methyl groups would have the same geometric factor and therefore the same dipolar shift. However, distortion of the D_{4d} coordination polyhedron to a D_2 polyhedron by folding about one diagonal of each square face, as observed in crystalline $Zr(acac)_4$[12] and β-$U(acac)_4$,[14] results in different values of θ for the two acetylacetonate methyl groups. Calculated values (Table I) of the geometric factor for an *ssss*-D_2 stereoisomer having the D_2 coordination polyhedron found for crystalline β-$U(acac)_4$ predict dipolar shifts of the same sign for the two methyl groups and a dipolar shift of opposite sign for the ring proton. The relative magnitudes of the dipolar shifts for the methyl and ring protons depend upon whether or not the chelate ring folds about the *s* edges (O···O) of the polyhedron; however, the signs of the dipolar shifts for the methyl and ring protons remain opposite for chelate ring dihedral angles (α) of $\lesssim 11°$. Best quantitative agreement between the dipolar shifts and the calculated geometric factors is obtained for the $h_1h_1p_2p_2$-C_2 bicapped trigonal prismatic stereoisomer found in the α crystalline form, with a chelate ring folding angle of $\sim 9.5°$. The rings are folded away from the quasi-$\bar{8}$ axis as is observed in both α[22] and β[14] crystalline forms. Our results suggest, therefore, that $U(acac)_4$ exists in solution as the same $h_1h_1p_2p_2$ stereoisomer found in the α crystalline form and that the paramagnetic shifts are predominantly dipolar. The absolute sign of the shifts (upfield for CH_3, downfield for $-CH=$) indicates that $\chi_{\parallel}$ is greater than $\chi_{\perp}$.

Total line-shape analysis of the methyl resonances of $U(acac)_4$ between -157 (where $k = 69\ s^{-1}$) and -106 °C (where $k = 2.8 \times 10^5\ s^{-1}$) has afforded the following activation parameters for exchange of methyl groups between the two methyl environments: $\Delta H^* = 6.0 \pm 0.1$ kcal/mol, $\Delta S^* = 3.6 \pm 0.8$ eu, and ΔG^* (-110 °C) $= 5.43 \pm 0.04$ kcal/mol. For $Zr(acac)_4$, rate constants vary from $7.2\ s^{-1}$ at -152 °C to $147\ s^{-1}$ at -128 °C, and activation parameters are $\Delta H^* = 4.1 \pm 0.3$ kcal/mol, $\Delta S^* = -18.7 \pm 2.5$ eu, and ΔG^* (-110 °C) $= 7.18 \pm 0.06$ kcal/mol. These rearrangements are intramolecular as evidenced by the fact that exchange of acac ligands between the complexes and free acetylacetone is slow on the NMR time scale at temperatures (-50 °C for $Zr(acac)_4$ and -106 °C for $U(acac)_4$) above the coalescence region.

$Ce(acac)_4$ and $Th(acac)_4$ exhibit a single time-averaged methyl resonance at -169 °C, but limiting slow-exchange spectra have been observed for several other zirconium(IV) and uranium(IV) β-diketonates. For example, the ^1H spectrum of $Zr(acac)_2(NO_3)_2$ below -144 °C is consistent with the *mmmm*-C_2 dodecahedral structure found in the solid state,[23] and the ^{19}F spectrum of $Zr(CF_3COCHCOCH_3)_4$ at -155 °C indicates the presence of more than one stereoisomer. Our work in this area is continuing.

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

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Robert C. Fay,* John K. Howie
Department of Chemistry, Cornell University
Ithaca, New York 14853

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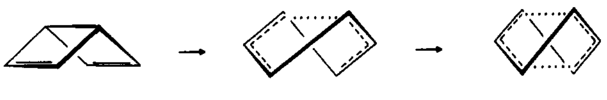
Thermolysis of Bicyclo[2.2.0]hexa-2,5-diene (Dewar Benzene)[1]

Sir:

The isomerization of Dewar benzene to benzene, apparently a symmetry-forbidden yet facile process, can be rationalized in various ways, some of them already published.[2] Independent experimental tests of such hypotheses are less common. We here report results of the first homogeneous gas phase thermolysis study of this precursor, of isotope labeling experiments that exploit its 1,2,4-trideuterio derivative, and of associated secondary deuterium kinetic isotope effect determinations. These severely restrict the useful range of continuing speculation.

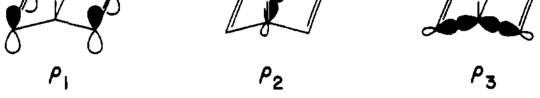
Isotopic scrambling of the precursor, for example, is suggested by two rather different hypotheses. One of them would replace the symmetry-forbidden $_{\sigma}2_s + _{\pi}2_s$ transformation by a spin-forbidden thermal crossing, initially to the lowest triplet state of the product.[2c,d] Experimentally, this triplet was detected through the fluorescence of 9,10-dibromoanthracene which it induces.[2c] The close correspondence between the observed $\Delta H^{\ddagger}$ (23 kcal/mol)[3] and the estimated $\Delta H°$ (≈ 25 kcal/mol)[2c] allows this first step also to be reversible and, hence, detectable by isotopic scrambling.

An earlier hypothesis provided a more topological escape from the pericyclic selection rule and a more explicit prediction of isotopic scrambling.[2b] Stretching of the central bond "accompanied by a quasi-conrotatory skewing distortion" (e.g., **1** → **1a**) would generate two mutually orthogonal allylic radicals, coupled only weakly and in an acyclic way across the residual bond. In retrospect, **1a** provides an alternative explanation for the subsequently discovered unsymmetrical substituent effects on reaction rate.[3,4] The weakly coupled allylic fragments can be stabilized by level splitting and by charge transfer. Isotopic scrambling becomes mandatory if distortion reaches the structure shown as **1b**, the "twist" transition state of a Cope rearrangement.[5]



1 1a 1b

An isotopically rearranged product instead is suggested by a third hypothesis and by its supportive experimental data.



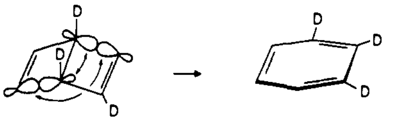
$$\psi(8a_1) = 0.88\ \rho_1 - 0.30\ \rho_2 + 0.33\ \rho_3 + \cdots$$

Table I. Kinetics of Dewar Benzene Isomerization at 61.2 °C

Pressure, Torr	10^4k (s^{-1})[a]	P_0[a,b]	R factor[c]
526	1.78 ± 0.05	0.97 ± 0.02	0.018
53	1.78 ± 0.05	0.99 ± 0.02	0.023
4.2	1.69 ± 0.08	0.99 ± 0.03	0.029
0.46	1.22 ± 0.08	1.00 ± 0.04	0.040

[a] Uncertainties are standard deviations. [b] Initial purity of Dewar benzene. [c] W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964, p 157.

Photoelectron spectroscopic analysis of Dewar benzene reveals the important contribution of p_3 to the highest occupied of its totally symmetric orbitals.[6] The unhappy correlation of this orbital with a benzene antibonding orbital[7] can then be avoided by the ${}_{\sigma}2_a + {}_{\sigma}2_s$ alternative (eq 1) to disrotatory cyclodissociation.



(1)

Despite failures to detect this mechanism elsewhere,[8a,b] the recently discovered rearrangement of 1,4-pentamethylene Dewar benzene to benzcycloheptene[8c] encourages hope that it might yet be found.

Other alternatives are better considered in conjunction with the experimental data that exclude them. For example, a "quantum-chain" mechanism[9] is excluded by the insensitivity of k to a tenfold reduction of pressure (526 → 53 Torr, Table I). These data also lend some generality to the activation parameters, previously obtained in tetrachloroethylene solution ($\Delta H^{\ddagger} = 23.0$ kcal/mol, $\Delta S^{\ddagger} = -5$ cal/mol·deg, whence $k^{61.2\,°C} = 5.0 \times 10^{-4}$).[3] Experimentally, k was here obtained by nonlinear least-square fitting of Dewar benzene attributable fractional ^{1}H NMR areas (f_D) to

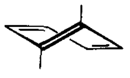
$$f_D = P_0 e^{-kt} \tag{2}$$

The absence of extraneous peaks in such spectra and the closely similar cyclodissociation rate of benzvalene ($k^{61.2°}_{\text{heptane}} = 1.78 \times 10^{-4}$)[10] exclude this isomer as a potential intermediate. Prismane is excluded because it reacts too slowly.[11] 3,3′-Bicyclopropenyl is reasonably presumed to be even more sluggish.[12]

Kinetics were followed into the low pressure region, in part to confirm unimolecularity but also to probe a more general hypothesis. Whether described as a "twixtyl",[13] "continuous biradical",[14] or in other ways,[15] a relatively flat potential energy surface surrounding the transition state region of a forbidden reaction has become an increasingly popular speculation. The necessary consequence of this suggestion—an unusually high density of vibrational states—suggests three possible observations: (a) onset of the bimolecular activation region at unusually high pressures, (b) an increased multiplicity of products in this region, (c) a more conspicuous statistical weight isotope effect in this region.[16]

Dewar benzene cyclodissociation satisfies none of these expectations. The pressure falloff is not significantly different from that observed in the pyrolysis of other 12-atom hydrocarbons.[17] Both at 481 Torr and at 0.46 Torr, only benzene-*1,2,4*-d_3 was detected, contaminated by <2.4% of its 1,2,3 isomer and by <3.5% of its 1,3,5 isomer.[18] ^{1}H NMR spectra of the reactant, recovered after 51% cyclodissociation at 481 Torr and after 22% at 0.46 Torr, revealed <5% contamination by any isotopic isomer. The experimental secondary deuterium isotope effects (k_{d_0}/k_{d_3}) obtained at 146 Torr (1.25 ± 0.03) or at 0.46 Torr (1.37 ± 0.16)[19] differ inappreciably from each other and from what would be expected for a mechanistic α-d_2 isotope effect associated with central bond cleavage at this temperature.[16,20]

It necessarily follows from these results that there is no single-step pericyclic alternative to disrotatory cyclodissociation. Potential multistep mechanisms are limited to those that would require rate-limiting formation of either *trans,cis,cis*-cyclohexa-1,3,5-triene (**2**) or *trans*-(Dewar benzene) (**3**). The results are sufficiently similar to those of bicyclo[2.2.0]hex-2-ene as to dispel much of the aura hitherto attributed to unusual exothermicity[2] (71 kcal/mol for Dewar benzene vs. 35 kcal/mol for its dihydro derivative).[21] The activation enthalpy is appropriately affected (by 9 kcal/mol) but not the choice of reaction mechanism.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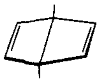
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The triplet benzene hypothesis can be reconciled with these conclusions most simply in a quantitative way. The data that support it apply to at least 0.02% of the reaction;[2c] those that we report apply to at least 93% of the reaction. As long as the sum remains less than unity, all such mechanisms might well coexist. Alternatively, the still incompletely elucidated structure of the benzene triplet[22] provides even more ample opportunities for its accommodation to the mechanistic conclusions defined by this work.

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Supplementary Material Available: Reaction scheme for the synthesis of Dewar benzene-*1,2,4*-d_3, infrared spectroscopic comparisons of benzene-d_3 isomers, and kinetic and isotope effect data (13 pages). Ordering information is given on any current masthead page.

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(18) By infrared spectroscopic comparison with authentically synthesized samples.

(19) This is reduced to 1.30 ± 0.05 if one value is deleted from the set of six. All isotope effects were derived from low-voltage mass spectral analysis of benzene-d_0 and benzene-d_3 obtained after 5–13% pyrolysis of the corresponding isotopic mixture of precursors. Appropriate care was taken to exclude the consequences of mass spectrometric isotopic discrimination.

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(21) (a) Both values assume that ΔH_f(bicyclo[2.2.0]hexadiene) − ΔH_f(bicyclo[2.2.0]hexene) = ΔH_f(bicyclo[2.2.0]hexene) − ΔH_f(bicyclo[2.2.0]hexane) = ΔH_f(cyclobutene) − ΔH_f(cyclobutane) = 30.6 kcal/mol. Neglect of "superstrain"[21b] implies that both are *minimal* estimates of exothermicity. Agreement with the MINDO/3 estimate of Dewar benzene cyclodissociation exothermicity (70 kcal/mol)[21c] is as fortuitous as was the previous agreement of 60 kcal/mol between a different empirical estimate[2c] and the MINDO/2 value[21d] for the same reaction. Experimental data would greatly be preferred. (b) J. F. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976). (c) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1294 (1975). (d) N. C. Baird and M. J. S. Dewar, *ibid.*, **91**, 352 (1969). (e) Still more recent MNDO calculations predict −61.6 kcal/mol for the cyclodissociation of Dewar benzene. They also require the trans isomer (**3**) to be less stable than the cis by 85.8 kcal/mol. **3** would therefore be excluded as a potential intermediate unless the latter value were in error by >63 kcal/mol (M. J. S. Dewar, private communication).

(22) The structure of the ($^3B_{1u}$) benzene triplet is most often regarded as that of a D_{2h}-distorted ground state. Distortions in the sense of **2** or **3** have not explicitly been considered. Cf. P. J. Vergragt and J. H. van der Waals, *Chem. Phys. Lett.*, **36**, 283 (1976), and references there cited.

(23) Taken in part from the Ph.D. thesis of R.S.L., Cornell University, 1977; U.S. Public Health Service Trainee, 1973–1976.

M. J. Goldstein,* R. S. Leight[23]
Department of Chemistry, Cornell University
Ithaca, New York 14853

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A Partial Optical Resolution of a Hydrocarbon by Free-Radical Kinetic Resolution

Sir:

The optical resolution of racemic hydrocarbons must normally be accomplished via indirect and tedious methods.[1] Because of the chemical inertness of hydrocarbons toward standard resolving agents, the direct formation of separable diastereomers is usually precluded. Hydrocarbons do, however, react with free radicals in hydrogen abstraction reactions. Therefore, if there is a significant difference in energy between the two different diastereotopic transition states formed upon approach of a chiral hydrogen abstracting radical to the two enantiomeric forms of the racemic hydrocarbon, it is hypothetically possible to partially resolve the hydrocarbon. If a limiting amount of the hydrogen abstracting species is used, hydrocarbon remaining unreacted should be enriched in the enantiomer which reacts more slowly with the chiral radical. We report here a direct partial resolution of 2-phenylbutane by taking advantage of the difference in the rates of reaction of the two enantiomers with optically active 2-phenyl-2-butoxy radical. This is the first example, to our knowledge, of kinetic resolution[2] reported for hydrogen abstraction by free radicals.

Alkyl hypochlorites have been extensively studied[3] as reagents for effecting free-radical chlorination and react via the chain reaction shown below.

$$\mathrm{ROCl} \xrightarrow{h\nu} \mathrm{RO\cdot} + \mathrm{Cl\cdot}$$

$$\mathrm{RO\cdot} + \mathrm{R'-H} \rightarrow \mathrm{ROH} + \mathrm{R'\cdot}$$

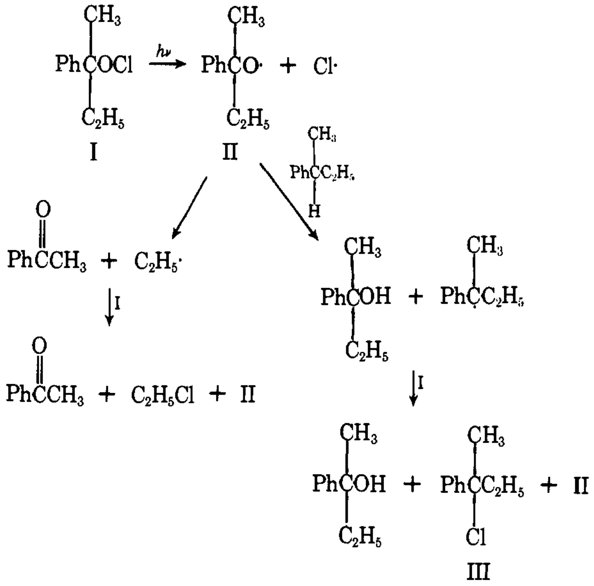
$$\mathrm{R'\cdot} + \mathrm{ROCl} \rightarrow \mathrm{RO\cdot}\ \mathrm{R'\text{-}Cl}$$

If the alkoxy radical contains moieties which can form relatively stable radicals, extensive fragmentation occurs, forming ketones and free radicals. Thus, when a carbon tetrachloride solution of racemic 2-phenyl-2-butyl hypochlorite (I, 5 M) and 2-phenylbutane (II, 0.5 M) which had been degassed by three freeze–thaw cycles was immersed in a 20 °C water bath and photolyzed with a sun lamp, acetophenone and ethyl chloride are produced predominately (~90% of the original hypochlorite). The 2-phenylbutane was 45.2% consumed, and a 38% yield of 2-chloro-2-phenylbutane (III) was produced.

Table I. Results of Photolysis of (+)-2-Phenyl-2-butyl Hypochlorite with Racemic 2-Phenylbutane

Optical purity of hypochlorite, %	27.2	86.2
Starting weight 2-phenylbutane, g	5.36	2.20
Residual weight 2-phenylbutane, g	2.88	1.10
Recovered from gas chromatograph, g	1.90	0.90
Observed rotation, deg	+0.475[b]	+0.31[c]
Specific rotation, deg	+1.24	+4.29
(+) isomer,[a] %	4.4	15.4

[a] Based on a rotation of optically pure 2-phenylbutane of ±28.0 °C: D. Seyferth and Y: M. Cheng, *J. Am. Chem. Soc.*, **95**, 6763 (1973). [b] 1.90 g/5 mL of CCl_4. [c] 0.65 g/9 mL of CCl_4.



Two samples of 2-phenyl-2-butanol of differing optical purity (A, $[\alpha]_D^{25}$ +4.75° (27.2% optically pure[4]), and B, $[\alpha]_D^{25}$ +15.05° (86.2% optically pure[4])), which were resolved by the method of Davies et al.,[5] were converted into the hypochlorites.[6] Solutions of these partially resolved hypochlorites and 2-phenylbutane (10:1 mole ratio) in carbon tetrachloride were photolyzed under the conditions described above. The experimental results are summarized in Table I. The unreacted hydrocarbon was isolated by spinning-band distillation and samples used for determination of optical rotation were collected by gas chromatography to further ensure their purity. Upon second attempted chromatographic separation, no impurities were detected.

By assuming that an initial rate approximation holds and that the rate constant k_+ for reaction of (+)-2-phenylbutane with (+)-II is identical with that of (−)-2-phenylbutane with (−)-II and that the rate constant k_- for reaction of (−)-2-phenylbutane with (+)-II is identical with that of (+)-2-phenylbutane with (−)-II one can derive the expression

$$\frac{\%\ (+)\text{-2-phenylbutane reacted}}{\%\ (-)\text{-2-phenylbutane reacted}} = \frac{k_-(R) + k_+}{k_- + k_+(R)}$$

where R is the original ratio of +/− hypochlorite. The approximation of using a constant ratio of optical purity of the hypochlorite should be valid since at least 90% of the alkoxy radicals derived from the hypochlorite reacts via a first-order decomposition to acetophenone and ethyl radical. When our experimental results are treated in this manner, the ratio k_-/k_+ from expt A is 1.42 and that from expt B is 1.41. This allows