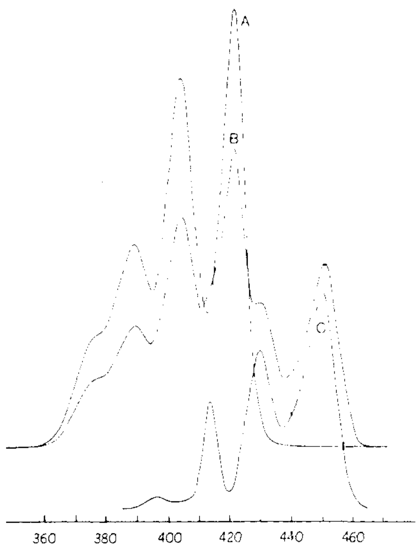

Figure 2. The uv spectra of the photolysis of NMA ($\sim 7 \times 10^{-3}$ *M*) in EtOH-MeOH (9:1) mixture at −150° with 405 nm narrow band light. The spectra were monitored with a Cary 14 spectrophotometer: (a) before the irradiation, (b) after 28 min irradiation, (c) the uv absorption curve of the intermediate isolated from spectrum b with a Du Pont 310 Curve resolver.

ed by irradiation through a Pyrex filter; a steady state of the intermediate absorption bands were observed and 65% of the total decrement of **1** decomposed irreversibly. At 25° the monochromatic irradiation (405 nm) of **1** resulted in the irreversible decomposition in about the same rate as that observed in the −150° irradiation suggesting that a monophotonic process had superceded in a more energetic environment. Preparatively since photodecomposition of **1** in the same alcohol solvent at *ca.* −150° gave the same type of products as those observed in the photolysis at room temperature, the primary photochemical process is judged to be the same for both cases, *i.e.*, the homolysis of the N–N bond.

The spectroscopic properties of the trapped intermediate[13] is compatible with the unstable rotamer **2**. Lack of luminescence[1b] of **1** at 77°K suggests that the lowest excited state *1 preferentially undergoes radiationless transition processes.[14] The conceptual scheme of Figure 1 indicates that a low temperature ***1** undertakes a nonvertical radiationless transition[14] reaching the vicinity of A from which a part relaxes along the new potential energy surface and is eventually trapped in the minimum **2**. Irradiation of **2** at −150° raises it to the new electronically excited level ***2** from where a radiationless transition imparts a sufficient energy to decay along the dissociation potential surface[15] as in **2*** → B → **3**. The transition to the monophotonic process at 25° may be simply interpreted that additional vibrational energy assists ***1** to traverse along the reaction coordinate within its lifetime to another point from where it follows a nonvertical radiationless transition overcoming the dissociation energy barrier B. In a broad sense, the observation described above is similar to photochromism[16] involving a metastable intermediate. However, the clear demonstration of the transition from biphotonic to monophotonic process along the temperature change provides a good deal of information on decay processes of the excited states. Obviously quantum yield determinations and their temperature dependency may give interesting information on these competing decay processes.

Acknowledgment. The authors wish to thank the National Research Council of Canada and the Defence Research Board of Canada for financial support.

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(9) Conceptually this pathway is the same as the reaction of "hot" species. See the discussion in p 388 of ref 7; the readers are referred to the excellent general discussion of radiationless decay described in ref 7.

(10) Examples pertinent to such trapping experiments are known. See O. L. Chapman, J. C. Clardy, T. L. McDowell, and H. E. Wright, *J. Amer. Chem. Soc.*, **95**, 5086 (1973), and the previous reports.

(11) For the isolation of the energy, the emission of superpressure Hg lamp OSRAM HBO 200-W was filtered through an Oriel narrow band interference filter 4047Å/100Å no. 2. Nitrosamide 1 has n → π* transition bands at 373, 387, 403, and 421 nm.

(12) Generally the sample was irradiated for less than 10 min to cause ~20% transformation to the intermediate during which isosbestic points at 422, 413, and 355 nm were observed in the spectrum. A longer irradiation also resulted in excitation of the intermediate absorption band at 414 nm which led to some irreversible decomposition.

(13) (a). Using an infrared spectroscopic monitor, the intermediate was observed to absorb at 1712 and 1555 cm^{-1} and 1 at 1738 and 1505 cm^{-1}. (b). A bathochromic shift of 18 nm for the n → π* absorption from *N*-nitroso-*N*-methylbutyramide to *N*-nitrosopyrrolidone (R. Huisgen and J. Reinertshofer, *Justus Liebigs Ann. Chem.*, **575**, 197 (1952)) is in general agreement with the proposed conformational change 1 → **2**.

(14) Since the potential energy surfaces of the lowest excited states *1 and *2 are obscure, they are simply shown with a horizontal line in Figure 1. A detailed picture of an internal conversion is difficult to guess; a model based on the "funnel" hypothesis has been discussed by Michl[8] and should be of both conceptual and practical value.

(15) The lack of reversibility in the second photoprocess does not allow us to make a closer scrutiny of this step. Alternative explanation is that the N–N bond dissociates from nonbonding excited states. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N.Y., Chapter 3, 1966.

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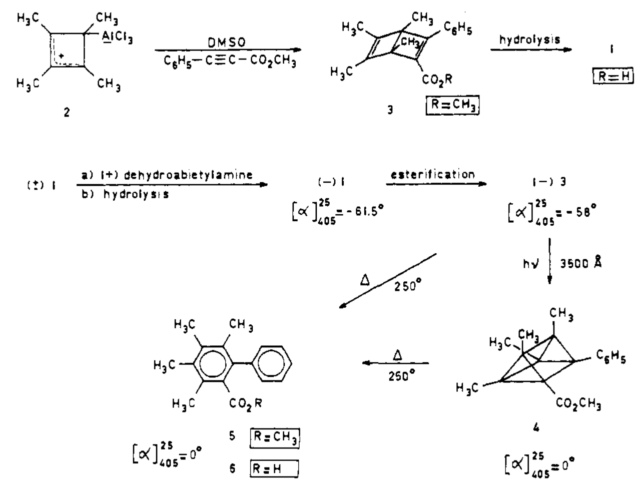
Synthesis and Resolution of a Chiral "Dewar" Benzene

Sir:

We have prepared an optically active "Dewar" benzene[1] in order to use chiroptical methods to study quantitatively the pathways between valence bond isomers of benzene.[1] This communication reports on the synthesis and resolution of 1,4,5,6-tetramethyl-3-phenylbicyclo[2.2.0]hexa-2,5-diene-2-carboxylic acid (**1**), as well as the conversion of its methyl ester **3** to a benzene **5** (thermally) and to a prismane **4**[2] (photochemically). To our knowledge **1** is the first optically active derivative of a valence bond isomer of benzene.

Using essentially van Bekkum's method[3] for the synthesis of tetramethyl (Dewar phthalates), we have prepared a number of chiral "Dewar" benzenes. Thus, when the complex **2**[3,4] was treated at 0–5° with DMSO in the presence of an excess of methyl phenylpropiolate, the monoester **3** was obtained in 75% yield (Scheme I). After extensive chromatography,[5] pure **3** was obtained and hydrolyzed by boiling with a methanolic KOH solution for 7 days. The acid **1** (mp 172–178°)[6] was obtained in 85% yield. *Anal.* Calcd for

Scheme I



$C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.15; H, 7.24. The nmr data of **1**, **3**, and **4** are compiled in Table I.

A solution of **1** (298 mg) in absolute alcohol (9 cm^3) was treated with a solution of 334 mg of (+)-dehydroabietylamine[7] ($[\alpha]^{20}{}_{405}$ +139.2°, *c* 9.7 in pyridine) in absolute alcohol (4 cm^3) and refluxed for 30 min. Water (4 cm^3) was added and the solution cooled overnight at −20° furnishing 290 mg of a white crystalline solid ($[\alpha]^{20}{}_{405}$ +47.5°), mp 93-101°. A further crystallization from 70% ethyl alcohol gave 149 mg of the diastereomeric salt ($[\alpha]^{20}{}_{405}$ +29.4°), which was decomposed by treatment with 2*N* hydrochloric acid, yielding 70 mg of (−)-**1**. The free optically active acid **1**[8] (with a superimposible ir spectrum with that of racemic **1**) showed an $[\alpha]^{20}{}_{405}$ of −61.5° (*c* 0.26 in absolute alcohol). The CD and uv spectra of resolved **1** are recorded in Figure 1.

(a) The circular dichroism spectra of optically active molecules, better than any other spectral technique, give detailed insight in the distribution of polarizable matter within the molecule.[9] Thus, in the "Dewar" benzene **1** the CD spectra might afford a clue as to the overlap of the π orbitals of the two cyclobutene moieties in the molecule **1**, information which cannot be obtained by inspection of uv spectra.[10] In the case at hand, the CD spectrum of (−)-**1** clearly shows two separate optically active transitions at 218 and 282 nm, respectively. The latter transition may safely be attributed to the "cinnamic acid" chromophore of **1**. The low wavelength transition may be due to olefinic π—π overlap. However, definite proof must await further work.

(b) Racemization of an optically active "Dewar" benzene can proceed by a number of pathways. Thermal, photochemical, and metal catalyzed paths may furnish prismanes, benzenes, other valence bond isomers, or a mixture of these. In addition racemization could proceed by a flapping motion of the "Dewar" benzene. It is clear therefore that the measurement of the disappearance of rotation of optically active **3**[11] by itself is insufficient for the complete elucidation of the "pathway" problem. We have determined first the products obtained when **3** was subjected to heat and light. Thus, at 250° **3** was converted to the diphenyl **5** (mp 79-80°). The remarkably high yield (>90%) conversion of **3** to the prismane **4** (mp 75-80°)[6,13,14] is especially noteworthy. The reaction is carried out by irradiation at 350 nm in ether at room temperature and is complete within 1 hr. This virtually quantitative conversion of **3** to **4** is undoubtedly due to the large difference in λ(max) of starting material and product allowing irradiation of **3** at a wavelength at which **4** does not absorb appreciably, a condition which does not obtain with "Dewar" benzenes studied previously.[1b] When these two experiments were repeated with optically active (−)-**3**, complete loss of optical activity was observed, a consequence of the achirality of **4** and **5**. We are working on the synthesis of chiral prismanes.[15]

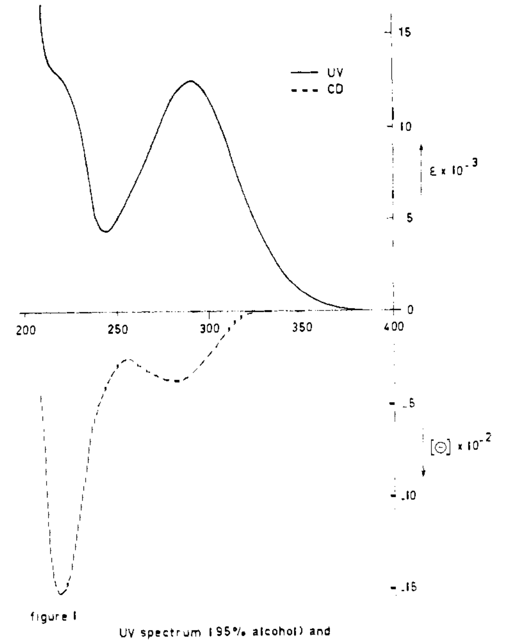


Figure 1. Uv spectrum (95% alcohol) and CD spectrum (*n*-hexane) of **1**.

Table I. Nmr data of **1**, **3**, and **4**[a]

Compound	CH_3 (C_1,C_4)	CH_3 (C_5,C_6)	$COOCH_3$	C_6H_5
1	1.32 (s)	1.68 (q)		7.33 (m, 3 H)
	1.34 (s)	1.73 (q)	—	8.02 (m, 2 H)
		$J_{5,6} \cong 1$ Hz		
3	1.28 (s)	1.66 (q)	3.72 (s)	7.28 (m, 3 H)
	1.32 (s)	1.70 (q)		7.88 (m, 2 H)
		$J_{5,6} = 1.3$ Hz		
	CH_3 (C_4,C_5)	CH_3 (C_1,C_6)		
4	1.24 (s)	1.36 (s)	3.56 (s)	7.18 (m, 5 H)

[a] Solutions in carbon tetrachloride (**3**, **4**) and acetone-d_6 (**1**); chemical shifts are expressed in δ values.

Acknowledgment. We wish to thank Dr. P. Wade and Dr. R. M. Kellogg for valuable comments and Dr. L. A. Hulshof for recording the CD spectrum.

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(5) Using basic Alumina (Merck, act 1) and cyclohexane as eluents.

(6) The "melting points" of **1** and **4** may well represent the melting ranges of a mixture of **1** and **6** and **4** and **5**, respectively.

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(8) The optical purity has not yet been determined. The resolved acid (−)-**1** is optically stable at room temperature for at least 3 weeks in the dark.

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(15) Note Added in Proof. (a) We have recently obtained **1** with a $[\alpha]^{20}{}_{405}$ of $-136.7°$ (*c* 0.3 in abs. alcohol). (b) The conversion of **4** to **5** proceeds as shown in Scheme I in high yield. Positional isomers of the diphenyl **5** have not yet been detected.

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On the Mechanism of the Electrochemical Reduction of Cyclooctatetraene

Sir:

It has been known for some time that the ultimate product of the electrochemical reduction of cyclooctatetraene (COT) is a mixture of 1,3,5- and 1,3,6-cyclooctatriene.[1] However, the mechanism of this reduction has not been definitely elucidated. In particular it is not clear whether the eec (eq 1) or ece (eq 2) mechanism predominates in aprotic solvents containing tetraalkylammonium salts, other than methyl, as supporting electrolyte. In dimethylformamide

$$\mathrm{COT} \xrightleftharpoons{e^-} \mathrm{COT}\cdot^- \xrightleftharpoons{e^-} \mathrm{COT}^= \xrightarrow{H^+} \mathrm{HCOT}^- \xrightarrow{H^+} \mathrm{H_2COT} \tag{1}$$

$$\mathrm{COT} \xrightleftharpoons{e^-} \mathrm{COT}\cdot^- \xrightarrow{H^+} \mathrm{HCOT}\cdot \xrightleftharpoons{e^-} \mathrm{HCOT}^- \xrightarrow{H^+} \mathrm{H_2COT} \tag{2}$$

(DMF),[2] dimethyl sulfoxide (DMSO),[2] acetonitrile (MeCN),[3] tetrahydrofuran (THF),[3] and hexamethylphosphoramide (HMPA) solutions containing the tetra-*n*-propyl- or -butylammonium ion $(\mathrm{TBA})^+$ in the supporting electrolyte, two distinct one-electron reduction waves are observed polarographically at approximately -1.65 and -1.95 V *vs.* an aqueous saturated calomel electrode.[4] The eec mechanism was originally proposed by Allendoerfer and Rieger[2] to explain the two observed electrochemical steps and is supported by the known stability of $\mathrm{COT}\cdot^-$ in these solvents as demonstrated by esr and by the consistency of the AC polarographic rate data,[2,5] with this mechanism. The ece mechanism was proposed by Theilen and Anderson[3] where the first proton source is the quaternary ammonium ion and is supported by the observation that only one polarographic reduction wave is observed when this proton source is removed by substituting the tetramethyl ammonium ion (TMA^+) in the supporting electrolyte for TBA^+.

The correct mechanism for the reduction can be determined by simultaneous electrochemical electron spin resonance (SEESR).[6] Using this technique the esr signal intensity from $\mathrm{COT}\cdot^-$ can be monitored during a cyclic potential scan. It was shown[6] that for a diamagnetic → paramagnetic reduction where the product was stable, the esr-voltage curve closely resembled the integral of the current-voltage curve, *i.e.*, resembled a charge-voltage curve where increasing negative charge corresponds to an increase in esr signal.

Figure 1 shows, in the upper most curve, a standard cyclic voltammogram of 10^{-3} *M* COT in HMPA using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte on a hanging mercury drop electrode. The voltage sweep rate was 150 mV/sec. The sweep rate dependence of the curve is identical in every respect with that reported previously for DMF, TPAP solutions[2] except that the second reduction product is stable so its reoxidation may be observed even on slow scans. The central curve is a cyclic voltammogram recorded for the same solution at the same scan rate in our SEESR cell on a 15-cm^2 amalgamated gold electrode. The construction details of this cell will be described elsewhere.[7] For the experiments described herein, it performs identically with that previously described by Goldberg and Bard.[6] The lower most curve shows the intensity of the esr signal of $\mathrm{COT}\cdot^-$ as a function of voltage, recorded simultaneously with the current-voltage curve. The magnetic field of the esr spectrometer was adjusted to sit on a first derivative peak of the central line of the $\mathrm{COT}\cdot^-$ nonet throughout the experiment. No other esr spectra are observed by continuous electrolysis at any potential, so the esr signal intensity plotted is entirely due to $\mathrm{COT}\cdot^-$.

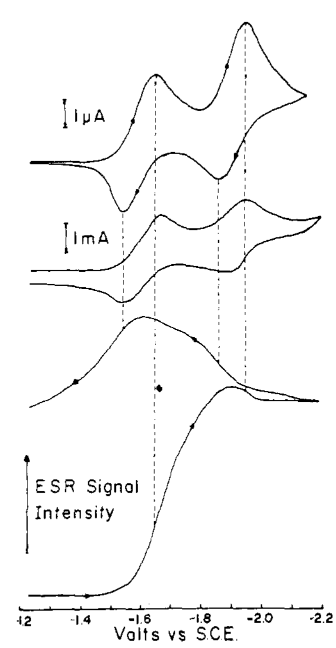

Figure 1. (Uppermost curve) Cyclic voltammogram of COT in HMPA on hanging mercury drop electrode. (Central curve) Cyclic voltammogram of same solution on 15 cm^2 amalgamated gold electrode in SEESR cell. (Lowermost curve) Esr-voltage curve recorded simultaneously with the voltammogram in SEESR cell.

This esr-voltage curve is identical with that shown by Goldberg and Bard[6] for two separate reversible one-electron reductions uncomplicated by following chemical reactions and thus confirms the eec hypothesis. Under the ece mechanism, the steady state concentration of $\mathrm{COT}\cdot^-$ would be determined by the rate of its production relative to the rate of its reaction with the proton donor so the esr signal intensity would be expected to follow the current-voltage curve at first and go through a maximum at the first cathodic peak potential. Thereafter, it should decrease monotonically as diffusion limits the amount of $\mathrm{COT}\cdot^-$ produced. Since the esr signal clearly does not decrease until a potential corresponding to the second reduction peak, $\mathrm{COT}\cdot^-$ must be stable until it becomes the electroactive species at the second peak in accordance with the eec mechanism. The subsequent sharp increase in the esr signal when the potential is again swept anodic of the second peak indicates the $\mathrm{COT}\cdot^- + e^- \rightleftharpoons \mathrm{COT}^{2-}$ reaction is reversible.

Thus I have shown, contrary to the suggestion of Theilen and Anderson,[3] that the COT radical anion is stable in the presence of TBAP and can be reversibly reduced electrochemically to the dianion. Since the single dc polarographic reduction wave of COT in the presence of TMA^+ discussed by Theilen and Anderson[3] in MeCN solution and confirmed by Hayes, *et al.*,[8] for DMF solutions can no longer be explained in terms of the irreducibility of $\mathrm{COT}\cdot^-$, another ex-