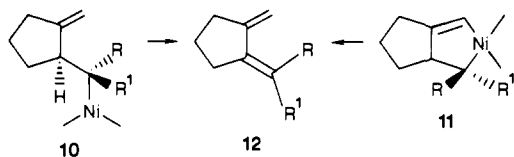
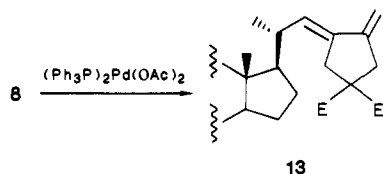


selectivity exists. For example, esters, ketones, sulfones, and free hydroxyl groups are all tolerated. Whereas, a carboethoxy group on the acetylene appears to promote reaction (entry 6), such a group on the olefin hinders reaction. Olefin geometry plays a role in terms of 1,3- vs. 1,4-diene formation in comparing entries 4 and 5. Unfortunately, without a defined mechanism, it is difficult to rationalize this observation. If we propose either an acyclic **10** or cyclic **11** intermediate which arises by a *cis* addition to the



olefin and propose that elimination proceeds by a *cis* elimination of nickel hydride, kinetically a *trans* olefin would lead to **12** R = H, R¹ = CH₃ and a *cis* olefin to **12** R = CH₃, R¹ = H. The steric congestion of placing the methyl group *syn* with respect to the diene in the case of the *Z* olefin, then, disfavors 1,3-diene formation. Finally, cyclization of enyne **8** in entry 10 led only to the cyclopentene **9**⁸ with no other double bond isomers detectable. Furthermore, analysis by 500-MHz ¹H and 125-MHz ¹³C NMR spectroscopy reveals a high diastereoselectivity (88:12). Upon the basis of the ¹³C chemical shift of C (21) (δ 18.5) and mechanistic considerations, we tentatively assign the stereochemistry depicted for the major isomer. While we cannot rule out isomerization of an exocyclic double bond, such an isomerization has not been observed in any other case even when the products were exposed to an active catalyst system for prolonged periods. This example also differs substantially from the Pd-(2+)-catalyzed reaction in terms of the regioselectivity of the hydrogen migration as shown in the diene **13**.²



The definition of the actual catalyst remains unclear. Neither tetrakis(triphenylphosphine)nickel nor tris(triphenylphosphine)nickel(1+) chloride⁹ are active catalysts. On the other hand, addition of chromous chloride to either generates a catalyst, but one which is less active than treating the nickel(2+) complex **2** with chromous chloride. A mixed metal complex like (Ph₃P)₃NiCrCl₄ or (Ph₃P)₃NiCrCl₃ would account for the special role of chromium chloride salts in generating active catalysts.¹⁰

Acknowledgment. We thank the National Science Foundation for their generous support of our programs.

Supplementary Material Available: Experimental procedures for preparation of the polymeric catalyst and of 4,4-dicarbo-methoxy-1,2-dimethylenecyclohexane; spectral data for products of entries 7, 8, and 9 of Table I (3 pages). Ordering information is given on any current masthead page.

(8) IR (CDCl₃) 1725, 1660, 1615 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.71 (s, 1 H), 5.46 (s, 1 H), 4.95 (d, J = 9.8 Hz, 1 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 2.79 (dd, J = 13.9, 7.9 Hz, 1 H), 2.44-2.23 (m, 4 H), 2.08-1.98 (m, 3 H), 1.85-1.77 (m, 3 H), 1.70-1.25 (m with methyl, s at δ 1.67 and 1.65, 12 H), 1.23-0.91 (m with methyl, s at 1.19, 9 H), 0.56 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) 199.2, 172.2, 171.8, 171.2, 149.0, 136.0, 127.6 (CH), 123.7 (CH), 122.5 (CH), 65.2, 58.6 (CH), 55.4 (CH), 53.9 (CH₂), 52.5 (CH₂), 46.6 (CH), 43.5, 39.8 (CH₂), 38.6 (CH₂), 35.9 (CH), 35.7 (CH₂), 33.9 (CH₂), 32.8 (CH₂), 31.9 (CH₂), 24.7 (CH₂), 24.1 (CH₂), 21.0 (CH₂), 18.5 (CH₃), 17.3 (CH₃), 15.2 (CH₃), 13.1 (CH₃).

(9) (a) D'Aniello, M. J., Jr.; Barefield, E. K. *J. Am. Chem. Soc.* **1978**, *100*, 1474. (b) Kanai, H.; Kushi, K.; Sakanoue, K.; Kishimoto, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2711.

(10) A mixed metal complex between Ni(1+) and stannous chloride is known. See ref 9a.

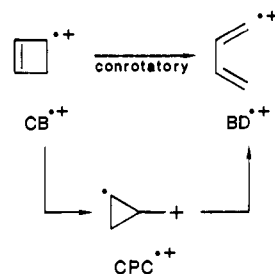
The Conrotatory Electrocycloreversion of the *cis*-3,4-Diarylcyclobutene Cation Radical¹

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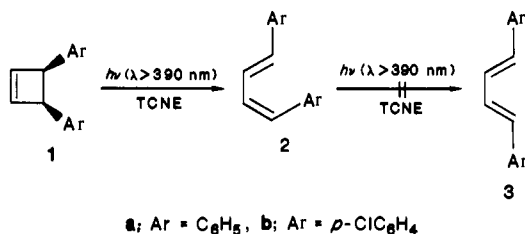
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Received February 17, 1987

Theoretical analyses² predicted that the ground-state electrocycloreversion of a cyclobutene radical cation (CB^{•+}) to a 1,3-butadiene radical cation (BD^{•+}) would occur preferably in a conrotatory manner^{2b} if the cycloreversion is a direct pathway or would occur in a two-step process passing through a cyclopropylcarbinyl (CPC^{•+}) radical cation intermediate^{2c} independent of symmetry constraints. There is, however, no experimental



investigation that tested those theoretical predictions in terms of stereochemistry.³⁻⁶ We examined this, and for the first time, report the stereospecific conrotatory electrocycloreversions of *cis*-3,4-diarylcyclobutene radical cations **1**^{•+} to *cis,trans*-1,4-diaryl-1,3-butadienes **2**. The process occurred either by the photoexcitation of the electron donor-acceptor (EDA) complexes of **1** and tetracyanoethylene (TCNE) or under photoinduced electron-transfer conditions. **1a**^{7,8a} and **1b**^{8b,9} exhibited the charge-



a: Ar = C₆H₅; b: Ar = *p*-ClC₆H₄

(1) Organic Photochemical Reaction no. 81. For no. 80, see: Yamashita, Y.; Ikeda, H.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, in press.

(2) (a) Haselbach, E.; Bally, T.; Lanyiova, Z. *Helv. Chim. Acta* **1979**, *62*, 577. (b) Dunkin, I. R.; Andrews, L. *Tetrahedron* **1985**, *41*, 145. (c) Bellville, D. J.; Chelsky, R.; Bauld, N. L. *J. Comput. Chem.* **1982**, *3*, 548. Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

(3) Although there are many experimental investigations of the reactions of cyclobutene radical cations, most of them are of the gas-phase reactions by using mass spectroscopic techniques⁴ or of reaction in frozen media.⁵ However, a putative electrocycloreversion of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene radical cation in solution was recently reported.⁶

(4) (a) Hoffman, M. K.; Bursey, M. M.; Winter, R. E. K. *J. Am. Chem. Soc.* **1970**, *92*, 727. (b) Mandelbaum, A.; Weinstein, S.; Gil-Av, E.; Leffin, J. H. *Org. Mass. Spec.* **1975**, *10*, 842. (c) Gross, M. L.; Russel, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 2082. (d) Dass, C.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5724. (e) Dass, C.; Sack, T. M.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 5780.

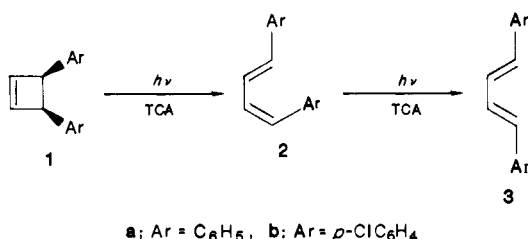
(5) Haselbach, E.; Bally, T.; Gschwind, R.; Hemm, U.; Lanyiova, Z. *Chimia* **1979**, *33*, 405.

(6) Kawamura, Y.; Thurnauer, M.; Schuster, G. B. *Tetrahedron* **1986**, *42*, 6195.

(7) Brauman, J. I.; Archie, W. C., Jr. *Tetrahedron* **1971**, *27*, 1275. **1a** used in this report was prepared by electrolysis of β-truxinic acid which was prepared according to the procedure reported.^{8a}

(8) (a) Nishikubo, T.; Takahashi, E.; Miyaji, T.; Iizawa, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3399. (b) Nakanishi, F.; Nakanishi, H.; Tsuchiya, M.; Hasegawa, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3096.

transfer (CT) absorption at 420 and 450 nm (shoulder), respectively, when mixed with TCNE in dichloromethane. Upon separate irradiation (>390 nm)¹⁰ in dichloromethane at 0 °C of those CT absorptions by using a 2 kW Xe lamp, the new CT absorptions of **2a** ($\lambda_{\max}^{\text{CT}} = 635 \text{ nm}$)¹¹ and **2b** ($\lambda_{\max}^{\text{CT}} = 625 \text{ nm}$)¹² rapidly appeared as those of **1a** and **1b** rapidly diminished, and those transformations were complete within 10 min.¹³ However, even upon prolonged irradiation, those resulting CT absorptions did not shift to the CT absorption maxima of **3a**¹¹ and **3b**¹⁴ which appear at 695¹⁵ and 670 nm, respectively. In fact, preparative scale photolyses of **1a** and **1b** resulted in quantitative formation of **2a** and **2b**, respectively. Those results indicate that the photoexcitations of the EDA complexes conveniently involved only the efficient electrocycloreversions of **1**⁺ to **2**⁺ without the secondary cis-trans isomerizations of **2** to **3**.¹⁶



Similar results were obtained in photoinduced electron-transfer reactions of **1** by using 2,6,9,10-tetracyanoanthracene (TCA) as a sensitizer. The fluorescence of TCA was quenched either by **1a** ($E_{1/2}^{\text{ox}} = 1.96 \text{ V vs. SCE}$)¹⁷ or by **1b** ($E_{1/2}^{\text{ox}} = 1.94 \text{ V vs. SCE}$),¹⁷ giving Stern-Volmer slopes 186 and 196 M⁻¹, respectively, which indicate that **1a** and **1b** are effective quenchers of the TCA singlet.¹⁸ An acetonitrile solution of TCA (0.1 mM) and **1a** (3.8 mM) was irradiated (>410 nm)¹⁰ by a 2 kW Xe lamp at 0 °C, and the progress of the reaction was monitored by liquid chromatography. Thus, **1a** quantitatively gave **2a** until 50% conversion of **1a**, and a mixture of **2a** (67%) and **3a** (5%) was obtained after 73% conversion. On the other hand, upon irradiation (>390 nm)¹⁰ of an acetonitrile solution of TCA (0.2 mM) and **1b** (24 mM), the formation of **3b** was not observed until 70% conversion of **1b**, and a 9:1 mixture of **2b** and **3b** was quantitatively obtained when **1b** was completely consumed. Upon prolonged irradiation, both **2a** and **2b** then slowly isomerized to **3a** and **3b**, respectively.^{19,20}

(9) **1b** was prepared by electrolysis of 4,4'-dichloro- β -truxinic acid which was prepared according to the procedure reported.^{8b} **1b**: mp 58–61 °C; ¹H NMR (90 MHz, in CCl₄) δ 4.38 (s, 2 H), 6.44 (s, 2 H), 6.72 (d, 4 H, $J = 9 \text{ Hz}$), 6.97 (d, 4 H, $J = 9 \text{ Hz}$). Satisfactory elemental analyses were obtained for new compounds, **1b** and **2b**.

(10) A Toshiba L-42 cutoff filter was used for irradiation by light longer than 390 nm from a 2 kW Xe lamp. Toshiba cutoff filters L-39 and B-46 were used for irradiation at 406 nm from a 75 W Hg lamp. A Toshiba Y-43 cutoff filter was used for irradiation by light longer than 410 nm from a 2 kW Xe lamp.

(11) Pinckard, J. H.; Wille, B.; Zechmeister, L. *J. Am. Chem. Soc.* **1948**, *70*, 1938.

(12) **2b**: mp 50–52 °C; ¹H NMR (400 MHz, in CCl₄) δ 6.41 (dd, 1 H, $J = 10.7, 11.5 \text{ Hz}$), 6.48 (d, 1 H, $J = 11.5 \text{ Hz}$), 6.66 (d, 1 H, $J = 15.4 \text{ Hz}$), 7.19 (dd, 1 H, $J = 15.4, 10.7 \text{ Hz}$), 7.25–7.37 (m, 8 H); UV (in CH₃CN), $\lambda_{\max} = 321 \text{ nm}$ (log $\epsilon = 4.51$).

(13) An acetonitrile solution of **1** (25 mM) and TCNE (50 mM) was irradiated. **1a** and **1b** isomerized very slowly to **2a** and **2b** in acetonitrile at room temperature in the dark, but **1a** and **1b** were stable either in the presence or in the absence of TCNE at 0 °C in the dark.

(14) Kamigata, N.; Ozaki, J.; Kobayashi, M. *J. Org. Chem.* **1985**, *50*, 5045.

(15) Aiga, H.; Matsuo, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 271.

(16) A similar result was obtained when irradiated either in the less polar benzene or in the more polar acetonitrile, indicating that the solvent polarity does not influence the stereochemical course.

(17) Half-wave oxidation potentials were measured by cyclic voltammetry at a platinum electrode with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte in dry acetonitrile.

(18) ΔG values for the electron transfers from **1** to ¹TCA* are calculated to be -10.8 and -11.3 kcal/mol for **1a** and **1b**, respectively, in acetonitrile.

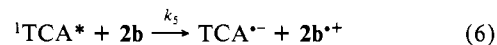
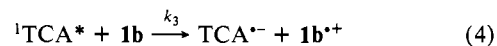
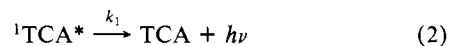
(19) Mechanistic details of the cis-trans isomerizations of **2** to **3** will be reported separately.

Those results clearly demonstrate that the initial rapid formation of **2** followed by the slow secondary isomerizations of **2** to **3** occurred in sequence in the photoinduced electron-transfer reactions of **1**. Stereochemical integrity of the cycloreversion was further confirmed by the irradiation (406 nm)¹⁰ of **1b** by using a 75 W Hg lamp under the TCA-sensitized conditions, which involved only the cycloreversion of **1b** to **2b** without the isomerization of **2b** to **3b**. The initial stereospecific formation of **2a** and **2b** at the initial stage are consistent with the results obtained by the photoexcitations of the EDA complexes. The observed stereospecificity can not be accounted for by a stepwise mechanism which intervenes a CPC⁺ or ring-opened allyl radical-methylene cation (or allyl cation-methylene radical) intermediate in which an allyl moiety is orthogonal to a cation moiety. The latter intermediate is favored as the least motion intermediate in a stepwise mechanism but is regarded also as a transition state for the cis-trans isomerization and should afford a photostationary mixture of **2** and **3** or the more thermodynamically stable **3** exclusively. The activation energy for the conrotatory cycloreversion of **1**⁺ to **2**⁺ is roughly estimated to be less than 7–13.8 kcal/mol if the ring opening of 3-phenylcyclobutene radical cation in the gas phase^{4d} is taken into account, which is significantly lower than that estimated for the ring opening of 1,2-diphenylcyclobutene.⁶

In order to gain further insight into the initial cycloreversion step, the irradiation of **1b** at 406 nm by a 75 W Hg lamp under the TCA-sensitized conditions was kinetically investigated by using **1b** containing about 7% **2b** in acetonitrile.

If electron-transfer processes sequentially occur as shown in Scheme I, the relative quantum yield (Φ_{rel}) for the formation of **2b** at an early stage can be expressed by eq 9 where α is the ratio

Scheme I



$$\Phi_{\text{rel}}^{-1} \propto (k_3 + \alpha k_5)/k_3 + (k_1 + k_2)/k_3[\mathbf{1b}]_0 \quad (9)$$

of the initial concentrations of **2b** and **1b** (i.e., $[\mathbf{2b}]_0/[\mathbf{1b}]_0$). From the intercept and slope of the observed straight line for the Φ_{rel}^{-1} vs. $[\mathbf{1b}]_0^{-1}$ plots, $(k_3 + \alpha k_5)\tau$ is calculated to be 270 M⁻¹. Because α and $k_5\tau$ are 0.08 and 349 M⁻¹, respectively, $k_3\tau$ becomes 242 M⁻¹. This value does not deviate far from the Stern-Volmer slope, $k_q\tau = 196 \text{ M}^{-1}$, obtained from the TCA fluorescence quenching by **1b**, indicating the efficient cycloreversion of **1b**⁺ to **2b**⁺, as denoted by the eq 5. Because the oxidation potential of **2b** ($E_{1/2}^{\text{ox}} = 1.34 \text{ V vs. SCE}$)¹⁷ is much lower than that of **1b**, the chain reaction, which can be initiated by the back electron-transfer from **2b**⁺ to **1b**, is unlikely to occur.

(20) One referee pointed out the possible generation of a "distonic" radical cation species (an allyl radical-methylene cation or an allyl cation-methylene radical) as an intermediate in which an allyl moiety is orthogonal to a cation moiety. This intermediate, however, cannot explain the stereospecific formation of the less thermodynamically stable **2**. If this species is involved as an intermediate, the formation of a photostationary mixture of **2** and **3** or the exclusive formation of the more thermodynamically stable **3** should be expected because this species can be regarded also as a transition state for the cis-trans isomerization between **2** and **3**.