8.7 (1 H, broad, OH); uv max (CH_3OH), 231 nm (ϵ 2.4×10^4).[11]

Presumably, in the absence of excess $IrCl_6^{2-}$ to intercept the intermediate **3**, the latter decomposes in accord with eq 7 or, alternatively, by an equivalent stepwise mechanism involving the release of a benzyl radical (according to eq 4), which is subsequently trapped by one of the DH^- ligands of **3**. Some support for the suggestion that the latter alternative is at least a contributing pathway is provided by the accompanying formation of traces of bibenzyl.

$$Co(DH)_2(H_2O)R^+ + H^+ \longrightarrow Co^{2+} + DH_2 + \mathbf{4} + H_2O \quad (7)$$

Para-substituted benzyl analogs of **1**, *i.e.*, $Co(DH)_2(H_2O)(p\text{-}CH_2C_6H_4X)$, were found to undergo analogous reactions with $IrCl_6^{2-}$, the reactivities increasing somewhat, as expected, with increasing electron-donating ability of X. With the cobalt compound initially in excess over $IrCl_6^{2-}$, the stoichiometry in each case corresponded to that of eq 6 and, in each case, an organic product, whose nmr spectrum, elemental analysis, and molecular weight were consistent with those expected for the corresponding para-substituted analog of **4**, was isolated in quantitative yield. With $IrCl_6^{2-}$ initially in excess over the cobalt complexes, the reactions of the para-substituted compounds exhibited stoichiometries intermediate between those of eq 1 and 6, the organic products being mixtures (ranging from *ca.* 1:2 to 2:1) of the para-substituted benzyl alcohols and the corresponding derivatives of **4** (together with equivalent amounts of DH_2). $Co(DH)_2(H_2O)(p\text{-}CH_2C_6H_4NO_2)$ reacted only very slowly with $IrCl_6^{2-}$. $Co(DH)_2(H_2O)(CH_3)$ was virtually unreactive.

Recent interpretations[12,13] of vitamin B_{12}-dependent reactions, such as the deamination of ethanolamine, have invoked mechanisms involving the homolytic cleavage of the cobalt–carbon bond of vitamin B_{12} coenzyme with formation of a 5′-deoxyadenosyl free radical which plays an important role in the catalytic transformation of the substrate. The observations described in this communication suggest another possible route (*i.e.*, oxidative dealkylation), in addition to those already considered, through which such radical-generating cobalt–carbon bond cleavage might occur.

Acknowledgment. We are grateful to Mr. Daniel Roberts for technical assistance and to the National Institutes of Health and the National Science Foundation for financial support.

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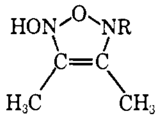
[11] An alternative structural assignment, which is somewhat less readily reconciled with the uv spectral evidence but which cannot be excluded, is that of the closely related cyclic isomer of **4**, *i.e.*



It is planned to establish the structure conclusively by X-ray crystallography.

[12] B. M. Babior, *J. Biol. Chem.*, **245**, 6125 (1970).

[13] P. Y. Law, D. G. Brown, E. L. Lien, B. M. Babior, and J. M. Wood, *Biochemistry*, **10**, 3428 (1971), and references cited therein.

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p-Benzyne. Generation as an Intermediate in a Thermal Isomerization Reaction and Trapping Evidence for the 1,4-Benzenediyl Structure

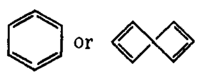
Sir:

We wish to report that *cis*-1,5-hexadiyn-3-ene (**2**) undergoes a striking thermal degenerate rearrangement which requires that it pass through, at least on the average, a species with a new C_2 symmetry axis; *i.e.* *p*-benzyne (**1**).[1] Furthermore, we have obtained evidence that **1** is a true intermediate with a lifetime long enough to allow trapping by external reagents. These trapping reactions suggest that **1** is best represented by the benzene-1,4-diyl structure[2] **1c**. Finally, our data also allow us to estimate a maximum heat of formation for this diradical.

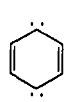
1a

1b

1c

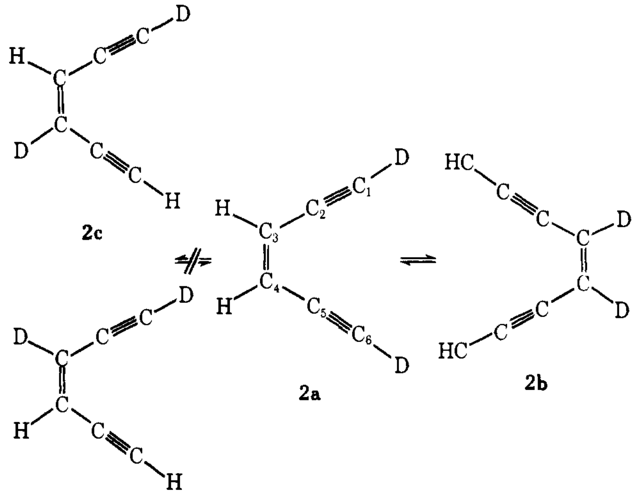


1d



1e

Reaction of 3-hydroxy-1,5-hexadiyne[3] with *p*-toluenesulfonyl chloride in pyridine and treatment of the tosylate with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in triethylene glycol-O-d_2, followed by reexposure of the products[4] to the deuterated medium, produced a 40:60 mixture of **2a** and its trans isomer **3**, >99% deuterated[5] in the acetylenic positions. Gas-phase pyrolysis in a flow system at 300° (atmospheric pressure, contact time



2c **2a** **2b** **2d**

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[1] (a) J. D. Roberts, A. Streitwieser, Jr., and C. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952); (b) M. J. S. Dewar and C. DeLlano, *ibid.*, **91**, 789 (1969); (c) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1003 (1965); (d) I. P. Fischer and F. P. Lossing, *J. Amer. Chem. Soc.*, **85**, 1018 (1963); (e) R. Hoyos de Rossi, H. E. Bertorello, and R. A. Rossi, *J. Org. Chem.*, **35**, 3328 (1970).

[2] (a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); (b) M. D. Gheorghin and R. Hoffmann, *Rev. Roum. Chim.*, **14**, 947 (1969). A correlation diagram using the orbital energy arrangement for **1c** predicted by these workers[2a] suggests that the **2** $\rightleftharpoons$ **1c** interconversion is a symmetry-allowed process. Conversion of **2** into **1a** is predicted to be forbidden.

[3] F. Sondheimer, Y. Amiel, and Y. Gaoni, *J. Amer. Chem. Soc.*, **84**, 270 (1961).

[4] W. H. Okamura and F. Sondheimer, *ibid.*, **89**, 5991 (1967).

[5] Nmr analyses were performed on a Varian A60-A instrument. Mass spectral analyses were carried out on a gas chromatography–mass spectrometry apparatus employing Hewlett-Packard 7620A and EAI Quad-300 instruments.

30 sec) caused complete scrambling[6] of deuterium between the acetylenic and vinyl positions of **2** and *no* such rearrangement in the trans isomer **3** (<1% detectable). The cis scrambling reaction is rapid even at temperatures 100° lower; the label is approximately half-equilibrated after 30-sec exposure at 200°. No scrambling in either isomer took place on ultraviolet irradiation ($\lambda > 220$ nm) in either cyclohexane or benzene solution. Repeated exposure of a sample of **2a**, which has been subjected to pyrolysis, to DBN–triethylene glycol (under conditions shown in independent control experiments to completely replace only the acetylenic deuterium in **2** with hydrogen) produced molecules containing only zero and two deuterium atoms (<2.5% d_1 species). This demonstrated that the scrambling reaction interconverts only **2a** and **2b**; no single-exchange products (**2c** and **2d**) are formed. *These data require that* **2a** *is being transformed via an intermediate or transition state* **1** *in which C-1, C-3, C-4, and C-6 are chemically equivalent.*[6a]

Compound **2** polymerizes at moderately high concentrations in solution even at 25°. When kept sufficiently dilute, however (<0.01 *M*), the material can be heated to 200° without extensive decomposition. In hydrocarbon solvent (2,6,10,14-tetramethylpentadecane), a new product, benzene, begins to appear at the expense of **2a**. This suggests that **1**, like the diradical generated on pyrolysis of *p*-cyclophane,[7] is capable of abstracting hydrogen atoms from a donor solvent. Reaction of **2** in toluene produces diphenylmethane as a major product, and in CCl_4 only 1,4-dichlorobenzene is observed. All these are typical free-radical reactions[8] and are best understood by assuming that the symmetrical intermediate produced on thermolysis of **2** is the 1,4-benzenediyl diradical **1c**. Even when given a choice of behaving as a polar or radical species, the intermediate selects the latter: reaction in methanol at 200° gives mostly benzene and some benzyl alcohol, but *no* anisole.[9]

From the contact time needed to approximately half rearrange **2a** at 200°, one can estimate that $\Delta F^{\neq}$ ($\cong \Delta H^{\neq}$)[10] for the reaction is about 32 kcal/mol. The heat of formation of **2** can be reliably estimated using group equivalent techniques[11] to be +126 kcal/mol. This requires that the maximum $\Delta H_f°$ possible for **1** is the enthalpy of the transition state leading to it, *i.e.*, +158 kcal/mol. However, $\Delta H_f°$ for benzene-1,4-diyl can be estimated[12] by adding two phenyl C–H bond energies (each 112 kcal/mol[11a]) to $\Delta H_f°$ for benzene[13] (+19.8 kcal/mol) and subtracting the bond energy of H_2. The result is +140 kcal/mol, indicating that $\Delta H°$ for the $\mathbf{2} \rightleftharpoons \mathbf{1c}$ reaction is only $\cong$+14 kcal/mol. If the activation energy and endothermicity of this reaction are truly so different, **1c** may lie in an appreciable (18 kcal/mol?) unimolecular energy well and may be capable of detection by spectroscopic techniques, especially if it has a triplet ground state.[2b] Attempts at such detection are under way.

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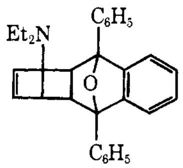
[6] Cis–trans isomerization of **2** becomes detectable only at temperatures ~150° higher than those required for the deuterium scrambling reaction.

[6a] NOTE ADDED IN PROOF. Compound **2** was shown to contain >95% d_2 species both before and after pyrolysis, demonstrating the absence of exchange with adventitious protium on the vessel walls. Further evidence for the unimolecular nature of the $\mathbf{2a} \rightleftharpoons \mathbf{2b}$ reaction has been obtained by thermolysis of a sample of partially deuterated **2** containing 44% d_2, 12% d_1, and 44% d_0 species. No excess d_1 species (limits of detection, 2%) was found in the pyrolysate. We are grateful to Professor Martin Stiles for suggesting this experiment.

[7] H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 3517 (1969).

[8] W. A. Pryor, "Free Radicals," McGraw-Hill, New York N. Y., 1966.

[9] R. Breslow and J. Napierski have prepared 1-chlorobicyclo[2.2.0]hexa-2,5-diene. On treatment with lithium diethylamide in the presence of diphenylisobenzofuran, compound i is produced. If



i

p-benzyne is an intermediate in this reaction, it apparently has a different structure when generated under these conditions than it has in the neighborhood of 200°. We are grateful to Professor Breslow for communicating these results to us prior to publication.

[10] Because no free rotational modes need to be frozen out in the transition state leading from **2** to **1**, the activation entropy ($\Delta S^{\neq}$) is undoubtedly very close to zero for this reaction.[11a] Kinetic studies are being carried out to verify this assumption.

[11] (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

[12] For a discussion of estimates of the heats of formation of other diradicals, and the assumptions involved, see (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968); (b) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970); (c) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18 (1963).

[13] N. S. Osborne and D. C. Ginnings, *J. Res. Nat. Bur. Stand.*, **39**, 453 (1947).

[14] (a) National Science Foundation Predoctoral Fellow, 1969–1971; (b) Alfred P. Sloan Foundation Fellow, 1970–1972; Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1970–1975.

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Structure and Reactivity of Organic Ions in Gas-Phase Radiolysis. V. The Structure and Formation Process of the $C_7H_7^+$ Ion from Toluene[1]

Sir:

The structure of the abundant $C_7H_7^+$ ion derived from toluene and higher alkylbenzenes has attracted a great deal of research interest in the field of mass spectrometry as well as that from other C_7H_8 isomers including cycloheptatriene, and considerable evidence has accumulated which demonstrates that the $C_7H_7^+$ ion is not a benzyl ion but a symmetrical tropylium ion.[2,3] Much of this evidence has been obtained from the isotope labeling studies on the decomposition process

$$C_7H_7^+ \xrightarrow{-C_2H_2} C_5H_5^+$$

For toluene, the isotope retentions in the $C_7H_7^+$ ions from deuterated toluenes indicate that the eight hydro-

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[1] For paper IV, see S. Takamuku, K. Nakamura, and H. Sakurai *Bull. Chem. Soc. Jap.*, in press.

[2] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 453.

[3] A recent study is, for example, A. S. Siegel, *J. Amer. Chem. Soc.*, **92**, 5277 (1970).