

Southwestern Analytical Chemicals, Inc.), was purified in the same manner.

Before each experiment, the electrolyte was dried for 4 h at 80 °C under high vacuum, and the solvent was degassed by using a three-cycle freeze-pump-thaw sequence. The platinum and glassy carbon electrodes (Atomergic Chemetals Corp.) were cleaned with nitric acid and were then polished with aluminum polishing powder (0.3 μm).

Instrumentation. Electrochemistry was performed on a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a Universal Programmer. The current-voltage curves were recorded on a Houston Instruments X-Y recorder, and current flow was monitored with a PAR Model 179 digital coulometer. The electrochemical cell was a standard three-electrode cell (volume 3–20 mL) with an adaptor for adding solids attached to the side. The cell was equipped with a glassy carbon working electrode (0.05 cm²), a platinum coil counterelectrode, and a silver wire reference electrode when cyclic voltammograms were obtained. For preparative oxidations, a platinum mesh working electrode, a platinum coil counterelectrode (with surface area twice that of the mesh), and a silver wire reference electrode were used.

Electron spin resonance (ESR) measurements were made with a Varian E-9 EPR spectrometer equipped with a Varian E-101 microwave bridge in a conventional or a specially constructed cell designed to allow simultaneous electrolysis and ESR monitoring.

Cyclic Voltammetry. A standard three-electrode cell was equipped with clean electrodes and 0.1 g of purified electrolyte (vide supra). The degassed solvent was then added via syringe. The solvent window (between -3.5 and +2.5 V for CH₃CN) was scanned to ensure the absence of air, water, or other impurities. Solid 1 or 2 was added to the solvent-electrolyte mixture to make a solution approximately 5 mM in hydrocarbon. 2 was transferred to the cell in a helium-filled drybox in order to completely exclude oxygen from the system. The electrochemical measurements were conducted at varying temperatures and scan rates (-78 °C to ambient temperatures; 0.2–10 V/s). Each experiment was referenced, after all scans had been taken, by adding ferrocene (5 mM), a compound whose redox behavior is known.¹⁷

Controlled Potential Electrolysis of 1. The standard two-chamber electrochemical cell was charged with solvent (5 mL of CH₃CN), electrolyte (230 mg of TBAFB, 0.17 M), and 1 (5 mg, 5 mM) as described above. After the mixture was cooled to -20 °C, a constant potential of 0.6 V was applied at the working

platinum electrode, and the current passed was measured by standard coulometry. When current flow ceased, 0.8 Faraday/mol had been taken up. The resulting solution was quickly transferred, under an inert atmosphere, to an argon-filled ESR tube and frozen by immersion in liquid nitrogen. The sample so obtained was transferred to the cavity of the ESR spectrometer. No interpretable signals were observed as the solution warmed from -78 °C to room temperature.

The coulometry was also conducted in a specially designed cell in which two platinum wires were inserted into a standard ESR tube. The cell was charged with a degassed solution of 1 (3.5 mg) and TBAFB (32 mg) in 1 mL of CH₃CN and inserted into the cavity of the ESR spectrometer. Current flow was monitored as the electrooxidation proceeded at room temperature. No interpretable ESR signals were detected. The oxidation ceased when 0.8 Faraday/mol of 1 had been taken up.

Calculations. The calculations were carried out by using the standard MNDO⁸ format. All geometries were optimized by the standard Davidson-Fletcher-Powell procedure, with no assumptions of any kind being made. All stationary points were characterized by using force-constant calculations, i.e., by diagonalization of the Hessian matrix. Local minima on the potential surface were characterized as possessing only positive eigenvalues. Transition states were identified as structures possessing one and only one negative eigenvalue. Reaction path calculations for the 6⁺ to 7⁺ (Figure 6) and the 6⁺ to linear C₄H₄⁺ (Figure 7) conversions were accomplished by progressive expansion of the C₁-C₂ bond length and the C₁C₂C₃C₄ dihedral angle, respectively.

Acknowledgment. Work done at the University of Texas at Austin was generously supported by the National Science Foundation and the Robert A. Welch Foundation. M.A.F. is also grateful for the support as an Alfred P. Sloan Foundation Research Fellow and as a Camille and Henry Dreyfus Teacher-Scholar. The assistance of Professor E. P. Kyba in the drybox manipulations described here is gratefully acknowledged.

Registry No. 1, 66809-06-1; 2⁺, 72952-86-4; 6⁺, 80826-01-3; 7⁺, 34531-09-4; 8⁺, 82323-59-9.

Supplementary Material Available: Appendixes I-III containing bond lengths, bond angles, and dihedral angles for the tetrahedrane, cyclopropylcarbinyl, and cyclobutadiene radical cations (2 pages). Ordering information is given on any current masthead page.

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Photolysis of the Cyclooctadienyl Anion

Marye Anne Fox* and Nancy J. Singletary

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

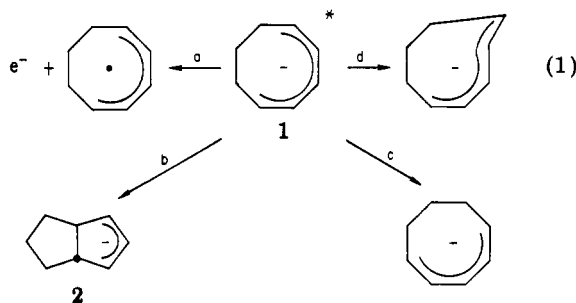
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Visible or long-wavelength ultraviolet excitation of alkali metal salts of cyclooctadiene leads to electron exchange. Primary photoinduced electron transfer has been used to initiate the geometrical isomerization of *cis*-stilbene and the photosubstitution of aryl halides. Mechanistic details for these reactions are presented. Electron exchange so dominates the excited-state reactivity of this pentadienyl anion that neither potential pericyclic reaction (i.e., electrocyclicization or sigmatropic shifts) nor photoinduced *cis*-*trans* isomerization can be detected.

The photochemistry of stable carbanions has been incompletely characterized,¹ and the factors which dispose an excited anion to prefer one possible reaction path to others are completely unknown. We have examined in detail the photoreactions of the cyclooctadienyl anion 1,

in order to examine how excitation energy in a typical delocalized anion is partitioned among several possible reaction modes. This represents the first mechanistic study of a resonance-stabilized anion in which photoinduced intramolecular pathways, i.e., eq 1, electrocyclicization, sigmatropic shifts, and/or *cis*-*trans* isomerization might reasonably be expected to compete with intermolecular electron exchange. We have found that the

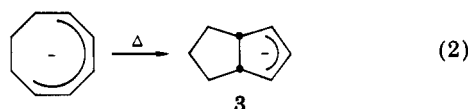
(1) Fox, M. A. *Chem. Rev.* 1979, 79, 253.



excited-state chemistry of 1 is dominated by electron transfer (eq 1a) even though formally allowed pericyclic reactions could have been envisioned.

Background

Treatment of 1,3-, 1,4-, or 1,5-cyclooctadiene with strong base or with alkali metals²⁻⁴ gives rise to alkali metal salts of 1. The NMR spectrum of the lithium salt shows 1·Li⁺ to contain a nonplanar π system with a puckered ring,² and its thermal conversion to a cis-fused bicyclic anion 3 (eq 2) has been described.⁴



At temperatures below 0 °C, anion 1 is stable for long periods (at least 2 weeks) in degassed, aprotic solvents, e.g., ammonia or tetrahydrofuran. In the presence of electron acceptors having reduction potentials less negative than about -1.7 V (e.g., nitrobenzene), however, a rapid reaction ensues in which the intense red color characteristic of alkali metal salts of 1 fades. This subset of acceptors includes a variety of functional groups (e.g., alkyl halides, carbonyl compounds, aryl bromides and iodides, easily reducible aromatic hydrocarbons, etc.), and so far no clear mechanistic distinction between single electron transfer and nucleophilic attack in these reactions of 1 has been made. Nonetheless, in the absence of acceptors, 1 resists intramolecular reaction, and its photochemistry can be studied conveniently.

Results

In the absence of an electron acceptor, broad-band ultraviolet-visible irradiation of 0.01 M solutions of the lithium, potassium, or magnesium salts of 1 at 0 °C in NH₃ or THF led to no discernible change even after 24 h, and a mixture of 1,4- and 1,3-cyclooctadiene could be recovered essentially quantitatively after quenching the reaction mixture with water. When the 3-deuterated salts 4 were similarly irradiated in an NMR tube at 20 °C for 72 h, no NMR signals indicative of a nondegenerate [1,6] sigmatropic shift (eq 3) could be detected.

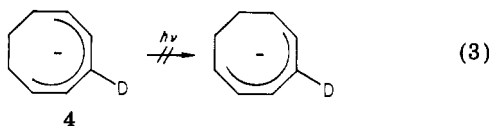
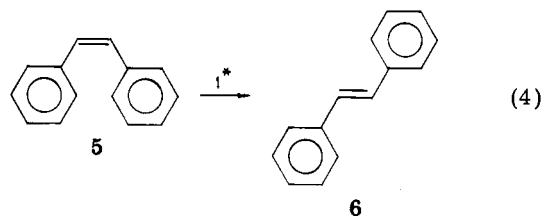


Table I. Photolysis of Cyclooctadienylpotassium and *cis*-Stilbene^a

irradn time	absolute recovery of <i>cis</i> -stilbene and conversion to products, %			
	5	6	7, 8	9
30 min	high	ca. 2	neg	neg
70 min	46	14	5	neg
90 min	66	16	8	neg
110 min	63	18	12	neg
3 h	67	14	11	neg
5 h	47	15	18	8
14 h	1	5	20	63
0 h ^b	84	2	4	neg

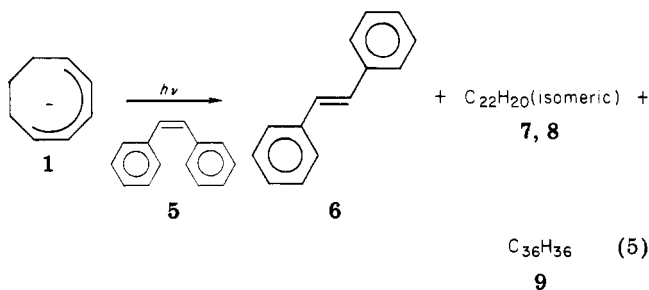
^a 0.04 M 1·K⁺ and 0.01 M 5 in THF, -65 °C, $\lambda > 360$ nm, followed by water quench. ^b Dark reaction: mix mixture held at -65 °C for 14 h.

When 1 is excited with long-wavelength ultraviolet light ($\lambda > 360$ nm) for relatively short periods (10 min to 3 h) in the presence of *cis*-stilbene (5), isomerization to *trans*-stilbene (6) occurred (eq 4). (Under these condi-



tions, 1 absorbs >99% of the incident light.) A parallel excitation of a 1/6 mixture gave essentially no isomerization to *cis*-stilbene; i.e., the initial rate of the *trans* → *cis* isomerization was at least 20 times greater than the reverse isomerization. When the 1/*cis*-stilbene photolysis mixture was quenched with D₂O, no deuterium incorporation (<1%) into the photoproduct *trans*-stilbene was observed. If a heavily deuterated 1 (*d*₇-*d*₉)/5 mixture was similarly irradiated, the isolated *trans*-stilbene remained undeuterated. Flash photolysis of a 1/5 mixture with a N₂ laser produced an absorptive transient at ca. 500 nm.

After longer irradiation periods (2–20 h), adduct formation (eq 5) was found to accompany the geometrical



isomerization. Both 1:1 and 1:2 adducts of 1 and stilbene were observed (eq 5). The relative yields of the three products varied with time. As shown in Table I, the formation of 6 peaked at 20% absolute conversion of *cis*-stilbene and then declined. The formation of the 1:1 adduct (7, 8) increased more slowly, but plateaued at about 20% conversion. The 1:2 adduct (9) was formed more slowly but became the predominant product at complete conversion. The 1:1 adduct was isolated as an inseparable mixture of isomers (see Experimental Section), but the isolation of pure 1:2 adduct was frustrated by polymerization during workup.

Geometrical isomerization of 5 was also observed upon heating a mixture of 1 and 5 to room temperature or above, but competing side reactions (i.e., ring closure of 1 and

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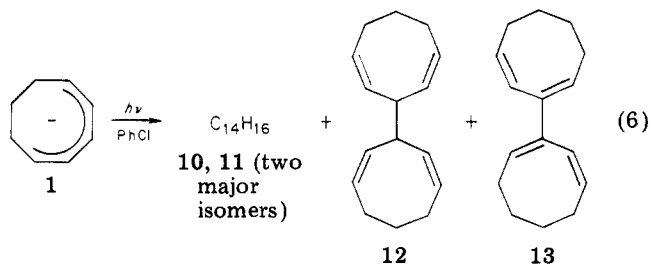
(4) Bates, R. B.; McCombs, D. A. *Tetrahedron Lett.* 1969, 977.

(5) Förster, T. Z. *Elektrochem.* 1950, 54, 531.

(6) Brauman, J. I.; Schwartz, J.; van Tamelen, E. E. *J. Am. Chem. Soc.* 1968, 90, 5328.

polymerization) made quantation of the reaction difficult.

Low-temperature photoexcitation of a 1:1 mixture of the lithium or potassium salts of **1** and chlorobenzene (2-h irradiation with a filtered medium-pressure mercury arc ($\lambda > 400$ nm) as 0.01 M solutions in THF) gave rise to a mixture of isomeric alkylated products **10** and **11** (eq 6).



No alkylation could be observed under the reaction conditions in the absence of light. This cross-coupling was accompanied by formation of $C_{10}H_{22}$ tetraenes **12** and **13**.³ The mixture of the latter compounds was identical with that obtained upon mixing **1** with nitrobenzene.

Similar reactivity could also be observed with other more easily reduced aryl halides. Upon mixing **1** with 9-bromoanthracene at -70 °C, for example, 9-(cyclooctadienyl)-9,10-dihydroanthracene (**14**, 78%) was isolated along with dimers **12** and **13**. The dark reaction of **1** with 1-bromonaphthalene at 0 °C gave rise to naphthalene (54%), 1-(cyclooctadienyl)naphthalene (**15**, 24%), and dimers **12** and **13** (10–15%), but no net reaction was observed at -70 °C (although an immediate color change from red-orange to black occurs upon mixing of the reagents). The products obtained in eq 6 could also be isolated from irradiation of a bromobenzene/**1** mixture at -70 °C or by warming such a mixture to 0 °C for 2 h.

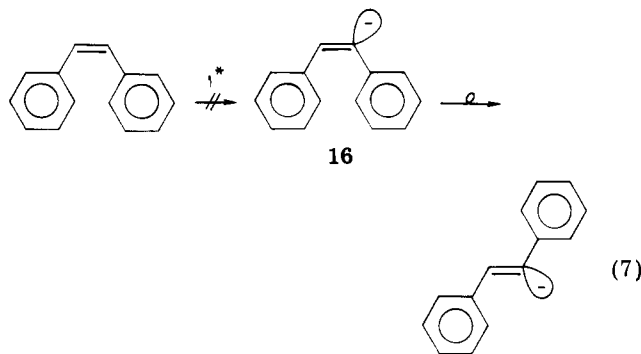
Discussion

At first glance, the efficient intermolecular photoreactions of **1** (as a sensitizer for the geometrical isomerization of *cis*-stilbene and as an alkylative participant in the photosubstitution of chlorobenzene) seem to bear little resemblance to each other and appear to contrast sharply with the resistance of **1** to intramolecular photorearrangement. In fact, however, the range of reactivity can be easily understood if the dominant primary photoprocess involves excited-state oxidation (i.e., electron loss).

Electron-Transfer-Initiated Geometrical Isomerization of Stilbene. Consider first the sensitized geometrical isomerization of *cis*-stilbene (eq 4). This conversion can be explained in several ways. Among these are (1) photoenhanced basicity in excited **1** leading to deprotonation of stilbene and isomerization of the resulting vinyl anion, (2) energy transfer from excited **1** to stilbene, (3) excitation of a charge transfer complex of **1**/stilbene in which geometric isomerization occurs, or (4) a photoinduced electron transfer (eq 1a) in which the acceptor radical anion isomerized to its geometric isomer before restoring its electron to oxidized **1**.

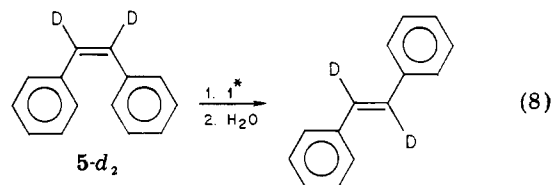
In the first mechanism, the excited state of **1** becomes sufficiently basic to deprotonate stilbene, generating a vinyl anion **16** in which rapid geometrical isomerization could occur (eq 7).

Examples are known in which enhanced basicity is observed in the excited state,^{1,5,6} and similar reactivity changes have been invoked to explain the photochemistry of cyclopentadienide⁷ and cyclononatetraenide.⁸ Fur-



thermore, although the stilbenyl anion is conformationally stable in the presence of proton donors,⁹ it rapidly isomerizes in THF at low temperature in the absence of quenchers.^{10,11}

If our photoinduced geometrical isomerization proceeds entirely through the stilbenyl anion, this anion must either persist through the photolysis or be protonated as it is generated by some acid present in the photolysis mixture. A persistent vinyl anion is excluded by the absence of deuterium incorporation in photoproducted *trans*-stilbene obtained after a D_2O quench, by the absence of 1,2-diphenylpropene when the photolysis mixture was quenched with methyl iodide, and by the retention of two deuterium atoms in the *trans*-stilbene generated after an H_2O quench of the mixture obtained after the excitation of **1** in the presence of $5-d_2$ (eq 8). Independent generation of the



stilbenyl anion **16** in THF at about -65 °C, followed by a D_2O quench, shows major ($\sim 90\%$) incorporation of deuterium (*trans*-stilbene-*d*).

These experiments also render the involvement of a transient vinyl anion unlikely, for such a species remains a permissible intermediate only if it is rapidly reprotonated as it is formed. The incorporation of deuterium upon D_2O quenching of independently prepared **16** implies that neither THF nor any side product derived from the deprotonated stilbene can reprotonate **16**. The only alternate proton source at low conversion is photogenerated cyclooctadiene. The absence of deuterium incorporation ($< 1\%$) in the *cis*- and *trans*-stilbenes recovered upon photolysis of heavily deuterated cyclooctadienide (predominately d_7 - d_8), followed by an H_2O quench, indicates that any transient vinyl anion is not reprotonated by cyclooctadiene. We conclude, therefore, that the isomerization cannot proceed solely through the vinyl anion.

The second mechanistic possibility requires that an excited state of **1** transfer its energy to *cis*-stilbene, generating an excited state from which geometrical isomerization results (eq 9). The absorption band ($\lambda_{max} \sim 470$ nm) for **1** places the energy of its first excited singlet state below 61 kcal/mol, a result in accord with the position of the 0,0 band in its fluorescence spectrum. The triplet energy of **1** is unknown, but if comparable singlet-triplet

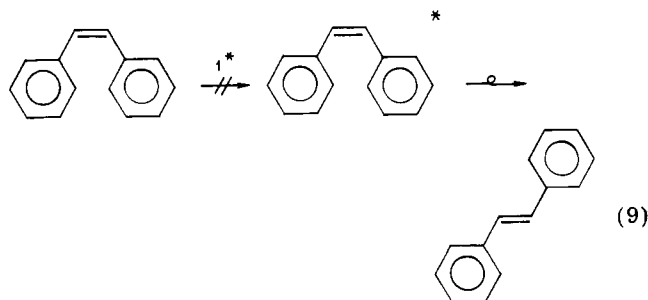
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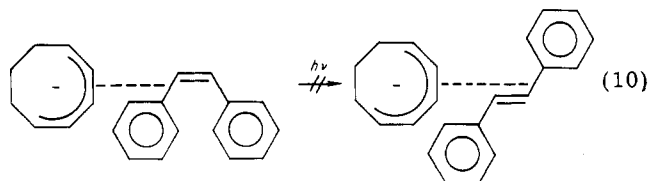
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splitting is encountered in the anion and in the related neutral hydrocarbon, we can estimate E_T for 1 as ~ 25 kcal/mol. Since the singlet and triplet energies for stilbene are 94¹² and 57¹³ kcal/mol, respectively, conventional energy transfer in either the singlet or triplet modes or through a "stilbene phantom triplet" ($E_T = 49\text{--}57$ kcal/mol) should be endothermic. Furthermore, the classical studies by Hammond et al.¹³ of the triplet-sensitized isomerization of stilbene have clearly shown that the steady-state *cis/trans* ratio depends on the triplet energy of the sensitizer. In our photoreaction, the initial rate of conversion of *cis*- to *trans*-stilbene is at least 20 times greater than the reverse isomerization. Thus, were photoequilibrium established, a *trans/cis* ratio >20 would be observed. Conventional triplet sensitization leads to photostationary mixtures dominated by the *cis* rather than the *trans* isomer. With low-energy sensitizers ($E_T < 45$ kcal/mol), a *trans/cis* ratio greater than 1 has been reported, but the mechanism, which has not been investigated, clearly differs from that observed with conventional triplet sensitizers.

The third option involves isomerization within an excited charge-transfer complex (eq 10).

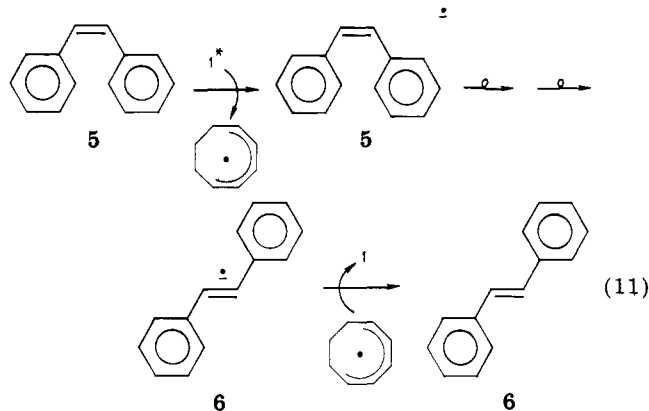


Ground-state charge-transfer intermediates are probably not involved since the visible absorption maximum of cyclooctadienylpotassium in THF of -25 °C remains unchanged by a sixfold excess of *cis*-stilbene. Nor could any evidence for exciplex formation between 1 and 5 be obtained.

Marked color changes which accompany the low-temperature mixing of 1 with several arenes or aryl halides, however, suggest that charge-transfer complexation may be involved with other electrophiles. Exciplex-intermediated radical-ion-pair formation between stilbene and electron-rich aromatic donors has been observed with CIDNP techniques.¹⁴

The fourth option, photoinduced electron transfer from 1 to 5, is mechanistically appealing. In this process (eq 11) the radical anion of 5, formed upon electron donation from 1,* isomerizes to the *trans* radical anion before back-transferring the photoejected electron.

The evaluation of such an electron exchange requires that both the reduction potential of 5 (-2.2 V vs. SCE)¹⁵



and the oxidation potential of 1 be known. An irreversible wave was found by cyclic voltammetry by using the solvent system and techniques described by Breslow¹⁶ (glassy carbon, TBAP, HMPA/THF, -70 °C) for the lithium salt of 1 at -1.7 ± 0.1 V (vs. SCE). This value compares with -1.6 ± 0.1 V observed for the oxidation potential of the allyl anion¹⁶ and implies that extension of the conjugated system from three to five atoms does not profoundly alter the difference in resonance stability between such an anion and its oxidation product (the delocalized free radical).

Although the oxidation of 1 in the absence of acceptors is irreversible, and hence its peak potential lacks thermodynamic relevance, we can use the observed potential to roughly gauge the efficiency of electron exchange.¹⁷ Using these potentials, we conclude that the transfer of an electron from 1 to 5 should be endothermic by about 12 kcal/mol. While this process is thermally insignificant at -65 °C, it can easily be driven by the energy available from light absorption at 470 nm. Furthermore, an absorptive transient at 500 nm (3^- absorbs at 490 nm)^{15,18} can be observed when a 1 + 5 mixture is flashed with a N_2 laser.

If the radical anion of *cis*-stilbene can be formed, a nearby complete isomerization to 6 should ultimately be expected, for Szwarc has shown that $5^{\cdot-}$ can be converted directly or stepwise through a stilbene dianion to $6^{\cdot-}$.¹⁹ Since 6 is reduced at a more negative potential than that at which 1 is oxidized, reverse thermal electron transfer (from $6^{\cdot-}$ to the cyclooctadienyl radical) will give rise to the observed products, 1 and *trans*-stilbene. Since subsequent reaction can occur, it is not surprising that the photoactivation with visible light at low temperature initiates an electron-transfer-mediated reaction.

For the same reason, thermal activation, i.e., heating a mixture of 1 and 5 in THF above room temperature, also leads to the geometrical isomerization of 5. This thermal reaction is complicated, however, by ring closure of 1 and by side polymerization of cyclooctadiene and of 5. A clear advantage for photochemical initiation of this electron transfer thus exists. That electron exchange also occurs thermally can be established, however, by the observation

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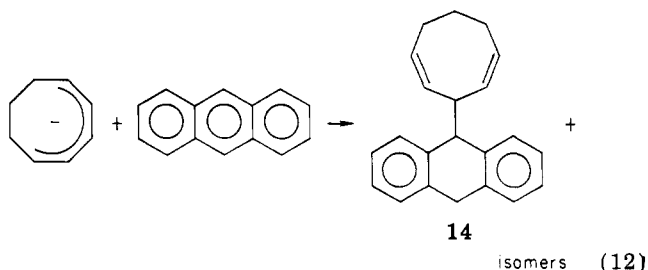
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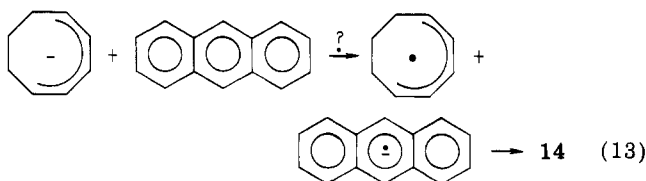
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of the previously described ESR spectrum of the stilbene radical anion^{20,21} upon mixing 1 with 5 at the ambient probe temperature of an ESR cavity ($\sim 30^\circ\text{C}$).

When the reduction potential of a potential aromatic hydrocarbon acceptor becomes less negative, electron exchange should be efficient. With anthracene ($E_{\text{pc}} = -1.95$ V vs. SCE²²), for example, adduct formation occurs upon mixing (eq 12). No distinction has been made about



whether such reactions^{23,24} occur by initial single electron transfer (eq 13) or by conventional nucleophilic (two electron) addition. Nonetheless, signals characteristic of

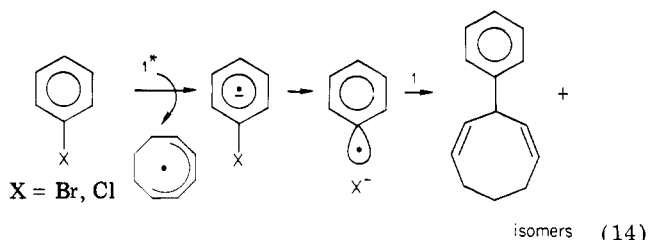


the anthracene radical anion²³ appear during adduct formation if the thermal reaction of 1 and anthracene is monitored in an ESR cavity.

Additional support for the involvement of radicals in the reaction of 1 with *cis*-stilbene can be found in the formation of a mixture of double bond isomers of dicyclooctadienyl³ and of 1:1 and 1:2 cyclooctadiene/stilbene adducts as side products of the isomerization. These products are identical with those obtained by independent generation of the cyclooctadienyl radical in the presence of cyclooctadiene and *cis*-stilbene, respectively. The formation of 1:2 adduct has precedent in the isolation of an analogous species from the thermal reaction of an alkyl-lithium with *trans*-stilbene.²⁵

Electron-Transfer-Initiated Reactions with Aryl Halides. If the primary photoprocess observed upon excitation of 1 involves electron ejection, the photoreaction of 1 with chlorobenzene and other aromatic halides can also be readily understood. The radical anions of aryl halides are known to rapidly cleave to aryl radicals and halide ions,²⁶ making the photoinduced electron transfer to chlorobenzene essentially irreversible and allowing the formation of ion-radical coupling products (eq 14).

This reaction is the photochemical analogue of thermal electron transfers observed by Russell²⁷ and is clearly related to Winkler's photochemical addition of butyllithium



to anthracene,^{23,24} to Tolbert's photomethylation of triarylmethyl anions in Me_2SO ,²⁸ and to Bunnett's photoinduced $\text{S}_{\text{RN}}1$ reactions.²⁹

An electron-transfer pathway also provides a convenient rationalization for the relative ease with which 1 reacts with the series of aryl halides. Consider the series of aryl bromides for example: 1 reacts rapidly upon being mixed at -70°C with 9-bromoanthracene (17), but heating to 0°C is required for thermal activation of the reaction of 1 with 1-bromonaphthalene (18) or bromobenzene (19). When mixed with 1 at -70°C , 18 immediately forms an intensely colored charge-transfer complex, but no such color develops upon mixing 1 with 19. This reactivity ordering is consistent with an increasing degree of electron transfer as 1 interacts with 19, 18, and 17. Although the bond-dissociation energies for the aryl bromide bond decrease along this series (70.3, 65.6, and 60.2 kcal/mol, respectively³⁰), the reactivity difference is more significant than would be expected for a 5-kcal/mol energy difference. The reduction potentials of these compounds (-2.2 , -1.85 , and -1.33 V, respectively³⁰) also follow the same order but provide a more acceptable rationale for the difference in reactivity seen in the series. Given the observed oxidation potential of 1 (*vide supra*), one would predict that the thermal electron exchange should occur rapidly and irreversibly with 17, reversibly with 18, and very slowly with 19, i.e., exactly the reactivity ordering observed. That products characteristic of electron-transfer-initiated Ar-X cleavage can be observed upon photoactivation of 1 in the presence of bromo- or chlorobenzene ($E_{\text{pc}} \approx 2.5$ V vs. SCE³¹) again supports photoinduced electron transfer as the primary photoprocess in the photolysis of 1.

Alternate Reaction Pathway. Electron photoejection in the absence of electron acceptors is expected to be followed by recombination too rapid to allow diversion of the pentadienyl radical to coupling products or to other products. In addition, however, several alternate energy-dissipating pathways are conceivable in 1: (a) an orbital topology controlled electrocyclization to form a highly strained bicyclic anion (eq 1b), (b) a photochemical *cis*-*trans* isomerization about one of the partial double bonds of the pentadienyl system (e.g., eq 1d), or (c) a photoinduced suprafacial 1,6 hydrogen shift (eq 1c).

Neither spectroscopic monitoring (an unaltered low-temperature NMR of the photolysis mixture obtained after exhaustive irradiation of 1) nor product analysis (nearly quantitative recovery of 1,3- and 1,4-cyclooctadiene after proton quenching) gave evidence supportive of electrocyclization (eq 1b). The difficulty in electrocyclization cannot be attributed to a lack of interaction between the ends of the pentadienyl system, for the thermal formation of the *cis*-fused isomer⁴ (eq 2) attests to the geometric feasibility of some interaction.

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Exclusive formation of anion **3** in the thermal reaction involves stereochemistry consistent with that predicted in an orbital topologically controlled electrocyclicization of this 6- π -electron system, and many examples are known in which such considerations dictate the stereochemical course of anionic thermal reactions.³² Rearrangement to ion **3** would also be predicted, however, by thermodynamic considerations. The strain introduced by trans fusion in **2** is unknown, but the energy difference between cis- and trans-fused bicyclo[3.3.0]octanes is about 6 kcal/mol.³³ The introduction of three sp²-hybridized atoms will increase this strain appreciably: MNDO calculations³⁴ indicate that **2** is 25 kcal/mol less stable than **3**. On this basis, and assuming comparable solvation in 1-3, we estimate that the conversion of the **1** to **2** would be endothermic by at least 20 kcal/mol. Since a significant fraction of this strain would be encountered as well in the transition state for ring closure, the absence of significant amounts of cyclization product **20** can be easily rationalized. Thus, photocyclization does not appear to be an attractive route for the preparation of highly strained anions.

Photochemical cis-trans isomerization (path 1d) is known both for the parent diene³⁵ and for acyclic anions.^{36,37} *cis,trans*-Cyclooctadiene is sufficiently stable to allow its analysis by GLC, but much lower barriers for rotation are encountered about the partial double bonds (of anions³²) than in dienes. The absence of detectable *cis,trans*-cyclooctadiene in the acid-quenched mixture obtained after a 3-h low-temperature photolysis of **1** thus implies either the absence of geometric isomerization, a low quantum yield for the photoconversion (i.e., that thermal equilibration of the *cis,trans*-cyclooctadienyl anion **20** is fast enough to swamp out its rate of formation), or that preferential protonation of **20** occurs at (1) to give only *cis,cis*-1,3-cyclooctadiene.

A distinction between the first and the latter two possibilities would be possible if **20** could be generated independently. Unfortunately, bases of sufficient strength to deprotonate *cis,trans*-cyclooctadiene acted as nucleophiles rather than bases, leading to isolable adducts.

A photochemical [1,6] sigmatropic hydrogen shift (eq 1c) would result in degenerate rearrangement of **1**. As such, this process would only be observable if **1** were appropriately labeled. Although such shifts are known in pentadienyl anions when a thermodynamic driving force exists,³⁸ a degenerate shift (as in **1**) has never been established. Deuteration at the 3-position of **1**, however, lifts the degeneracy and allows detection of isomerized product. Since the resonances for the C(2) hydrogens of **1** (δ 5.6) appear significantly downfield from that of the C(3) hydrogen (δ 2.9),² spectroscopic monitoring of the intensity of the C(2) signal and its splitting pattern will easily demonstrate the occurrence of the sigmatropic shift illustrated in eq 3. The absence of any change in the NMR spectrum after prolonged irradiation of the potassium salt

of **1** shows that the sigmatropic shift does not represent a significant pathway for the deactivation of the excited state. Although some complexity in the δ 5.6 region developed after 48 h of irradiation of the lithium salt of **1**, the complete splitting pattern characteristic of rearrangement could not be observed. If the altered NMR signals do represent rearrangement, the efficiency of the conversion is at least 100 times lower than the electron-transfer pathway discussed above.

Clearly, neither pericyclic reactions nor *cis/trans* isomerizations represent reaction pathways efficient enough to compete successfully with electron exchange in determining the photoreactivity of **1**.

Conclusions

These reactions provide the first systematic study of the chemical consequences of photoinduced electron transfer in stable carbanions in systems where alternate intramolecular pericyclic reactions are possible. In anion **1**, photoinduced electron exchange completely supercedes other possible reaction modes. In view of the apparent ubiquity of such photooxidations from carbanionic excited states, the main utility of anion photochemistry will probably be found in the generation of reactive free radicals and in the stimulation of catalytic redox reactions.

Experimental Section

Instrumentation. Proton nuclear magnetic resonance (NMR) spectra were obtained at ambient probe temperature on a Varian EM390 (90 MHz), on a Perkin-Elmer R12 (60 MHz), or on a Nicolet NT200 (200 MHz) spectrometer. Low-temperature ¹H NMR spectra were obtained on a Varian A60 60-MHz spectrometer.

Electron spin resonance (ESR) spectra were obtained on a Varian E-9 EPR spectrometer equipped with a Varian E-101 microwave bridge. UV-visible spectra were recorded on a Cary-14 spectrometer. IR spectra were recorded on a Beckman Acculab 7 spectrophotometer. Gas chromatography-mass spectroscopic analysis was performed on a Finnigan Model 4023 automated GC/MS with an INCOS data system. Spectra reported here were obtained with the assistance of Dr. James Hudson, Department of Chemistry, University of Texas at Austin. Low-resolution mass spectra were obtained with a Du Pont 21-491 mass spectrometer.

Laser flash photolysis was performed with a N₂ laser at the Center for Fast Kinetics Research at the University of Texas at Austin with the assistance of James Lynch and Dr. M. Rodgers. Transient absorptions were monitored at right angles with an Oriol xenon lamp, a programmable shutter, a Bausch and Lomb monochromator, and a Hamamatsu Corp. R928 or RCA IP 28 photomultiplier tube.

Vapor-phase chromatography (VPC) was carried out on a Varian Aerograph 920 gas chromatograph with a thermal-conductivity detector or on an Antek 400 gas chromatograph with a flame-ionization detector (FID). Peak integration was performed by triangulation of peak areas or with an Autolab 6300 digital integrator equipped with a teletype. Column conditions and liquid phases are specified where pertinent. Solid supports were Chromosorb P and W.

High-pressure liquid chromatography (HPLC) was carried out with a Waters Associates chromatography pump equipped with a Waters R401 differential refractometer and a Porasil A-packed preparative column.

Cyclic voltammetry was accomplished with a Princeton Applied Research Model 173 potentiostat equipped with a universal programmer (PAR Model 175). Cyclic voltammograms were recorded with a Houston Instruments X-Y recorder.

The 450-W medium-pressure Hanovia lamp used in many of the irradiations was equipped with an Ace Glass Water-flo Cut-off safety device.

Solvents and Reagents. Tetrahydrofuran (THF) and ether (MCB reagents) were distilled under nitrogen from potassium or lithium aluminum hydride. Skelly B was cleaned by stirring with concentrated sulfuric acid, followed by stirring over sodium bi-

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carbonate, filtration through a column of alumina, and distillation. For aqueous work-ups, ether was used as received.

The *n*-butyllithium (*n*-BuLi) was obtained as a 1.6 N solution in hexane from Aldrich. Normality was determined by titration. Potassium *tert*-butoxide (K-*t*-OBu), obtained from Aldrich or Alfa, was dried under vacuum with heating and stored under argon.

cis-Stilbene (**5**) was used as received from Aldrich or distilled under vacuum from calcium hydride or, if discolored, chromatographed from silica gel or alumina and then vacuum distilled from calcium hydride. Other reagents were commercially available and used as received.

General Procedure. All carbanion reactions and preparations were carried out under an argon atmosphere. Most other reactions were carried out under a nitrogen or argon atmosphere. Argon was bubbled through concentrated sulfuric acid and then passed through potassium hydroxide and calcium chloride.

A standard aqueous workup consisted of extraction of an organic solution (usually Skelly B or ether) by aqueous NaHCO₃, saturated NaCl solution, or water, followed by extraction twice with water, with the total volume of aqueous extractions equaling the volume of the organic layer. The organic solution was subsequently dried over MgSO₄. The solvent was removed by distillation or by rotary evaporation. Solutions were concentrated by rotary evaporation to a volume of 1–3 mL for VPC analysis.

Preparation of 1-K⁺. General Procedure. The THF solution of roughly 0.04 M 1-K⁺ was prepared by crystallization of the salt from the reaction of 1,3-cyclooctadiene (**21**) with complex base^{40,41} in THF.

Typically, 0.9 mL (7.5 mmol) of **21** was added to 0.9 g (8.0 mmol) of K-*t*-OBu in 15 mL of THF. With cooling in an ice bath, 10 mL (16 mmol) of 1.6 N *n*-BuLi was added. Stirring at 0 °C was continued for 45 min. With cooling at –70 °C and continued stirring to prevent separation of the THF and hexane layers the yellow salt precipitated from the deep red solution. Vacuum filtration was accomplished by tilting the flask 90° and opening the stopcock to the vacuum. The salt was washed with dry ether and again filtered under vacuum. The salt was dissolved at –60 to –70 °C in 50 mL of THF which was added to the flask with a dropping funnel. The yield and concentration of 1-K⁺ were estimated by titration of an aliquot of the stock solution with diphenylacetic acid in THF⁴² or from the NMR spectrum² with benzene as an internal standard. Yields varied from 20% to 65%.

The visible absorption spectrum obtained at –25 °C (λ_{\max} = 470 nm) was identical with that previously reported⁴³ and remained unchanged by the addition of **5**.

Preparation of 3-Deuterio-1,4-cyclooctadiene (22-3-d). (a) From 1-K⁺. A solution of 1-K⁺ (0.24 mol) in about 50 mL of THF was maintained at 0 °C. Stirring was continued for 30 min, and then the reaction was quenched with about 10 mL of D₂O in 15 mL of THF. The solution was taken up in 250 mL CCl₄, and the resulting solution was extracted with water and dried over MgSO₄. The solvent was removed by distillation under reduced pressure (about 20 mm) provided by a water aspirator. Distillation of the residue [35–38 °C, (20 mm)] yielded 21.4 g (0.20 mol, 83% recovery) of a mixture of **21** and 1,4-cyclooctadiene (**22**) of undetermined deuterium content.

The double bond isomers were separated by silver nitrate complexation of the 1,4 isomer.⁴⁴ The distillate was stirred with 25 g (73 mmol) of 50% aqueous AgNO₃ under argon overnight. The resulting gray-white solid, 1,4-cyclooctadiene-(AgNO₃)₂, was filtered and washed with water. The filtrate was taken up in ether, and the ether layer was extracted once with water. The ether layer contained predominantly **21** and a minor amount of **22**. The aqueous layer and the solid were separately treated with cold concentrated aqueous ammonia. The combined aqueous solutions were taken up in ether. The ethereal solution was extracted with water, and the ether was removed by distillation. Distillation of the residue under reduced pressure (20 mm) gave 3.22 g (30 mmol, 12%) of 1,4-cyclooctadiene-3-d: ¹H NMR (60 MHz) δ 5.2–5.8 (m,

4 H), 2.75 (m, 1 H), 2.2 (m, 4 H), 1.4 (m, 2 H).

(b) Potassium Metal Reduction of 21. The anion 1-K⁺ was isolated as a yellow precipitate according to the method of Nakamura and co-workers.³ The yellow salt, 1-K⁺, was dissolved in THF and quenched with D₂O. After an aqueous workup, 5.47 g (30% recovery) of a mixture of **21** and **22** was collected by distillation from CaH₂ at 44 °C (30 mm). On the basis of the NMR spectrum and VPC (15% FFAP, 3 m × 0.25 in., column temperature (T) = 70 °C) the mixture contained 60% 22-3-d and 40% **21**.

The mixture of isomers (4.6 g) was separated by AgNO₃ complexation of the 1,4 isomer as described above. Distillation yielded 1.3 g (12 mmol, 28%) of 22-3-d virtually free of **21**.

Generation of 4-Li⁺. The anion **4** was prepared by deprotonation of 22-3-d with *n*-BuLi. Butyllithium (1.6 N, 6 mL, 9.6 mmol) was added to 0.8 mL (6.6 mmol) of 22-3-d in 2 mL of THF-d₈ at 0 °C. Upon warming, the solution separated into two layers. The solution was cooled to 0 °C, and aliquots of roughly 0.5–1 mL of the bottom layer were transferred via Teflon tubing to five medium-walled NMR tubes each containing 0.27 mg (0.33 mmol) of benzene. The tubes, lengthened at the top with 5-cm glass tubing for the purpose, were sealed with a flame. A 60-MHz NMR spectrum was obtained at –3 °C for each solution: ¹H NMR δ 5.7 [Br d, 2 H, HC(2), J (HC(2)–HC(1)) = 9 Hz], 2.9 (m, 6 H, HC(1) and allylic H), 2.3 (t, <0.4 H, HC(3), J (HC(3)–HC(2)) = 7 Hz]. Upfield resonances were obscured by hexane. On the basis of the integration of the triplet at δ 2.3, the anion 1-Li⁺ constituted less than 25% of the mixture predominated by 4-Li⁺.

Preparation of 1-MgBr⁺. Compound 1-K⁺ was prepared by the customary procedure. The precipitated salt (15 mmol) was dissolved at 0 °C in 30 mL of THF. The Grignard salt, 1-MgBr⁺, was prepared from 1-K⁺ by counterion exchange.⁴⁵ Upon addition of a THF solution of 1-K⁺ to precipitated freshly prepared MgBr₂⁴⁵ the deep red solution rapidly became bright pale yellow.

Irradiation of 1-K⁺. Irradiation of 0.1 M of 1-K⁺ in THF was carried out in a quartz, a Pyrex, and a foil-covered test tube. The tubes, each containing 5 mL of the stock solution, were suspended about 8 in. from a 450-W medium-pressure Hanovia lamp in a water-cooled quartz condenser. Photolysis was continued for 28 h at 27 °C. The solutions had not changed perceptibly in color from the original bright red. The solutions were quenched with water and an ethereal solution was extracted with saturated NaCl and water. Internal standards for VPC determination of recovery and yield were 1,5-cyclooctadiene and biphenyl. Equal "dark" formation of **3** was observed in all cases.

Photolysis of 4-Li⁺. Two of the tubes described above were covered in foil, and all five tubes were suspended in a Pyrex Dewar flask containing 2-isopropyl alcohol (IPA) cooled to –25 °C with a Flexicoil cooling apparatus. The tubes were irradiated in a Rayonet Photochemical Reactor equipped with 16 350-nm lamps for 110 h. The NMR spectrum was essentially unchanged from the initial spectrum in both the irradiated and dark tubes.

By use of the above procedure, 4-Li⁺ was transferred to a quartz NMR tube containing 0.030 mL (0.33 mmol) of benzene. The tube was capped, and the cap was sealed with parafilm. The NMR tube was suspended in an IPA-filled Dewar container with a quartz window. Cooling to –13 °C was accomplished with a Flexicoil cooling probe. Irradiation by a 450-W medium-pressure Hanovia lamp in a water-cooled quartz condenser about 4 in. from the window was continued for 86 h. The NMR spectra at 14 h (60 MHz, 0 °C) and at 62 and 86 h (90 MHz, ambient probe temperature) showed no significant changes compared to the initial spectrum.

Photolysis of 1-MgBr⁺. Three 5-mL aliquots of 1-MgBr⁺ were transferred by syringe to a quartz, a Pyrex, and a foil-covered test tube. Two aliquots were transferred to two Pyrex NMR tubes. All tubes were suspended about 8 in. from a 450-W medium-pressure Hanovia lamp in a water-cooled quartz condenser.

The white solid, KBr, eventually settled in each tube. Irradiation was continued for 36 h. The solutions were quenched with water and taken up in ether. An aqueous workup followed. No products were detected by VPC other than **21** and **22** and minor yields of unresolved dimers **12** and **13**.

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Preparation of *cis*-Bicyclo[3.3.0]oct-2-ene (3).⁴ The solution of 4-Li⁺ which had been irradiated through quartz for 86 h was allowed to warm to room temperature. At 6.5 h a broad singlet (HC(2) of 28-3-d) about equal in intensity to the doublet at δ 5.7 (about 50% conversion) appeared at δ 5.4. After 5 days, the doublet at δ 5.7 and the multiplet at δ 2.85 had disappeared.

The solution was quenched with H₂O and taken up in Skelly B. The organic layer contained 21, 22, and 3. Preparative VPC (15% FFAP, 3 m \times 0.25 in., 90 °C) yielded 0.0132 g of 2-3-d: ¹H NMR (90 MHz) δ 5.35 [br s, 1 H, H-C(2)], 3.0 [br s, 1 H, H-C(1)], 2.45 [m, 2 H, HC(4)], 1.0–2.2 [m, 8 H (7 H expected)]⁴.

Analogous reaction of 1-K⁺ (vide supra) gave rise to 2 identical with that reported by Bates.⁴

Reaction of *cis,trans*-1,3-Cyclooctadiene (23) with Base. Method 1. Reaction with *n*-BuLi. Addition of 1.5 mL (2.4 mmol) of 1.6 N *n*-BuLi to 0.175 mL (1.5 mmol) of *cis,trans*-1,3-cyclooctadiene (23)^{46,47} in 20 mL of THF at -60 °C caused the solution to turn bright yellow. Addition of about 0.1 g of K-*t*-OBu caused the yellow solution to turn orange. The solution was quenched with water and taken up in Skelly B. Preliminary VPC analysis (15% TCEP, 3 ft \times 1/8 in., T = 53 °C, injector temperature = 110 °C) of the organic layer showed that 23 was recovered along with C₄H₁₀ adduct(s).

Analogous reaction with 1 equiv of complex base gave only recovered 24 and C₄H₁₀ adduct.

Method 2. A solution of 0.100 mL (0.83 mmol) of 23, 0.6 mL (0.96 mmol) of 1.6 N *n*-BuLi, and 0.103 g (0.92 mmol) of K-*t*-OBu in 8 mL of THF was prepared at -70 °C in a 25-mL round-bottomed flask with a Y-shaped adapter leading to two 10-mL round-bottomed flasks. The solution was poured into the two flasks by tilting the 25 mL flask. One of the flasks was covered in foil. The apparatus was suspended in a dry ice/IPA-filled Dewar flask with a quartz window. Irradiation was carried out on an optical bench equipped with a focussing lens, a 250-W medium-pressure mercury arc, and a Corning 0-54 filter. The bath was maintained at -50 °C or below. The solutions were quenched with D₂O and taken up in Skelly B. Under a variety of VPC column conditions, the photolyzed and dark solutions were identical. The relative yields of products were as follows: 28% 21 + 22, 22% C₁₂H₂₂, and 51% C₁₆H₂₂₋₂₆.

Irradiation of 1-K⁺ and *cis*-Stilbene (5). Aliquots (15 mL) of a solution of about 0.05 M 1-K⁺ in THF at 70 °C were transferred via Teflon tubing to Pyrex tubes containing 30 mg (0.167 mmol) of 5 in about 0.5 mL of THF. The solutions were degassed through three freeze-pump-thaw cycles, and the tubes were sealed under vacuum and irradiated at -65 °C by filtered long-wavelength UV light ($\lambda > 360$ nm). A control experiment demonstrated that isomerization by direct irradiation of 5 could account for <3% of the geometric isomerization observed here.

Solutions were quenched with D₂O in THF and taken up in 100 mL of ether and 30 mL of saturated NaCl. The ether layer was subsequently extracted twice with water, dried over MgSO₄, and concentrated for VPC analysis by rotary evaporation.

The 2:1 adduct 9 was detected by VPC (50 cm \times 3 mm column, 5% OV-101, T(initial) = 50 °C, heating at 10 deg/min to 275 °C, retention time 16.5 min for 9 compared to 10.5 min for 7 and 8, for a 2 ft \times 1/8 in. column (15% FFAP, T(initial) = 80 °C, heating at 6 deg/min to 220 °C) retention times for 9 and 7 were 8 and 15 min, respectively. 9 was identified as 2:1 adduct from GC/MS: *m/e* 468 (P).

Resolution of 5 and *trans*-stilbene (6) from 7 and 8 was accomplished on 5–10-ft 15% FFAP columns. Absolute yields and recoveries were obtained by VPC with fluorene or biphenyl as standards. Reported yields are based upon a stoichiometry of 1 mol of stilbene to 1 mol of product. Product distributions are listed in Table I.

The product solutions of two separate photolyses were combined and 2 mg of pale yellow liquid (7 + 8) was collected by preparative VPC (5% SE-30, 3 ft \times 0.25 in., T = 200 °C): 200-MHz NMR (CDCl₃) δ 7.0–7.8 (m, 10 H), 5.5–5.95 (m, 3 H), 3.57 (t, H_B, J_{BA} = J_{BA'} = 7.4 Hz), 3.65 (t, H_B, J_{B'A'} = J_{B'A'} = 7.4 Hz,

combined area of 2 t = 1 H), 3.2 (dd, 2 H, J = 14, 7.4 Hz), 3.07 (dd, J = 15, 8 Hz); mass spectrum, *m/e* 288 (P), 197 (base).

Generation of Stilbenyl Anion. (i) Reaction of 5 with Complex Base. To a solution of 0.13 g (1.1 mmol) K-*t*-OBu and 0.150 g (0.75 mmol) of 5 in 30 mL of THF at -60 °C was added 0.8 mL (2.0 mmol) of 1.3 N *n*-BuLi. The solution was allowed to stand at -40 °C for 30 min and then quenched with 22 mg (0.8 mmol) of methyl iodide. A standard aqueous workup followed. Other than 5 and 6 (20% and 30%, respectively, by VPC: 5 ft \times 1/8 in., 15% FFAP) the major product was α -methyl-*trans*-stilbene (50% by VPC).

Similarly, the reaction of 30 mg (0.17 mmol) of 5 with 2 equiv each of *n*-BuLi and K-*t*-OBu was carried out as described above and, after 5 min, was quenched with D₂O. After a standard aqueous workup, the product mixture was analyzed by VPC and mass spectroscopy. The mixture contained 6 (78% by VPC). Mass spectral analysis indicated predominantly *trans*-17-d.

(ii) Reactions of 1-K⁺ with 5-d₂. Compound 5-d, was prepared by thermolysis⁴⁹ of the ethyl orthoformate of hydrobenzoin-d₂.⁵⁰

A solution of 0.05 M 1-K⁺ in THF at -70 °C was prepared according to the usual procedure. Aliquots of approximately 15 mL were transferred to 35 cm \times 20 mm tubes containing 20 mg (0.11 mmol) of 5-d₂ in 1 mL of THF at -70 °C. One tube was irradiated for 2 h at -65 °C by long-wavelength UV light ($\lambda > 360$ nm), and a second was held in the dark at -65 °C for the same period. The reactions were quenched with H₂O. Two additional tubes were warmed to 0 °C, allowed to stand at 0 °C for 5 min, and quenched in one case with methyl iodide. The FID VPC and GC/MS results showed nearly identical deuterium incorporation in unreacted 5, recovered 5, and recovered 6.

ESR Spectra of Solutions of 1-K⁺ and 5 and of 1-K⁺ and 5-d₂. Solutions of approximately 0.1 M stilbene and 0.1 M 1-K⁺ were prepared at room temperature by the addition of 10 mg (0.06 mmol) of *cis*-17 or *cis*-17-d₂ to 0.5-mL aliquots of 0.1 M 1-K⁺ in THF prepared according to the standard procedure. ESR spectra were obtained at ambient probe temperature promptly after mixing. The ESR signal obtained in the reaction of 1-K⁺ and *cis*-17 was assigned as that of the 5 radical anion.

Flash Photolysis of a Solution of 1-K⁺ and 5. The apparatus employed for flash photolysis of 1-K⁺ and 5 in THF consisted of a 1-cm quartz cell with four polished sides joined at 90° angles to a cylindrical 1-cm tube. The cell was dried by heating under vacuum, and it was then filled with argon. A 2-mL aliquot of 0.05 M 1-K⁺ in THF was added to the tube. The solution was cooled to a -70 °C, and 50 mg (0.28 mmol) of 5 was added. The solution was degassed under vacuum through three freeze-pump-thaw cycles, and the apparatus was sealed with a flame under vacuum.

The transient absorption spectrum of the solution upon room-temperature flash photolysis at 337 nm with a N₂ laser was obtained. A transient absorption maximum appeared at 495–500 nm. The reported λ_{\max} of the 6 radical anion ranges from 480 to 500 nm^{15,19} while the λ_{\max} of the *cis*-17 radical anion has been determined to be 516 nm.¹⁵

Reactions of 1-K⁺ and Aromatic Electrophiles. General Procedure for Carrying Out Reactions. A general procedure was followed for carrying out the reaction of 1-K⁺ with various electrophiles. A solution of 1-K⁺, roughly 0.05 M in THF, was prepared from the filtered salt precipitated as previously described. The approximate molarity of the solution was determined as before by NMR. One, two, or excess equivalents of 1-K⁺ were added to a solution of the electrophile in THF, or the electrophile in THF or as a neat liquid was added to the carbanion salt solution. A reaction temperature of -70 °C was provided by a dry ice/(wet) 2-propyl alcohol bath. The reactions were quenched with several milliliters of water and taken up in 100–200 mL of Skelly B or ether. A standard aqueous workup followed.

Reaction with Anthracene. Excess 1-K⁺ was added at -70 °C to 0.084 g (0.47 mmol) of anthracene in THF. The reaction was quenched after being allowed to stand at -70 °C for 1.25 h. On the basis of the NMR spectrum of the crude product, anthracene was quantitatively converted to a mixture of isomers

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of 9-cyclooctadienyl-9,10-dihydroanthracene.

Reaction with 9-Bromoanthracene (17). Reaction with Excess 1-K⁺. About 1.1 mmol of 1-K⁺ in THF at -70 °C was added to 0.54 mmol of 19. The reaction was quenched after being allowed to stand for 2 h at -70 °C. In the NMR spectrum of the crude mixture the only resonances in the aromatic region were attributable to the double bond isomeric mixture of adducts of 9-cyclooctadienyl-9,10-dihydroanthracene: mass spectrum (mixture), *m/e* 178 (base), 285 (P - 1).

The reaction was repeated with a 1:1 molar ratio of 1-K⁺ to 5 (roughly 5 mmol of 1-K⁺ in THF with 5 mmol 19 at -25 °C), and was quenched with water after 5 min. Reduction product (anthracene) rather than adduct was obtained.

Reaction with 1-Bromonaphthalene (18). Mixing of 1-K⁺ (excess in THF) and 0.135 g (0.65 mmol) of 18 at -70 °C was accompanied by a dramatic color change from bright orange to deep red to black. After 20 min at -70 °C the solution was quenched with water. Only 18, 22, 23, and a minor amount of naphthalene were apparent in the NMR spectrum of the crude product.

The reaction mixture from 0.060 mL (0.43 mmol) of 18 with 8–10 mL of 0.05 M 1-K⁺ for 3.5 h at 0 °C was analyzed on 15% FFAP (10 ft × 1/8 in.). The absence of 1,4-cyclooctadiene (by VPC) indicated that the anion was completely consumed in the reaction. The major volatile products were naphthalene (relative amount 54%), C₁₆H₂₂ tetraenes, 12 and 13 (10–15%), and a product (24%) tentatively identified as cyclooctadienyl-naphthalene: mass spectrum (mixture), *m/e* (relative intensity) 234 (P, adduct, 20), 128 (P, C₁₀H₈, 100). A multiplet at δ 3.6 in the NMR spectrum of the crude mixture was attributed to the adduct: NMR δ 7.2–7.8 (m, 7–8 H), 5.2–6.0 (m, ca. 5 H), 3.6 (m, 0.5–1 H), 1.0–2.8 (m). Decomposition occurred upon repeated attempts to purify this product.

Reaction with Bromobenzene (19). Bromobenzene (45 mg, 0.5 mmol) was added to 8 mL of roughly 0.05 M 1-K⁺ (0.4 mmol) in THF cooled to -70 °C. The reaction was allowed to stand at -70 °C for 1 h. The solution was quenched, and a standard aqueous workup followed. On the basis of an NMR spectrum of the crude mixture only, 19, 22, and 23 were recovered.

Bromobenzene (45 mg, 0.43 mmol) was added to about 8 mL (0.4 mmol) of 0.05 M 1-K⁺ in THF at 0 °C. The solution was allowed to stand at 0 °C for 1.5 h before quenching with water. On the basis of VPC analysis (15% FFAP, 10 ft × 1/8 in.) two major products (partially resolved) were obtained in about 70% yield. GC/MS [mixture, *m/e* (relative intensity) 184 (P, C₁₄H₁₆ adduct, 30), 91 (100)] suggested the formation of phenylated cyclooctadienes. Minor products were C₁₆H₂₂ tetraenes identified by coinjection with authentic material (products of reaction of 1-K⁺ with nitrobenzene).

Reaction with Chlorobenzene. Chlorobenzene was distilled under argon from CaH₂. Aliquots of 15–20 mL of roughly 0.05 M 1-K⁺ in THF were added at -70 °C to 20 cm × 13 mm test tubes (each with two constrictions) containing 0.05 mL (0.49 mmol) of 23 in 0.5–1 mL of THF. The solutions were degassed through three freeze-pump-thaw cycles, and the tubes were irradiated for 4 h at -65 °C by long-wavelength UV light as described previously. Three samples were analyzed: (a) one obtained by irradiation at -65 °C for 4 h, (b) one held in the dark at -65 °C for 4 h, and (c) one held at 0 °C for 4 h.

VPC analysis (15% FFAP, 5 ft × 1/8 in. column, T(initial) = 90 °C, heating at 10 °C/min, biphenyl as a standard, isothermal heating at 50 °C) detected no more than a trace of benzene (by coinjection, possibly no benzene at all) in the photolyzed solution. The lower recovery of 1,4-cyclooctadiene from the photolyzed solution compared to that for the "dark" solution indicated that more anion had been consumed in the photolysis than in the dark reaction. Accordingly, approximately a 20% yield of products (C₁₄H₁₆ adduct) and a rough yield of 20% of C₁₆H₂₂ tetraenes 12 and 13 (by retention times) were obtained in the photolytic reaction compared to 5% yields of each in the dark reaction. Although the products could not be easily resolved on a preparative VPC column, excellent resolution was achieved on a capillary column: sample a; *hν*, -65 °C. The distribution of C₁₆H₂₂ tetraenes was the same as for sample b (dark, vide infra). Two major products (I and II) with similar mass spectra were identified as isomers of 3-phenyl-1,4-cyclooctadiene on the basis of mass

spectra: mass spectrum (I), *m/e* (relative intensity) 184 (P), 155 (100); mass spectrum (II), *m/e* (relative intensity) 184 (P, 55), 91 (100).

For sample b (dark, -65 °C), the only long retention time peaks (ca. 19 min) detected by GC/MS were assignable to unresolved C₁₆H₂₂ tetraenes on the basis of the mass spectrum showing a molecular ion at *m/e* 214: mass spectrum (unresolved isomers), *m/e* (relative intensity) 214 (P, 3), 79 (100).

For sample c (0 °C), the reaction yielded a mixture of I and II similar to that obtained with low-temperature photolysis. The yield of C₁₆H₂₂ tetraenes relative to C₁₄H₁₆ adducts was lower than for sample a, however.

Preparation of Dimers 12 and 13. (i) **Reaction of 1-K⁺ with Nitrobenzene.** To a solution of about 20 mmol of 1-K⁺ in THF was added nitrobenzene (5.6 mL 55 mmol) at 0 °C. After 2 h at 0 °C, the reaction was quenched with water and taken up in Skelly B. A standard aqueous workup followed. By VPC (15% FFAP, 10 ft × 1/8 in. column, CT = 200 °C, biphenyl as standard) two unresolved product peaks of a combined yield of 9.1 mmol (33% yield based on a stoichiometry of 2:1 reactant to product) were detected. This mixture was isolated by silica gel chromatography with Skelly B: NMR δ 5.5 (m, 4 H), 3.2 [m, ca. ~0.5 H, H-C(3) and H-C(1') of 12], 2.2 (m, 4 H); mass spectrum, *m/e* 214 (P, C₁₆H₂₂, 12 and 13).

The liquid collected by silica gel chromatography above was partially separated into components 12 and 13 by high-pressure liquid chromatography (HPLC) on Porasil A with Skelly B. Recycling through the column six times was necessary. The faster moving product 13 (the slower eluting product by VPC) was collected free of 12: NMR δ 5.1–5.9 (m, 3 H), 2.2 (m, 3 H, expected 4 H for 33), upfield resonances obscured by solvent. Assignment was based upon comparison with the literature NMR spectrum for 2-(1,7-cyclooctadienyl)-1,3-cyclooctadiene.³

The second HPLC fraction contained predominantly 12³⁰ (70% based on a multiplet at 3.3 ppm): NMR δ 5.3–6.1 (m, 8 H), 3.3 (m, 6.4 H), 2.4 (m, 8 H), upfield resonances obscured by Skelly B. The presence of a minor amount of 13 (and possibly other isomers) was confirmed by VPC.

(ii) **Reaction of 1-K⁺ with O₂.** A solution of about 0.05 M 1-K⁺ in THF was divided into two portions. One aliquot (1–2 mmol of 1-K⁺) was stirred for about 5 min, until the color of the solution was quenched, under a stream of O₂ passed through CaCl₂. The solution was taken up in water. The second aliquot was quenched directly with water. After an aqueous workup of the two solutions the relative amounts of 21 and isomers 12 and 13 were determined by VPC (10% FFAP, 2 m × 1/8 in. column, T(initial) = 90 °C, heating at 8 °C deg/min): 27:73 21/12 + 13.

Anodic Oxidation of 1-Li⁺ at a Vitreous Carbon Electrode. The oxidation potential of 1-Li⁺ was determined by cyclic voltammetry according to the procedure of Breslow.¹⁶ A three-compartment cell equipped with a silver quasi-reference electrode, a platinum foil counterelectrode, and a vitreous carbon working electrode with an area of 0.08 cm² and a magnetic stirrer in the working electrode compartment was employed. Lithium perchlorate (0.568 g, 5.3 mmol) was dried overnight under vacuum (0.01–0.05 mm) at ca. 40 °C. THF (20 mL, distilled under argon from LiAlH₄) was added to the argon-filled cell with a dropping funnel. Hexamethylphosphoramide (HMPA), 5 mL, distilled from CaO under nitrogen) was added via syringe. The cell was cooled in dry ice/CCl₄ to -20 °C. A cyclic voltammogram of solvent and electrolyte was obtained. The potential sweep of 500 mV/s between +1.4 and -2.4 V was initiated at 0 V in the anodic direction. No impurity peaks were observed.

A solution of about 0.5 M 4-Li⁺ was prepared at 0 °C by reaction of 2.5 mmol 4-3-d (0.5 mL of a mixture of 60% 4-3-d and 40% 22) in 5 mL of THF with 1.8 mL (2.9 mmol) of 1.6 N *n*-BuLi. An aliquot of 0.350 mL (0.2 mmol of 1-Li⁺) of this solution was added to the cell with a gas-tight syringe. Potential sweeps of 200 mV/s were initiated from -2.2 V toward the anodic direction. A weak anodic wave appeared for 4-Li⁺, whose potential (*E*_{pa} = -1.7 V vs. SCE) was determined relative to the known redox potential of ferrocene (lit. *E*_{pa/2} = +0.51 V vs. SCE¹⁶) added after completion of the cyclic voltammogram.

Calculations. Heats of formation of 2 and 3 were calculated with the standard MNDO format.³⁴ Geometries were optimized by the standard Davidson-Fletcher-Powell procedure with no

assumptions of any kind being made.

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Registry No. 1, 28927-63-1; 1 Li, 82338-17-8; 1 K, 82338-18-9; 1 MgBr, 82351-39-1; 2-3-d, 82338-19-0; 4 Li, 82338-20-3; 5, 645-49-8; 17, 1564-64-3; 18, 90-11-9; 19, 108-86-1; 22-3-d, 73908-49-3; 23, 3806-60-8; chlorobenzene, 108-90-7; nitrobenzene, 98-95-3; naphthalene, 91-20-3; stilbene radical anion, 34467-73-7; anthracene, 120-12-7; anthracene radical anion, 34509-92-7; 1,3-cyclooctadiene, 1700-10-3; potassium *tert*-butoxide, 865-47-4; butyllithium, 109-72-8; potassium, 7440-09-7; 1,4-cyclooctadiene(AgNO₃)₂, 82338-21-4; magnesium bromide, 7789-48-2; cyclooctadienylnaphthalene, 82338-22-5.

Reaction and Interconversion of Norditerpenoid Dialactones, Biologically Active Principles Isolated from *Podocarpus* Plants¹

Yuji Hayashi* and Takeshi Matsumoto

Faculty of Science, Osaka City University, Sumiyoshiku, Osaka 558, Japan

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The reactions of the B/C ring system and the ring A functional groups of the norditerpenoid dialactones isolated from *Podocarpus* plants are described. The interconversion of the three structural types of the natural dialactones is also presented, being focused on the transformation of type A (8(14),9(11)-dienolides) and type B (7 α ,8 α -epoxy-9(11)-enolides) into type C (7(8),9(11)-dienolides) dialactones, minor constituents but biologically the most interesting type of the dialactone members.

Since 1968, there have been reported more than 40 norditerpenoid dialactones isolated from various species of *Podocarpus* plants.²⁻¹¹ Particularly, the constituents of the species *P. nagi* (Thunberg) Pilger⁸ have been investigated most extensively in relation to their remarkable biological activity, including antitumor activity,^{9,12} plant growth inhibitory activity,¹³⁻¹⁵ termiticidal activity,¹⁶ and insect toxicity.¹⁷ The dialactones are classified into three

major subgroups in accordance with the structure of the B/C ring part: A, α -pyrone [8(14),9(11)-dienolide] type; B, 7 α ,8 α -epoxy-9(11)-enolide type; C, 7(8),9(11)-dienolide type.¹⁵ It should be noted that the dialactone members in each of these structural types show fine differences in their biological activity. For example, type B, e.g., nagilactone E (5), and type C, e.g., nagilactone F (6), generally show stronger activity than type A for antitumor or plant growth inhibitory activity; especially for the latter effect, types B and C exhibit a simple inhibitory effect (≥ 0.005 ppm) proportional to the dialactone concentration, while type A dialactones, e.g., nagilactone B (2), show a dual activity, inhibitory (> 0.5 ppm) or promotive (< 0.05 ppm) depending on the concentration,¹⁵ which may indicate their role as a growth regulator in the plant. The termiticidal activity has been found for only inumakilactone A (11, type B)¹⁶ and nagilactone D (4, type A)¹⁸ in spite of their natural cocurrence with other dialactones. Nagilactone D (4) is also sufficiently toxic (ED₅₀ 0.7 ppm) for larvae of housefly and Lepidoptera,^{17c} while the other 11 dialactones tested were 10-10² times less active than 4.

It is worthwhile to study the chemical reactivity and the interconversion of the three types of the dialactone members, since minor dialactones, particularly type C, were to be derived from other types of members for practical purposes, e.g., the synthetic study of nagilactone F (6)¹⁹ and various biological investigations. Only a limited number of publications has dealt with the reactivities of the dialactones except for the preparation of simple functional derivatives for structure determination. This would be due to the poor content of the dialactone components in plant materials. Fortunately, we have collected a considerable quantity of seeds and root bark of *P. nagi*, which

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