-H), 6.17 (d, J = 5 Hz, 1H, 2-H), 7.1–7.5 (m, 10H, phenyl-H).

$C_{22}H_{24}$ (288.4) Calcd. C 91.81 H 8.44 Found C 91.61 H 8.39
Calcd. 288.188 Found 288.189 (MS)

r-3-tert-Butyl-c-4-[(E)-3,3-dimethyl-1-butenyl]-1,t-4-diphenyl-1-cyclohexene (**2i**): ^{1}H NMR (80 MHz): δ = 0.93 (s, 9H, *t*Bu), 1.05 (s, 9H, *t*Bu), 1.6–3.0 (m, 5H, 3-H, 5, 6-H$_2$), 5.36 (s, 2H, vinyl-H), 6.26 (br. d, J = 4.5 Hz, 1H, 2-H), 7.0–7.5 (m, 10H, phenyl-H).

r-3-tert-Butyl-t-4-[(E)-3,3-dimethyl-1-butenyl]-1,c-4-diphenyl-1-cyclohexene (**3i**): ^{1}H NMR (80 MHz): δ = 0.66 (s, 9H, *t*Bu), 1.05 (s, 9H, tBu), 1.6–3.0 (m, 5H, 3-H, 5, 6-H$_2$), AB system (δ$_A$ = 5.40, δ$_B$ = 5.73, J_{AB} = 18 Hz, vinyl-H), 6.36 (br. d, J = 4 Hz, 1H, 2-H), 7.0–7.5 (m, 10H, phenyl-H).

$C_{28}H_{36}$ (372.6) Calcd. C 90.08 H 9.59
Found C 90.26 H 9.74

trans-3-Phenyl-4-[(E)-styryl]-1-cyclohexene (**2j**): ^{1}H NMR (80 MHz): δ = 1.5–2.8 (m, 5H, 4-H, 5, 6-H$_2$), 3.56 (m$_c$, 1H, 3-H), 5.82 (m$_c$, 2H, 1, 2-H), 6.14 (s, 2 styryl-H), 7.2 (br., 10H, phenyl-H).

cis-3-Phenyl-4-[(E)-styryl]-1-cyclohexene (**3j**): ^{1}H NMR (80 MHz): δ = 1.5–2.8 (m, 5H, 4-H, 5, 6-H$_2$), 3.23 (m$_c$, 1H, 3-H), 5.82 (m$_c$, 2H, 1, 2-H), AB system (δ$_A$ = 5.95, δ$_B$ = 6.30, J_{AB} = 15 Hz, styryl-H), 7.2 (m, 10 H, phenyl-H).

$C_{20}H_{20}$ (260.4) Calcd. C 92.22 H 8.04 Found C 92.26 H 7.74

1,t-4-Dimethyl-r-3-phenyl-c-4-[(E)-styryl]-1-cyclohexene (**2k**): ^{1}H NMR (60 MHz): δ = 1.18 (s, 3H, 4-CH$_3$), 1.71 (br. s, 3H, 1-CH$_3$), 1.4–2.3 (m, 4H, 5, 6-H$_2$), 3.25 (br. s, 1H, 3-H), 5.43 (br. s, 1H, 2-H), 6.10 (s, 2H, styryl-H), 7.0–7.4 (m, 10H, phenyl-H).

1,c-4-Dimethyl-r-3-phenyl-t-4-[(E)-styryl]-1-cyclohexene (**3k**): ^{1}H NMR (60 MHz): δ = 0.78 (s, 3H, 4-CH$_3$), 1.71 (br. s, 3H, 1-CH$_3$), 1.4–2.3 (m, 4H, 5, 6H$_2$), 3.36 (br. s, 1H, 3-H), 5.43 (br. s, 1H, 2-H), 6.23 (s, 2H, styryl-H), 7.0–7.4 (m, 10H, phenyl-H). – IR (film): ν = 1595 cm^{-1}, 1560, 1490, 1445, 1370, 965, 745, 695.

$C_{22}H_{24}$ (288.2) Calcd. C 91.76 H 8.50
Found C 91.61 H 8.39

1,t-4-Diisopropyl-r-3-phenyl-c-4-[(E)- styryl]-1-cyclohexene (**2l**): ^{1}H NMR (80 MHz): δ = 0.96, 1.11 [2 d, J = 7 Hz, 2 × 6 H, CH(C*H*$_3$)$_2$], 1.3–2.3 (m, 6H, 2C*H*(CH$_3$)$_2$, 5, 6-H$_2$), 3.43 (m$_c$, 1H, 3-H), 5.33 (br. s, 1H, 2-H), 5.90 (s, 2H, styryl-H), 6.9–7.5 (m, 10H, phenyl-H).

1,c-4-Diisopropyl-r-3-phenyl-t-4-[(E)-styryl]-cyclohexene (**3l**): ^{1}H NMR (80 MHz): δ = 0.70, 0.91 (2 d, J = 7 Hz, 2 × 6 H, CH(C*H*$_3$)$_2$), 1.3–2.3 (m, 6H, 2C*H*(CH$_3$)$_2$, 5, 6-H$_2$), 3.25 (m$_c$, 1H, 3-H), 5.33 (br. s, 1H, 2-H), AB system (δ$_A$ = 6.01, δ$_B$ = 6.33, J_{AB} = 15 Hz, styryl-H), 6.9–7.5 (m, 10H, phenyl-H). – IR (film): ν = 2960 cm^{-1}, 1610, 1495, 1450, 955, 750, 690.

$C_{26}H_{32}$ (344.5) Calcd. C 90.70 H 9.24
Found C 90.64 H 9.36

1,t-4-Di(tert-butyl)-r-3-phenyl-c-4-[(E)-styryl]-1-cyclohexene (**2m**): ^{1}H NMR ([D$_6$]benzene, 80 MHz): δ = 0.94, 1.05 (2s, 2 × 9H, 2 *t*Bu), 1.6–2.4 (m, 4H, 5, 6-H$_2$), 3.68 (br. d, J = 5 Hz, 3-H), 5.63 (br. d, J = 5 Hz, 2-H), AB system (δ$_A$ = 6.10, δ$_B$ = 6.28, J_{AB} = 17.0 Hz, styryl-H), 6.9–7.6 (m, 10H, phenyl-H).

1,c-4-Di(tert-butyl)-r-3-phenyl-t-4-[(E)-styryl]-1-cyclohexene (**3m**): ^{1}H NMR ([D$_6$]benzene, 80 MHz): δ = 0.61, 1.01 (2s, 2 × 9H, 2 *t*Bu), 1.6–2.4 (m, 4H, 5, 6-H$_2$), 3.65 (br. d, J = 5 Hz, 3-H),

5.53 (br. d, J = 5 Hz, 2-H), AB system (δ_A = 6.20, δ_B = 6.43, J_{AB} = 17.0 Hz, styryl-H), 7.0–7.6 (m, 10H, phenyl-H).

$C_{28}H_{36}$ (372.6) Calcd. C 90.65 C 9.72
Found C 90.26 H 9.74

1,r-3,t-4-Triphenyl-c-4-[(Z)-styryl]-1-cyclohexene (**5a**): Colorless prisms, mp. 116–118°C. – ^{1}H NMR (80 MHz): δ = 2.2–2.5 (m, 4H, 5, 6-H_2), 3.97 (br. d, J = 5 Hz, 1H, 3-H), AB system (δ_A = 5.82, δ_B = 6.47, J_{AB} = 12.5 Hz, styryl-H), 6.35 (br. d, J = 5 Hz, 1H, 2-H), 6.6–7.6 (m, 20H, phenyl-H). – IR (KBr): ν = 3060 cm^{-1}, 3030 (CH), 1640, 1595, 1575, 1490, 1445, 1075, 760, 700.

$C_{32}H_{28}$ (412.5) Calcd. C 92.84 H 6.95
Found C 93.16 H 6.84

1,r-3,c-4-Triphenyl-t-4-[(Z)-styryl]-1-cyclohexene (**6a**): Colorless prisms, mp. 182–183°C. – ^{1}H NMR (80 MHz): δ = 1.7–2.8 (m, 4H, 5, 6-H_2), 3.78 (br. d, J = 5 Hz, 1H, 3-H), AB system (δ_A = 6.15, δ_B = 6.68, J_{AB} = 12.5 Hz, styryl-H), 6.5–7.6 (m, 20 H, phenyl-H). – IR (KBr): ν = 3010 cm^{-1}, 1600, 1580 (C=C), 1490, 1445, 1175, 880. $C_{32}H_{28}$ (412.5) Calcd. C 93.23 H 6.99
Found C 93.16 H 6.84

r-3-(tert-Butyl)-c-4-[(Z)-3,3-dimethylbutenyl]-1,t-4-diphenyl-1-cyclohexene (**5b**): ^{1}H NMR (80 MHz): δ = 0.92, 1.05 (2s, 2 × 9 H, 2 *t*Bu), 2.0–2.9 (m, 5H, 3-H, 5, 6-H_2), 5.50 (s, 2H, vinyl-H), 6.27 (m_c, 1H, 2-H), 7.0–7.7 (m, 10 H, phenyl-H).

r-3-(tert-Butyl)-t-4-[(Z)-3,3-dimethylbutenyl]-1,c-4-diphenyl-1-cyclohexene (**6b**): ^{1}H NMR (80 MHz): δ = 0.66, 1.05 (2s, 2 × 9 H, 2 *t*Bu), 2.0–2.9 (m, 5H, 3-H, 5, 6-H_2), 5.57 (s, 2H, vinyl-H), 6.27 (m_c, 1H, 2-H), 7.0–7.7 (m, 10 H, phenyl-H). – IR (film): ν = 2950 cm^{-1}, 1650, 1595, 1490, 1440, 1360, 750, 695.

$C_{28}H_{36}$ Calcd. 372.282 Found 372.284 (MS)

Kinetic Studies of the Dimerization

^{1}H-NMR Method: An exact quantity (100–150 mg) of the diene and dioxane (ca. 30 mg) as an internal standard were put into an NMR tube and diluted with C_6D_6 to a combined volume of exactly 1.0 ml. The tube was sealed under argon and placed into a thermostat. At appropriate intervals, the tube was removed from the bath, chilled with ice/water and a ^{1}H-NMR spectrum was recorded. The product analysis was based on the relative integrals of the $=CH_2$ signals of the diene and the combined 2-H + 3-H signals of the dimer. To make sure that no side reactions had occurred, the integrals of diene + dimer were correlated with the integral of the dioxane singlet. No loss of material could be detected in this way.

Titrimetric Method: **9** (312.8 mg) was dissolved in 100 ml of benzene. The titer of the solution was determined by titrating 9,10-dimethylanthracene (18.8 mg, 0.091 mmol) in benzene (2.00 ml). 4.16 ml of the solution was consumed, so it was 0.022 M. **1a** (600 mg) was dissolved in benzene (15.0 ml) and the solution was divided among 14 ampoules, which were sealed under argon and placed into a thermostat at 60°C. After 5 min, the first ampoule was removed, and its contents were titrated to give c_0 (0.101 mol/l). Every 20 min, an ampoule was removed and titrated to furnish c_t. The $1/c_t$ values correlated linearly with t. The rate constant was $2.72 \cdot 10^{-4}$ lmol^{-1} s^{-1} compared to $2.62 \cdot 10^{-4}$ lmol^{-1} s^{-1} obtained by the ^{1}H-NMR method.

In each kinetic run, the reaction was followed up to ca. 90% conversion and 10–15 data points were registered. The linearity of the time/concentration relationship was checked by determining the regression coefficient r, which was > 0.99 in all cases. The accuracy of the rate constants was estimated to be about ± 5%. The same procedure was applied in the kinetic studies of the 1,5-H shifts of **4c**, **d** (vide infra).

1,5-H Shift: The kinetic measurements were performed in C_6D_6 by the ^{1}H-NMR method, using the $=CH_2$ signals of **4c**, **d** and the CH_3 singlet in **10a**, **b** for product analysis. Again, dioxane was used as an internal standard to check the clean conversion of **4c**, **d** to **10a**, **b**. After completion of the rearrangement, the solvent was evaporated and the residue was distilled at 12 Torr to furnish **10a** and **b** as colorless oils.

(E,E)-2-Phenyl-2,4-hexadiene (**10a**): ^{1}H NMR (80 MHz): δ = 1.81 (d, J = 6.5 Hz, 3H, CH_3), 2.11 (s, 3H, CH_3), 5.45–6.10 (m, 1H, 5-H), 6.33 (dd, J = 11.0, 16.5 Hz, 1H, 4-H), 6.38 (d, J = 11.0 Hz, 1H, 3-H), 7.1–7.5 (m, 5H, phenyl-H). – IR (film): ν = 3030 cm^{-1}, 1595, 1030, 960, 755.

$C_{12}H_{14}$ Calcd. 158.1095 Found 158.109 (MS)

(E)-2-Phenyl-5-methyl-2,4-hexadiene (**10b**): ^{1}H NMR: δ = 1.81 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 6.21 (d, J = 11.5 Hz, 1H, 4-H), 6.70 (d, J = 11.5 Hz, 1H, 3-H), 7.0–7.4 (m, 5H, phenyl-H). – IR: ν = 2960 cm^{-1}, 1625, 1595, 1490, 1375, 760.

$C_{13}H_{16}$ (172.3) Calcd. C 90.64 H 9.36 Found C 90.12 H 9.59

Crystal Structure Analysis of **2a**: A single crystal (0.3 × 0.4 × 0.4 mm) from ethanol was analyzed on a Nicolet P3 diffractometer. 2071 independent reflections were obtained, 1251 of which had $I \geq$

Table 10. Fractional atomic coordinates for **2a**

Atom	X/A	X/B	X/C
C1	0.23997(51)	-0.36011(42)	1.04253(24)
C2	0.33456(54)	-0.32075(43)	1.00941(25)
C3	0.32884(51)	-0.20777(44)	0.97515(26)
C4	0.22609(51)	-0.12730(43)	1.00298(25)
C5	0.08874(51)	-0.19268(45)	0.99980(27)
C6	0.17040(53)	-0.29598(45)	1.04481(27)
C7	0.20251(53)	-0.02273(46)	0.95866(24)
C8	0.25812(55)	0.07743(46)	0.97258(27)
C9	0.23721(52)	0.17637(45)	0.92854(25)
C10	0.18748(60)	0.16911(51)	0.85990(29)
C11	0.166657(66)	0.26705(54)	0.82073(31)
C12	0.19848(62)	0.37173(52)	0.84999(30)
C13	0.24954(60)	0.37932(49)	0.91816(28)
C14	0.26881(55)	0.28286(47)	0.95674(26)
C15	0.27967(53)	-0.09225(44)	1.07626(25)
C16	0.19377(59)	-0.02475(50)	1.10760(28)
C17	0.23649(62)	0.01376(51)	1.17260(29)
C18	0.36381(60)	-0.01684(50)	1.20847(28)
C19	0.44924(59)	-0.09505(50)	1.17887(29)
C20	0.40740(56)	-0.12302(46)	1.11269(26)
C21	0.26249(52)	-0.46716(44)	1.08104(25)
C22	0.39642(56)	-0.50752(47)	1.10474(26)
C23	0.41922(59)	-0.60868(49)	1.13844(28)
C24	0.30945(61)	-0.67145(51)	1.15280(29)
C25	0.17811(67)	-0.63151(55)	1.13227(31)
C26	0.15225(58)	-0.53138(50)	1.09626(28)
C27	0.29332(51)	-0.21940(44)	0.89877(25)
C28	0.20261(54)	-0.30200(47)	0.86803(26)
C29	0.16775(61)	-0.30679(52)	0.79817(30)
C30	0.22617(65)	-0.23234(55)	0.75859(31)
C31	0.31862(65)	-0.15329(54)	0.78864(30)
C32	0.35305(58)	-0.14581(48)	0.85816(28)

$2\sigma(I)$. The structure was solved by direct methods using the SHELXTL program and refined by least squares methods anisotropically to converge at $R_1 = 0.078$ and $R_2 = 0.079$. The fractional atomic coordinates are listed in Table 10. Table 11 contains some selected bond distances and bond angles[17].

Table 11. Selected bond lengths [Å] and angles [°] in the crystal structure of **2a**

C1–C2	1.310(8)	C8–C–9	1.454(7)
C2–C3	1.494(7)	C4–C15	1.524(7)
C3–C4	1.549(8)	C3–C27	1.514(7)
C4–C5	1.530(7)	C1–C21	1.474(7)
C5–C6	1.506(8)	C5–H5A	1.103(5)
C6–C1	1.499(7)	C3–H3	1.054(5)
C4–C7	1.512(7)	C7–H7	1.149(5)
C7–C8	1.305(8)	C8–H8	1.112(5)
C2–C1–C6	121.3(5)	C5–C4–C15	108.6(4)
C1–C6–C5	113.6(5)	C4–C15–C7	109.6(4)
C5–C4–C3	106.8(4)	C4–C15–C3	112.4(4)
C3–C4–C2	110.6(4)	C3–C27–C2	111.6(4)
C3–C2–C1	125.2(5)	C3–C27–C4	112.0(4)
C7–C8–C4	126.6(4)	C8–C9–C7	125.9(5)
C1–C21–C2	121.1(5)	C1–C21–C6	117.5(5)

Crystal Data: $C_{32}H_{28}$, $M_{calc} = 412.54$, monoclinic, space group $P2_1/c$, $a = 9.702(6)$, $b = 11.711(8)$, $c = 20.044(13)$ Å, $\beta = 100.34(05)°$, $V = 2252$ Å^3, $d_{calc} = 1.22$ gcm^{-3}, $Z = 4$, μ(Mo-K_α) = 0.6 cm^{-1}, $T = 240$ K, $\lambda = 0.71069$ Å, graphite monochromator, $2° < 2\Theta < 42°$, ω scan with $2.4 \leq \dot{\omega} \leq 29.3°$ min^{-1}.

CAS Registry Numbers

1a: 35632-82-7 / **1b**: 84313-01-9 / **1c**: 84313-03-1 / **1d**: 84313-05-3 / **1e**: 84313-07-5 / **1f**: 84313-09-7 / **1g**: 116669-43-3 / **1h**: 70588-46-4 / **1i**: 84313-14-4 / **1j**: 16939-57-4 / **1k**: 68036-69-1 / **1l**: 69366-50-3 / **1m**: 69366-51-4 / **2a**: 116780-00-8 / **2b**: 116780-01-9 / **2c**: 116780-02-0 / **2d**: 116780-03-1 / **2e**: 116780-04-2 / **2f**: 116780-05-3 / **2g**: 84313-16-6 / **2h**: 116669-44-4 / **2i**: 116669-45-5 / **2j**: 116780-06-4 / **2k**: 116669-46-6 / **2l**: 116669-47-7 / **2m**: 116669-48-8 / **3a**: 116781-87-4 / **3b**: 116780-09-7 / **3c**: 116780-10-0 / **3d**: 116780-11-1 / **3e**: 116780-12-2 / **3f**: 116780-13-3 / **3h**: 116780-14-4 / **3i**: 116780-15-5 / **3j**: 116780-16-6 / **3k**: 116781-88-5 / **3l**: 116780-17-7 / **3m**: 116780-18-8 / **4a**: 21035-05-2 / **4b**: 84313-26-8 / **4c**: 84313-24-6 / **4d**: 84313-25-7 / **5a**: 116780-07-5 / **5b**: 116780-08-6 / **6a**: 116780-19-9 / **6b**: 116780-20-2 / **10a**: 116669-49-9 / **10b**: 116669-50-2

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