Scheme III

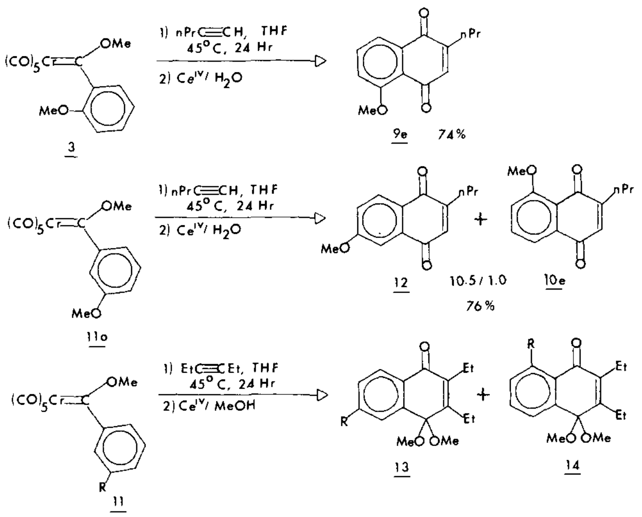


Table II. Regioselectivity of Complex 11[a]

carbene complex	R	yield (13 + 14), %	*13/14*
11a	OMe	81[b]	2.1[d]
11b	Me	79[c]	1.2[e]
11c	F	70[c]	7.5[e]
11d	CF_3	55[b]	25.5[f]

[a] With procedure described in ref 3. [b] Isolated yield. [c] HPLC yield with internal standard. [d] Ratio of isolated products. [e] Ratio by HPLC with internal standard. [f] Ratio by GC (FID); uncorrected.

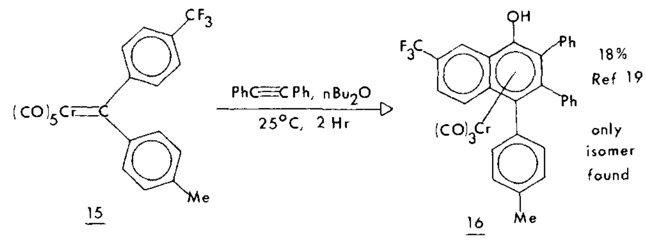
ambiguously confirm the structural assignments for the acetals **7** and **8**. We have done this by carrying out an independent synthesis of **8** from 1-hydroxy-2-acetonaphthone in nine steps.[15]

We have investigated in more detail the regiochemistry of the reactions of the ortho-methoxy carbene complex **3** with unsymmetrical acetylenes, and the results are presented in Table I. The reaction of **3** with 2-pentyne also gives both possible isomeric products; in this case the naphthoquinones **9a** and **10a** in a 1.5:1.0 ratio. The regioselectivity increases with increasing steric differences in the acetylene substituents until in the case of terminal acetylenes the reaction is in fact highly regioselective. The reaction of carbene complex **3** with 1-pentyne gives a single isomer that was identified as **9e** by comparison with an authentic sample prepared from 5-methoxy-2-allyl-1-naphthol.[16,17] This corresponds to a selective incorporation of the largest acetylene substituent (*n*-propyl) α to the carbonyl derived from a carbon monoxide ligand.

Meta substitution of the carbene complex introduces a second regiochemical aspect to this reaction. For the metamethoxyl carbene complex **11a** cyclization can occur at either of the two ortho hydrogens, and thus upon reaction with an unsymmetrical acetylene four isomeric naphthoquinones could be produced. The reaction of **11a** with 1-pentyne, however, gives only the two naphthoquinones **12** and **10e**. Exclusive cyclization to the position ortho to the methoxyl group with concomitant indiscriminate incorporation of 1-pentyne would give the quinones **10e** and **9e**. The fact that **9e** was not formed in this reaction reveals that complex **11a** also reacts regioselectively with 1-pentyne.[18]

The substituent effect on the direction of cyclization was examined in the reactions of several meta-substituted carbene complexes with 3-hexyne, and the results are presented in Table II. In all cases cyclization away from the meta substituent predominates to give the acetal **13** as the major product. A steric argument could account for this but not for the fact that the meta-fluoro complex **11c** gives a ratio of *13/14* six times greater than that of the meta-methyl complex **11b**. This indicates that cyclization preferentially occurs at the more electron-rich position. This observation and conclusion is in direct contrast to the report by Dötz that the diarylcarbene complex **15** reacts with diphenylacetylene to give only **16**, the product resulting from cyclization to the more electron-deficient ring.[19]

Scheme IV



The differences in selectivity between the reactions of complex **11a** with 1-pentyne and 3-hexyne is intriguing. It is not clear how the substituents on the acetylene can affect the direction of cyclization via either the proposed mechanism for this reaction[20] or any of the reasonable alternatives. Therefore, we are continuing an investigation of this and other aspects of this reaction. We have shown here that the reaction of the ortho-methoxy carbene complex **3** with terminal acetylenes gives 2-substituted-5-methoxy-1,4-naphthoquinones in good yields and with high regioselectivity. We are currently employing this result in anthracycline synthesis.

Acknowledgment. This work was supported in part by the Research Corporation, American Cancer Society Institutional grant (IN-41-U-3), and the Louis Block Fund (The University of Chicago). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by NCI via The University of Chicago Cancer Research Center (CA-14599).

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[15] An account of this synthesis will be presented in a full paper on this work.

[16] Eisenhuth, W.; Schmid, H. *Helv. Chim. Acta* **1958**, *41*, 2021-2041.

[17] The crude mixture from this reaction was submitted to an HPLC analysis (Waters RCM radial pak B, ether/methylene chloride/hexane, 1:1:4.7, 6.0 mL/min, retention time of **9e** 5.9 min. By comparison with the retention time of **10e** (3.9 min) it was determined that **10e** was not present in greater than 0.9%.

[18] On this basis the other naphthoquinone produced in this reaction has been assigned the structure **12**.

[19] Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517-2526.

[20] Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449-1457.

First Evidence for the Existence of Intramolecular C-H-C Hydrogen Bonds: Carbanions of [1.1]Ferrocenophane, 1-Methyl[1.1]ferrocenophane, and 1,12-Dimethyl[1.1]ferrocenophane

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We wish to report the observation of rapid proton transfer between two carbon atoms, which we believe to constitute the first case of an *intra*molecular C-H-C hydrogen bond. *Inter*molecular hydrogen bonding between strongly acidic sp-hybridized carbons as in acetylenes and strong acceptor sp carbon functionalities in compounds such as isonitriles has been known for a long time,[1,2] but intramolecular hydrogen bonds between carbon atoms only have, at least to our knowledge, never been observed up to now, although their presence has been postulated occasionally.[3]

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[1] Ferstandig, L. L. *J. Am. Chem. Soc.* **1962**, *84*, 3553.

[2] Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 1715.

[3] For instance, an intramolecular H bond has been assumed to account for the preferred endo conformation of allylpotassium and allylcesium compounds: Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1978**, *98*, 4674.

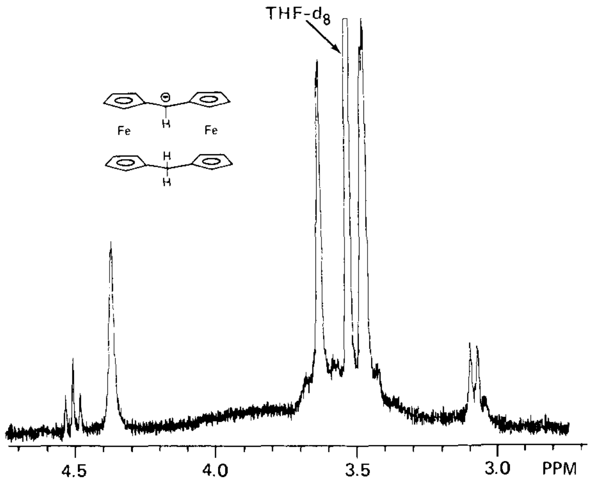
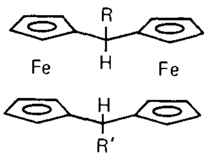


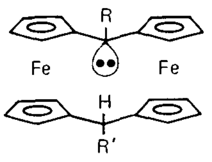
Figure 1. Proton NMR spectrum of the carbanion **2** in THF-d_8 at 360 MHz and 22 °C. The high field doublet corresponds to the two exo protons and the triplet to the bridging endo proton.

Saturated hydrocarbon centers not carrying electron-withdrawing substituents are generally considered to be too weak proton donors to form hydrogen bonds even with strong proton acceptors, such as carbanions.[4,5] Nevertheless, the interaction between a saturated, sp^3-hybridized carbon as the proton donor and a carbanion, which possesses a pair of electrons either in a p- or sp^3-type orbital, does correspond to the three-center, four-electron bonding situation in hydrogen bonds of the usual type as, for instance, in N–H–N systems.[6]

The compound in which we first found evidence for unusual C–H–C interactions is the lithium salt of the carbanion **2** of [1.1]ferrocenophane (**1**). This deep red anion[7] can be obtained by reacting [1.1]ferrocenophane[8,9] with butyllithium in THF. Chemically, we were able to obtain proof for the fact that one and only one proton had been removed in this reaction from one of the bridging methylene groups: reaction of the anion **2** with methyl iodide exclusively produced the bridge methylated 1-methyl[1.1]ferrocenophane (**3**). Even after treating **1** with a large excess of butyllithium and then with methyl iodide, only this derivative was obtained, without any ring methylated or doubly methylated species being formed.[11]



1, R = H; R' = H
3, R = H; R' = CH$_3$
5, R = CH$_3$; R' = CH$_3$



2, R = H; R' = H
4, R = H; R' = CH$_3$
6, R = CH$_3$; R' = CH$_3$

Evidence for the existence of a rapid proton exchange in **2** comes from the 360-MHz proton NMR spectrum[12] at 22 °C in THF-d_8 (Figure 1). Five groups of resonances are observable: the ferrocene ring protons appear as two narrow multiplets at 3.6 and 4.3 ppm of four protons each and an eight-proton multiplet at 3.4 ppm. The three bridge protons form a doublet at 3.09 ppm and a triplet at 4.51 ppm, with a coupling constant of 9.0 Hz and an intensity ratio of 2:1. Double-resonance experiments show that irradiation at the center of the triplet at 4.51 ppm leads to the collapse of the doublet at 3.09 ppm into a singlet. The ^{13}C NMR spectrum of **2** in THF-d_8 at 22 °C and 50.3 MHz was obtained both in the proton coupled and in the decoupled mode. The decoupled spectrum showed only *one* line for the bridge carbon atoms at 29.5 ppm, one signal for the tertiary ferrocene carbons at 99.3 ppm, and four closely spaced signals for the other ferrocene carbon atoms at 63.3, 63.6, 63.7, and 64.3 ppm. The proton-coupled spectrum shows a pattern of four equally intense lines, centered at 29.5 ppm, for the two bridge carbon atoms. This pattern can be analyzed to be a doublet of a doublet with the coupling constants 130.4 and 63.9 Hz. The 130.4-Hz coupling constant clearly results from the interaction of the bridge carbon atoms with their respective "permanent" outer proton. In addition, *both* carbon atoms interact with the inner proton and show a splitting of $J_{\mathrm{C-H}} = 63.9$ Hz. The C–H$_{\mathrm{inner}}$ coupling constant is close to one-half the value of the C–H$_{\mathrm{outer}}$ coupling, which is to be expected from the spreading of this interaction over two carbons instead of one. The value of 130.4 Hz for the C–H$_{\mathrm{outer}}$ coupling shows that *both* bridge carbons are essentially sp^3 hybridized (26% s character).

The parent [1.1]ferrocenophane **1** undergoes a particularly rapid syn to syn exchange, which is evident from its NMR spectra.[9,13,14] From the ^{1}H and ^{13}C spectra of the carbanion **2** we can deduce quite clearly that the anion has become so rigid that the syn–syn exchange no longer occurs and that, on the NMR time scale, this system now possesses not only a vertical plane of symmetry but also a second, horizontal one. This high degree of apparent symmetry can only be understood by assuming that **2** exists as a solvent separated ion pair and that the endo hydrogen is shared between the two bridge carbon atoms so that the proton NMR spectrum shows the two outer protons 1-exo and 12-exo as a doublet due to their equal interaction with the central proton, which appears as a triplet. If the C–Li bond in the anion **2** were covalent,[15] one would, for instance, expect to see the bridge protons

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[4] Pimentel, C. G.; McClellan, A. L. "The Hydrogen Bond"; W. H. Freeman and Co.: San Francisco, 1960.

[5] Green, R. D. "Hydrogen Bonding by C-H Groups"; Wiley: New York, 1974.

[6] Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1970**, *92*, 4849.

[7] The parent [1.1]ferrocenophane **1** has two weak absorptions at 439 and 320 nm (ε 178 and 245, respectively).[10] For the anion **2**, we observe two much more intense peaks at 543 and 408 nm with extinction coefficients of approximately 3100 and 4700, respectively.

[8] Mueller-Westerhoff, U. T.; Nazzal, A.; Prössdorf, W. *J. Organomet. Chem.* **1981**, *205*, C21.

[9] Cassens, A.; Eilbracht, P.; Nazzal, A.; Prössdorf, W.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1981**, *103*, 6367.

[10] Barr, T. H.; Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1969**, *25*, 6001.

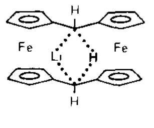
[11] Reaction of **2** with SiCl$_4$ leads to 1-trichlorosilyl[1.1]ferrocenophane, which we have used for the modification of semiconductor surfaces (Nazzal, A.; Mueller-Westerhoff, U. T., unpublished).

[12] Dilute solution (approximately 10 mg/mL) in THF-d_8 without Me$_4$Si. Samples were prepared in the NMR tubes in the following way: butyllithium in hexane (a 1.3:1 molar ratio of butyllithium to ferrocenophane guarantees complete conversion of the neutral compound to its anion) was freed of solvent at 0.01 Torr, then cooled to -70 °C, and diluted with THF-d_8; solid ferrocenophane was added, the sample was briefly warmed to 0 °C to ensure complete reaction, cooled again to -70 °C, and then sealed under vacuum.

[13] Mueller-Westerhoff, U. T.; Nazzal, A.; Prössdorf, W.; Cassens, A.; Mayerle, J. J.; Collins, R. L., submitted for publication.

[14] Molecular models show that the anti form of **1**, which has never been observed, is completely rigid and sterically very unfavorable (repulsion of the inner α protons), while the syn form is flexible and allows a facile and concerted rotation around the methylene bridges, leading to syn–syn exchange. This motion averages not only the exo and endo bridge protons but also the inner and outer α protons as well as the β protons of the ferrocenes in **1**. As a consequence, the ^{1}H NMR spectrum of **1** shows only two narrow multiplets for the ferrocene protons and a sharp singlet for the methylene bridges. From a variable-temperature NMR study, the activation barrier for the syn–syn exchange in **1** can be estimated to be less than 5 kcal/mol.

[15] In spite of our argument for the existence of **2** as a solvent separated ion pair, one should, however, also consider the case of a four-center, four-electron bond as in i, where, in addition to the C–H–C bond, a C–Li–C bond exists.



Several facts speak against **2** having the covalent structure i: Firstly, the NMR spectra of **2** would have to be more complex than they are; especially the α protons could no longer be magnetically equivalent. Furthermore, **2** is completely insoluble in hexane and other hydrocarbons, and it crystallizes from THF solvated by several molecules of THF. This leads us to assume that **2** is unusually ionic in solution as well as in the solid and exists as a solvent separated ion pair.

as one singlet and a pair of doublets, as was found in the case of the carbocation derived from **1**.[13] The same pattern would results for an ionic ase without C–H–C exchange. The NMR data, therefore, clearly establish the presence in **2** of rapid intramolecular proton transfer between the carbon atoms of the bridges. While there can be no doubt that the transition state for this transfer process corresponds to a symmetric hydrogen bond, the above data suggest, but do not prove, that the ground state of **2** also possesses a C–H–C hydrogen bond. Qualitatively, an extrapolation from the known O–H–O and N–H–N bond lengths to a C–H–C system makes it appear likely that the ring–ring distance of 3.31 Å in ferrocene,[16] which dominates the distance of the two syn-oriented methylene groups, would allow the formation of a hydrogen bond in **2**, particularly since the ^{13}C data show that the anionic sp^2 carbon apparently has rehybridized to achieve more sp^3 character. A bonding interaction of this orbital containing a pair of electrons with the endo proton of the opposite methylene group seems to be the reason for the formation in **2** of a C–H–C bond.

An intramolecular hydrogen bond in **2** could be either symmetric or rapidly exchanging between two equivalent positions (single- vs. double-well potential). Considerations of proton donor and acceptor strengths[5] do not rule out a single minimum potential but tend to favor a double minimum potential for the case of a C–H–C hydrogen bond, where the barrier for proton exchange would depend on the C–C distance and the strength of the C–H–C interaction. Either situation would lead to a NMR spectrum of this anion showing a doublet–triplet pattern for the bridge protons, as long as the exchange is rapid. To obtain some information about the exchange rate, a temperature-dependence study of the NMR spectrum of **2** was carried out. We find that over the entire 100 °C range, from +30 to −70, the spectrum remains unchanged. Due to the limited solubility of **2** in THF, all signals broaden below −70 °C. The invariance of the NMR spectrum shows that the barrier for proton exchange in this C–H–C system must be smaller than we would have expected.

Evidence that we indeed are dealing with a C–H–C hydogen bond and not just rapid proton exchange can be found in the proton NMR spectra of the carbanions **4** and **6** derived from 1-methyl[1.1]ferrocenophane (**3**) and 1,12-dimethyl[1.1]-ferrocenophane[9] (**5**), respectively. Reaction of the monomethyl[1.1]ferrocenophane[17] with butyllithium in THF produces the anion **4**. The 90-MHz ^{1}H-NMR spectrum of the deep red solutions of **4** in THF-d_8 at 22 °C shows that a proton has been abstracted from the unsubstituted bridge and also that, in contrast to what was found for the anion **2**, no proton exchange between the two bridge carbon atoms appears to occur. The secondary bridge carries most of the negative charge so that the somewhat broadened singlet of the C–H proton appears at 2.64 ppm, 0.84 ppm upfield from the corresponding bridge signal in neutral **3**. No change is observed in the signal of the methyl group (doublet with $J = 7$ Hz at 1.20 ppm). The corresponding quartet of the endo proton appears at 4.30 ppm, at a position 0.58 ppm downfield from the quartet in **3**. Due to the rigidity of **4** and the absence of proton exchange, eight types of ferrocene protons are observed at 3.26, 3.44, 3.50, 3.54, 3.66, 3.72, 3.86, and 4.85 ppm. Irradiation into the quartet not only produces the obvious collapse of the methyl group doublet into a singlet but also leads to a sharpening of the C–H singlet at 2.64 ppm by approximately 25%. It is this latter observation together with the significant downfield shift of the bridging proton which leads us to believe that in **4** we have come across one extreme of a hydrogen bond: C–H–C interaction exists, but no visible proton exchange takes place. The best description would be that of a quite unsymmetric double-well potential, where the bridging proton predominantly occupies the lower well.[18,19]

Although we can see in the anion **4** that the methyl group destabilizes a negative charge, the symmetrically substituted 1,12-dimethyl[1.1]ferrocenophane (**5**) is readily deprotonated by butyllithium in THF to give the carbanion **6**. As in the case of the parent anion **2**, the ^{1}H NMR spectrum of **6** in THF-d_8 shows that a symmetric double-well potential exists, with rapid proton exchange taking place on the NMR time scale. The ferrocene protons appear as only three multiplets at 4.6 (4 H), 3.8 (4 H), and 3.7 ppm (8 H); the two methyl groups form only one doublet at 1.52 ppm, coupling equally with the bridging central proton ($J = 4.5$ Hz), which appears at 4.70 ppm as a septet. Irradiation into the methyl group doublet leads to the collapse of the septet and vice versa.[20]

It is noteworthy that the chemical shifts of the bridging protons in **2**, **4**, and **6** are so similar, in spite of the differences in substitution and proton exchange rates. At 4.50 ± 0.2 ppm, they are shifted 0.6–1.0 ppm to lower field with respect to their neutral precursors. The possibility that proton exchange alone would be the cause of this shift difference can be excluded because of the absence of rapid exchange in **4**.

The ^{13}C spectra of the carbanions **4** and **6** were recorded at 50.3 MHz and 22 °C. As expected, the latter spectrum is very simple, reflecting the high apparent symmetry of **6** and therefore provides little information beyond that obtained for the parent carbanion **2**. On the other hand, the ^{13}C spectrum[21] of the unsymmetric anion **4** is quite informative. The two carbon atoms of the substituted bridge are accidentally degenerate ($\delta = 31.6$) and appear as a doublet with $J_{\text{C-H}} = 122$ Hz for the bridge carbon and a quartet with $J_{\text{C-H}} = 124$ Hz for the methyl group; the anionic bridge doublet at 33.9 ppm has $J_{\text{C-H}} = 130$ Hz. This last value shows clearly that, in spite of the fact that proton exchange is not ob-

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(16) Seiler, P.; Dunitz, J. D. *Acta. Crystallogr., Sect. B* **1979**, *B35*, 1068.

(17) Only one isomer of **3** exists, because the rapid syn-to-syn exchange equilibrates the exo and endo positions for the methyl group. The ambient temperature 90-MHz ^{1}H NMR spectrum of **3** in $CDCl_3$ shows a doublet and quartet pattern for the CH_3CH group at 1.20 and 3.72 ppm, respectively, with $J = 7$ Hz, a singlet at 3.48 for the CH_2 group, and the 16 ferrocene protons as 2 multiplets at 4.14 ppm (12 H) and 4.54 ppm (4 H). Since, in spite of the syn–syn exchange, the exo and endo bridge protons cannot be magnetically equivalent, their appearance as a singlet must be due to an accidental degeneracy of the chemical shifts. This is confirmed by the 360-MHz spectrum, where this signal is resolved into two doublets with a geminal coupling constant of 18.5 Hz.

(18) Looking for an increase in exchange rate, we raised the sample temperature to 60 °C. Unfortunately, decomposition becomes very rapid above 50 °C, presumably due to reaction of the anion or excess (see ref 12) butyllithium with the solvent. Solutions of **2**, **4**, and **6** in THF can be kept at −70 °C for several weeks. At room temperature, decomposition occurs rapidly.

(19) Reaction of this anion with methyl iodide stereospecifically produces only the exo–exo isomer of **5**. This fact again substantiates our interpretation of the NMR data, from which we conclude that the anion **4** is frozen in the syn conformation with the methyl group in the exo position, while most of the negative charge is localized on the unsubstituted bridge.

(20) Going from the neutral, nonexchanging **5** to the carbanion **6**, the CH_3–CH coupling constant decreases from 7.0 to 4.5 Hz. In the anion **6**, the proton–proton interaction is spread out over both bridges, leading to this decrease in the coupling constant.

(21) The assignment of the three bridge carbon resonances is complicated by the accidental degeneracy of the chemical shifts of the methyl group and its neighboring bridge carbon and by the similarity of their coupling constants. The decoupled spectrum shows a two-carbon signal at 31.6 ppm and the third bridge carbon at 33.9 ppm. In the coupled spectrum, seven peaks are grouped at 35, 33, 30 and 28 ppm, representing the expected two doublets and one quartet. The assignment becomes unambiguous through a reduction of the coupling constants by off-resonance decoupling, whereby the 33.9-ppm signal becomes a doublet and the 31.6-ppm signal resolves into a doublet and a quartet. Selective decoupling at the frequency of the anionic bridge proton (2.64 ppm) collapses the 33.9-ppm signal to a singlet, while irradiation at the proton quartet (4.30 ppm) reduces the complex signal at 31.6 ppm to a quartet and a singlet. With this information, we can unambiguously assign the bridge carbon signals, whereby the coupling constants have an accuracy of ±1 Hz. In the ferrocene carbon portion of the ^{13}C spectrum, we find all except the tertiary carbons shifted to higher field (2 carbons each at 67.9, 67.4, 64.9, 64.5, 63.9, 63.0, 59.9, and 59.4 ppm) with respect to neutral **3**. The tertiary carbons on the substituted side remain practically unchanged (99.5 vs. 93.1 ppm in **3**). An large downfield shift is found for the tertiary carbons adjacent to the anionic bridge carbon: they are displaced by 22.4 ppm from 86.6 ppm in **3** to 109.0 ppm in **4**. This shift corresponds to what we observe for the symmetric parent anion **2**, where all four tertiary carbons are shifted from 87.7 ppm in **1** to 99.3 ppm in **2** ($\Delta\delta$ 11.6), about one-half the shift found in the localized anion **4**, where this effect is limited to two carbons instead of four. In the ^{13}C spectra of all three carbanions it is noteworthy that the bridge carbons, in spite of their negative charge, have chemical shifts very close to those in their neutral presursors but that in each case the adjacent tertiary carbons show a significant downfield shift. It is tempting to speculate that the downfield shifts are due to an increase in conjugation and that this effect is approximately balanced for the bridge carbons by the upfield shift due to the negative charge.

servable, the unsubstituted bridge carbon is essentially sp^3 hybridized, maximizing in this way the overlap between its electron pair and the proton of the opposite bridge.

Although there appears to exist no previous proof for the existence of an intramolecular hydrogen bond between carbon atoms only, we believe that the data presented here find their most attractive interpretation in a three-center, four-electron C–H–C hydrogen bond.

Acknowledgment. Support of this work through a NATO Postdoctoral Fellowship, administered by the DAAD, to W.P. is gratefully acknowledged. U.M.-W wishes to thank Professor Manfred Schlosser (University of Lausanne) for many very helpful discussions and for providing us with 360- and 90-MHz NMR spectra of various ferrocenophanes. Further 360-MHz proton and 50-MHz ^{13}C spectra were obtained at the NMR facility of the University of California at Davis. We thank Dr. Gerry Matson and Dr. Jerry Dallas at UC Davis for their cooperation and help.

Oxygen-Atom-Transfer Reactions from a Carbonyl Oxide (Produced from a 1,2,3-Trioxolane) to Electron-Deficient Unsaturated Compounds

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Many recent studies have focused attention on the transfer of an oxygen atom from carbonyl oxides, a reaction believed to be a model for certain reactions catalyzed by monooxygenase enzymes.[1] Carbonyl oxides are produced in the ozonolysis[2] of alkenes, alkynes, and ketenes and during the photooxidation of diazo compounds.[3-5] Carbonyl oxides transfer oxygen atoms to alkanes,[3] alkenes,[4-6] sulfides,[5,7] and aromatic compounds,[5,8] but until recently very little was known about the characteristics of this reaction. Ogata et al.[5] have recently shown that carbonyl oxides are nucleophilic oxygen-atom-transfer agents.

Oxygen-atom-transfer reactions are relevant to the mechanism of ozonolysis of certain olefins as well. For example the ozonolysis of haloolefins leads to high yields of epoxides,[9] and the ozonation of certain olefins in the presence of tetracyanoethylene (TCNE) produces the epoxide of TCNE.[10a] It is generally not possible to identify the actual oxygen-atom-transfer agent in olefin ozonation reactions; ozone, 1,2,3-trioxolane, and the carbonyl oxide are all potential oxygen-atom-transfer agents, and all three coexist under normal ozonolysis conditions. Furthermore, the competing reaction of the carbonyl oxide with aldehydes to form stable ozonides makes it difficult to study the oxygen-transfer reaction of carbonyl oxides under ozonolysis conditions.

We therefore have examined the decomposition of ozone-free samples of the trioxolane of *trans*-di-*tert*-butylethylene (**1**) in the presence of various electron-deficient oxygen acceptors. Compound **1** is an unusually stable trioxolane,[11] stable to −60 °C, and its decomposition in a polar solvent does not yield stable ozonides.[12] Using ESR, product isolation, and carbonyl oxide trapping experiments we show that the carbonyl oxide **2** and not trioxolane **1** is the actual oxygen-atom-transfer agent in our systems (see eq 1, Scheme I).

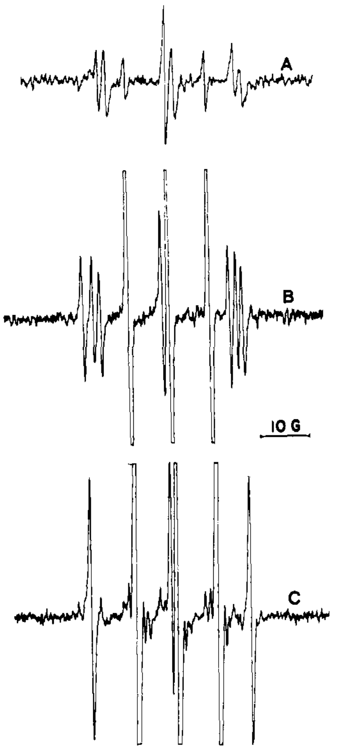

Figure 1. ESR spectra recorded during the decomposition of trioxolane **1** in the presence of PBN. (A) Spectrum recorded at −60 °C; (B) at −30 °C; (C) spectrum recorded on a sample that has been warmed at 20 °C for 5 min.

When a degassed sample of trioxolane **1** in dichloromethane at −90 °C is allowed to warm up in the ESR cavity, free radical signals are not observed, confirming the result of Murray and Ramachandran.[12] However, when **1** is allowed to warm in the presence of α-phenyl-*tert*-butyl nitrone (PBN), a well-known spin trap,[13] ESR signals begin to appear at about −60 °C. The spectrum obtained at −60 °C shows (Figure 1A) a triplet of doublets ($a^{\mathrm{N}} = 13.40$ and $a^{\mathrm{H}} = 1.25$ G) and a triplet ($a^{\mathrm{N}} = 7.85$ G); these two signals can be ascribed to the peroxyl radical spin adduct of PBN[14] and an acyl radical spin adduct of 2-methyl-2-nitrosopropane (NtB).[15] As the temperature is raised above −60 °C, these signals grow and a second triplet ($a^{\mathrm{N}} = 15.84$ G) due to di-*tert*-butyl nitroxide appears (Figure 1B). As the reaction mixture is warmed to room temperature, the triplet of doublets slowly disappears, as would be expected of a peroxyl radical spin adduct,[14] but the other signals remain (Figure 1C).

The formation of di-*tert*-butyl nitroxide indicates that NtB and *tert*-butyl radicals are produced in this system. The appearance of a blue color in the reaction mixture, characteristic of nitroso compounds, also indicates the formation of NtB. The decomposition of **1** in the presence of NtB in the dark gives an acyl-*tert*-butyl nitroxide and di-*tert*-butyl nitroxide but not a peroxyl radical spin adduct. This result indicates that the acyl nitroxide produced in the presence of PBN probably is not benzoyl-*tert*-butyl nitroxide (PBNOx);[15] rather, it seems likely that the acyl nitroxide

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(1) (a) Hamilton, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 3391. (b) Hamilton, G. A. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 405.

(2) (a) For a comprehensive review on the ozonolysis of carbon–carbon double bonds, see: Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1. (b) Bailey, P. S. *Chem. Rev.* **1958**, *58*, 925.

(3) Hamilton, G. A.; Giacin, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 1584.

(4) Murray, R. W.; Ramachandran, V.; Hinirichs, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 1282.

(5) Ogata, Y.; Kato, H.; Sawaki, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832.

(6) Hamilton, G. A.; Keay, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 6876.

(7) Ando, W.; Kohmoto, S.; Nishizawa, K. *J. Chem. Soc., Chem. Commun.* **1978**, 894.

(8) (a) Murray, R. W.; Hoyt, R. A.; Chaudhary, S. K. *Tetrahedron Lett.* **1976**, 4235. (b) Jerina, J. W.; Jerina, D. M.; Witkop, B. *Experimentia* **1972**, *28*, 1129.

(9) See ref 2a, Chapter X.

(10) (a) For a discussion, see ref 2a, p 135. (b) Reference 2a, pp 83–88.

(11) (a) Criegee, R.; Schroder, G. *Chem. Ber.* **1960**, *93*, 689. (b) Bailey, P. S.; Thompson, J. A.; Shouders, B. A. *J. Am. Chem. Soc.* **1966**, *88*, 4098.

(12) Murray, R. W.; Ramachandran, V. *J. Am. Chem. Soc.* **1978**, *100*, 2197.

(13) (a) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31. (b) Janzen, E. G. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1980: Vol. IV, Chapter 4.

(14) (a) Merrit, M. V.; Johnson, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3713. (b) Howard, J. A., Tait, J. C. *Can. J. Chem.* **1978**, *56*, 176.

(15) Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481 and references therein.

0002-7863/81/1503-7681$01.25/0