and *cis*-2-pentene does not react readily with **5** at 25 °C.

We should note that the activities of these alkylidyne complexes for acetylene metathesis are far greater than those reported for the heterogeneous[2] or $Mo(CO)_6$/phenol[3] catalysts, possibly in part because our catalyst is a well-defined, stable complex which is present in high concentration. While we cannot conclude that the heterogeneous or $Mo(CO)_6$/phenol catalyst systems contain metal(VI)–alkylidyne complexes, it would now seem worthwhile entertaining that possibility.

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Thermoneutral Dyotropic Transfer of Hydrogen in a Hydrocarbon

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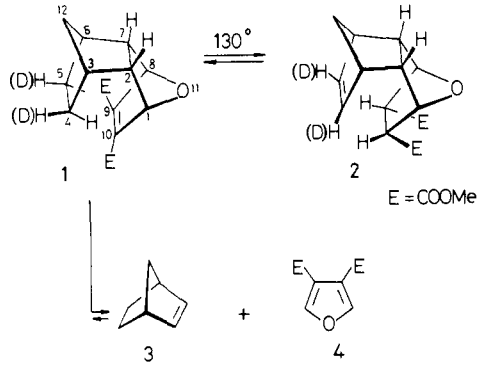
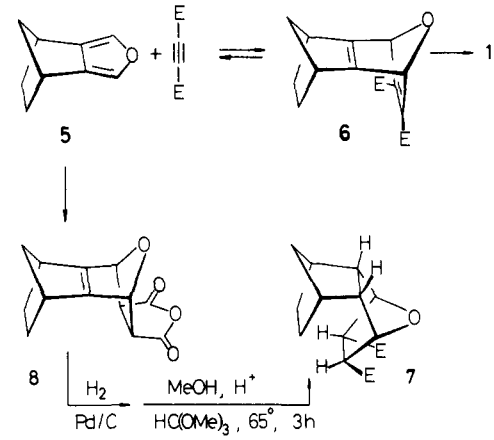
The concerted transfer of two hydrogen atoms from an ethane to an ethylene group in a process suprafacial on both reactants is a thermally "allowed" pericyclic reaction.[1] The diimide reduction of olefins[2] is an example, and analogous reactions with hydrocarbons have also been reported; they are all highly exothermic processes involving the formation of aromatic compounds.[1,3] We report an intramolecular, thermoneutral [$_\sigma 2_s + {}_\sigma 2_s + {}_\pi 2_s$] dyotropic transfer of hydrogen in the *endo,endo*-11-oxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecenes **1** ⇄ **2**. This pericyclic



reaction competes with a cycloreversion yielding 2-norbornene (**3**) and dimethyl 3,4-furandicarboxylate (**4**).[4]

The addition of dimethyl acetylenedicarboxylate to 2-norborneno[*c*]furan (**5**)[5] was highly endo selective (>98%) and gave the diene **6** which could be hydrogenated selectively into **1**.[6] When heated in benzene-d_6 at 130–160 °C, **1** rearranged into **2** (at 130



± 0.2 °C, $k(\mathbf{1} \rightarrow \mathbf{2}) = (2.0 \pm 0.1)10^{-6}$ s^{-1}, by ^{1}H NMR spectroscopy) about 30 times more rapidly than it underwent cycloreversion to yield **3** + **4**. The isomer **2** could be isolated by chromatography on SiO_2 and its structure was deduced from its elemental analysis and spectral data. Catalytical hydrogenation (H_2, Pd–C, acetone, 20 °C) of **2** gave **7**, a compound prepared independently from **8**,[7] the adduct of maleic anhydride to the furan **5**. The structure of **8** has been established by single-crystal X-ray diffraction.[6] Heated in benzene, pure **2** was isomerized into **1** and slowly fragmented into **3** + **4**. An equilibrium constant of 1.1–1.2 was evaluated for **2**/**1** at 130 °C in C_6D_6 [$k(\mathbf{1} \rightarrow \mathbf{2}) \simeq 2.4 \times 10^{-6}$ s^{-1}, **2**/**1** ≃ 3 at 130 °C in MeOH-d_4; **2** is more polar than **1**). At 160 ± 0.2 °C, a rate constant $k(\mathbf{1} \rightarrow \mathbf{2}) = (3.3 \pm 0.2)10^{-5}$ s^{-1} was measured in C_6D_6, thus giving $\Delta H^{\ddagger}$ = 35–39 kcal/mol and $\Delta S^{\ddagger}$ = 2–11 eu. The positive activation entropy term is consistent with an intramolecular mechanism.

The rate constant of the rearrangement **1** ⇄ **2** was not affected by the concentration (0.05–1.2 M), presence of air, SiO_2, or traces of water. This suggested also an intramolecular rather an intermolecular process. When the 4,5-*exo*-dideuterio derivative **1**-*d* was used,[8] the isomer **2**-*d* was deuterated exclusively at the olefinic centers C(4,5). A stepwise mechanism involving the transfer of one endo hydrogen atom and the formation of a diradical intermediate would require a $\Delta H^{\ddagger} \geq 52$ kcal/mol.[11] This is significantly higher than the activation enthalpy observed for **1** → **2**. Thus, thermochemical factors as well as the deuterium labeling

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(8) **1**-*d* was prepared by DN=ND[9] reduction of *trans*-5,6-bis(chloromethyl)-2-norbornene[10] which was transformed into 5,6-*exo*-dideuterio-2,3-dimethylenenorbornane. Photooxidation followed by treatment in AcOH yielded the corresponding dideuterated furan **5**.[5] An eventual kinetic isotope effect on the rearrangement **1** ⇄ **2** (vs. **1**-*d* ⇄ **2**-*d*) could not be detected (by ^{1}H NMR spectroscopy).

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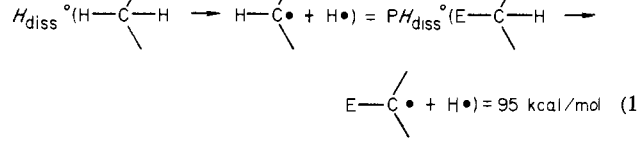
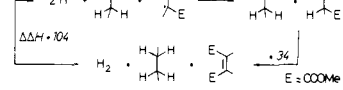
(11) This value [$\Delta\Delta H = \Delta H_f$(diradical) − ΔH_f(**1**)] was estimated by assuming the following homolytic bond dissociation enthalpies:



$H_{diss}°(H_2)$ = 104 kcal/mol[12] and a hydrogenation enthalpy of maleic acid of 34 kcal/mol.[13]



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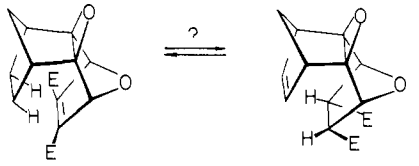
experiment are consistent with a concerted intramolecular mechanism involving the stereospecific 4,5-endo ⇄ 9,10-endo hydrogen double migration. To our knowledge, this is the first case of a thermoneutral [$_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s$] dyotropic transfer of hydrogen in a hydrocarbon.

The lack of a driving force is probably compensated by the compressed structures of **1** and **2**. The distance separating C(4) and C(10) is evaluated [assuming dihedral angles of 112° for C(2,1,10) and C(2,3,4) and 120° for C(1,2,3)[6]] to be a short as 1.8 Å. Consequently, the hydrogen transfer **1** ⇄ **2** must be a short motion. The adduct **6** reacted with air or *m*-chloroperbenzoic acid to yield the epoxide **9**.[6,14] When heated in benzene, **9** did not



9 10

rearrange into **10**. At 180 °C, it slowly decomposed. The apparently retarded dyotropic transfer **9** ⇄ **10** might be due to an unexpected lower stability of **10** compared with that of **9**. Another hypothesis is to invoke a higher activation energy for **9** ⇄ **10** than for **1** ⇄ **2** because of the larger C(4)–C(10) distance in **9**, **10** than in **1**, **2** (dihedral angle C(2,3,6,7)–C(1,2,7,8) being larger in **9**, **10** than in **1**, **2**).

Acknowledgment. We are grateful to Hoffmann-La Roche and Co., Basel, the Swiss National Science Foundation (FN. 2'456-0.79), and Fonds Herbette, Lausanne, for generous support.

Supplementary Material Available: Spectral data and elemental combustion analyses of compounds **2** and **7** (3 pages). Ordering information is given on any current masthead page.

(14) In contrast, the diimide reduction of the C(2,7) double bond in **6** was a very slow reaction and did not compete with the cycloreversion **6** → **5** + EC≡CE. See also: Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.

The New Amino Acid β-Carboxyaspartic Acid (Asa). Laboratory Synthesis and Identification in the Ribosomal Proteins of *E. coli*

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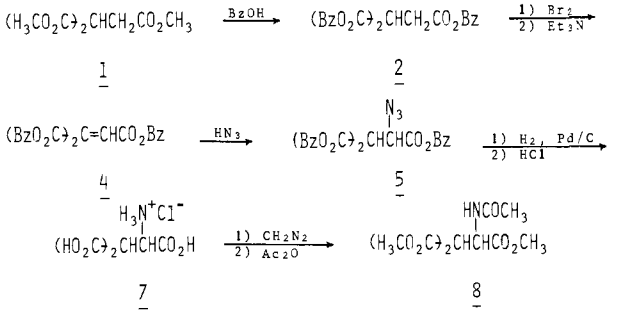
β-Carboxyaspartic acid (Asa) is the homologue of γ-carboxyglutamic acid (Gla), a biologically important amino acid. Gla is formed by the vitamin-K-mediated post-translational γ carboxylation of glutamyl residues in blood coagulation proteins (prothrombin, factors IX, X). The resulting γ-carboxyl groups are essential for calcium binding and blood coagulation.[1,2] Gla has also been identified in bone[3,4] and other tissues[5] and appears to be universally distributed in ribosomal proteins.[6,7] In this laboratory, comparison of alkaline and acid hydrolysates of *E. coli* ribosomal proteins revealed an excess of aspartic acid in the acid hydrolysate. Since Asa, like Gla, can be expected to be stable in alkali but readily decarboxylated in acid, it was theorized that the excess Asp resulted from decarboxylation of Asa, a previously unknown amino acid. We now report that amino acid analysis of alkaline hydrolysates of *E. coli* ribosomal proteins gives a ninhydrin-positive peak coinciding with that of racemic Asa, synthesized by addition of hydrazoic acid to 1,1,2-tris(carbobenzyloxy)ethylene followed by catalytic hydrogenation. Mass spectral studies have confirmed the identity of the synthetic and naturally occurring Asa.

Scheme I



The synthetic approach to Asa shown in Scheme I was suggested by the recent report of Hall and co-workers[8] that methanol adds regiospecifically to 1,1,2-tris(carbomethoxy)ethylene to give 1,1,2-tris(carbomethoxy)-2-methoxyethane. We proposed that a nitrogen nucleophile would react similarly. The initial objective was the preparation of a protected DL-β-carboxyaspartic acid in which the protecting groups could be removed rapidly and simultaneously by catalytic hydrogenation, since the presumed Asa from natural sources was expected to be quite labile with respect to decarboxylation.

The starting material, 1,1,2-tris(carbomethoxy)ethane (**1**), was prepared as described by Hall and co-workers by the nucleophilic substitution reaction of sodium dimethylmalonate with methyl chloroacetate.[9] Transesterification of **1** in refluxing benzyl alcohol for 4 h at 60 °C under reduced pressure (5×10^{-2} torr) catalyzed with potassium hydroxide gave pure tris(carbobenzyloxy)ethane (**2**, 98%).[10] Bromination of **2** with 1.01 equiv. of bromine in refluxing carbon tetrachloride for 2 h with total exclusion of light yielded 1-bromo-1,2,2-tris(carbobenzyloxy)ethane (**3**, 88%).[11] When light was present the yield of **3** was substantially reduced by competitive bromination at the benzylic positions as indicated by the formation of benzaldehyde upon aqueous workup. Compound **3** was purified by TLC using Merck silica gel F 254 preparative layer plates eluting with 3:1 v/v methylene chloride–ether. Subsequent reaction of **3** in ether at 0 °C with 1 equiv of triethylamine for 3 h yielded pure tris(carbobenzyloxy)ethylene (**4**, 100%).[12] Compound **4** was reacted with hydrazoic acid by

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(10) Compound **2** has the following physical properties: mp 40.5–42 °C; IR ($CHCl_3$) 5.78 μm; ^1H NMR ($CDCl_3$) δ 3.04 (d, J = 7.5 Hz, 2 H) 3.98, (t, J = 7.5 Hz, 1 H), 510 (s, 2 H), 5.15 (s, 4 H), 7.30 and 7.33 (2s, 15 H); mass spectrum (70 eV), *m/e* (relative intensity) 197 (45), 107 (74), 91 (base), 78 (10), and 65 (16).
(11) Compound **3** has the following spectroscopic properties: IR ($CHCl_3$) 5.73 and 12.70 μm; ^1H NMR ($CDCl_3$) δ 3.46 (s, 2 H), 5.02 (s, 2 H), 5.09 (s, 4 H), 7.23 and 7.27 (2s, 15 H); mass spectrum (70 eV), *m/e* (relative intensity) 107 (24), 91 (11), 90 (base), and 64 (13).
(12) Compound **4** has the following physical properties: mp 44–45 °C; IR ($CHCl_3$) 5.8 μm; ^1H NMR ($CDCl_3$) δ 5.11 (s, 4 H), 5.19 (s, 2 H), 6.89 (s, 1 H), and 7.19–7.29 (m, 15 H); mass spectrum (70 eV), *m/e* (relative intensity) 430 (M^+, 0.1), 107 (11), 91 (20), and 90 (base).

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