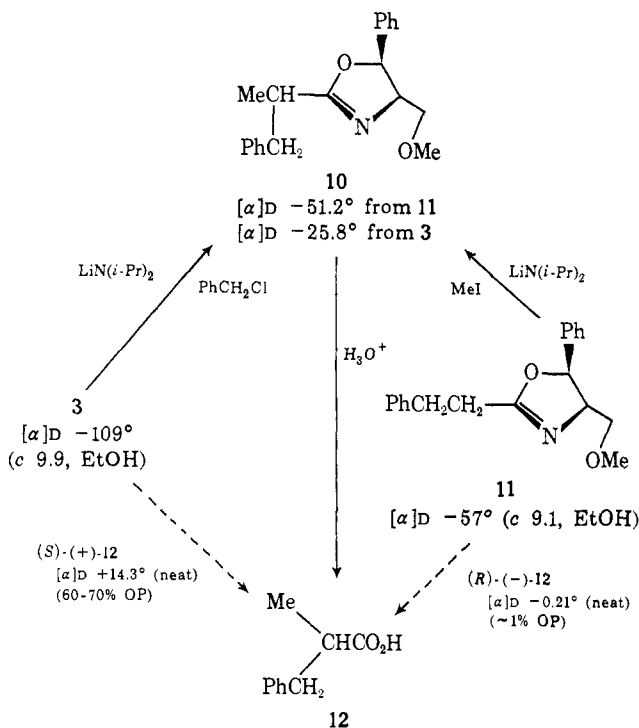


yield. The sequential acid-base-acid cleavage of oxazolines currently appears to be the choice method for preparing the acids, **6**, since direct acid hydrolysis of **5** results in 5–10% racemization of the ester **8**.⁷

The order in which the alkyl groups are introduced into the chiral oxazoline was found to be critical to the success of the asymmetric synthesis. For example, when **3** was treated with base to form the lithio salt, **4** or **4a**, and then alkylated with benzyl chloride, the oxazoline **10** was smoothly formed which gave, after direct acidic cleavage, 2-methyl-3-phenylpropionic acid (**12**) in 60–70% optical purity.⁸ However, when the 2-phenethyloxazoline (**11**) (*via* alkylation of the 2-methyl-oxazoline with benzyl chloride; BuLi, -78° , THF) was treated with base and methyl iodide (-78° , THF), the oxazoline **10** was formed which gave essentially racemic 2-methyl-3-phenylpropionic acid (**12**). These results



imply that the nature of the 2-alkyl groups originally present in the oxazoline (**3** or **11**) has a considerable effect upon the reactivity of the lithio anions.⁹ Other data in hand also confirm the fact that 2-substituents on the oxazoline *larger than ethyl* also lead to nearly racemic products. The structures drawn for the lithio-oxazolines (**4** and **4a**) should, therefore, not be considered firm at this time, although they do represent a reasonable working hypothesis.¹⁰ Further studies are

(7) Evidence for racemization in the ester intermediate **8** was gathered by hydrolysis under different time intervals. The longer the ester was heated in 4.5 N HCl, the lower the optical purity of the acid, although the acids themselves were found to be completely stable to racemization under these conditions.

(8) M. B. Watson and G. W. Youngson, *J. Chem. Soc. C*, 258 (1968), report $+20.4^\circ$ (neat) for this acid.

(9) The nearly racemic acid obtained from **11** could also be due to the small electrophile being introduced (*i.e.*, methyl) which may enter the molecule from one of several approaches. However, alkylation of **4** with the slightly larger ethyl iodide gave 2-methylbutanoic acid (**6**) ($R = Et$) in high optical yield (Table I).

(10) The corresponding *trans*-4-methyl-5-phenyloxazoline [$[\alpha]_D +81^\circ$] obtained by resolution of norephedrine was evaluated as a source of chiral carboxylic acids and found to give only 10–12% optically pure material. The absence of the methoxyl function in this oxazoline coupled with the poorer optical yields lends some credence to the structures depicted for the lithio salts **4** and **4a**.

in progress to evaluate the effect of a wide variety of substituents and scope of this method.

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Supplementary Material Available. Complete experimental details on all compounds described in this communication will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-268.

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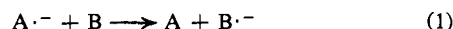
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Received September 12, 1973

Electron-Transfer Catalyzed *Cis-Trans* Isomerization of Stilbene. The Stability of Sodium *cis*-Stilbenide and the Existence of Sodium Salts of *cis*- and of *trans*-Stilbene Dianions

Sir:

Electron transfer from a radical anion, $A^{\cdot-}$, to an aromatic acceptor, B , *viz.*



is extremely fast when the electron affinity of B , $EA(B)$, is greater than that of A . Nevertheless, techniques for studying its kinetics are available.^{1–3} The reverse reaction is inaccessible to a direct kinetic investigation when $EA(B) \ll EA(A)$, because the equilibrium concentration of $B^{\cdot-}$ is then exceedingly low. However, if some reaction different than the reverse of 1 rapidly removes $B^{\cdot-}$, reaction 1 might become rate determining and its progress could be measured then, *e.g.*, by the disappearance of B .

Having this strategem in mind, we decided to investigate the kinetics of electron transfer from sodium anthracenide, $A^{\cdot-}, Na^+$, to *cis*-stilbene, C , leading to the isomerization of the latter. This reaction was followed spectrophotometrically by monitoring the absorbance at 285 nm. At this wavelength the decimal extinction coefficients of *cis*- and *trans*-stilbenes are 1.02×10^4 and $2.45 \times 10^4 M^{-1} cm^{-1}$, respectively, and the absorbance of the anthracenide is at minimum, $\epsilon 0.35 \times 10^4 M^{-1} cm^{-1}$. The starting *cis* isomer was purified by vpc and contained about 6% of the *trans* isomer (determined spectrophotometrically at $\lambda 320$ nm).

It is known⁴ that *cis*-stilbene isomerizes into *trans*-stilbene, T , when in contact with radical anions, and

(1) S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

(2) S. Arai, D. A. Grev, and L. M. Dorfman, *J. Chem. Phys.*, **46**, 2572 (1967).

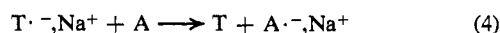
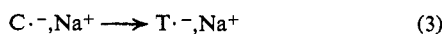
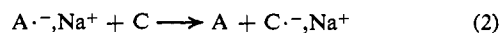
(3) G. Rämme, M. Fisher, S. Claesson, and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **327**, 467 (1972).

(4) M. A. Doran and R. Waack, *J. Organometal. Chem.*, **3**, 94 (1965).

Table I. Isomerization of *cis*-Stilbene; $[C] \sim 2-3 \times 10^{-3} M$

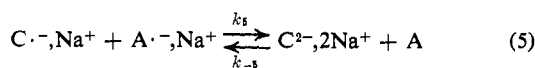
$10^3[A\cdot^-,Na^+], M$	$10^3[A], M$	$[A\cdot^-,Na^+]/[A]$	$10^3k_{ap}, \text{sec}^{-1}$	$k_{ap}/\{[A\cdot^-,Na^+]/[A]\}^2 = k_{isom}K_2K_5 (\text{sec}^{-1})$
9.7	3.1	3.16	53.5	5.35×10^{-3}
3.12	0.965	3.25	53.0	5.0×10^{-3}
2.12	1.06	2.00	25.8	6.4×10^{-3}
6.6	3.2	2.06	22.6	5.30×10^{-3}
4.85	3.5	1.38	10.9	5.72×10^{-3}
2.87	3.17	0.82	4.35	5.30×10^{-3}
0.332	3.19	0.107	0.074	6.43×10^{-3}
2.03	2.4	0.84	4.7	6.6×10^{-3}

therefore the following sequence of events could be expected

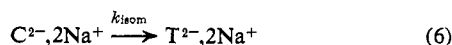


The relative electron affinities of *cis*- and of *trans*-stilbene have been determined polarographically⁵ and both are substantially lower than that of anthracene. Therefore the stationary concentrations of $C\cdot^-,Na^+$ or $T\cdot^-,Na^+$ should be negligible in the reacting solution, even if C is in excess (see Table I for the pertinent data). Indeed, we found the isomerization to be catalyzed by sodium anthracenide; no reaction was observed in its absence. (No change was observed in a solution of *cis*-stilbene kept in the sample compartment of a Cary-14 spectrophotometer with the analyzing beam on for 10 hr. We know an example of photolysis resulting from the irradiation of a sample by the analyzing beam of a Cary-14 spectrophotometer.⁶) The addition of *cis*-stilbene did not affect the concentration of $A\cdot^-,Na^+$ which remained constant during the reaction. The isomerization was virtually completed within 10–30 min and in each run $\ln [C]$ was strictly linear with time, even at 95% of conversion. However, the pseudo-first-order rate constant, $k_{ap} = d \ln [C]/dt$, instead of being proportional to $[A\cdot^-,Na^+]$ and independent of $[A]$, was found to be proportional to $\{[A\cdot^-,Na^+]/[A]\}^2$ provided $[A] > 2 \times 10^{-3} M$. This relation is verified by the data collected in Table I which lists also the ratios $k_{ap}/\{[A\cdot^-,Na^+]/[A]\}^2$.

Apparently the sodium salt of *cis*-stilbenide, $C\cdot^-,Na^+$, is stable and does not isomerize in the course of our experiments. However, $C\cdot^-,Na^+$ may be reduced further (or disproportionate) to $C^{2-},2Na^+$



and the salt of the dianion, $C^{2-},2Na^+$, isomerizes then in a rate-determining step



The stationary-state treatment (reaction 2 is assumed to maintain the equilibrium concentration of $C\cdot^-,Na^+$) gives

$$k_{ap} = k_{isom}K_2K_5\{[A\cdot^-,Na^+]/[A]\}^2/(1 + k_{isom}/k_{-5}[A])$$

For sufficiently high concentration of A, $k_{-5}[A] \gg k_{isom}$ and then the approximation $k_{ap} = k_{isom}K_2K_5$

(5) R. Dietz and M. E. Peover, *Discuss. Faraday Soc.*, **45**, 154 (1968).

(6) W. Bracke, J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *Chem. Commun.*, 77 (1970).

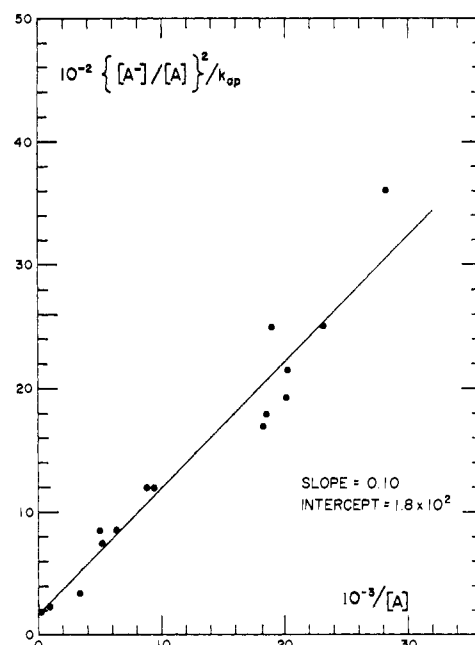
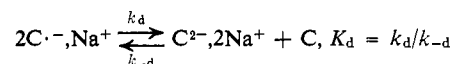


Figure 1. Plot of $\{[A\cdot^-]/[A]\}^2/k_{ap}$ vs. $10^{-3}/[A]$: slope = $1/k_{-5}K_2K_5$; intercept = $1/k_{isom}K_2K_5$; slope/intercept = $k_{isom}/k_{-5} = 2 \times 10^{-3} M$.

$\{[A\cdot^-,Na^+]/[A]\}^2$ is valid. Apparently this approximation applies when $[A] > 2 \times 10^{-3} M$ since the values of $k_{isom}K_2K_5$ given in Table I are constant.

On the whole, k_{ap} obeys the relation $\{[A\cdot^-]/[A]\}^2/k_{ap} = (k_{isom}K_2K_5)^{-1} + (k_{-5}K_2K_5)^{-1}[A]$, verified by Figure 1. This confirms the proposed mechanism. Had the formation of $C^{2-},2Na^+$ been due to disproportionation



the kinetics would be given by

$$-d \ln [C]/dt = k_{isom}K_2^2K_d\{[A\cdot^-]/[A]\}^2/(1 + k_{isom}/k_{-d}[C])$$

where $K_2^2K_d = K_2K_5$. The reaction would acquire then a second-order character in its last stages, contrary to our observation. If the electron transfer and the disproportionation contribute to the formation of $C^{2-},2Na^+$, their relative contributions are given by $(k_5/k_d)([C]/[A])$ and our kinetic scheme could be affected had this ratio been small. Apparently this is not the case under our experimental conditions.

Further evidence for the proposed mechanism is provided by the experiments involving sodium pyrenide, $\pi\cdot^-,Na^+$, instead of anthracenide. The isomerization was much faster, but otherwise retained all its previous

characteristics. It is easy to verify that the resulting $k_{ap}/\{[\pi^{\cdot-}, Na^+]/[\pi]\}^2 = k_{isom}K_2'K_5'$ is related to the previously determined $k_{isom}K_2K_5$ by the relation

$$k_{isom}K_2'K_5'/k_{isom}K_2K_5 = (K_{A,\pi})^2$$

where $K_{A,\pi}$ is the equilibrium constant of the reaction



Thus calculated $K_{A,\pi}$ was found to be 140; whereas the direct determination⁷ led to the value of 110.

In conclusion, neither *cis*-stilbene nor its radical anion salt isomerize spontaneously within the time period of our experiments, while its dianion salt does. We derive from Figure 1 $k_{isom}/k_{-5} = 2 \times 10^{-3} M$ and therefore $k_{isom} \leq 5 \times 10^6 \text{ sec}^{-1}$ because k_{-5} is probably diffusion controlled, *i.e.*, $k_{-5} \approx 10^{10} M^{-1} \text{ sec}^{-1}$. Hence, the lifetime of the sodium salt is $2 \times 10^{-7} \text{ sec}^{-1}$ or more. The principle of microscopic reversibility demands therefore the existence of four thermodynamically distinct species: *cis*-stilbene \cdot^-, Na^+ , *trans*-stilbene \cdot^-, Na^+ , *cis*-stilbene $^{2-}, 2Na^+$, and *trans*-stilbene $^{2-}, 2Na^+$. The relative stability of *cis*-stilbene $^{2-}, 2Na^+$, surprising in view of its endowment with two antibonding electrons, is tentatively attributed to the binding of both phenyl groups by the sodium counterions.

Acknowledgment. The support of this study by the National Science Foundation is gratefully acknowledged.

(7) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

G. Levin, T. A. Ward, M. Szwarc*

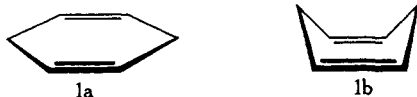
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Received September 27, 1973

Stereochemistry of 1,4-Cyclohexadienes. Confirmation via Rare Earth Shift Reagents

Sir:

A considerable amount of controversy exists concerning the conformational preferences of 1,4-cyclohexadiene (1) and its derivatives. A planar structure, **1a**, has been proposed by several investigators¹⁻⁷ using various techniques including nmr⁵ and electron diffraction.⁶ However, a subsequent conflicting electron



diffraction study of **1**⁸ and nmr studies of several deriva-

(1) H. Gerding and F. A. Haak, *Recl. Trav. Chim. Pays-Bas*, **68**, 293 (1949).

(2) B. J. Monostori and A. Weber, *J. Mol. Spectrosc.*, **12**, 129 (1964).

(3) H. D. Stidham, *Spectrochim. Acta*, **21**, 23 (1965).

(4) R. C. Lord, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. PHYS 74.

(5) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967).

(6) E. W. Garbisch, Jr., and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1958).

(7) Very recently a planar form has been predicted for **1** on the basis of calculations [N. L. Alliner and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972)] and for a highly substituted derivative by X-ray analysis [M. J. Bennett, J. T. Purdham, S. Takada, and S. Masamune, *ibid.*, **93**, 4063 (1971)].

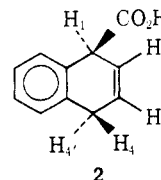
(8) H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).

tives⁹⁻¹¹ have resulted in the suggestion of a boat conformation, **1b**.

Thus far, the nmr studies on derivatives of **1** have considered only the ratio of the homoallylic *cis* and *trans* (H_1 to H_4) coupling constants. It was on this basis that boat conformations were postulated, and Marshall, *et al.*,¹¹ suggested that 1,4-dihydrobenzoic acid exists in a boat with the substituent pseudoequatorial. Unfortunately, there has been some disagreement^{6,10,11} concerning the "predicted value" of the J_{cis}/J_{trans} ratio expected for the planar form.¹²

A major difficulty in the nmr analysis of 1-substituted-1,4-cyclohexadienes is the fact that the several derivatives reported all show a deceptively simple spectrum. Typically, the methine proton appears as a triplet (H_1 , $J \sim 8-9$ Hz) coupled to the methylene protons (H_2, H_4') which appear as a corresponding doublet. Hence, H_4 and H_4' appear to have the same chemical shift and also appear to be equally coupled to H_1 . In addition, the vinyl protons often have approximately the same chemical shift, and neither the vicinal nor allylic coupling constants have been determined. In fact, even the homoallylic coupling constants are difficult to obtain and have only been measured by preparing deuterated compounds.^{12,14,15}

In an attempt to prepare a cyclohexadiene that might be more suitable for nmr analysis, Marshall and Folsom¹⁴ prepared 1,4-dihydro-1-naphthoic acid (**2**) and



concluded, from the vicinal coupling constants ($H_1H_2 = 4.59$ Hz, $H_3H_4 = 4.60$, $H_3H_4' = 2.44$) together with the Karplus equation, that the ring was boat shaped with the CO_2H pseudoaxial. Later, however, the homoallylic coupling constants were accurately determined using deuterium substitution ($J_{1,4} = 3.84$, $J_{1,4'} = 4.36$), and, since the homoallylic *cis/trans* ratio was very close to the predicted value for a flat ring (see ref 12), a "flattened boat" was proposed.¹⁵

We would now like to report the first complete nmr analysis of a 1-substituted-1,4-cyclohexadiene, which we were able to accomplish with the use of the rare earth shift reagent $Eu(fod)_3$.¹⁶ Birch reduction of benzoic acid followed by $LiAlH_4$ reduction resulted in 1,4-dihydrobenzyl alcohol (**3**).¹⁷ The complete nmr analysis of **3** was accomplished by adding $Eu(fod)_3$, and under these conditions the H_4 and H_4' protons appeared as an AB quartet (H_4 assigned to the signal

(9) L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Commun.*, 456 (1965).

(10) D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969).

(11) J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970).

(12) Recently, Sternhell has calculated a value of $J_{cis}/J_{trans} = 1.12$ on the basis of an INDO treatment.¹³ See ref 15.

(13) M. Barfield and S. Sternhell, *J. Amer. Chem. Soc.*, **94**, 1905 (1972).

(14) J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, **36**, 2011 (1971).

(15) J. L. Marshall, A. M. Ohrig, and P. N. Jenkins, *J. Org. Chem.*, **37**, 1863 (1972).

(16) For a review, see W. D. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

(17) All new compounds gave satisfactory spectral data and elemental analysis.