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The Cyclobutene/Butadiene Anion Radical Electrocyclic Reaction

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Abstract: The generalized cyclobutene anion radical/butadiene anion radical electrocyclic reaction has been explored experimentally and theoretically. Its preferred stereochemical course is conrotation. Simple theoretical methods are discussed for treating radical electrocyclic reactions, but SCF reaction path calculations are also described. The HOMO method, alone among the theoretical approaches evaluated, is found to be unsatisfactory.

The stereochemistry of an electrocyclic reaction of a free radical was first discussed in 1965.¹ Applying the now familiar concept of HOMO,^{1,2} the allyl/cyclopropyl radical interconversion was predicted to occur conrotatorily. Shortly thereafter an orbital correlation diagram analysis of the same transformation was presented.³ Neither rotatory pathway was found "allowed" but conrotation was again predicted on the basis of estimated relative energies of the two cyclopropyl radical excited states with which the respective dis- and conrotatory cyclizations of the allyl radical "intend" to correlate. Reaction path calculations of the extended Hückel type also envision conrotation,¹ but MINDO⁴ and an *ab initio*⁵ calculation generate the contrary disrotatory prediction. No definitive experimental results are available for this or other uncharged radical systems. Study of the stereochemistry of electrocyclic reactions of anion radicals has been more fruitful, however, and in one case in particular, the generalized cyclobutene/butadiene anion radical system, the results are clear and instructive.^{6,7} These are now reported in full.

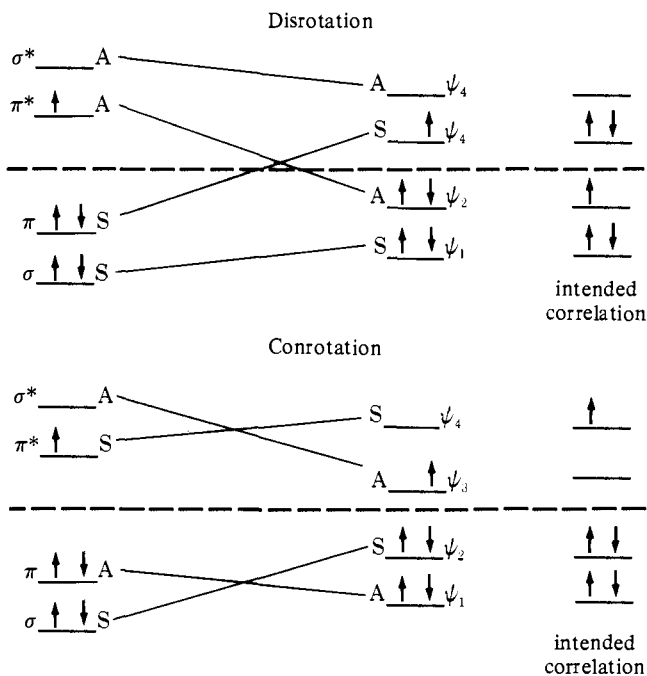
Theoretical Section

The butadiene anion radical HOMO is symmetric, eliciting a HOMO prediction of disrotation. Orbital correlation diagrams for the cyclobutene/butadiene anion radical reaction (Scheme I) do not find the decision quite so straightforward. As in the cyclopropyl/allyl radical case, neither reaction mode

is allowed. A variety of quantitative treatments, however, select the conrotatory mode as favored, in contradiction to HOMO's prediction. One such treatment amounts to a quantitative extension of the orbital correlation diagram approach. With reference to Scheme I, the intended product of the disrotatory cleavage of the cyclobutene anion radical is what will be designated the 212 excited state of the butadiene anion radical. In this notation the ground state is 221, the successive numbers representing electron populations of the diene π MO's as they increase in energy from left to right. The intended correlation for the conrotatory path is with the 2201 excited state. The Hückel energies of these states are 2.618 and 2.858 β , respectively. The conrotatory route is thus favored by 0.240 β . This kind of treatment, incidentally, finds the two cyclopropyl radical pathways degenerate.⁸

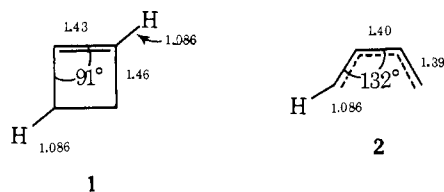
A second means of ordering the energies of the dis- and conrotatory transition states relies on the Zimmerman concept according to which conrotatory transition states are likened to cyclic Möbius systems and disrotatory ones to systems of Hückel topology.⁹ The HMO energies of the Möbius and Hückel topologies of the cyclobutadiene anion radical are 4.24 and 4.00 β , respectively. The difference, 0.24 β , is exactly the same as derived via the quantitative orbital correlation diagram approach and, again, conrotation is foreseen. The Hückel/Möbius comparison can also be made using INDO energies. The Möbius state is calculated by assigning one nearest

Scheme I. Orbital Correlation Diagrams for the Cyclobutene/Butadiene Anion Radical Transformation



neighbor p_z/p_z resonance integral the negative of its normal value and executing an otherwise normal INDO calculation.¹⁰ Using the square geometry (1.42 Å, the INDO optimum for *square* cyclobutadiene) the energies are: Möbius -30.1836; Hückel -30.0198 au. Conrotation is favored (by 103 kcal/mol).

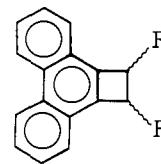
The most fundamental approach, of course, is to perform reaction path calculations for both rotatory reaction modes. This has been done using the INDO MO method.¹¹ The reactant (**1**) and product (**2**) geometries were optimized except



for carbon-hydrogen bond lengths and angles.¹² For intermediate states a linear relationship between bond stretching, rotation, and rehybridization was assumed. This assumption has been validated by extensive checking in the cyclobutene/butadiene (neutral) electrocyclic reaction. Calculations were carried out at 1° intervals of the rotational angle θ ($\theta = 0$ for the cyclobutene geometry, $\theta = 90^\circ$ for the butadiene one) in regions of interest. The transition state for conrotation was located at 37° and that for disrotation at 39°, the former being 40.19 kcal lower in energy than the latter (the lower barrier to conrotation is calculated as 151.39). The E vs. θ curve is smooth at the transition state for conrotation, but is discontinuous at the disrotatory transition state. Examination of the wave function reveals that this is a region of HOMO crossing. In the conrotatory case this crossing takes place well before the transition state thus avoiding a transition state discontinuity. Unsymmetrical rotatory processes ($\theta_1 \neq \theta_2$; the term "lag rotatory" will be adopted herein)¹³ have also been explored, though less extensively. In the conrotatory case these paths are uniformly of higher energy than the symmetrical path, but in the disrotatory case the lag mechanisms all have lower barriers, culminating in the semiroductory path ($\theta_1 = 0^\circ$, $\theta_2 = 90^\circ$) which is of lower energy than any disrotatory path (35 kcal lower than the symmetrical disrotatory path). Finally, Matsen's intriguing

Hückel-Hubbard reaction path calculations also favor the conrotatory path.¹⁴ The conclusion derived from all of the theoretical treatments considered (except HOMO) is that the preferred electrocyclic mode is the same as that for neutral cyclobutene, viz., conrotation.

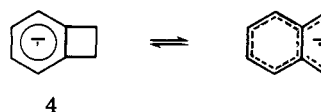
The experimental test which has been carried out involves the substituted ($R = \text{Ph}$) phenanthrocyclobutene **3**. The orbital



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correlation diagrams for this system ($R = \text{H}$) are shown in Scheme II and may be seen to closely parallel the essential characteristics of the prototype system.

The benzocyclobutene anion radical (**4**) merits some addi-

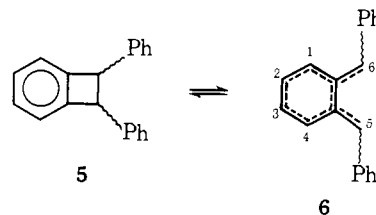


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tional comment. The electrocyclic conversion of this species to the *o*-quinodimethane anion radical is *allowed* in the conrotatory mode (Scheme III). The HOMO in **4** is, incidentally, experimentally verified (ESR) to be symmetric.¹⁵ This is the first radical species observed to possess an allowed electrocyclic mode.⁶ As in the prototype (cyclobutene anion radical) system, but now in direct contradiction to the unequivocal orbital correlation diagram prediction, HOMO predicts a favored disrotatory cleavage. A reaction path calculation similar to that for the cyclobutene system gives the barrier to conrotation as only 0.5 kcal, whereas that for disrotation is 23.7 kcal. Once more, all theoretical approaches investigated except HOMO concur in predicting conrotation. In view of the miniscule barrier calculated for conrotation, the unfavorable interaction between the reaction termini envisioned by HOMO must be considered quantitatively irrelevant. The results of the reaction path calculations are nicely consistent, however, with the allowed nature of this reaction mode as treated by orbital correlation diagrams. The experimental test applied in this series involves *cis*- and *trans*-3,4-diphenylbenzocyclobutene. The odd electron in these anion radicals is expected to occupy the same symmetric type antibonding HOMO of the benzocyclobutene system as in benzocyclobutene itself, rather than an ABMO on one of the phenyl substituents. This follows from the greater solution electron affinity of benzocyclobutene than toluene or even benzene.¹⁶

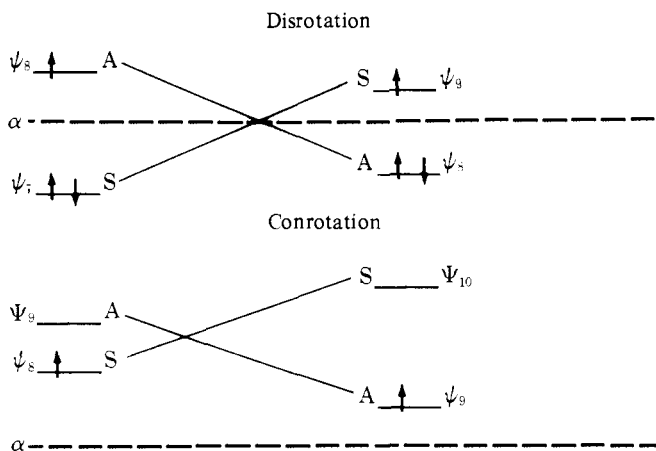
Results and Discussion

cis- and *trans*-3,4-diphenylbenzocyclobutene (**5**) were prepared by the method of Carpino.¹⁷ Birch reduction ($\text{Na}/\text{NH}_3/\text{EtOH}$) of each at -78°C gave *o*-dibenzylbenzene in 100% yield, indicating facile cleavage of the 3,4 bond of the cyclobutane ring of *cis*- and *trans*-**5**⁻ at -78°C . Attempts

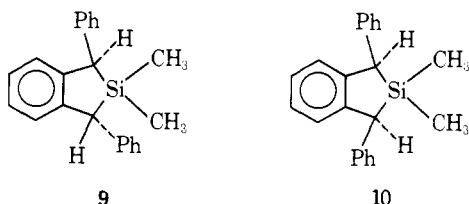


to observe these anion radicals by the usual alkali metal/etheral solvent ESR procedures were totally unsuccessful,

Scheme II. Partial Orbital Correlation Diagrams for the Phenanthrocylobutene/9,10-Phenanthraquinodimethane Anion Radical Transformation

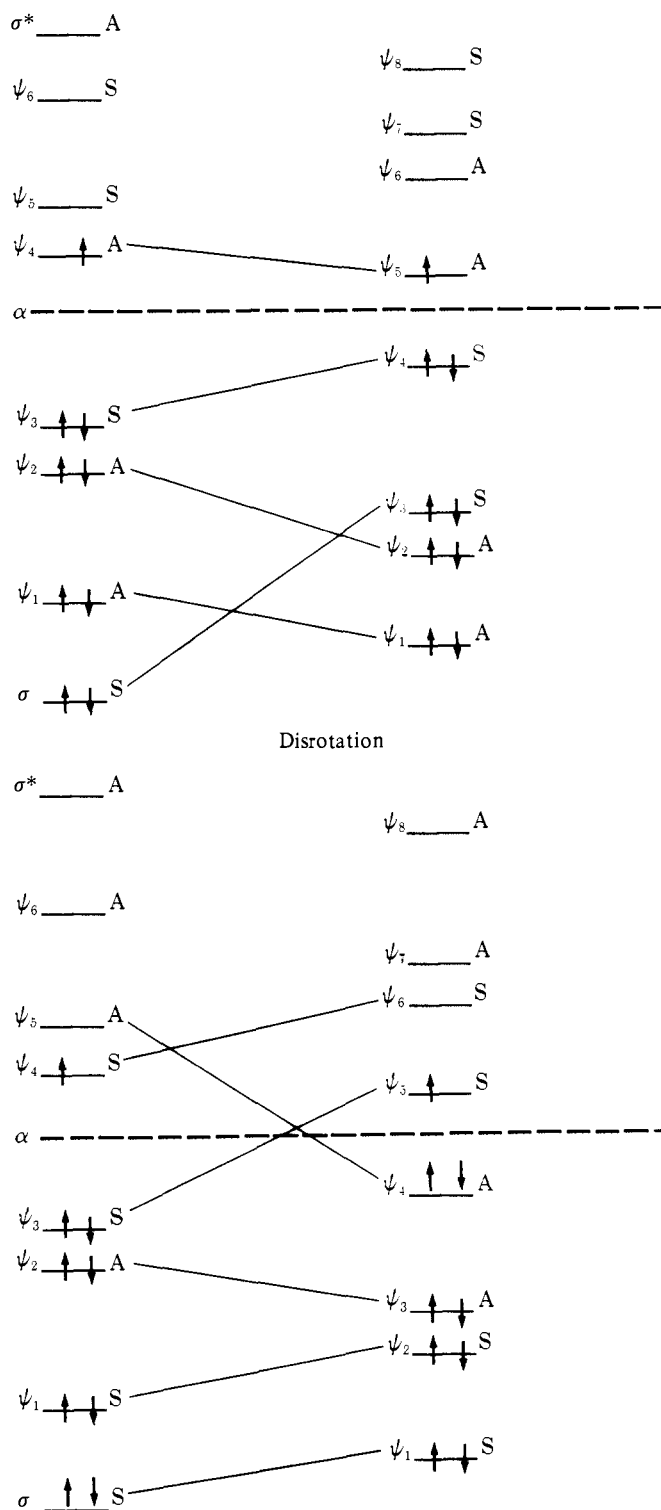


thus confirming the instability of these anion radicals and, together with the Birch reduction results, suggesting that they rapidly cyclorevert to $6^{\cdot-}$, which is, in turn, converted to diamagnetic 6^{2-} . The reaction of *cis*- and *trans*-**5** with potassium in 2-methyltetrahydrofuran (MTHF) at -78°C in vacuo were complete in 2 h. The resulting deep red solutions contained essentially only anions of general structure 6^{2-} , as indicated by quenching experiments with methyl iodide and also D_2O . The expected dimethyl and dideutero compounds (**7** and **8**, respectively) were obtained in $>90\%$ yield. The absence of monomethylated product was confirmed by independent synthesis. The two diastereoisomers of **7** were produced in roughly the same proportion from either *cis*- or *trans*-**5** and have NMR (CDCl_3) τ 2.4–3.0 (14 H, m), 5.6 (2 H, q, $J = 7$, 8.4 (6 H, d, $J = 7$, 25% of this isomer), 8.6 (6 H, d, $J = 7$, 75%) and mass spectrum m/e 286 (M). The dianions from *cis*- and *trans*-**5** can be confidently assigned the (*Z,E*)- 6^{2-} and (*E,E*)- 6^{2-} structures, respectively, on the basis of their reactions with dimethyldichlorosilane (-78°C , MTHF, vacuum line). The dianion from *cis*-**5** gave silanes **9** (84%) and **10**



(16%) in $>90\%$ total yield, while that from *trans*-**5** yielded **9** (30%) and **10** (70%), also in high yield. Silane **9** has NMR (CS_2) τ 2.7–3.15 (14 H, m), 6.15 (2 H, s), 9.9 (6 H, s) and mass spectrum m/e 314 (M), while **10** has NMR (CS_2) τ 2.6–3.1 (14 H, m), 6.35 (2 H, s), 9.6 (3 H, s), 10.4 (3 H, s) and mass spectrum m/e 314 (M). The silyl methyl groups of the *trans* cyclic silane **9** are, of course, equivalent, whereas those of the *cis* silane **10** are not. Even though the silane quenching reaction is not likely to be concerted, any partial stereospecificity should obviously be in favor of suprafacial (*cis*-1,4) addition. The most likely reaction sequences are therefore *cis*-**5** \rightarrow *cis*- $5^{\cdot-}$ \rightarrow (*Z,E*)- $6^{\cdot-}$ \rightarrow (*Z,E*)- 6^{2-} and *trans*-**5** \rightarrow *trans*- $5^{\cdot-}$ \rightarrow (*E,E*)- $6^{\cdot-}$ \rightarrow (*E,E*)- 6^{2-} and both retroelectrocyclic reactions (of *cis*- and *trans*- $5^{\cdot-}$) must be preferentially conrotatory. Though some of the alternate cyclic silane is obtained in each instance, it is most likely that incomplete stereospecificity in the stepwise quenching reaction is responsible for this. In view of the difficulty in forming simple alkyl substituted benzenoid anion radicals by alkali metal reduction, the possibility of formation and electrocyclic

Scheme III. Orbital Correlation Diagrams for the Benzocyclobutene/*o*-Quinodimethane Anion Radical Transformation Conrotation

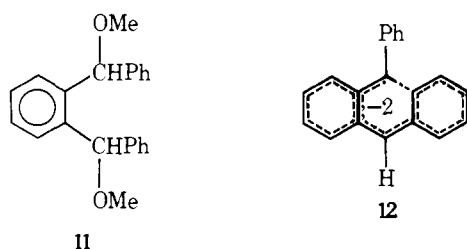


cleavage of the dianion of **5** can be confidently rejected. Such dianions are unprecedented. It may also be noteworthy that the benzocyclobutene anion radical is not further reduced by excess metal.

Further confirmation of the dianion structural and stereochemical assignments and evidence that both retroelectrocyclic reactions are highly stereospecific is provided by NMR studies on the respective dianions in $\text{THF}-d_8$. The ions were prepared on a vacuum line and studied in sealed tubes at temperatures ranging from -78°C to ambient. The dianion (*E,E*) from

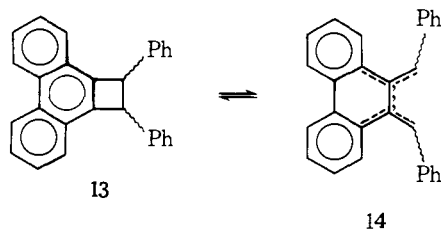
trans-**5** has NMR τ 2.7 (4 H, m, meta), 3.4 (6 H, m, ortho), 3.93 (2 H, m, H_{2,3}), 4.40 (2 H, m, H_{1,4}), 5.77 (2 H, s, H_{5,6}). The dianion from *cis*-**5** (viz., the *Z,E* dianion) has NMR τ 2.8 (4 H, m, meta), 3.5 (6 H, m, para + ortho), 4.1 (4 H, m, H₁₋₄), 5.77 [1 H, s, H₅ (outside)], 6.28 (1 H, s, H₆). Except for the benzylic protons the positional assignments should be regarded as tentative inasmuch as they are, in part, based on MO calculations of charge density. The large upfield shifts of all of the aromatic protons except the meta ones are noteworthy. Still more significantly, H_{5,6} (the benzylic protons) are equivalent in the *E,E* but not in the *Z,E* dianion. The dianions are obtained free of each other if the reaction vessel and later the NMR tube are kept close to -78°C .

Incidentally, two alternate, convenient, and stereoselective routes to (*Z,E*)-**6**²⁻ have been devised. Reaction of *o*-dibenzylbenzene with excess butyllithium in MTHF at room temperature gives, along with smaller amounts of the monoanion, mainly (*Z,E*)-**6**²⁻ as shown by methyl iodide quenching and also reaction with dimethyldichlorosilane (83% **9**, 17% **10**). Similarly, reaction of the diether **11** with potassium in MTHF



at 0°C gives the *Z,E* dianion cleanly. Silane quenching gives 87% **9** and 13% **10**. These two results pointedly suggest that the *Z,E* dianion is more stable than the *E,E* isomer (product development control leads to the preferential formation of the *Z,E* isomer). This is most astonishing when one considers the steric congestion associated with the *Z,E* framework. Two different effects may contribute to this stability. Firstly, the portion of the negative charge delocalized into the phenyl substituents may interact strongly with the two lithium gegenions if the phenyl substituent is in a *Z* but not an *E* position. Thus the *Z,E* isomer should be preferentially stabilized in relation to the *E,E* one. Presumably the *Z,Z* isomer would be sterically untenable. Secondly, the *Z,E* isomer could have a long range interaction (see **12**) which would set up a Möbius eight π electron system. Such an interaction would be unprecedented for a dianion and, in the absence of a special ion pairing effect such as that proposed above, would probably be dominated by Coulombic repulsions between the interacting, negatively charged termini. The combined effects, however, represent a likely explanation.

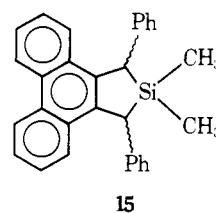
As previously mentioned, the experimental model of the parent cyclobutene system in the present investigation is the 3,4-diphenylphenanthrocyclobutene system **13**. The trans



isomer was already known: mp $195\text{--}197^\circ\text{C}$; NMR (CDCl₃) τ 1.25–1.42 (m, 2 H), 2.33–2.58 (m, 6 H), 2.87 (s, 10 H), 6.5 (s, 2 H). The previously unknown *cis* isomer was prepared by lithium aluminum hydride–aluminum chloride reduction of the known dibromide of **13** obtained by the action of *N*-bromosuccinimide on *trans*-**13**: mp $158\text{--}160^\circ\text{C}$; NMR (CDCl₃)

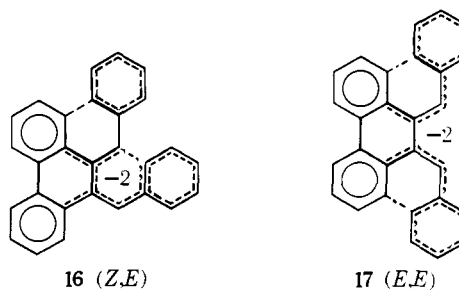
τ 1.25–1.42 (m, 2 H), 2.35–2.6 (m, 6 H), 3.13 (s, 10 H), 4.9 (s, 2 H). Isomerization of *cis*- to *trans*-**13** occurs in *tert*-butoxide–tetrahydrofuran at room temperature.

Reduction of *cis*-**13** at -78°C with potassium, sodium, or lithium biphenyl (anion radical) gives *cis*-**13**^{•-}: ESR (THF) 4.22 G (4 H; H₁, H₈, saturated methines), 2.85 (2 H, H₃, H₆), 0.48 (4 H). The positional assignments are based on HOMO eigenfunctions for the phenanthrene system. The hyperfines are reassuringly similar to those of the phenanthrene anion radical: 4.43, 3.71, 2.88, 0.63, 0.43 (2 H each). After complete reduction, *cis*-**13** was regenerated in 80% yield by aqueous quenching, thus demonstrating the absence of degradation in the predominant reduction reaction. The anion radical is stable indefinitely at -78°C and resists decomposition up to about 0°C . In significant contrast, *trans*-**13** gave no detectable paramagnetic species, even at -78°C , upon similar reduction. The mode of decomposition of transient *trans*-**13**^{•-} was identified as electrocyclic by quenching the reduction product with aqueous ammonium chloride. An 84% yield of 9,10-dibenzylphenanthrene was obtained. Dimethyldichlorosilane quenching gave **15**. The ultimate reduction product of *trans*-**13**



is thus **14**²⁻. Even at -78°C this dianion undergoes rapid *Z,E* \rightleftharpoons *E,E* equilibration, invalidating the silane quench as a stereochemical mechanistic probe, as the following data and discussion reveal. Table I lists product compositions for the silane quenching of solutions of **14**²⁻ prepared in various ways. Considering first the cyclic silanes, there are essentially only two product distributions. When sodium or potassium is the cation, irrespective of whether the reducing agent is an alkali metal or an anion radical, a 50:50 mixture of *cis* and *trans* silanes results. When the gegenions are lithium the ratio is 3:1 (*cis*:*trans*). Moreover, **14**²⁻ is initially prepared from potassium metal and then a large excess of lithium biphenyl added, silane quenching resulting in the characteristic lithium gegenion composition (3:1). The latter result verifies equilibration of the two stereoisomeric dianions.

In **14**²⁻, the *Z,E* configuration is of comparable stability to the *E,E* one, not, as in **6**²⁻, significantly more stable. A plausible rationalization would include the recognition of new but less potent Möbius eight π electron interactions involving the (*E*)-phenyl substituents of **16** and **17**. Incidentally, the “triene

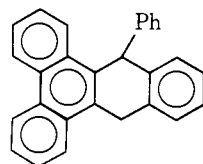


dianion” HOMO is more heavily weighted at the benzylic carbon involved in the interaction with a (*Z*)-phenyl substituent than at the phenanthrene ring positions interacting with the (*E*)-phenyls. Consequently a *Z,E* preference should still exist in terms of the π electronic interaction.

One may note also in Table I that the reduction product (9,10-dibenzylphenanthrene) is obtained in far smaller quantity when lithium is employed as the gegenion, as opposed

to sodium or potassium, and also when the reducing agent is an anion radical, as opposed to an alkali metal. These appear to be rather general results and are highly likely to be due to varying amounts of deprotonation of the substrate (e.g., **13**) by the dianion (e.g., **14**²⁻). Light (lithium) ion pairing should stabilize the dianion toward such abstractions. The use of a less polar solvent (e.g., 2-methyltetrahydrofuran as opposed to tetrahydrofuran) has a similar effect. The advantage of anion radicals as reducing agents, in this connection, is presumably that all of the substrate is reduced (to the anion radical) virtually at once and very little neutral substrate remains as a proton source.

Eventually, at 0 °C, *cis*-**13**⁻ does decompose, as observed by ESR and quenching studies. Aqueous quenching yields some (30%) 9,10-dibenzylphenanthrene but mainly (70%) the pentacyclic substance **18**, previously obtained by Cava in the



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thermolysis of *trans*-**13**. The required cyclization can readily be envisaged from the *Z,E* configuration of **14**, but the *Z,E* dianion (**14**²⁻) has already been observed and fails to undergo such a transformation. The likeliest possibility seems therefore to be cyclization of (*Z,E*)-**14**⁻. This would require a conrotatory cleavage of *cis*-**13**⁻, as predicted theoretically. The quenching product composition would then depend on the relative rates of cyclization of (*Z,E*)-**14**⁻ and of the reduction of the latter to the corresponding dianion, which is stable prior to quenching.

The dramatically different rates of cleavage of *cis*- and *trans*-**13**⁻ form the basis for a relatively secure assignment of reaction stereochemistry as follows. Despite the greater thermodynamic stability of *trans*- than *cis*-**13**, *trans*-**13**⁻ cleaves far more rapidly. This phenomenon is a familiar aspect of the profile of the conrotatory cleavages of neutral 3,4-diphenylcyclobutene derivatives and is well understood on the basis of strong steric repulsions encountered by the (*Z*)-phenyl substituent in the conrotatory opening of the *cis* isomer. Both phenyl substituents can occupy *E* positions in the conrotatory cleavage of the *trans* isomer. The stabilizing π interaction present in the dianion is absent in the anion radical,¹⁸ and the normal destabilizing effect of steric repulsions prevails.

Conclusions

The stereochemical results for the general cyclobutene/butadiene anion radical electrocyclic reaction are gratifyingly straightforward. Theoretical and experimental studies decisively concur in finding a preferred conrotatory mode. An interesting incidental observation is that HOMO generates the erroneous prediction of disrotation. Since the original report of this, similar failings of HOMO have been reported among singlet species.¹⁹ The inability of HOMO to properly treat radical electrocyclic reactions generally will be discussed more fully in a sequel paper. It is, nevertheless, already clear that HOMO depends for its validity on a circumstance that is not generally realized, namely, the alternation of orbitals in (S or A) symmetry type. Various, still quite simple, alternative procedures are available for analyzing electrocyclic reaction stereochemistry. Two examples, namely the quantitative orbital correlation diagram and Zimmerman-Hückel-Möbius approaches are discussed in the theoretical section, in addition to INDO reaction path calculations. It should, perhaps, be stressed that orbital correlation diagrams do not suffer from

Table I. Product Distribution in the Reduction and Silane Quenching of **14**²⁻

Reducing agent	Product composition, %		
	<i>cis</i> - 15	<i>trans</i> - 15	9,10-Dibenzylphenanthrene
Lithium biphenyl anion radical	78.4	21.6	0.0
Sodium naphthalene anion radical	46.3	41.8	11.9
Potassium naphthalene anion radical	28.5	28.5	43.0
Lithium	37.0	14.5	48.5
Sodium	15.0	15.0	60.0
Potassium	25.0	25.0	50.0

the flaws of HOMO and do appear to be generally valid where applicable.

The dianions generated in the experimental study are of unprecedented structure. The phenomenon of *Z,E* \geq *E,E* in configurational stability may signal on unprecedented electronic effect, that of Möbius eight π electron aromaticity.

Theoretical studies on other radical electrocyclic reactions of interest, including the cyclobutene/butadiene cation radical, and the cyclopropyl/allyl radical transformations will be discussed in a subsequent paper.

Experimental Section

Equipment. NMR spectra were obtained using a Perkin-Elmer R-12-A spectrometer, with Me₄Si as internal standard. ESR spectra were obtained using a Varian E-9 spectrometer. Mass spectra were obtained at low resolution on a Bell and Howell C.E.C. Model 21-491 spectrometer (70 eV). Melting points are uncorrected. CN/INDO calculations were carried out using the standard Pople program available from QCPE, modified for use on the CDC-1604/CDC-6600 computers in use at the University of Texas.

3,4-Dibromo-3,4-diphenyl-9,10-phenanthrocylobutene. To 4.2 g (0.012 mol) of *trans*-3,4-diphenyl-9,10-phenanthrocylobutene²⁰ dissolved in 270 ml of dry CCl₄, contained in a 500-ml round-bottomed flask equipped with condenser and magnetic stirrer, was added 4.2 g (0.022 mol) of *N*-bromosuccinimide and a spatula tip of dibenzoyl peroxide. The suspension was stirred and heated at reflux under nitrogen for 1 h, then cooled to room temperature and filtered to remove succinimide. The solvent was removed at room temperature under vacuum, and the crude product, owing to its instability, was used immediately in the next, reduction, step.

***cis*-3,4-Diphenyl-9,10-phenanthrocylobutene (*cis*-**13**).** In a 500-ml three-necked flask equipped with a condenser and a 150-ml addition funnel, 2 g (0.053 mol) of lithium aluminum hydride was added to 200 ml of anhydrous diethyl ether under dry nitrogen. This mixture was then cooled to 0 °C in an ice bath and stirred magnetically. Then, 7.03 g (0.053 mol) of anhydrous AlCl₃ was added, and the mixture was allowed to warm to room temperature. All of the previously prepared crude dibromide (0.012 mol theoretically) was suspended in 100 ml of anhydrous diethyl ether and added through the addition funnel to the LAH/AlCl₃ solution at room temperature with stirring. After all of the dibromide solution had been added, the reaction was stirred at room temperature overnight and then worked up by the dropwise addition of water at 0 °C. Water was added until no further evolution of hydrogen was noted. The reaction mixture was then poured into 500 ml of ice-water and extracted several times with diethyl ether. The ether extracts were combined, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator, giving a yellow solid residue. Recrystallization of the crude product from a Skellysolve B-benzene solvent mixture gave 1.1 g (26% overall yield for two reactions) of a white crystalline solid: mp 158–160 °C; NMR (CDCl₃) τ 1.25–1.42 (m, 2H), 2.35–2.60 (m, 6H), 3.13 (s, 10H), 4.9 (s, 2H); mass spectrum *m/e* 356 (M = 356).

Base Isomerization of *cis*-13** to *trans*-**13**.** Dry THF (30 ml), freshly distilled from potassium metal, was placed in a 100-ml round-bottom flask equipped with a condenser and two glass stoppers. Then, 0.15 g (0.00042 mol) of *cis*-**13** and 1 g (0.0089 mol) of potassium *tert*-butoxide was added under dry N₂ gas. The reaction mixture was

stirred at room temperature for 2 h. The reaction was worked up by pouring into 250 ml of ice-water and extracted several times with diethyl ether. The ether extracts were combined, dried over anhydrous sodium sulfate, and concentrated with a rotary evaporator, giving 1.5 g of crude product. The NMR of the crude product showed it to consist of 92% **13** and 8% **12**.

Preparation of Anion Radical Reducing Species. A. Lithium Biphenyl. In a 150-ml three-necked round-bottom flask equipped with a condenser, a rubber septum, and a glass stopper, 2.5 g (0.016 mol) of biphenyl was dissolved in 80 ml of dry THF, freshly distilled from potassium. Dry N₂ gas was passed through the system throughout the reaction. Then, 0.14 g (0.020 mol) of freshly cut lithium metal was added at room temperature. Initiation of the reaction was indicated by a dark green coloration of the solution. The reaction mixture was stirred magnetically at room temperature for 3 h before use. The theoretical concentration of lithium biphenyl is 0.2 M. From titrations of several previous mixtures, the concentration of lithium biphenyl anion radical under these conditions is 0.13–0.16 M.

B. Sodium Naphthalene. The general procedure outlined in A was followed. A total of 1.93 g (0.015 mol) of naphthalene in 50 ml of dry THF was used. Then, 0.5 g (0.022 mol) of freshly cut sodium was added at room temperature. The reaction was stirred at room temperature for 3 h before use. The theoretical concentration of sodium naphthalene anion radical is 0.30 M.

C. Potassium Naphthalene. The general procedure outlined in A was used. A total of 1.93 g (0.015 mol) of naphthalene in 50 ml of dry THF was used. A total of 0.75 g (0.019 mol) of freshly cut potassium was added at room temperature. The reaction was stirred at room temperature for 3 h prior to use. The theoretical concentration under these conditions is 0.3 M.

Reaction of *cis*- and *trans*-13 with Anion Radical Reducing Species. A. Lithium Biphenyl Anion Radical. (1) Ammonium Chloride Quenching. In a three-necked 100-ml round-bottom flask equipped with a condenser, a rubber septum, and a ground glass stopper, 0.5 g (0.0014 mol) of *cis*-**13** was dissolved in 30 ml of dry THF. Dry N₂ gas was slowly passed through the system throughout the reaction. The solution was then cooled to -78°C using a dry ice-acetone bath, and 23 ml (0.0030–0.0037 mol) of lithium biphenyl was introduced through the rubber septum with a hypodermic syringe. The same procedure was repeated with 0.5 g of *trans*-**13**. Each reaction was stirred at -78°C for 1 h and then quenched by dropwise addition of saturated ammonium chloride solution through the septum. The ammonium chloride solution was added until the solutions had lost their dark green coloration. Both reactions were worked up as follows. The reaction was allowed to warm to room temperature, poured into ~250 ml of ice-water, and extracted several times with diethyl ether. The ether extracts were combined, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator, giving a solid white residue. The crude product was then chromatographed on a silica gel column. The column was first eluted with pure Skellysolve B which produced, after concentration, pure biphenyl. Subsequent elutions with an 80% Skellysolve B, 20% benzene solvent eluted the phenanthrene-type products from the column. For the reaction of *cis*-**13**, the product was 0.3933 g of a white crystalline material, shown by NMR to consist of 100% starting material. For the reaction of *trans*-**13**, the product was 0.296 g of a white solid, shown by NMR to consist of a mixture of 68% starting material and 32% 9,10-dibenzylphenanthrene: NMR (CDCl₃) τ 1.15–1.4 (m, 2 H), 1.82–2.08 (m, 2 H), 2.38–2.63 (m, 4 H), 2.89 (s, 10 H), 5.48 (s, 4 H); mass spectrum *m/e* 358 (M = 358).

(2) **Dichlorodimethylsilane Quenching.** Only the reaction with *trans*-**13** was carried out. The procedure outlined in (1) was used with the following exceptions. A total of 0.3 g (0.00084 mol) of *trans*-**13** was dissolved in 10 ml of dry THF. A total of 13.8 ml (0.0018–0.0022 mol) of lithium biphenyl was used. The reaction was quenched after 1 h at -78°C using neat dichlorodimethyl silane (Aldrich Co.). There were two product fractions eluted from the column. The first consisted of 0.085 g of starting material. The second fraction consisted of a mixture of 78.4% *cis* cyclic silane [NMR (CS₂) τ 1.2–1.4 (m, 2 H), 1.9–2.15 (m, 2 H), 2.3–2.65 (m, 4 H), 2.9 (s, 10 H), 5.5 (s, 2 H), 9.45 (s, 3 H), 10.35 (s, 3 H)] and 21.57% *trans* [NMR (CS₂) τ 1.2–1.4 (m, 2 H), 1.9–2.15 (m, 2 H), 2.3–2.65 (m, 4 H), 2.95 (s, 10 H), 5.5 (s, 2 H), 10.0 (s, 6 H)].

B. Sodium Naphthalene. Only the reaction with *trans*-**13** was carried out. The same procedure as outlined in A was used with the following exceptions. A total of 0.35 g (0.00098 mol) of *trans*-**13** in 20

ml of dry THF was used. A total of 10 ml (0.003 mol) of reducing solution was added at -78°C . The reaction was quenched after 1.5 h at -78°C with dichlorodimethylsilane. The NMR of the product showed it to consist of a mixture of 11.9% dibenzylphenanthrene, 46.3% *cis* silane, and 41.8% *trans* silane.

C. Potassium Naphthalene. Only the reaction with *trans*-**13** was carried out. The same procedure outlined in A was used with the following exceptions. A total of 0.20 g (0.00056 mol) of *trans*-**13** in 10 ml of dry THF was used. A total of 5 ml (0.0015 mol) of reducing solution was added at -78°C . The reaction mixture was quenched with dichloromethyl silane after 2 h at -78°C . The NMR of the product showed it to consist of mixture of 43% dibenzylphenanthrene, 28.5% *trans* silane, and 28.5% *cis* silane.

Reaction of *cis*- and *trans*-13 with Alkali Metals. A. Potassium (Ammonium Chloride Quenching). The same procedures as previously described were used with the following exceptions. A total of 0.25 g (0.0007 mol) of substrate in 10 ml of dry THF was used. Freshly cut potassium metal (0.15 g, 0.0038 mol) was used. The two reactions were kept at -78°C for 1 h, followed by 0°C for 2 h prior to quenching. Both reactions were quenched with saturated ammonium chloride solution. For the reaction with *trans*-**13**, the product was 0.16 g (64% yield) of dibenzylphenanthrene. For the reaction with *cis*-**13**, the product was a white solid, shown by NMR to consist of a mixture of 30% dibenzylphenanthrene and 70% of **17**: NMR (CS₂) τ 1.3–1.6 (m, 2 H), 1.75–2.05 (m, 2 H), 2.35–3.15 (m, 13 H), 4.05–4.15 (s, 1 H), 5.5–5.7 (s, 2 H).

Birch Reduction of *trans*-3,4-Diphenylbenzocyclobutene (5). A solution of **5** (1.0 g, 3.9 mmol) in ether (20 ml) was added slowly to sodium (0.23 g, 10 mmol) in liquid ammonia (50 ml) at -78°C . The mixture was warmed to -33°C , and the ammonia was allowed to evaporate. Water (20 ml) was added, and the ether layer was washed with water, dried (Na₂SO₄), and concentrated to give 1.1 g (100%) of virtually pure *o*-dibenzylbenzene: mp 77.8–78.5 $^{\circ}\text{C}$ (EtOH) (lit.²¹ 78–9 $^{\circ}\text{C}$); NMR (CCl₄) τ 2.94 (m, 14 H), 6.12 (s, 4 H); mass spectrum *m/e* 258 (M = 258); mixed melting point undepressed.

NMR Studies on Dianions (6²⁻). *cis*- or *trans*-**5** (200 mg) was loaded into capillaries and placed in a vacuum line reaction vessel with sidearms for sodium/potassium and an NMR tube. The vessel was evacuated and sodium/potassium alloyed formed and distilled into it by heating the appropriate sidearm with a burner. Tetrahydrofuran-*d*₈ (2 ml) was then distilled from a solvent reservoir into the cooled (liquid nitrogen) reaction vessel. The vessel was then warmed in dry ice-acetone for 2 h to effect the reaction. The deep red solution resulting was then poured into the cooled (-78°C) NMR sidearm and the latter sealed off and analyzed.

Quenching Studies. *cis*- or *trans*-**5** (70 mg) was dissolved in tetrahydrofuran or 2-methyltetrahydrofuran (3 ml) in a reaction vessel kept under dry nitrogen at -78°C . An excess of potassium metal was added, and the mixture was stirred for 1.5 h. A large excess (several ml) of the appropriate quenching agent (D₂O, methyl iodide, or dimethyldichlorosilane) was then added and stirring continued until the dianion color faded (a few minutes at most). The excess potassium was mechanically removed, water was added, and the mixture was extracted with ether. After being dried (Na₂SO₄), the ether solution was concentrated. The crude product was examined by NMR and then purified by alumina chromatography. The semi-solid cyclic silane mixtures were eluted by Skelly B, not being separated even by this nonpolar eluent. Crystallization attempts also proved unsuccessful. Therefore the substances were characterized only by their NMR spectra (cited in the text).

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Calculations of Steric Hindrance in Ester Hydrolysis Based on Estimation of van der Waals Strain Energies of Alkanes

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Abstract: Steric hindrance is traditionally defined by the Taft E_s values, which are derived empirically from rates of acid-catalyzed hydrolysis of esters: $E_s = -\log(k/k_0)$, where k is the rate constant for any ester RCOOEt and k_0 is for ethyl acetate. We have explored the utility of hydrocarbon models for calculating E_s for R alkyl and cycloalkyl. The postulate is that E_s is proportional to $\Delta\Delta H = [\Delta H_f^\circ(\text{neoalkane}) - \Delta H_f^\circ(\text{isoalkane})]$, where neoalkane is RC(CH₃)₃. The neoalkane is intended to reflect the degree of steric strain in the tetrahedral intermediate and the isoalkane that is in the ester. Empirical procedures for estimating ΔH_f° prove relatively useless for these calculations. However, ΔH_f° estimated from molecular mechanics does provide good values: for example, $E_s = 4.419 + 0.552\Delta\Delta H$ has a standard deviation of 0.4 for a total range of 4, and the correlation coefficient is 0.95 for 24 esters.

The present study continues our calculations of steric hindrance and steric acceleration.¹ The Taft E_s values, based on relative rates of acid-catalyzed ester hydrolysis, have long served as an important empirical measure of steric hindrance:² $E_s = -\log(k/k_0)$ where k is the rate constant for any ester RCOOEt and k_0 is for CH₃COOEt. E_s values are relatively independent of reaction conditions and have a standard deviation of the order of 0.1 over a range of 4. The group R may be alkyl or cycloalkyl and may have benzene rings, halogens, or other substituents. However, R may not be aryl or hydrogen; Taft gives a separate E series for benzoic acids.

Several reported attempts to relate E_s values to empirical van der Waals radii have given no generally useful results.^{1,3} In this paper we develop a procedure for calculating E_s values for R alkyl or cycloalkyl based on hydrocarbon models, the isoalkane RCH(CH₃)₂ being taken as the structural analogue of RCOOEt, and the neoalkane RC(CH₃)₃ as the analogue of RC(OH)₂OEt, the tetrahedral intermediate. A previous attempt based on RCH₂CH₂Et-RCMe₂CH₂Et pairs gave relatively poor results,⁴ but might be improved by the techniques we have used.

The postulate is that the difference in "strain" energies between neoalkane-isoalkane pairs, computed for the gas phase at 298 K, may parallel activation energy differences between starting esters and their tetrahedral intermediates. This requires that solvation and entropy factors remain constant or proportional to "strain" energies for all esters treated. There is no a priori way to calculate that this condition will hold. It is also clear that isoalkanes are not the best possible structural analogues for esters; acids RCOOH, for example, are closer. We will report later on the use of such "improved" models.

For present purposes we will use enthalpies of formation,

(ΔH_f°) as the thermodynamic property related to E_s . The justification is that we are interested in strain energy differences, and much of the strain energy is reflected in the enthalpy of formation.

Hydrocarbon models have an especially important advantage: there are more extensive data and better estimation procedures for the thermodynamic properties of hydrocarbons than of any other class of compounds.⁵ Direct experimental values, however, are available for only a few trivial pairs, and it is therefore necessary to resort to estimation. Many dozens of empirical recipes have been used for estimating enthalpies of formation of hydrocarbons⁶ and the powerful methods of molecular mechanics have also been explored by several groups.¹²⁻¹⁸ It was our hope that by focusing initial efforts on a critical use of hydrocarbon models we could maintain a reasonable check against temptation to resort to procedures only weakly grounded on experimental data.

Any success of relating $\Delta\Delta H$ to E_s depends primarily on how well the strain component can be evaluated. Examination of typical empirical procedures for estimating enthalpies of formation shows that their success is oblivious to serious deficiencies in treating strain. The strain component is only a small fraction of the total enthalpy of formation and can be absorbed by other terms. These deficiencies would become apparent if experimental data were available for a sufficient range of strained molecules, but such all-important data are scarce indeed.

As an example, the Franklin protocol⁷ predicts a total of just three distinct $\Delta\Delta H$ values for the 24 neoalkane-isoalkane pairs to which it is applicable, and in consequence provides no correlation at all with E_s values. As another example, of all the methods we have used, the Allen protocol⁸ provides the best calculated enthalpies of formation for the compounds in Table