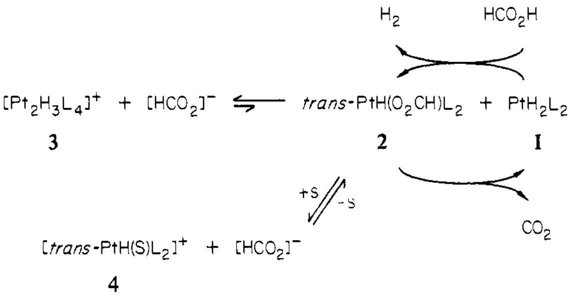
Scheme I. Proposed Equilibria in the Catalysis of $HCO_2H \rightarrow H_2 + CO_2$ ($L = PEt_3$; $S = HCO_2H$, $(CH_3)_2CO$, or CH_3OH)



In solution under 1 atm of ethylene, **3a** quantitatively converts to $Pt(C_2H_4)L_2$ after 24 h (reaction 3). We have shown[6] that

$$\underset{\mathbf{3}}{[Pt_2H_3L_4]^+} + [HCO_2^-] \xrightleftharpoons[CH_3CN]{} \underset{\mathbf{1}}{PtH_2L_2} + trans\text{-}PtH(O_2CH)L_2 \xrightarrow[-CO_2]{C_2H_4} 2Pt(C_2H_4)L_2 + 2H_2 + CO_2 \quad (3)$$

ethylene reacts rapidly with **1** to yield $Pt(C_2H_4)L_2$ and H_2. This apparently drives reaction 3. It is important to note that under identical conditions, **3b**, in the absence of HCO_2^-, did not react with ethylene. Solutions of **3a** placed under 1 atm of $^{13}CO_2$ also rapidly incorporate ^{13}C into the formate counterion. Dimer **3a** therefore appears to react via the small equilibrium concentrations of PtH_2L_2 and $PtH(O_2CH)L_2$.

The complex *trans*-$PtH(O_2CH)[P(i\text{-}Pr)_3]_2$ catalyzes the decomposition of formic acid to hydrogen and carbon dioxide,[3a] a reaction relevant to water–gas shift catalysis.[3,4] The complex $PtCl_2[P(n\text{-}C_4H_9)_3]_2$ has been reported[12] to slowly catalyze formic acid decomposition at high temperatures. Solutions of **3b** show no such catalytic activity after 14 h at 20 °C.[13] However, when sodium formate was added ($[HCO_2^-]:[\mathbf{3}] = 200$), immediate sustained catalysis occurs at a turnover rate of 3.3 ± 0.5 (mol HCO_2H/mol **3**) per hour *at 20 °C*. This rate decreases as the pressure of CO_2 and H_2 above the solution increases, but when these gases are removed, the original catalytic rate returns. Several hundred turnovers were observed with no significant change in activity. A mechanism based on the equilibria described above is diagrammed in Scheme I. Catalytically active platinum species are proposed to be the monomers **1** and **2** present in equilibrium with dimer **3a**. Formate ion promotes catalysis by its reaction with **3** to produce small steady state quantities of **1** and **2**. We independently established that **1** reacts rapidly with formic acid to evolve hydrogen and produce formate ion.[14] Because **2** and **4** should also be in equilibrium in coordinating solvents, excess formate ion should further promote the catalysis by driving this equilibrium toward **2**. Loss of carbon dioxide from **2** completes the cycle. The catalytic cycle can in fact be entered by adding an excess of sodium formate to **4** (as [*trans*-$PtH((CH_3)_2CO)L_2][BF_4]$). Note that the proposed catalytic species **1** and **2** were not detectable by $^{31}P\{^1H\}$ NMR spectroscopy of these solutions, and their concentrations relative to **3** must be quite small. This implies that the turnover rate per molecule of **1** or **2** must be much greater than the turnover rate calculated on the basis of added platinum.[15] The dimerization reaction thus traps and inactivates the catalytic species.[16]

Acknowledgment. We thank the National Science Foundation (Grants CHE 78-01615 and 81-050698) for support of the work and Johnson Matthey, Inc., for a generous loan of platinum.

Registry No. 1, 62945-61-3; **2**, 81768-78-7; **3a**, 81800-04-6; **3b**, 81800-05-7; CO_2, 124-38-9; HCO_2H, 64-18-6.

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(12) Coffey, R. S. *Chem. Commun.* **1967**, 923–924.

(13) $[\mathbf{3b}]_0 = 0.0063$ M, $[HCO_2H]_0 = 9.8$ M, methanol solvent.

(14) In this reaction, a mixture of **3** and **4** rapidly forms. We believe **1** reacts with formic acid to give **4**, either by direct protonation and loss of H_2 or by oxidative addition of HCO_2H and reductive elimination of H_2, with intermediate formation of **2**. (This accords with observations of the reactivity of **1**: ref 6.) Complex **4** (or **2**) can then react with unreacted **1** to give **3**.

(15) On the basis of our limits of detection by $^{31}P\{^1H\}$ NMR spectroscopy of 1%, the turnover rate based on **1** or **2** would be *at least* 2 orders of magnitude greater than the turnover rate based on **3** or **4**.

(16) If these monomeric species were anchored to a rigid support to prevent dimerization, a dramatic increase in catalytic activity should be observed. This possibility is being investigated.

[2 + 2] Cycloaddition Reactions of Homoazulene. A New Synthesis of the Homoheptalene Ring System

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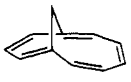
Recent studies on homoazulene (**1**)[1] have significantly advanced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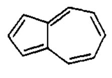
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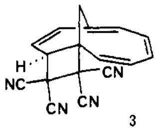
the modern view of π-torsional effects on cyclic conjugation.[2] This unusual hydrocarbon and its derivatives have also provided the first clear data on the effects of nonalternant transannular interactions in cyclic π systems; several parallels between the spectroscopic properties of **1** and those of azulene (**2**) have been noted.[3] By the synthesis developed in our laboratory,[2e,f] homoazulene has now become available in sufficient quantity to permit much more extensive physical and chemical investigation of its unique properties, and we have recently reported on the novel thermal behavior of **1**.[4] Herein we describe the first intermolecular chemical reactions of homoazulene, one of which leads to a crystalline [4*n*]annulene derivative.

At room temperature, homoazulene reacts instantaneously with tetracyanoethylene (TCNE). By conducting the reaction at −45 °C in tetrahydrofuran (0.03 M in each component) for 45 min, we obtained a 1:1 adduct in quantitative yield. Spectroscopic analysis (see Table I) permits assignment of structure **3** to this adduct; the stereoisomer of **3** with an exo tertiary hydrogen is geometrically infeasible.



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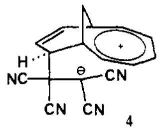

4

Although symmetry forbidden as a concerted reaction, [2 + 2] cycloaddition of TCNE to alkenes frequently occurs via zwitterionic intermediates.[5] In the present case, formation of an aromatic homotropylium ion[6] very likely facilitates the electrophilic attack and accounts for the site of initial C–C bond formation (**4**). The observed periselectivity corresponds to that reported by Hafner et al. in the stepwise [2 + 2] cycloaddition of dimethyl acetylenedicarboxylate (DMAD) to azulene,[7] and the exo stereoselectivity conforms with that observed in the electro-

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(1) Homoazulene = bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene; homoheptalene = bicyclo[5.5.1]trideca-1,3,5,7,9,11-hexaene.

(2) (a) For a discussion of the geometry of homoazulene, see: Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893. (b) Masamune, S.; Brooks, D. W.; Morio, K.; Sobczak, R. L. *Ibid.* **1976**, *98*, 8277. (c) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239. (d) Scott, L. T.; Brunsvold, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 4320. (e) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 274. (f) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216.

(3) Scott, L. T., unpublished results; see also ref 2c and 2f.

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(5) Bartlett, P. D. *Chem. Soc. Quart. Rev.* **1970**, *24*, 473 and references cited therein.

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(7) Hafner, K.; Diehl, H.; Süss, H. U. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 104.

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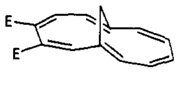
Table I. Physical and Spectroscopic Properties of Cycloadduct 3 and Homoheptalene Diester 5

3 (mp 120 °C dec)
^{1}H NMR ($CDCl_3$) δ 7.08 (d, 1, J = 10 Hz), 6.58–5.98 (m, 5), 5.71 (dd, 1, J = 10, 4 Hz), 4.30 (d, 1, J = 4 Hz), 3.07 (d, 1, J = 12 Hz), 2.67 (d, 1, J = 12 Hz)
^{13}C NMR (CD_3COCD_3) δ 136.8 (d), 132.9 (s), 130.1 (d), 129.2 (d), 126.8 (d), 126.7 (d), 125.1 (d), 115.3 (d), 110.5 (s), 109.9 (s), 108.6 (s), 108.1 (s), 52.3 (d), 49.2 (s), 46.0 (s), 38.1 (s), 30.3 (t)
IR (KBr) 2995, 2915, 2890, 2215, 1447, 1333, 1277 (s), 1075 (s), 930 (vs), 886 (vs), 767 (vs), 730 (vs), 717 (vs) cm^{-1}
UV (CH_3CN) λ_{max} 230, 298
5 (mp 139 °C)
^{1}H NMR ($CDCl_3$) δ 7.19 (s, 1), 7.00 (d, 1, J = 4 Hz), 6.13 (m, 2), 5.93 (d, 1, J = 4 Hz), 5.64 (m, 3), 5.10 (d, 1, J = 12 Hz), 4.95 (d, 1, J = 12 Hz), 3.72 (s, 3), 3.69 (s, 3)
^{13}C NMR ($CDCl_3$) δ 168.4 (s), 167.6 (s), 145.2 (s), 144.3 (d), 144.1 (d), 143.9 (s), 137.2 (d), 136.0 (d), 130.5 (d), 130.4 (s), 130.3 (s), 129.5 (d), 129.3 (d), 126.0 (d), 52.2 (q), 52.1 (q), 31.7 (t)
IR (KBr) 2975, 2920, 1708 (s), 1685 (s), 1585, 1417, 1225 (s), 1055, 915, 772 cm^{-1}
UV (CH_3CN) λ_{max} 226 sh, 270, 413

philic attack on other bridged annulenes.[8]

DMAD adds much more slowly than TCNE to homoazulene. At 82 °C, however, (refluxing $ClCH_2CH_2Cl$, 36 h) the reaction proceeds smoothly to give the homoheptalene diester **5** in 91% yield, presumably via the [2 + 2] cycloadduct **6**. The spectroscopic properties of this blood-red product (see Table I) support the assigned structure. Of special interest are the low-field ^{1}H NMR signals for the CH_2 bridge in **5** (δ ca. 5.0), which reflect a paramagnetic ring current[9] in the newly created [4n]annulene perimeter and contrast sharply with those for the CH_2 bridge in homoazulene (δ ca. −1.0). ^{1}H NMR spectroscopy rules out an α,β-disubstituted homoheptalene derived from the expected [2 + 2] cycloadduct **7**. The addition of DMAD probably follows a stepwise course via an intermediate analogous to **4**, but the zwitterion cyclizes to form **6** rather than **7** for reasons that are presently not clear.



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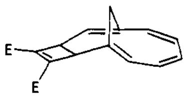

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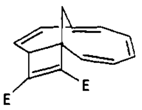

7

E = $COOCH_3$

Structure **5** accounts well for the small coupling constant (J = 4.1 Hz) associated with the clean olefinic AB quartet in the ^{1}H NMR spectrum of this homoheptalene derivative.[10] A significantly larger coupling constant would be expected for the alternative Kekulé structure (**8**) or the fully delocalized structure (**9**).[10] The appearance of an NMR singlet (δ 7.19) and a doublet (δ 7.00) at abnormally low field further strengthens the conclusion that this molecule exists predominantly, if not exclusively, in the bond-localized form **5**.[11]

8

9

Vogel and co-workers have previously prepared the unsubstituted homoheptalene molecule by an elegant ten-step synthetic sequence.[12] The parent hydrocarbon exhibits an even more pronounced paramagnetic ring current (^{1}H NMR) and is likewise characterized by double-bond localization in the ground state (^{13}C NMR and X-ray).[12,13] Equilibration between the two isoenergetic (enantiomeric) Kekulé structures in this case was found to occur with $\Delta G^{\ddagger}$ = 5 kcal/mol.[12]

By the rules of orbital symmetry conservation,[14] disrotatory electrocyclic opening of the cyclobutene ring in **6** to give **5** constitutes a forbidden ground-state reaction. Most likely, therefore, the isomerization passes through a symmetry-allowed ten-electron pericyclic transition state, producing **8** as the initial product, which then rearranges by a low-energy bond-switching process to the thermodynamically more stable isomer **5**. Completely analogous periselectivity has been observed in the disrotatory opening of bicyclo[4.2.0]octa-2,4,7-triene derivatives to give substituted cyclooctatetraenes.[15]

In conclusion, we emphasize the similarity between the [2 + 2] cycloaddition reactions of homoazulene and the known reactions of azulene with electron-deficient cycloaddends. Our results represent the first *chemical* evidence to support the conclusion (previously drawn from spectroscopic data) that the electronic properties of homoazulene resemble those of the prototypical nonalternant hydrocarbon azulene. As a bonus, the DMAD cycloaddition provides a novel high-yield route to the 4n π-electron homoheptalene ring system, which should also be weakly nonalternant through homoconjugation; more thorough studies of homoheptalenes will now be possible.

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health (CA 23488), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Registry No. 1, 65754-71-4; 3, 81741-07-3; 5, 40985-77-1; TCNE, 670-54-2; DMAD, 762-42-5.

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(11) See ref 10, Chapter 3-3.

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Reactions of Aliphatic Radicals with Benzylaquocobaloxime: Kinetics of Coupling Reactions As Studied by Novel Kinetic Competition Methods

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Organocobaloximes[1] are good candidates to employ in a search for the rarely encountered bimolecular homolytic displacement reactions, because the leaving group is the stable cobalt(II) cobaloxime. Catalytic reactions of selected organocobaloximes with tetrahalomethanes[2] and arenesulfonyl chlorides[3] are characterized by products and other features that suggest that one step is a reaction between the cobaloxime and $\cdot CX_3$ or $ArSO_2\cdot$, respectively,

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(1) Cobaloxime is the trivial name given to bis(dimethylglyoximato)cobalt complexes [Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97], designated $Co(dmgH)_2$, where $dmgH^-$ is the monoanion of dimethylglyoxime (2,3-butanedione dioxime).

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