obtained in this way demonstrate that the rate constants cited above are composite values for the reaction of two or more $C_4H_4^+$ isomers. In both hexadiynes and pyridine, there is present a $C_4H_4^+$ species which reacts with benzene-d_6 with the same rate constant as that measured for the reactive $C_4H_4^+$ component produced in pure benzene and a $C_4H_4^+$ population which is unreactive with benzene-d_6. With a nominal electron energy of 15 eV, the fraction of reactive $C_4H_4^+$ ions in benzene, 1,5-hexadiyne, 2,4-hexadiyne, and pyridine was, respectively, 60 ± 5%, 65 ± 5%, 60 ± 10%, and 50 ± 10%.

In order to assess the effect of internal energy on the relative abundance of the two $C_4H_4^+$ populations in benzene, $C_6H_6^+$ ions were produced by charge transfer from CO^+ (CO ionization energy = 14.0 eV), N_2^+ (N_2 ionization energy = 15.58 eV), and Ar^+ (Ar ionization energy = 15.75 eV) so that the range of energy content of the $C_6H_6^+$ ions formed in these experiments was 14.8–16.6 eV. The dissociative charge transfer involving CO^+, whose recombination energy is close to the appearance potential of $C_4H_4^+$ in benzene (13.7 ± 0.2 eV), yielded mainly unreactive $C_4H_4^+$ (>95%). In sharp contrast, 82 ± 3% of the $C_4H_4^+$ ions formed in the dissociative charge transfer

$$Ar^+ + C_6H_6(B) \rightarrow Ar + C_4H_4^+ + C_2H_2 \quad (3)$$

react with benzene with the same rate constant as the reactive $C_4H_4^+$ ions formed in pure benzene [$k_{Rn} = (6 \pm 1)10^{-10}$ cm^3/(molecule s)]. An average value of 80 ± 2% was found for the abundance of the reactive isomer in similar experiments involving N_2^+ as charge donor. The relative abundances of the reactive and unreactive populations of $C_4H_4^+$ formed in the experiments with Ar^+ and N_2^+ as charge donors was independent of the Ar–C_6H_6 or N_2–C_6H_6 ratio from 5:1 to 40:1. Analogous charge-transfer experiments with the hexadiynes and pyridine could not be carried out because of the reactivity of the $C_4H_4^+$ ions with these compounds.

Because 3-buten-1-yne is the only $C_4H_4^+$ isomer known,[1,11] to have an ionization potential (9.58 eV) higher than that of benzene (9.24 eV), the observation of reaction 2 leads to the conclusion that the reactive $C_4H_4^+$ population consists entirely of ions having the 3-buten-1-yne structure. For information obtainment about the structure(s) of the $C_4H_4^+$ ions which are unreactive toward benzene, various aromatic molecules with ionization potentials[12] below that of benzene were added to a CO–benzene (30:1) mixture. *p*-Difluorobenzene (IP = 9.14 eV), bromobenzene (IP = 8.98 eV), and *p*-dichlorobenzene (IP = 8.89 eV) were found to be unreactive [$k_{Rn} < 10^{-12}$ cm^3/(molecule s)], while electron transfer to $C_4H_4^+$ was found to occur from the following compounds: toluene [IP = 8.82 eV; $k_{Rn} = (1.1 \pm 0.3)10^{-10}$ cm^3/(molecule s)], *p*-fluorotoluene [IP = 8.79 eV; $k_{Rn} = (2.6 \pm 0.3)10^{-10}$ cm^3/(molecule s)], ethylbenzene [IP = 8.77 eV; $k_{Rn} = (8 \pm 0.5)10^{-10}$ cm^3/(molecule s)], and 1,3,5-trimethylbenzene [IP = 8.41 eV; $k_{Rn} = 10 \pm 1$ cm^3/(molecule s)].

The rapid rise in k_{Rn} with an increase in the exothermicity of reaction is typical for near-thermoneutral charge-transfer reactions.[13] On the basis of these rate constant data, a value of 8.8 ± 0.05 eV is suggested for the "apparent" recombination energy of the "unreactive" $C_4H_4^+$ ions in benzene. This value is substantially below the known ionization energy of butatriene (9.20 ± 0.05 eV) and is nearly 1 eV higher than that estimated for methylenecyclopropene (7.96 ± 0.1 eV).[14] However, the apparent recombination energy can be reconciled with what is known about the ionization energies of C_4H_4 isomers if the charge-transfer reaction is written as follows:

$$[c\text{-}C_3H_2(=CH_2)]^+ + \text{aromatic} \rightarrow \text{aromatic}^+ + CH\equiv CCH=CH_2 \quad (4)$$

This is the only reaction which can be written for which the charge transfer to toluene would be near thermoneutral. It has been shown before that isomerization to produce thermodynamically favored configurations can occur in the course of electron-transfer reactions[15] or as the outcome of ion–molecule collisions.[16]

The appearance of a new reaction channel producing linear rather than cyclic $C_4H_4^+$ ions at higher energies is consistent with the pronounced increase in formation of $C_4H_4^+$ relative to other fragment ions in C_6H_6 isomers, which occurs at total energies above 15.6 eV.[4,17]

Apparently, $C_4H_4^+$ is not the only fragment ion from $C_6H_6^+$ which exhibits more than one structure. The $C_6H_4^+$ ion produced in the 30-eV mass spectrum of benzene shows a reactive component [$k_{Rn} = 4.6 \times 10^{-10}$ cm^3/(molecule s)] and an unreactive component [$k_{Rn} < 5 \times 10^{-13}$ cm^3/(molecule s)].

---

[11] Bieri, G.; Burger, F.; Heilbronner, E.; and Maier, J. P. *Helv. Chim. Acta* **1970**, *60*, 2213.

[12] Lias, S. G.; Ausloos, J. *J. Am. Chem. Soc.* **1978**, *100*, 6027.

[13] An extensive study (Lias, S. G., private communication) of charge transfer to aromatic molecules shows that 50% or more of the collisions lead to electron transfer when the exothermicity of reaction is greater than 0.01 eV. Thermoneutral charge-transfer reactions involving aromatic compounds occur with a collision efficiency of 0.05–0.1.

[14] This value is based on the assumption that the value of 7.7 ± 0.1 eV obtained for $\Delta H_f(C_4H_4^+)$ from appearance potential measurements[1-4] does indeed correspond to the heat of formation of the cyclic $C_4H_4^+$ ion. A value for the heat of formation of methylenecyclopropene of 4.18 eV was taken from ab initio calculations of Hehre and Pople W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6441.

[15] Sieck, L. W.; Searles, S. K.; Ausloos, P. *J. Am. Chem. Soc.* **1969**, *91*, 7627.

[16] Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540.

[17] Dannacher, J. *J. Chem. Phys.* **1978**, *29*, 339.

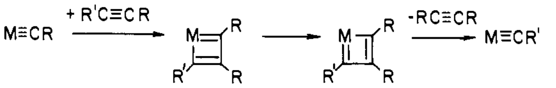
Metathesis of Acetylenes by Tungsten(VI)-Alkylidyne Complexes[1]

Jeffrey H. Wengrovius, José Sancho, and
Richard R. Schrock*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received February 23, 1981
Revised Manuscript Received April 30, 1981

The few reports of homogeneously catalyzed[2] alkyne metathesis in the literature[3] provide no clues as to what the mechanism of this reaction might be, but since olefins are metathesized by alkylidene complexes,[4,5] one might propose that acetylenes are metathesized by alkylidyne complexes via (according to one proposal[6]) the metallacyclobutadiene intermediates shown in eq 1. Recently we prepared some oxoalkylidene complexes of tungsten(VI) (counting the alkylidene ligand as a dianion) which metathesize olefins at 25 °C.[5] Therefore if an alkylidyne complex



(1)

---

[1] Multiple Metal–Carbon Bonds. 21. For part 20; see: Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965–966.

[2] The earliest reports were heterogeneously catalyzed metatheses at temperatures of the order of 400 °C with tungsten oxides on a support such as silica: (a) Pannella, F.; Banks, R. L.; Bailey, G. C. *J. Chem. Soc., Chem. Commun.* **1968**, 1548–1549. (b) Moulijn, J. A.; Reitsma, H. J.; Boelhouwer, C. *J. Catal.* **1972**, *25*, 434–436.

[3] (a) Mortreux, A.; Delgrange, J. C.; Blanchard, M.; Labochinsky, B. *J. Mol. Catal.* **1977**, *2*, 73. (b) Devarajan, S.; Walton, O. R. M.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *181*, 99–104.

[4] (a) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (b) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283. (c) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Ibid.* **1979**, *17*, 449. Rooney, J. J.; Stewart, A. *Catalysis (London)* **1977**, *1*, 277.

[5] (a) Third International Symposium on Metathesis, Lyons, Sept 10–12, 1979. (b) Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73–83. (c) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515–4516

[6] Katz, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 1592–1594.

0002-7863/81/1503-3932$01.25/0

Table I. Metathesis of Acetylenes[a]

acetylene (mmol)	solvent (mL)	catalyst (mmol)	rate[b]	equilibrium
PhC≡CEt (1.9)	toluene (6)	**5** (0.10)	0.15 min^{-1}	4 h
CyC≡CEt (2.1)	toluene (9)	**5** (0.076)	1.6 min^{-1}	~18 min
PhC≡Ctol (1.9)	toluene (6)	**5** (0.063)	0.6 min^{-1}	~1 h[c]
EtC≡CPr (78)	pentane (40)	**5** (0.034)	300 min^{-1}	~10 min[d,e]
PhC≡Ctol (3.5)	THF (2)	**1** (0.12)	~1 h^{-1} [f]	~2 h at 60 °C

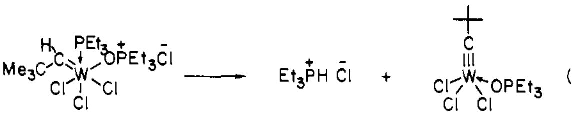
[a] Catalyst removed by passage through activated alumina before GLC analysis. In one 3-heptyne case the volatiles were removed from the catalyst and shown to consist of the expected products. T = 25 °C unless otherwise noted. Ph = C_6H_5; tol = *p*-C_6H_4Me; Pr = *n*-C_3H_7; Et = C_2H_5; Cy = C_6H_{11}. [b] Estimated initial turnover rate at time zero. [c] The *tert*-butyl containing products consisted of equal parts of PhC≡CCMe$_3$ and tolC≡CCMe$_3$ (~1 equiv total) and a trace of Me$_3$CC≡CCMe$_3$. [d] EtC≡CCMe$_3$ and PrC≡CCMe$_3$ were found in nearly equal amounts (1 equiv total). [e] In neat acetylene (13 g) using 50 mg of **5** (acetylene/W ≈ 1600), equilibrium was reached in less than 1 min at 25 °C. [f] Approximately 60% of expected initial metathesis products (1:1) were present after 1 h.

is to catalyze the metathesis of acetylenes, perhaps it too should contain tungsten(VI) (counting the alkylidyne ligand as a trianion). The only one which is known, [W(CCMe$_3$)(CH$_2$CMe$_3$)$_3$]$_2$,[7] is not the best candidate, since the alkyl ligands are potentially reactive. For this reason we have been searching for analogous alkylidyne complexes which do not contain alkyl ligands. Here we report the preparation and characterization of several such complexes and show that some of them do indeed metathesize acetylenes with remarkable and unprecedented ease.

A simple neopentylidyne complex was first prepared by the route shown in eq 2. Tetrachloroethylene, Et$_3$P$^+$HCl$^-$, and blue

$$\mathrm{W(O)(CHCMe_3)(PEt_3)_2Cl_2 + C_2Cl_6 \xrightarrow{THF} C_2Cl_4 + Et_3P^+HCl^- + \underset{\mathbf{1}}{W(CCMe_3)(O{=}PEt_3)Cl_3}} \quad (2)$$

1 all form nearly quantitatively. W(CCMe$_3$)(O═PEt$_3$)Cl$_3$ was characterized by NMR methods[8] and its reaction with PEt$_3$ to give blue W(CCMe$_3$)(O═PEt$_3$)(PEt$_3$)Cl$_3$ (**2**)[9] and with excess PMe$_3$ to give rather insoluble, yellow W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$ (**3**)[10] and Et$_3$P═O quantitatively. The object of the reaction shown in eq 2 was to form W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$[5c] and Et$_3$P$^+$ClCl$^-$.[11] We believe this is, in fact, the first step and that Et$_3$P$^+$ClCl$^-$ then attacks the oxo ligand in W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$ to give the intermediate shown in eq 3 from which **1** forms by loss of Et$_3$P$^+$HCl$^-$. Support for this intriguing mechanism consists of the fact that W(O)(CHCMe$_3$)(PEt$_3$)Cl$_2$ reacts with Pr$_3$P$^+$ClCl$^-$ in THF to give Et$_3$P$^+$HCl$^-$ and a product analogous to **1** which reacts with PMe$_3$ to give **3** and Pr$_3$P═O. We suspect that loss of the oxo ligand is possible largely because a tungsten–carbon triple bond replaces the tungsten–oxygen pseudo triple bond.



(3)

Under some conditions (e.g., in chlorobenzene) a minor product of the reaction shown in eq 2 is a blue salt in which Et$_3$P$^+$H is the cation. We postulated that the anion was [W(CCMe$_3$)Cl$_4$]$^-$ formed by displacement of Et$_3$P═O from **1** by Cl$^-$. This was confirmed by preparing a Et$_4$N$^+$ salt quantitatively by the route shown in eq 4. **4** reacts with PMe$_3$ to give **3** quantitatively.

$$\mathrm{W(CCMe_3)(CH_2CMe_3)_3 + 3HCl + NEt_4{}^+Cl^- \xrightarrow{ether} \underset{\mathbf{4}}{[Et_4N]^+[W(CCMe_3)Cl_4]^-}}{}^{12} \quad (4)$$

Treating W(CCMe$_3$)(CH$_2$CMe$_3$)$_3$ with 3 equiv of HCl in the presence of Et$_3$P═O gives **1**. We believe that **4**, like **1**, is likely to be a tetragonal pyramid with the neopentylidyne ligand at the apex.

[W(CCMe$_3$)Cl$_4$]$^-$ should prove to be a valuable starting material for the preparation of other neopentylidyne complexes. An example is shown in eq 5. Pale yellow, pentane soluble **5** is thermally stable and sublimable.

$$\mathrm{[Et_4N]^+[W(CCMe_3)Cl_4]^- + 3LiOCMe_3 \xrightarrow{THF} \underset{\mathbf{5}}{W(CCMe_3)(OCMe_3)_3}}{}^{13} \quad (5)$$

All of these tungsten(VI)–neopentylidyne complexes will react with diphenylacetylene to give the initial organic metathesis product and analogous benzylidyne complexes. For example, W(CCMe$_3$)(O═PEt$_3$)Cl$_3$ reacts with diphenylacetylene at 70 °C in toluene in 1 h to give >95% of the expected PhC≡CCMe$_3$ and a green solution. Addition of PMe$_3$ to the green solution gave yellow W(CPh)(PMe$_3$)$_3$Cl$_3$[14] in 90% yield. W(CCMe$_3$)(PMe$_3$)$_3$Cl$_3$ and W(CCMe$_3$)(O═PEt$_3$)(PEt$_3$)Cl react with PhC≡CPh but more reluctantly than **1** does. We think it likely that the phosphine and phosphine oxide ligands simply block the acetylene's access to the metal just as ligands block reaction between an alkylidene complex and an olefin.[15] Further evidence for this hypothesis is the fact that W(CCMe$_3$)(OCMe$_3$)$_3$ reacts readily with diphenylacetylene to give PhC≡CCMe$_3$ (1 equiv) and a high yield of sublimable, yellow W(CPh)(OCMe$_3$)$_3$.[16]

Given that the "stoichiometric metathesis" reactions proceed in high yield it was not surprising to find that all the tungsten(VI)–alkylidyne complexes will catalytically metathesize some acetylenes (Table I). What was surprising was the rate of some of these metathesis reactions. The most impressive is the metathesis of 3-heptyne with **5**. The amount of total acetylene at equilibrium equalled that we started with, i.e., no oligomers formed. A ^{13}C NMR spectrum of the yellow solution during the catalytic reaction shows alkylidyne α-carbon signals which we have tentatively ascribed to W(CPr)(OCMe$_3$)$_3$ and W(CEt)(OCMe$_3$)$_3$. The fact that 3-heptyne is metathesized much more rapidly neat (see footnote e, Table I) suggests the reaction is at least first order in catalyst and first order in substrate, as one might expect. The other results in Table I suggest, as one might further expect, that the rate of productive metathesis will depend sensitively on the steric and electronic properties of the acetylenes and the ligands on the catalyst. Further studies should elucidate these features of the acetylene metathesis reaction, which, superficially at least, are related to some features of the olefin metathesis reaction.

One limitation we have discovered so far is that methylacetylenes cannot be metathesized as efficiently as ethylacetylenes, most likely due to adverse reactions involving the 2-butyne product. 2-Butyne rapidly reacts with **5** to give a white, insoluble, and as yet unidentified polymer. We suspect that terminal acetylenes likewise will not be metathesized efficiently. Two other interesting findings are that we have metathesized acetylenes in acetonitrile

---

(7) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774–6776.

(8) ^{13}C NMR (ppm, C$_6$D$_6$) 329 (s, J_{CW} = 208 Hz, *C*CMe$_3$), 46.1 (s, C*C*Me$_3$), 34.9 (q, J_{CH} = 127 Hz, CC*Me*$_3$), 17.9 (dt, J_{CH} = 124, J_{CP} = 66, OP(*C*H$_2$CH$_3$)$_3$), 5.64 (q, J_{CH} = 124 Hz, OP(CH$_2$*C*H$_3$)$_3$. ^{31}P{^{1}H} NMR (ppm) 82.4.

(9) Anal. Calcd for WC$_{17}$H$_{39}$Cl$_3$OP$_2$: C, 33.38; H, 6.42. Found: C, 33.70; H, 6.46. C$_\alpha$ at 340 ppm (doublet) in C$_6$D$_6$ with J_{CP} = 14.5 Hz. ^{31}P{^{1}H} NMR (ppm) 63.9 (O═PEt$_3$), 33.2 (J_{PW} = 256 Hz, PEt$_3$).

(10) Anal. Calcd for WC$_{14}$H$_{36}$Cl$_3$P$_3$: C, 28.62; H, 6.18. Found: C, 29.08; H, 6.25. C$_\alpha$ at 400 ppm (quartet) in CDCl$_3$ with J_{CP} = 40 Hz. Its insolubility suggests it might be a salt, e.g., [W(CCMe$_3$)(PMe$_3$)$_3$ Cl$_2$]$^+$Cl$^-$.

(11) Appel, R.; Schöler, H. *Chem. Ber.* **1977**, *110*, 2382–2387.

(12) Anal. Calcd for WC$_{13}$H$_{29}$Cl$_4$N: C, 29.74; H, 5.57. Found; C, 30.28; H, 5.69. C$_\alpha$ at 337 ppm in CDCl$_3$.

(13) Anal. Calcd for WC$_{17}$H$_{36}$O$_3$: C, 43.23; H, 7.68. Found: C, 43.06; H, 7.69. C$_\alpha$ at 271 ppm in C$_6$D$_6$.

(14) Anal. Calcd for WC$_{16}$H$_{32}$P$_3$Cl$_3$: C, 31.63; H, 5.31. Found, C, 31.66; H, 5.20. C$_\alpha$ at 357 ppm in CDCl$_3$.

(15) Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440–1447.

(16) Anal. Calcd for WC$_{19}$H$_{32}$O$_3$: C, 46.35; H, 6.55. Found: C, 46.29; H, 6.67. C$_\alpha$ at 257 ppm in C$_6$D$_6$.

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.

Acknowledgment. We thank the National Science Foundation for support (CHE79-05307), the ITP Foundation (Spain) for a fellowship to J.S., and K. B. Sharpless for a gift of several acetylenes.

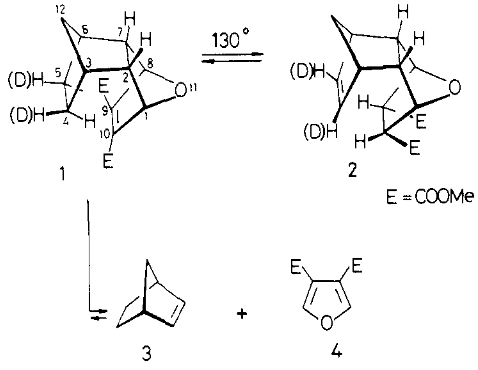
Thermoneutral Dyotropic Transfer of Hydrogen in a Hydrocarbon

Jean-Pierre Hagenbuch, Brigitte Stampfli, and Pierre Vogel*

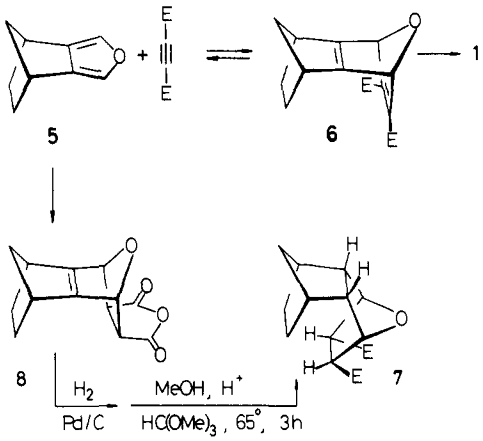
Institut de chimie organique de l'Université
CH-1005 Lausanne, Switzerland

Received February 20, 1981

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 ^1H 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

---

[1] Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Verlag Chemie, GmbH, Weinheim/Bergstr., 1970; p 141. See also: Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189. *Adv. Organomet. Chem.* **1977**, *16*, 33.

[2] Hünig, S.; Müller, H. R.; Thier, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 271. Franck-Neumann, M.; Dietrich-Buchecker, C. *Tetrahedron Lett.* **1980**, 671. Garbisch, Jr., E. W.; Schildcrout, S. M.; Patterson, D. B.; Sprecher, C. M. *J. Am. Chem. Soc.* **1965**, *87*, 2932.

[3] Mackenzie, K. *J. Chem. Soc. C* **1969**, 1784.

[4] Fikentscher, R.; Kröper, H.; Sand, J. *Methoden Org. Chem.* (*Houben-Weyl*), **1966**, *Vol. VI/4*, 674.

[5] Hagenbuch, J.-P.; Vogel, P. *Tetrahedron Lett.* **1979**, 561.

[6] Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta*, *in press*.

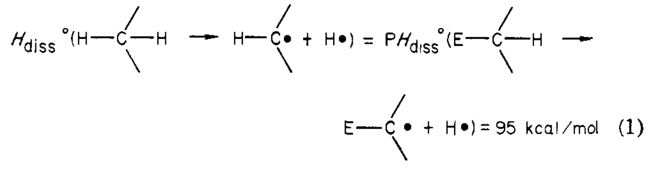
[7] Avenati, M.; Hagenbuch, J.-P.; Mahaim, C.; Vogel, P. *Tetrahedron Lett.* **1980**, 3167.

[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 ^1H NMR spectroscopy).

[9] Berson, J. A.; Poonian, M. S.; Libbey, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 5567.

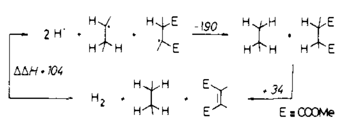
[10] King, R. B.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3590. Toda, T.; Ohya, T.; Mukai, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1561.

[11] This value [$\Delta\Delta H = \Delta H_f(\text{diradical}) - \Delta H_f(\mathbf{1})$] was estimated by assuming the following homolytic bond dissociation enthalpies:



$$H_{diss}{}^{\circ}(\mathrm{H{-}C{-}H} \rightarrow \mathrm{H{-}C\bullet} + \mathrm{H\bullet}) = PH_{diss}{}^{\circ}(\mathrm{E{-}C{-}H} \rightarrow \mathrm{E{-}C\bullet} + \mathrm{H\bullet}) = 95\ \mathrm{kcal/mol} \quad (1)$$

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



[12] Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516, 1537.

[13] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: 1970, London.

0002-7863/81/1503-3934$01.25/0