SYNTHESIS AND DEGENERATE COPE REARRANGEMENT OF 2,6-DIPHENYLBARBARALANE

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Abstract—The oxygen-sensitive 2,6-diphenylbarbaralanes 15 and 16 are synthesized from bicyclo[3.3.1]nonane-2,6-dione(9) via dibromide 14 in four steps with 46 and 54% overall yield, respectively. Crystalline 2,6-diphenylbarbaralane (15) is yellow at room temperature and decolourizes reversibly on cooling. Accordingly, the UV spectrum of *trans*-decalin solutions of 15 changes reversibly in the temperature range 295-450 K. The bromodiphenylbarbaralane 16 is shown to exist as a single valence tautomer. The ¹³C chemical shifts of 16 serve as estimates of the analogous shifts in the non-exchanging valence tautomer of 2,6-diphenylbarbaralane (15) itself. The barrier for the degenerate Cope rearrangement of 15 in $[D_2]$ dichloromethane has been determined from ¹³C-NMR line width measurements in the temperature range of 169-233 K to be $\Delta G_{200}^2 = 21.6$ kJ mol⁻¹. Hence phenyl substituents at the termini of the allylic parts of barbaralane accelerate the degenerate Cope rearrangement somewhat more than cyano groups.

We report an efficient synthesis of 2,6-diphenylbarbaralane (15) and show with the help of low temperature ¹³C-NMR spectra that it possesses an even lower activation barrier towards degenerate Cope rearrangement than 2,6-dicyanobarbaralane (11a).¹ Our results suggest, therefore, that appropriately placed phenyl groups are more effective than cyano groups in stabilizing delocalized structures of barbaralanes and semibulivalenes.

The concept of homoconjugation (through-space interaction) originated from the early work of Winstein and Adams on the solvolysis of cholesteryl chloride² and has developed since into a fundamental principle in organic chemistry.3 Roberts and Applequist invoked the resemblance of the cyclobutenylium to the cyclopropenylium cation in order to explain the special stability of the former.^{4,5} Extending homoconjugation to aromatic compounds. Winstein conceived the general notion of homoaromaticity.⁶ Accordingly, the σ -skeleton of neutral or charged aromatic systems may be interrupted by an sp³-carbon bridge at one or more sites resulting in mono-, bis-, tris-, etc., homoaromatic species. The concept of homoaromaticity initiated an impressive amount of both experimental and theoretical work.^{7,8} While the existence of homoaromatic cations is by now reasonably well established,⁸ that of homoaromatic anions has recently been questioned⁹ and is still subject to experimental scrutiny.¹⁰ A similar situation applies to neutral, potentially homoaromatic systems. Thus, Houk, Paquette and co-workers arrived at a pessimistic conclusion opposite to previous deductions about neutral homoaromaticity: "Homoconjugative interactions between neutral

† The results are taken from the projected Doctoral Thesis of E. Geissler and the projected Ph.D. Thesis of K. L. Colson. closed-shell π -systems are destabilizing!"¹¹ The implied elusiveness of neutral homoaromaticity originating from through-space interaction of *closed-shell* π -systems did not fortunately detract from the search for such homoaromatic compounds.¹²

A principally different concept of homoaromaticity in neutral molecules evolved from von E. Doering's and Roth's ingenious design of fluxional molecules undergoing fast degenerate Cope rearrangement.¹³ In fact, von E. Doering and co-workers considered the existence of a shallow minimum on top of the energy barrier separating the degenerate valence tautomers. Such minima would correspond to symmetrical intermediates with a negligible activation energy.^{13,14} Theoretical support for this hypothesis was provided by McIver who pointed out that, because transition states cannot have two negative force constants, a symmetric species must be a potential energy minimum between two maxima.15 Whatever the true nature of the lowest transition state for the non-constrained, archetypal Cope rearrangement may be,16 when the 1,5-hexadiene system (1)¹⁴ is subjected to increasing geometrical constraints as in the order cis-divinylcyclopropane (2),¹⁷ 3,4-homotropilidene (3),¹⁸ dihydrobullvalene (4c),¹⁹ barbaralane (4b),^{20,21} semibullvalene (4a),²² the Cope activation barrier dramatically decreases to as low as $E_s = 21.3 \text{ kJ}$ mol^{-1 22} found for the latter compound. Theoretical studies by Hoffmann and Stohrer²³ and Dewar and coworkers^{24,25} suggested that certain substitution patterns might continue this trend down to "negative activation energies". Specifically, extended-Hückel calculations supported the prediction that a semibullvalene of type 5 is likely to exist in the delocalized ground state 5⁺.²³ According to MINDO/2 calculations, electron acceptor substituents at C-2, 4, 6, 8, e.g. cyano, carboxy or trifluoromethyl groups,²⁴ or perhaps just two cyano groups at C-2 and C-6, 25 might provide for ground state delocalization. Furthermore,

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non-classical, delocalized structures were predicted for 2,6-diaza- and 3,7-diazasemibullvalene.²⁵ While similar delocalized, homoconjugated systems are invoked as transition states of numerous pericyclic reactions, the theoretical studies of Hoffmann and Dewar designed a novel type of neutral (bis)homoaromatic stable molecules. In fundamental contrast to Winstein's homoaromaticity this kind of neutral homoaromaticity is characterized by the homoconjugative (through space) interaction of *openshell* π -systems and may be termed Dewar-Hoffmann type in order to distinguish it from the former. Recent MNDO-C1 calculations of the localized and delocalized structures of cyano-substituted semibullvalenes²⁶ essentially agree with earlier studies.²³⁻²³

By long tradition, theoretical predictions stimulate experimental work. In fact, Hoffmann's and Dewar's design of delocalized homoaromatic semibullvalenes presents a considerable experimental challenge which is getting more attention in these and other laboratories.[†] We have synthesized 2,6-dicyanobarbaralane $(11a)^{27}$ and 2,6-dicyanosemibullvalene 6^{28} which for the first time enabled us to obtain a quantitative evaluation^{1,28} of the predicted¹³⁻²⁶ substituent effects. Moreover, the surprising temperature dependence of the UV spectrum of 6 indicated an equilibrium with a less stable (by 11 kJ mol⁻¹) isomer which was assigned the delocalized homoaromatic structure $6^{*,29}$ This assignment implies two unsymmetrical transition states for the Cope rearrangement of 6 and thus may be the first experimental evidence for McIver's theorem.¹⁵

Unlike cyano groups, phenyl substituents exert only small inductive and field effects. Therefore, variations in rates caused by their presence are essentially due to their conjugative ability and steric requirements. While numerous studies have been concerned with phenylsubstituted 1,5-hexadienes undergoing Cope rearrangement via chair-like transition states, ^{30–33} only a few phenyl-substituted systems are known for which geometric constraints require boat-like transition states. Furthermore, a few degenerately rearranging



† For a summary of leading references see Ref. 28.

compounds of this sort, e.g. 2,5-diphenyl-3,4homotropilidene,³⁴ the barbaralanes $8b^{34}$ and 19^{35} and the semibulivalenes 7b and c,³⁶ carry the phenyl groups at the *central* carbon of the allylic part where they exert only a minor, rate-*retarding* effect.^{34,36} Since the Cope transition states of semibulivalenes and barbaralanes resemble two more or less interacting allyl radicals,^{21,23-26,37} a sizeable decrease of the Cope activation barrier is anticipated if the phenyl groups are attached to the *termini* of the allylic parts. Here we describe the first such system (15). We have chosen to study the expected effect in the barbaralane series using only two phenyl groups, since, unlike the semibulivalene system²² or that with four phenyl substituents, the barrier is anticipated to be sufficiently high to allow determination by ¹³C spectroscopy.

Synthesis and properties of 2,6-diphenylbarbaralanes

Barbaralane (4b) and its derivatives have been obtained via a variety of routes employing as the key steps intramolecular carbene or carbenoid addition to cycloheptatrienes^{20,38,39} and cyclohexene derivatives,40 intramolecular [4+2]cycloaddition of a 7allenyl-1,3,5-cycloheptatriene,⁴¹ homo-1,4-elimination in triasterane derivatives,^{34,42} photo-isomerization tricyclo[3.2.2.0^{2,4}]nona-2,8-diene (homobarreof lene),43 di-n-methane rearrangement of bicyclo[4.2.1]nona-2,4,7-trienes44 and bicyclo[3.2.2]nona-2,6,8triene,45 photo-extrusion of molecular nitrogen, and ring-closure reactions between C-2 and C-7 of bicyclo[3.2.2]nonanes^{35,47} and between C-2 and bicyclo[3.3.1]nonane derivatives. 27,48-56 C-8 of of the well-developed syntheses of In view bicyclo[3.3,1]nonanes⁵¹ the latter route promised to provide the most straightforward access to barbaralanes. In fact, a barbaralane had already been obtained via dehydrobromination of a 3,4dibromobicyclo[3.3.1]nonadiene 20 years ago.48 Furthermore, a rational and flexible synthesis of 2,6disubstituted barbaralanes such as 15 may take advantage of the convenient availability of Meerwein's diketone, bicyclo[3.3.1]nonane-2,6-dione (9),52-55 which appears a logical precursor to 2,6-disubstituted bicyclo[3.3.1]nona-2,6-dienes suitable for ring closure to barbaralanes. The short, high-yield synthesis of the 2,6-dicyanobarbaralanes 1127 demonstrated the merits of this strategy. Consequently, we set out on an analogous route to 2,6-diphenylbarbaralanes.



To this end the diketone 9 was allowed to react with excess phenyllithium affording a 74% yield of a diol which was formed as a single, symmetrical diastereomer according to the ¹³C spectrum. The *endo,endo*-configuration of the hydroxy groups and hence structure 12 for the diol was inferred by analogy with similar cases. For instance, methylmagnesium iodide,⁵⁶ sodium borohydride^{57,56} and lithium aluminium hydride^{58,59} attack bicyclo[3.3.1]nonane-2-ones almost exclusively from the *exo* face affording the *endo*-alcohols with high diastereoselectivity. Likewise, sodium borohydride and lithium aluminium hydride differentiate the endo and exo faces of diketone 9 producing predominantly the endo,endo-diol⁶⁰ contrary to an earlier report.⁵⁵ Therefore, we assume that the bulky nucleophile phenyllithium a forteriori attacks from the exo face of 9 which thereby is converted to the endo,endo-diol 12.

Diol 12 was directly dehydrated to the diene 13 in 91% yield by a short treatment with an 8:2 mixture of acetic acid and concentrated sulfuric acid.⁶¹ The high yields in both steps contrast sharply to the 3.5% overall yield in an analogous sequence which transformed the 4,8-dimethyl homologue of diketone 9 to the 2,6dipbenyldiene.62 Without any doubt, the phenyl groups in 12 are essential for the smooth direct dehydration since this method failed⁵² or met only with limited success⁵⁵ in the case of a bicyclo[3.3.1]nonane-2,6-diol63 lacking the phenyl groups. N-Bromosuccinimide brominated diastereoselectively both allylic positions of the diene 13 yielding dibromide 14 as a single stereoisomer. The presence of symmetry was again deduced from the ¹³C spectrum which exhibited only five signals for the bicyclic ring system. The exo, exo-configuration of the bromine atoms and hence structure 14 are based on the steric requirement of bromine which strongly disfavours the endo,endoconfiguration, on the known predominance of exoattack (vide supra), and on the comparison with the dibromide 10b for which the exo, exo-dibromo configuration was established by an X-ray structure determination.27

The zinc-copper couple, useful for numerous dehalogenating cyclopropane forming reactions, 64,65 was the reagent of choice for the debromination of the dibromodinitrile 10b to afford the dicyanobarbaralane 11a,²⁷ as well as, for similar reactions leading to semibullvalenes, e.g. 628 and 7a.66 Accordingly, treatment of the dibromide 14 with the zino-copper couple in boiling ether followed by flash chromatography of the crude material yielded 68% of 2,6diphenylbarbaralane (15). The bicyclic dibromodiene 10b had also served as a precursor for the brominated barbaralane 11b via dehydrobromination using alkoxide bases. When the dibromodiene 14 was allowed to react with a solution of potassium t-butoxide in t-butanol the anticipated dehydrobromination proceeded smoothly affording the bromobarbaralane 16 which was also purified by flash chromatography. The structures of the new com-



pounds were confirmed by spectroscopic methods. In particular, the assignments in the ^{13}C spectra are based on single frequency off resonance (12) or fully protoncoupled spectra (13-16) and on selective decoupling experiments (13, 14, 16).

While the hydrocarbon 15 formed lemon-coloured crystals melting at 108-110°, the bromobarbaralane 16 resisted all attempts to induce crystallization and remained as a viscous oil. Surprisingly, both 2,6diphenylbarbaralanes were very sensitive towards atmospheric oxygen which precipitated a colourless, insoluble material from solutions of 15 even in the dark. The structure of the presumably polymeric, peroxidic product is still under investigation. On the other hand, the 4-bromo-2,6-diphenylbarbaralane (16) which is almost colourless or pale yellow turns yellow immediately when exposed to air. Consequently, preparation and purification of both 2,6-diphenylbarbaralanes had to be performed with strict exclusion of oxygen. The unexpected reactivity of the diphenylbarbaralanes 15 and 16 towards triplet oxygen is reminiscent of the similar behaviour of tri-t-butylcyclobutadiene,⁶⁷ syn-sesquinorbornadiene and triene derivatives,⁶⁸ octamethylsemibullvalene⁶⁹ and the semibulivalone 6.28 Furthermore, a non-crystalline compound which was assigned structure 18 was very air sensitive while its crystalline isomer 19 did not exhibit such properties.³⁵ The same principles hold for an isomer of 15, e.g. 3,7-diphenylbarbaralane (8b)^{34,50} and other barbaralanes. While the triplet oxygen products of semibullvalenes and barbaralanes are still unknown with the exception of that of octamethylsemibullyalene,⁶⁹ the striking substituent dependence of the enhanced reactivity of certain semibullvalenes and barbaralanes towards triplet oxygen suggests that it may be related to the stability of the allylic radical which is formed with simultaneous cyclopropane ring cleavage by a radical attack at one of the termini of the allylic parts.

Crystalline diphenylbarbaralane 15 shares with the semibullvalenes 628,29 and 2070,71 the remarkable yellow colour. Even more surprising, this colour disappears reversibly on cooling just as found for the semibullvalenes 6^{28,29} and 20.⁷¹ Corresponding changes in the UV spectrum have been observed also for solutions of 6. The reversible temperaturedependent appearance of a new long-wavelength band in the UV spectrum of 6 was rationalized in terms of an equilibrium with the delocalized, bishomoaromatic isomer 6^{*,29} The similarity in the temperaturedependent colour changes of crystalline 6 and 15 prompted an investigation of the UV spectrum of 15 in solution at various temperatures. As solvent we chose trans-decalin for ease of purification to a suitable UV transmittance, the broad temperature range of the liquid state,⁷² and the known density data between the freezing and boiling point.73 The UV spectrum of 2,6diphenylbarbaralane (15) (Fig. 1) shows a single maximum at 273 nm (e = 16,300). Since the parent barbaralane (4b) itself exhibits only end absorption above 200 nm³⁸ the long-wavelength band of 15 reflects the extension of the conjugated system by the phenyl groups and may be compared to that of 2,6diphenylbicyclo[3.3.1]nona-2,6-diene (13, λ_{max} 246 nm, $\varepsilon = 21,900$) and trans-styrylcyclopropane (λ_{max} 261 nm, $\varepsilon = 19,000$).⁷⁴ In line with the colour change of crystalline 15 on cooling, 10^{-3} - 10^{-2} M solutions of 15



Fig. 1. UV spectra of 2,6-diphenyibarbaralane (15) at 295, 350, 400 and 450 K in *trans*-decalin. The temperature dependence of the volume was taken into account by means of the density of trans-decalin.⁷⁵

show a completely reversible temperature dependence of the UV spectrum in the temperature range 295-450 K (Fig. 1). At higher temperatures, the absorption decreases in the maximum, which is slightly shifted to shorter wavelengths, and increases in the minimum as well as in the near UV. Although the temperaturedependent changes parallel those of the dicyanosemibullvalene 6 they are, however, much less pronounced than for the latter.²⁹ Nevertheless, they may be indicative of an equilibrium involving a less stable isomer. On the other hand, since the long-wavelength end of the absorption spectrum is due to transitions from thermally excited vibrational, levels of the electronic ground state and the population of such levels increases with rising temperatures, accorresponding increase of the absorption in this region at the expense of other regions can be generally expected. For example, the temperature dependence of the visible spectrum (460-560 nm) of neat cyclooetatetraene was explained in this way.⁷⁵ An equilibrium involving a less-stable isomer and the equilibrium between vibrational levels of the electronic ground state are both governed by the Boltzmann distribution function and. therefore, difficult to distinguish in the absence of other pieces of evidence. Hence a rationalization of the small temperature-dependent changes in the UV spectrum of 15 must await further experimentation.

Degenerate Cope rearrangement of 2,6-diphenylbarbaralane (15)

The ¹³C spectra at 90 and 100 MHz of 2,6diphenylbarbaralane (15) were examined as a function of temperature. In the temperature range accessible on the spectrometers used, the broad band decoupled ¹³C spectra of 15 yielded two single, equally populated, twosite exchange systems (C-2/C-6 and C-4/C-8) with an estimated chemical shift difference Δv of ca 9000 Hz at 90 MHz (vide infra). The spectra were run in the fastexchange limit where the rate constant for exchange can be calculated from the exchange broadening W_{exch} using Eq. (1).⁷⁶ The exchange broadening is derived from the measured line width of the exchange broadened signal by subtracting the effective line width of that signal in the absence of exchange, Wo. The latter is approximated by the line width of a similar ¹³C signal which is not or only very slightly influenced by the exchange process. Line widths at half height (Table 1) were determined by least squares fitting of the observed signal to a Lorentzian line shape

$$k = \pi (\Delta v)^2 / 2W_{\text{exch}}.$$
 (1)

The C-2 and C-6 signals provide the best information about the rate of the Cope rearrangement of 15. This is

calculated face constants at valices temperatures							
T [K]	2,6 Carbons ^a	<u>ipso</u> Carbon ^a	Wexch	10 ⁻⁵ k [s ⁻¹]			
169	60.8 (2.4)	2.6 (0.7)	58.2	20.5			
174.5	41.0 (3.9)	2.1 (0.6)	38.9	30.5			
179.5	34.8 (2.0)	2.6 (0.5)	32.2	37			
183	28.9 (1.5)	1.5 (0.5)	27.4	43.5			
191	24.0 (1.5)	1.5 (0.4)	22.5	53			
200	15.3 (1.9)	2.1 (0.6)	13.2	90			
203	12.5 (1.7)	2.3 (0.6)	10.2	117			
207.5	10.4 (1.0)	1.1 (0.5)	9.3	128			
213	9.5 (0.7)	1.9 (0.6)	7.6	157			
233	4.8 (1.0)	1.4 (1.0)	3.4	351			
251 ^b	3,4 (0.8)	1.1 (0.3)	2.3				

Table 1. Line widths at half height (Hz) of the 2,6 and *ipso*¹³C peaks, exchange broadening (W_{exch}) of the 2,6 ¹³C signals of 2,6-diphenylbarbaralane (15) and calculated rate constants at various temperatures

 $^{\rm a}$ The errors (in parenthesis) were calculated by the program DISNMRP 82 which is part of the Bruker software package. $^{\rm b}$ Not used for the calculation of the parameters of Equation 2.

because of their large chemical shift difference and, in particular, because, having no attached protons, their effective line widths in the absence of exchange are not very dependent on the efficiency of broad band decoupling. Furthermore, the line widths of the ipso phenyl carbon signals, which are virtually unaffected by exchange, can be used as convenient estimates for W_0 of the quaternary carbons C-2 and C-6. On the other hand, the protonated carbons which were equally unaffected by exchange (C-9, tertiary phenyl carbons) exhibited line widths two to three times larger than the ipso carbons. Use of such line widths as estimates of W_0 in the calculation of the exchange broadening of the C-4/C-8 signals introduces greater errors. Therefore, the exchange broadening of the tertiary carbons C-4/C-8 was not applied for the determination of rate constants although it was similar to that of the C-2/C-6 signal.

The low solubility of 2,6-diphenylbarbaralane (15) in dichloromethane-chlorodifluoromethane solutions at temperatures below 140 K precluded the determination of the chemical shift data for the non-exchanging valence tautomer. Thus, in order to extract the rates of exchange from line broadening in the "fast exchange" region it was necessary to obtain estimates for the chemical shifts in the low temperature limit. In a similar study of the Cope rearrangement of 2,6-dicyanobarbaralane (11a) we used a bromodicyanobarbaralane as a model for the non-rearranging valence tautomer because the bromo compound existed as only the non-degenerate valence tautomer 11b.¹ The absence of a significant temperature dependence of the ¹³C shifts now showed that the same was true for the bromodiphenylbarbaralane, i.e. it exists as the single valence tautomer 16. Inspection of the data in Table 2 reveals that the chemical shifts relative to that of C-9, which should be virtually the same in the two valence tautomers, have only a minor dependence on temperature. In particular, there is no change in the difference between the chemical shifts of C-2 and C-6. That the shifts of C-2 and C-6 for the bromobarbaralane 16 are indeed appropriate for the analogous nuclei in 2,6-diphenylbarbaralane (15) itself is confirmed by the agreement between the observed shift $(\delta = 87.9 \text{ ppm})$ for C-2/C-6 in this compound and the average ($\delta = 88.9$) of the two shifts in the model 16. Therefore, a value of $\Delta v = 96.2$ ppm, corresponding to

8710 Hz at 90.56 MHz, was used in the calculation of rate constants from exchange broadening. A very similar value for Δv may be calculated by adding appropriate correction terms^{77,78} for the influence of phenyl groups to the shift data recently reported for the non-rearranging valence tautomer of the parent barbaralane (4b).²¹

The much greater stability of the bromodiphenylbarbaralane 16 compared to its valence tautomer 17 can be interpreted in terms of double bond stabilization by bromine⁷⁹ in 16 and the unfavourable steric interaction of phenyl and bromine at the cyclopropane ring of 17.

Calculation of enthalpies and entropies of activation from rates determined by Eq. (1) can lead to serious errors,⁸⁰ and we therefore restrict our discussion of the barrier for the Cope rearrangement in 15 to a consideration of the rate constant and ΔG^{\ddagger} at 200 K. This temperature allows a convenient comparison of 15 with other "degenerate" barbaralanes (Table 3). The k and ΔG^{\ddagger} values at 200 K are calculated from the exchange broadening data in Table 1 by

$$\pi/2W_{\text{exch}} = k(\Delta v)^{-2} = a \cdot e^{-b/T}$$
(2)

which is obtained from Eq. (1) and the Arrhenius equation. A non-linear least squares treatment of the data in Table 1 afforded the parameters of Eq. (2) $[a = (1270 \pm 550)$ s, $b = (1850 \pm 90)]$. A short calculation shows that the error in ΔG_{200}^2 introduced by an uncertainty as large as 2 ppm in the estimated Δv value amounts to only 0.07 kJ mol⁻¹ and hence can be neglected when compared with the statistical error resulting from parameters *a* and *b* in Eq. (2).

Table 3 lists rates and free enthalpies of activation of the Cope rearrangement for barbaralane (4b) and some substituted derivatives. The difference in the free enthalpies of activation of 2,6-dicyano- (11a) and 2,6diphenylbarbaralane (15) is small but, most probably, significant because both experiments were run under identical conditions on the same spectrometer and in the same temperature range so that any systematic errors that might arise tend to cancel. It is seen that phenyl groups are somewhat more efficient than cyano groups in increasing the barrier, if attached to C-3 and C-7 as in 8b and a, respectively, as well as in lowering the Cope activation barrier, if placed at two opposite corners as in 15 and 11a, respectively. In fact the 2,6-

Table 2. Effect of temperature on the ¹³C chemical shifts of the tricyclic ring system in 4-bromo-2,6-diphenylbarbaralane (16) (CD₂Cl₂). The shifts (ppm) are expressed relative to that of C-9

	318 К	243 K	Difference
C-1	3.0	2.7	+0.3
C-2	19.5	19.3	+0.2
C-3	106.3	107.0	-0.7
C-4	93.6	93.7	-0.1
C-5	21.2	20.8	+0,4
C-6	115.7	115.5	+0.2
C-7	98.8	99.0	-0.2
C-8	11.2	11.1	+0.1
C-9	(0.0)	(0.0)	(0.0)

Cpd.	10 ⁻³ k	^k rel	∆G◆	Temp. Range (K)	Ref.
4b	26	1.00	31.5 ± 0.4	153 - 276	21
8a	18	0.72	32.0 ± 0.9	148 - 260	21
8b	4	0.15	34.5 ± 2.3	206 - 240	34, 81
11a	1950	76	24.2 ± 3.2	209 - 249	1
15	9400	360	21.6 ± 1.6	169 - 233	This work

Table 3. Rate constants and free enthalpies of activation at 200 K for the degenerate Cope rearrangement of some barbaralanes*

^a Rate constants k in s^{-1} , ΔG^+ in kJmol⁻¹.

diphenylbarbaralane (15) rearranges even faster than semibullvalene (4a) ($\Delta G_{200}^{1} = 24.6 \text{ kJ mol}^{-1}$).²² The rate-accelerating effects are in accord with the generally accepted transition state model resembling two more or less interacting allyl radicals, 21,23-26,37 as well as, with the order of the radical stabilization energies (RSE) and double bond stabilization parameters (DS) of the cyano (RSE = 54, 32b DS = 14.5 kJ mol⁻¹)⁷⁹ and the phenyl group (RSE = 59, 326 DS = 19 kJ mol⁻¹).⁷⁹ However, while in the ground state both types of substituents can exert their full interaction with one double bond and the appropriate Walsh orbitals of the cyclopropane ring, the radical stabilizing effect is greatly attenuated in the transition state.^{32b} This attenuation reflects the deviation of the real transition state from the hypothetical model consisting of interacting allyl radicals, and may be attributed to the homoconjugative (through space) interaction of the allylic fragments which mirrors the (bis)homoaromatic nature of the transition state.

While stable homoaromatic semibullvalenes as yet remain elusive, the results of the present investigation suggest that this final goal may perhaps be achieved (if at all) by using a substitution pattern different from (or in addition to) the one predicted by Hoffmann²³ and Dewar^{24,23} more than a decade ago. We shall report on semibullvalenes substituted similarly to **15** and higher substituted systems in due course.

EXPERIMENTAL

Pulsed Fourier transform 400.13 MHz ¹H and 100.61 MHz ¹³C spectra were obtained from CDCl₃ solns using a Bruker WM 400 NMR spectrometer. Chemical shifts are in ppm downfield from TMS as internal reference. The assignment of the ¹³C signals was confirmed by single frequency off resonance decoupled or proton coupled spectra. Protonproton coupling constants were derived by a first-order analysis.

The variable temp ¹³C spectra were recorded at 90.56 MHz on a Bruker WM 360 spectrometer using carefully degassed solns in CD₂Cl₂ prepared by vacuum line techniques in sealed NMR tubes. The temps were calibrated by means of a MeOH calibration sample. The Lorentzian line shape least squares fitting routine, which is part of the Bruker software package, was used to determine line widths.

IR spectra were recorded on a Beckman Acculab 4 IR spectrometer and calibrated with polystyrene. Dilute solns in CCl₄ and 10 mm quartz cells were used for the 4000–2600 cm⁻¹ range, solns in CH₂Cl₂ and 1 mm CaF₂ cells for the 2000–1500 cm⁻¹ range. Low resolution 70 eV mass spectra were obtained on a Varian MAT CH 7 mass spectrometer connected to an SS 200 data system. The exact mass of 16 was

determined using a Finnigan MAT 8200 high resolution mass spectrometer and perfluorokerosine calibration.

UV spectra at room temp were measured on a Perkin-Elmer 330 spectrometer using 0.1, 1 and 10 cm cells. UV spectra at higher temps were recorded on a Cary 17 spectrometer equipped with a high temp sample cell holder which was connected to a Lauda Ultrathermostat. The temp in the sample cell was measured by a Cr-Ni thermocouple which was calibrated with high precision thermometers. The transdecalin solns of 15 for UV spectra at higher temps were prepared in a closed apparatus, equipped with 0.1 and 1 cm quartz cells, repeatedly degassed under vacuum and ultrasonic irradiation, and saturated with purified Ar. The UV spectra were recorded immediately after the cell had attained the desired temp. After each UV spectrum the sample cell was cooled to room temp and the UV spectrum was scanned on the Perkin-Elmer 330 spectrometer in order to check the reversibility of temp-induced spectral changes and to screen for decomposition products. The temp dependence of the volume of the trans-decalin solns was accounted for using density data of trans-decalin.73

Uncorrected m.ps were determined in a Büchi apparatus in sealed capillary tubes, corrected m.ps on a Kofler hot stage from Optische Werke C. Reichert, Vienna, Austria.

Silica gel, 32-63 μ m (Woelm, Eschwege, F.R.G.), was used for flash chromatography.³¹ HPLC analyses were carried out on a Waters chromatograph equipped with a 254 nm UV detector. A Knauer HPLC column Nucleosil 5C₁₈ and MeOHwater (9:1) as eluant at a flow rate of 0.9 ml min⁻¹ were used. A Varian 1400 gas chromatograph equipped with a Shimadzu C-R1B integrator was applied to GLC analyses using 3 × 0.002 m glass columns containing 10% SE 30 on Volaspher A₂ (Merck, Darmstadt, F.R.G.).

The following solvents were distilled under purified Ar: diethylether, THF, pentane and pet. ether $(30-50^{\circ})$ from NaH, t-BuOH from CaH₂. In the synthesis and purification of 15 and 16, spectrograde quality solvents were used. The solvents, including the water for extraction of the organic layers, were repeatedly evacuated under ultrasonic irradiation and saturated with Ar.

trans-Decalin for UV measurements was obtained from a purified⁷² cis/trans decalin mixture (58.3:36.1 GLC) by vacuum distillation through an efficient vacuum-insulated 3 m distillation column. A fraction boiling at 86°/34 Torr and of 99.97% purity (GLC) was further purified by flash chromatography on active basic alumina (Woelm) and silica gel, 0.063–0.2 mm (Woelm).⁸³ The trans-decalin thus obtained showed an absorbance of 0.5–0.6 at 250 nm and a pathlength of 1 cm (reference water).

2,6-Diphenylbicyclo[3.3.1]nonane-2,6-diol(12). To 250 ml of a 0.80 M soln of PhLi in ether (0.2 mol), which was stirred under N₂, a soln of 9.4 g (62 mmol) 9^{54} in a mixture of 450 ml ether and 270 ml THF was added within 70 min. After 15 h stirring under reflux, the mixture was cooled to 0° and cautiously hydrolysed using dil NH₄Cl aq. The organic layer was washed twice with NH₄Cl aq and water and dried with MgSO₄. The partially oily product obtained after removal of the solvent using a rotary evaporator was dissolved in 85 ml boiling CCl₄. Cooling to 0° afforded 14.1 g (74%) colourless crystals, m.p. 137–139° (uncorr). Crystallization from cyclohexane raised the m.p. to 144–145° (corr). IR : 3605 (s) (O--H), 3095 (w), 3065 (ra), 3030 (w) (==C--H), 1602 (m), 1582 (w) cm⁻¹ (C==C). ¹H-NMR : 1.14 (ra, J_{1.9} = J_{3.9} = 3.1 Hz, 9-H), 1.89 (br., OH), 1.86, 2.25 (2 m, 4-H, 8-H), 2.16 (m, J_{1.8} = J_{4.4,5} = 5.3 Hz, 1-H, 5-H), 2.41, 2.51 (2 m, 3-H, 7-H), 7.32 (m, m-H), 7.53 (m, o-H). ¹³C-NMR : 24.4 (C-4, C-8), 27.8 (C-9), 33.7 (C-3, C-7), 38.3 (C-1, C-5), 75.3 (C-2, C-6), 126.0 (o-C), 127.1 (p-C), 128.2 (m-C), 147.6 (ipso-C). MS : m/e = 290 (3% M - H₂O), 272 (42, M - 2 H₂O), 244 (5), 231 (13), 185 (25), 170 (23), 158 (34), 155 (29, Ph--C₆H₆), 142 (15), 133 (25), 129 (17), 120 (16), 119 (16), 117 (24), 115 (15), 105 (100, PhCO), 91 (26), 77 (30). (Cack for C₂₁H₂₄O₂ (308.42): C, 81.78; H, 7.84. Found: C, 82.41; H, 8.20%)

2,6-Diphenylbicyclo[3.3.1]nona-2,6-diene (13). Diol 12 (10.2 g, 33 mmol) was shaken for 5 min with 35 ml of a freshly prepared mixture of AcOH and conc H₂SO₄ (8:2). The mixture was diluted with 200 ml water and extracted with two 300 ml portions of pet. ether (b.p. 30-50°). The organic layer was washed with NaHCO₃ aq and water and dried with MgSO₄. Removal of the solvent using a rotary evaporator yielded 8.24 g (91%) colourless, shining crystals, m.p. 90-92° (corr). Crystallization from MeOH raised the m.p. to 93-94° (corr). HPLC retention time 13.4 min. IR : 3070 (w), 3050 (m), 3020 (m) (==C-H), 1635 (w), 1593 (m), 1570 (w) cm⁻ (C=C). UV (hexane): $\lambda_{max} = 283$ nm (sh, 9000), 246 (22,000), 220 (sh, 16,300), 200 (40,300); $\lambda_{min} = 225$ (12,100). ¹H-NMR : 1.98(t, J_{1,9} = J_{5,9} = 3.1 Hz, 9-H), 2.07 (dd, $\begin{array}{l} J_{4made, 4xx0} = J_{8made, 8xx0} = 183, \ J_{3,4exm} = J_{7,8exm} = 5.1 \ Hz, \ 4-H_{exm}, 8-H_{exx0}, 2.45 \ (m, 4-H_{made}, 8-H_{made}), 3.10 \ (m, 1-H, 5-H), 5.96 \ (dd, J_{3,4exm} = J_{7,8exmb} = 2.4 \ Hz, 3-H, 7-H), 7.21 \ (p-H), 7.30 \ (m-H), 7.40 \ (o-H), 1^{3}C-NMR : 29.1 \ (J = 126.1 \ Hz, C-1, C-5), 29.7 \ (dd, J_{3,4exmb}) = 1.26.1 \ Hz, C-1, C-5, 20.7 \ (dd, J_{3,4exmb}) = 1.26.1 \ Hz, C-1, C-5, 20.7 \ (dd, J_{3,4exmb}) = 1.26.1 \ Hz, C-1, C-5, 20.7 \ (dd, J_{3,4exmb}) = 1.26.1 \ Hz, C-1, C-5, 20.7 \ (dd, J_{3,4exmb}) = 1.26.1 \ Hz, C-1, C-5, 20.7 \ (dd, J_{3,4exmb}) = 1.26.1 \ Hz, C-1, C-5, 20.7 \ (dd, J_{3,4exmb}) =$ $(^{1}J = 126.0 \text{ Hz}, \text{C-9}), 31.6 (^{1}J = 128.7 \text{ Hz}, \text{C-4}, \text{C-8}), 122.6 (^{1}J$ = 154.3 Hz, C-3, C-7), 125.8 (dt, ${}^{1}J = 157.5$, ${}^{3}J = 6.8$ Hz, o-C), 126.6 (dt, ${}^{1}J = 160.8$, ${}^{3}J = 7.6$ Hz, p-C), 128.2 (dd, ${}^{1}J = 159.2$, $^{3}J = 7.6$ Hz, m-C), 140.1 (C-2, C-6), 141.3 (ipso-C). MS: m/e $= 272 (100\%, M^+), 244 (10, M - C_2H_4), 231 (65, M - C_3H_3),$ 181 (15), 168 (19, M-Ph-CH=CH₂), 165 (17), 155 (74, Ph-C, H, 142 (51), 128 (23), 115 (49), 91 (35), 77 (23). (Calc for C₂₁H₂₀ (272.39): C, 92.60; H, 7.40. Found: C, 92.72; H, 7.52%.)

4,8-Dibromo-2,6-diphenylbicyclo[3.3.1]nona-2,6-diene (14). A stirred mixture of 8.5 g (31 mmol) of 13, 13.5 g (76 mmol) Nbromosuccinimide and 260 ml CCl4 was heated under reflux for 45 min, cooled and washed with two 170 ml portions of 2 M NaOH and with 200 ml water. Drying with MgSO₄ and removal of the solvent using a rotary evaporator yielded 13.4 g (100%) pale yellow crystals, dec.p. 184-189°. Crystallization from EtOAc afforded 11.7 g (87%) pale yellow prisms of dec.p. 188-190°. HPLC retention time 15.3 min. IR : 3085 (m), 3065 (m), 3035 (m) (=C-H), 1630 (m), 1600 (w), 1583 (m) cm⁻¹ $(C_{--}^{(m)}C)$.¹H-NMR : 2.54 (t, J₁, 9 = J₅, 9 = 3.1 Hz, 9-H), 3.58 (m, 1-H, 5-H), 4.65 (dd, J₁, 8 = J₄, 5 = 1.4, J₃, 4 = J₇, 8 = 5.0 Hz, 4-H, 8-H), 6.13 (d, 3-H, 7-H), 7.31-7.46 (m, Ph--H). ¹³C-NMR : $20.2 (^{1}J = 132.8 \text{ Hz}, \text{C-9}), 38.4 (^{1}J = 138.2 \text{ Hz}, \text{C-1}, \text{C-5}), 50.2$ $(^{1}J = 158.4 \text{ Hz}, \text{C-4}, \text{C-8}), 124.0 (^{1}J = 163.0, ^{2}J = 4.6, ^{3}J = 4.6$ Hz, C-3, C-7), 125.9 (dt, 1J = 157.8, 3J = 6.7 Hz, o-C), 128.6 (dt, ${}^{1}J = 161.2$, ${}^{3}J = 7.3$ Hz, p-C), 128.8 (dd, ${}^{1}J = 160.5$, ${}^{3}J = 7.4$ Hz, m-C), 137.9 (m, C-2, C-6), 139.2 (m, ipso-C). MS: m/e = 430 (0.3%, M+), 351 (30), 349 (30, M - Br), 271 (23), 270 (100, M -2 Br), 269 (28), 255 (26, M - 2 Br – Me), 254 (15), 241 (12), 240 (10), 239 (13), 193 (22, M-2 Br-Ph), 192 (23), 191 (22), 179 (36), 178 (28), 165 (26), 152 (14), 135 (17), 117 (22), 115 (49), 91 (33). (Calc for C₂₁H₁₈Br₂(430.18): C, 58.63; H, 4.22. Found : C, 58.49; H, 4.04%.)

2,6-Diphenyltricyclo[$3.3.1.0^{2.8}$]nona-3,6-diene (15). All operations were performed under purified Ar using carefully de-aerated solvents saturated with Ar. A mixture of 1.0 g (2.3 mmol) of 14, 2.3 g Zn-Cu couple⁴⁴ and 350 ml ether was refluxed for 3 h, cooled, filtered through a 6 cm layer of kieselguhr and washed with two 100 ml portions of water. After drying with K₃CO₃, the ether was distilled under normal pressure leaving 638 mg of a yellow residue. Flash chromatography 82 on a 20 × 2.5 cm silica gal column using CH₂Cl₂-pentane (3:2) as eluant afforded 425 mg (68%) of lemon-coloured crystals, m.p. 108-110° (uncorr). HPLC analysis did not show any impurities (retention time 11.8 min). IR : 3085 (w), 3060 (m), 3030 (m) (=C-H), 1630 (w), 1602 (m), 1578 (w) cm⁻¹ (C=C). UV (*trans-decalin*, Fig. 1), 295 K : λ_{max} 273 mm ($\varepsilon = 16,300$), λ_{min} 243 (7730); 350 K : ε_{273} 15,900, λ_{243} 7930; 400 K: ϵ_{272} 15,400, ϵ_{243} 8390; 450 K: ϵ_{270} 16,100, ϵ_{243} 9650; (hexane): λ_{223} 271 nm ($\epsilon = 17,500$), 218 (sh, 19,900); λ_{241} 241 (8500). ¹H-NMR: 1.42 (t, J_{1,9} = J_{5,9} = 2.5 Hz, 9-H), 3.02 (dt, J_{1,8} = J_{4,5} = 7.1 Hz, 1-H, 5-H), 4.26 (dd, J_{3,4} = J_{7,8} = 8.1 Hz, 4-H, 8-H), 6.03 (d, 3-H, 7-H), 7.22 (p-H), 7.33 (m-H), 7.43 (o-H). 13C-NMR : 18.9 (C-9), 29.2 (C-1, C-5), 79.1 (¹J = 164.0 Hz, C-4, C-8), 87.9 (C-2, C-6), 122.0 (dt, ¹J = 159.4, ${}^{3}J$ = 3.1 Hz, C-3, C-7), 126.35 (dt, ${}^{1}J$ = 160.6, ${}^{3}J$ = 7.6 Hz, p-C), 126.56 (dt, ${}^{1}J$ = 156.6, ${}^{3}J$ = 7.0 Hz, o-C), 128.4 (dd, ${}^{1}J$ = 159.8, ${}^{3}J = 7.7$ Hz, m-C), 143.0(*ipso-C*). MS : m/e = 271(22), 270(100, M *), 269(19), 255(27, M - Me), 254(14), 253(11), 241 (10), 240(10), 239(13), 193(20, M - Pb), 192(22), 191(20), 179 (38), 178 (28), 167 (13), 165 (25), 152 (13), 115 (39), 91 (23). (Calc for C21H18 (270.37): C, 93.29; H, 6.71. Found: C, 92.95; H, 6.86%.)

4 - Bromo - 2,6 - diphenyltricyclo[3.3.1.0^{2,8}]nona - 2,6 diene (16). All operations were performed under purified Ar using carefully de-acrated solvents saturated with Ar. To a stirred soln of 1.37 g (3.2 mmol) 14 in 50 ml THF, 5.45 ml of a 0.82 M soln of t-BuOK in t-BuOH (4.5 mmol) were added. After 4 h stirring, the mixture was extracted with 200 ml saturated aqueous potassium dihydrogen phosphate soln and 50 ml water. The aqueous layer was re-extracted with three 150 ml portions of ether. The combined organic layers were washed with two 100 ml portions of saturated NaCl aq and with 200 ml of dil NaCl aq and dried with MgSO₄. Evaporation of the solvent in vacuo left a yellow-orange oil which was flash chromatographed^{\$2} on a 20×2.5 cm silica column using pentane containing 1.5% ether as eluant to afford 0.6-0.7 g (ca 80%) of a pale yellow, viscous oil after removal of the last traces of solvent at 50°/10⁻⁵ Torr. The compound remained unchanged when kept under Ar. IR (film): 3075 (w), 3055 (m), 3025 (m) (=C-H), 1618 (w), 1602 (m), 1577 (w) (C=C). ¹H-NMR: 1.43 (dt, $J_{9a,9b} = 12.6$, $J_{1,9b} \simeq J_{5,9b} = 2.7$ Hz, 9-H_b), 1.73 (m, 9-H_a, H_a on the same side as bromine), 2.50 (t, $J_{1,8}$ $\simeq J_{7,8} = 7.3$ Hz, 8-H), 2.64(dq, $J_{1,8} = 7.6$, $J_{1,5} \simeq J_{1,9_8} \simeq J_{1,9_6}$ = 2 Hz, 1-H), 3.59 (tq, $J_{5,96} \simeq J_{5,96} = 2.8$, $J_{1,5} \simeq J_{3,5} \simeq J_{5,7}$ = 1.4 Hz, 5-H), 6.15 (d, J₃, $_{3}$ = 1.4 Hz, 3-H), 6.33 (dd, J₇, $_{8}$ = 7.1, J_{5,7} = 1.4 Hz, 7-H), 7.20-7.26 (m, 2 *p*-H), 7.29-7.37 (m, 2 *o*-H, 4 *m*-H), 7.58-7.62 (m, 2 *o*-H of 6-Ph). ¹³C-NMR (CD₂Cl₂): 21.3 $(tq, {}^{1}J = 133.2, {}^{2}J = {}^{3}J = 3.7 Hz, C-9), 24.3 ({}^{1}J = 168.2 Hz, C-9)$ 1), 32.5 (¹J = 167.5 Hz, C-8), 40.8 (C-2), 42.5 (¹J = 135.3 Hz, C-5), 114.8 (C-4), 120.1 (ddd, ¹J = 159.0, ³J_{1,7} = 1.6, ³J_{5,7} = 4.5 Hz, C-7), 125.8 (dt, ¹J = 155.9, ³J = 6.7 Hz, o-C of 6-Ph), 127.1 Hz, C-7), 125.8 (at, 3 = 155.7, 3 = 0.1, 127.44 (m, ${}^{1}J = 161.1$ Hz, p-(dt, ${}^{1}J = 160.8$, ${}^{3}J = 7.3$ Hz, p-C), 127.44 (m, ${}^{1}J = 161.1$ Hz, p-C), 127.54 (m, ${}^{1}J = 166.4$ Hz, C-3), 128.4 (dt, ${}^{1}J = 156.7$, = 7.0 Hz, o-C of 2-Ph) 128.93 (dd, ${}^{i}J = 159.2$, ${}^{3}J = 8.3$ Hz, m-C), 129.02 (dd, ${}^{1}J = 159.8$, ${}^{3}J = 6.5$ Hz, m-C), 137.0 (m, C-6), 139.8 (m, ipso-C of 6-Ph), 144.5 (m, ipso-C of 2-Ph). MS : m/e = 350, 348 (36%, 36%, M⁺), 269 (71, M - Br), 254 (27), 191 (62, $M - Br - C_6 H_6$, 165 (29), 115 (75, M - Br - 2 Ph), 91 (100, C₇H₇). Exact mass: calc for C₂₁H₁₇⁷⁹Br, 348.0513; found, 348.0517.

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