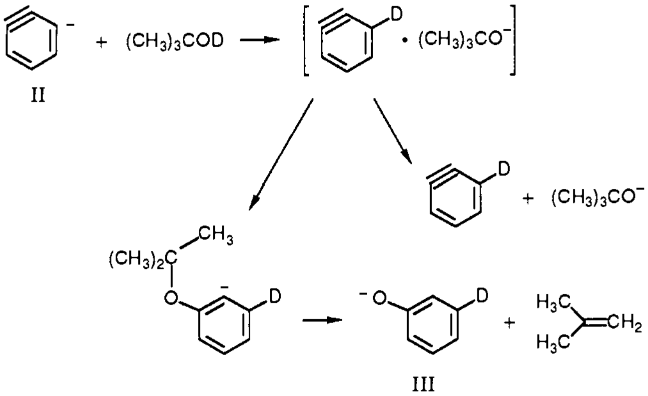
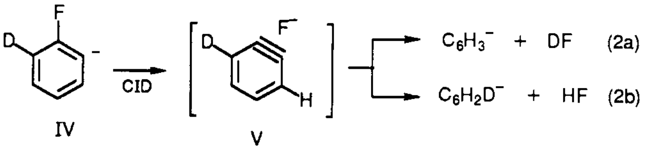
Scheme I



$\Delta G°_{acid}$(benzyne) = 372 kcal mol^{-1}, 19 kcal mol^{-1} more acidic than benzene and 2 kcal mol^{-1} more acidic than the methyl group in toluene.[6] From this gas-phase acidity and the reported heat of formation of benzyne,[7] we can calculate ΔH_f(II) = 131 kcal mol^{-1}.[8] Since the gas-phase acidities of carbanions correlate well with those in solution,[5] the dehydrophenyl anion could well be a useful synthetic intermediate. In fact, the lithium salt of the dehydrophenyl anion has been postulated as an intermediate in the reaction of 2 equiv of alkyllithiums with aryl sulfones.[9]

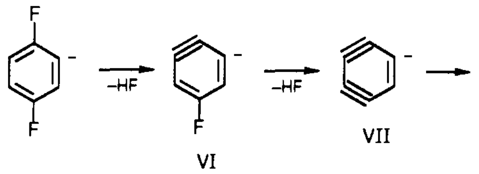
With other alcohols, II undergoes exothermic proton transfer with formation of an ion–dipole complex consisting of benzyne and an alkoxide ion, within which further reactions can occur. For example, *tert*-butyl alcohol-*O-d* reacts with II to give $C_6H_4DO^-$, which we formulate as the deuteriophenoxide ion (III), as well as some *tert*-butoxide anion (Scheme I). An analogous process is observed with ethyl and isopropyl alcohol in competition with hydride transfer within the benzyne–alkoxide complex to produce the phenyl anion. Reaction of II with *tert*-butyl mercaptan leads to thiophenoxide ion.

Benzyne is considerably less acidic than HF ($\Delta G°_{acid}$ = 366 kcal mol^{-1}), and it is therefore surprising that II rather than F^- is the nearly exclusive ionic product of the collision-induced dissociation of anion I. Indeed, if HF is added to the flow tube containing II, proton transfer to form F^- and addition to form $C_6H_4F^-$ occur readily. To test for the possible concerted loss of HF, we synthesized *o*-deuteriofluorobenzene, allowed it to react with HO^-, and injected IV (eq 2). When subjected to CID conditions, IV yields nearly equal amounts of deuterated and undeuterated ions, implicating the intermediacy of fluoride-benzyne complex V in the reaction. We do not understand why V does not merely lose F^-. However, simply proposing another structure for II does not eliminate the problem because II, whatever its structure, reacts readily with HF.[10]



Using ab initio techniques, we have investigated the structure of the 2,3-dehydrophenyl anion calculationally. An optimization at the 6-31+G* level[11] including a frequency analysis indicates that it is a minimum on the potential surface with the ring highly distorted compared to that in benzyne,[12] the angle between the three methynyl carbons being nearly 160°. Such a large geometry change upon protonation could account for its slow proton transfer rate.

Substituted dehydrophenyl anions can also be formed in this way. In particular, the carbanion formed by proton abstraction from *p*-difluorobenzene produces the fluorodehydrophenyl anion (VI). Loss of a second HF molecule occurs readily, to form C_6H^-. Because this ion shows none of the high reactivity of II, we believe an initially formed diynyl anion (VII) undergoes an electrocyclic ring opening to produce a polyacetylide ion, VIII (eq 3). Such a Woodward–Hoffmann allowed transformation to form a stable ion is possible from VII; an analogous reaction of II would produce a vinyl anion. Further experiments designed to shed light on the mechanism of HF loss in these ions are in progress.



$$HC\equiv C-C\equiv C-C\equiv C^- \quad (3)$$

VIII

Acknowledgment. We thank Michael Stronach for assistance in some of the experiments and Prof. Alex Harrison for providing unpublished results and participating in helpful discussions. We gratefully acknowledge the support of this work by the National Science Foundation (Grant CHE-8815459).

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[6] The absence of deuterium exchange with D_2O indicates that benzyne is at least 10–15 kcal mol^{-1} more acidic than H_2O ($\Delta G°_{acid}$ = 384 kcal mol^{-1}); see: Grabowski, J. J.; DePuy, C. H.; Van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384.

[7] The ΔH_f(benzyne) = 118 ± 5 kcal mol^{-1} is from the following: Pollack, S. K.; Hehre, W. J. *Tetrahedron Lett.* **1980**, *21*, 2483. $\Delta H_f(\mathrm{II}) = \Delta H°_{acid}$(benzyne) + ΔH_f(benzyne) − $\Delta H_f(H^+)$. $\Delta H°_{acid}$(benzyne) is determined from the measured $\Delta G°_{acid}$ and an estimate of the entropy of protonation; see: Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2.

[8] Because the proton transfers are slow and it is not practical to carry out bracketing from the reverse direction, our value of $\Delta G°_{acid}$(benzyne) must be termed an estimate and we cannot assign errors. The acidities of the alcohols used in this study have uncertainties of approximately ±2 kcal mol^{-1}.

[9] Stoyanovich, F. M.; Marakatina, M. A. *Zh. Org. Khim.* **1980**, *16*, 2251 and references therein; *J. Org. Chem. USSR (Engl. Transl.)* **1980**, *16*, 1915.

[10] Chloride and bromide ions are the exclusive product ions from analogous CID reactions of the chlorophenyl and bromophenyl anions.

[11] Optimizations were carried out by using Gaussian 86 and its internal basis sets: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohfling, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *GAUSSIAN 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

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Intramolecular Triplet State Cyclization of But-3-enoxyacetonaphthones

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Recently we reported that double bonds attached by a three-atom tether ortho or para on acetophenone quench the ketone triplet[1] and in the process undergo 2 + 2 cycloaddition to the benzene ring,[2] both very efficiently. We now find that 1-butenoxy-2-acetonaphthones and 2-butenoxy-1-acetonaphthones both undergo high-yield internal 2 + 2 cycloadditions from their triplet states, but with much different rate constants. These reactions represent the first examples of 1,2-addition of simple alkenes to triplet naphthalenes. The rate differences suggest significant radical character in the rate-determining step for cyclization.

The isomeric sets of ketones in Scheme I (prepared by standard S_N2 chemistry) produce high chemical yields (70–90% isolated) of the acetylbenzo-2-oxatricyclo[5.4.0.0^{1,5}]undecadienes upon near-UV irradiation in benzene.[3,4] These cyclizations are entirely

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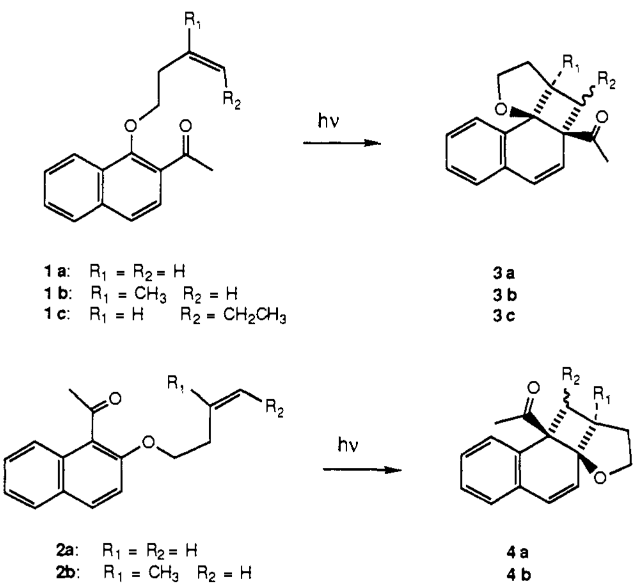
[1] Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 4044.

[2] Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 6528.

Scheme I



1a: R$_1$ = R$_2$ = H **3a**
1b: R$_1$ = CH$_3$ R$_2$ = H **3b**
1c: R$_1$ = H R$_2$ = CH$_2$CH$_3$ **3c**

2a: R$_1$ = R$_2$ = H **4a**
2b: R$_1$ = CH$_3$ R$_2$ = H **4b**
2c: R$_1$ = H R$_2$ = CH$_2$CH$_3$

Table I. Photokinetics for Some But-3-en-1-oxyacetonaphthones^a

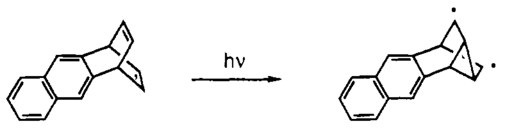
ketone	$\phi_{cyc}{}^a$	$1/\tau^{b,c}$	$k_q{}^{INT\,c,d}$	$k_{cyc}{}^{c,e}$
1a	0.23	8.8	7.8	2.0
2a	0.01	3.0	2.0	0.03
1b	0.17	6.7	5.7	1.1
2b	0.04	1.7	0.7	0.07
1c	0.31	12.5	11.5	3.8

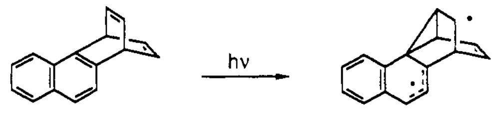
^{a}In benzene at 25 °C. ^{b}Direct decay measurement in CH$_3$OH. ^{c}All rate constants in units of 10^5 s^{-1}. $^d k_q{}^{INT} = 1/\tau - 1 \times 10^5$. $^e k_{cyc} = \phi/\tau$.

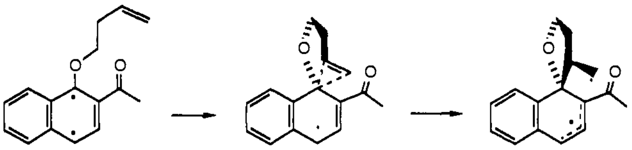
triplet-state reactions: product formation can be sensitized with Michler's ketone and is readily quenched by low concentrations of conjugated dienes or *trans*-stilbene, with $k_q\tau$ values of 4000–25 000 M^{-1} in benzene. The long triplet lifetimes were verified by flash kinetics.[5] Photokinetics data for the five compounds that cyclize are listed in Table I. Compound **2c** undergoes only cis–trans isomerization of the double bond. Compound **1c** forms an apparently equal mixture of both diastereomers of **3c**.

McCullough reported similar 2 + 2 intramolecular cycloadditions upon direct irradiation of the isomeric 2-, 4-, and 6-(2-oxa-4,5-dimethyl-4-hexenyl)-1-cyanonaphthalenes.[6] The first isomer is similar electronically to our compounds **2a–c** but photocyclizes in high quantum yield (0.69). These reactions are known to proceed from singlet exciplexes[6,7] and have rate constants of at least 10^8 s^{-1}, since 95% of monomer fluorescence is quenched by the double bond.[6] The lowest π,π^* singlet states of the naphthalenes have excitation energies >85 kcal/mol.[6] The lowest π,π^* triplets of **1a** and **2a** have excitation energies of only 58.1 and 56.7 kcal/mol, respectively.[8] It is remarkable that these low-energy excited states can cyclize, given the loss of resonance energy and the gain in ring strain that accompany cycloaddition. The only other well-characterized cycloaddition to triplet naphthalene is the 1,4-addition of α-morpholino- or α-(alkanethiyl)acrylonitriles to 1-acetonaphthone reported by Döpp.[9]

It is evident that the 1-alkenoxy-2-acetylnaphthalene triplets **1** react more rapidly and more efficiently than their positional isomers **2**. Since unsubstituted acetonaphthones have triplet lifetimes of 10 ns under the same experimental conditions, only some of the quantum inefficiency arises from triplet decay competitive with reaction. The values of $k_q{}^{INT}$ in the table equal the measured $1/\tau$ values minus 1×10^5 and represent internal reaction with the double bond. The k_{cyc} values represent the effective rate constants for cyclization. The fact that **2c** undergoes primarily cis–trans isomerization, while **1c** forms cycloadduct efficiently, indicates (1) that a biradical intermediate precedes cyclization, since the energetics forbid any electron or energy transfer to the double bond, and (2) that biradical closure is less efficient from the 2-alkenoxy system than from the 1-alkenoxy system.







The absolute values and the large positional dependence of these triplet rate constants require explanation. The lower rate constants for the triplet reactions relative to those for singlets probably reflect the lower energy content of the triplets but also may reflect different electron distributions and mechanisms for the two electronic states. Therefore the strong regioselectivity is particularly revealing. The same phenomenon is well-known in the di-π-methane rearrangement of triplet naphthobarrelenes.[10] Bonding of the α-naphthyl position to a double bond is faster than vinyl–vinyl bonding, which in turn is faster than bonding at the β-naphthyl position. The di-π-methane reaction appears to involve initial radical-like addition of the aromatic to a double bond;[11] the similarity in selectivity invites mechanistic comparison.

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(3) Solutions 0.04 M in C$_6$D$_6$ in argon-flushed NMR tubes were irradiated at 313 nm and followed by NMR. For preparative experiments, 250 mg of reactant in 50 mL of benzene was irradiated under nitrogen for 6–40 h at ambient temperature with a Hanovia 450-W medium-pressure mercury arc filtered by Pyrex. Conversion ranged from 50% to 100%.

(4) Major products were readily isolated by column or thin-layer chromatography; several minor byproducts have not yet been characterized. **3b**: IR 1700 cm^{-1}; MS m/e 171, 186 (base), 254 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 1.00 (s, 3 H, CH$_3$), 1.61 (ddd, J_{AB} = 12.5 Hz, J_{AX} = 11.0 Hz, J_{AY} = 7.4 Hz, 1 H, OCH$_2$CH_2), 1.68 (ddd, J_{AB} = 12.5 Hz, J_{BX} = 6.1 Hz, J_{BY} = 1.5 Hz, 1 H, OCH$_2$CH_2), 1.78 and 2.88 (AB quartet, 2 H, J = 12.5 Hz, cyclobutane CH$_2$) 2.13 (s, 3 H, CH$_3$CO), 3.96 (ddd, J_{AX} = 11.0 Hz, J_{AB} = 9.0 Hz, J_{AY} = 6.0 Hz, 1 H, OCH_2), 4.24 (ddd, J_{AB} = 8.9 Hz, J_{BX} = 7.2 Hz, J_{BY} = 1.5 Hz, 1 H, OCH_2), 5.66 and 6.48 (AB quartet, 2 H, J = 10.0 Hz, CH=CH), 7.05–7.10 (m, 1 H, aromatic), 7.15–7.30 (m, 3 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 22.1, 26.7, 38.0, 38.9, 51.4, 55.6, 68.9, 88.8, 125.9, 127.3, 128.2 (2), 128.9, 129.0, 132.2, 133.0, 206.0. **4b**: IR 1700 cm^{-1}; MS m/e 171, 186 (base), 254 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 1.18 (s, 3 H, CH$_3$), 1.59 (ddd, J_{Ab} = 12.2 Hz, J_{AX} = 11.0 Hz, J_{AY} = 7.7 Hz, 1 H, OCH$_2$CH_2), 1.72 (ddd, J_{AB} = 12.2 Hz, J_{BX} = 5.5 Hz, J_{BY} = 1.3 Hz, 1 H, OCH$_2$CH_2), 1.83 and 3.13 (AB quartet, 2 H, J = 12.5 Hz, cyclobutane CH$_2$), 2.00 (s, 1 H, CH$_3$CO), 3.91 (ddd, J_{AX} = 11.0 Hz, J_{AB} = 9.0 Hz, J_{AY} = 5.5 Hz, 1 H, OCH$_2$), 4.09 (ddd, J_{AB} = 9.0 Hz, J_{BY} = 1.4 Hz, J_{BX} = 7.7 Hz, 1 H, OCH$_2$), 5.56 and 6.54 (AB quartet, 2 H, J = 10.0 Hz, CH=CH), 6.78 (dd, 1 H, J = 7.5, 1 Hz, 1 H, aromatic), 7.07–7.25 (m, 3 H, aromatic); ^{13}C NMR (CDCl$_3$) δ 21.8, 26.9, 39.3, 40.5, 50.8, 55.7, 68.8, 88.9, 126.5, 126.8, 127.9, 128.4, 128.9, 129.6, 131.1, 137.8, 205.1. The chemical shifts and splitting of the vinyl AB quartet are almost identical with those reported for the similar cycloadduct reported in ref 6. Other products **3** and **4** had similar spectra.

(5) We thank Dr. Tito Scaiano at the NRC in Ottawa for his hospitality in allowing the use of his flash kinetics apparatus. The decay of triplet naphthalene absorption at 425 nm was monitored in methanol solvent.

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(11) For a thorough discussion of the di-π-methane reaction, see: Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 131.

Zimmerman ascribed the regioselectivity to a greater spin density at the α-position of excited naphthalenes,[10] as has since been made more evident from measured hyperfine interactions in triplet naphthalenes.[12]

If this reaction of triplet naphthalenes involves weak charge-transfer (CT) interaction of the excited aromatic with the double bond followed by radical addition to form a five-membered ring, as appears to be the case for the similar singlet reactions[5] and for analogous triplet benzenes,[1,13] both steps would be affected by the relative unpaired spin density at the carbon bearing the alkenoxy group. As in all such two-step processes,[14] it must be determined which step is rate-determining. We first must deal with any consequences of the slightly lower triplet energy of **2a** relative to **1a**. This difference would not affect the first step, since **2a**'s reduction potential is lower than **1a**'s, but it might affect the second step if bond formation were becoming endothermic. However, the di-π-methane rearrangement has no such energy difference yet shows the same selectivity. We suggest that the low rate constants and the high regioselectivity indicate a low driving force for the first CT step, such that the second step (biradical formation) is facilitated only slightly by charge separation and therefore dominates rate constants. The fact that terminal alkyl substitution on the double bond slightly enhances k_q^{INT} while a 3-methyl depresses it is further evidence for radical cyclization character in the rate-determining step.[12,15] The values of k_q^{INT} deduced for **1a** and **2a**, 8×10^5 and 2×10^5 s^{-1}, are in exactly the same ratio as the spin densities at the 1- and 2-positions in triplet naphthalenes, 0.23 and 0.06,[12] respectively; the **1b**/**2b** rate ratio is twice as large.

Acknowledgment. This work was originally supported by NSF Grants No. CHE 85-06703 and 88-15052 and recently by NIH Grant No. GM39821. The NMR spectrometers were funded by NIH Grant No. RR04750 and NSF Grant No. CHE88-00770.

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Near-Infrared Fourier Transform Raman Spectroscopy of Photolabile Organocobalt B_{12} and Model Compounds. 1. Detection of the Cobalt-Carbon Stretching Mode in the Solid State and in Solution

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The discovery that coenzyme B_{12} contains a stable Co–C bond[1] and the subsequent recognition of the homolysis of this bond in B_{12}-dependent catalysis[2] have stimulated a considerable amount of work aimed at elucidating factors promoting the enzymatic cleavage of this organometallic bond.[2] Valuable insights have come from structural studies of well-defined organocobalt B_{12} models by X-ray diffraction methods in the solid state and NMR spectroscopy in solution.[3] While vibrational spectroscopic techniques (i.e., IR and Raman) hold the promise of providing molecular information in both the solid state and solution, their utility in directly probing the nature of the Co–C moiety has been rather limited. Early IR studies of organocobalt complexes containing the $(DH)_2$ equatorial ligand system (DH = monoanion of dimethylglyoxime) revealed a Co–C-related absorption band.[4] Its assignment to the Co–C stretching mode remains controversial because the 320-cm^{-1} value is too low compared to those found in other organocobalt complexes and its isotopic shift (6 cm^{-1}, CH_3 vs CD_3) is significantly smaller than that expected for a stretching mode. Resonance Raman investigations of organocorrins with visible laser excitations inevitably ran into the trouble of photoinduced sample decomposition.[5] Even though photolysis could be alleviated by using the rapid-flow technique, the resonance Raman spectra obtained yielded no information about the Co–C bond.[6] A recent report[7] tentatively identified a Raman line at 506 cm^{-1} as the Co–CH_3 stretching mode in solid (4-*tert*-butylpyridine)$Co(DH)_2CH_3$, but the resonance Raman spectrum recorded with 514.5-nm excitation exhibited severe fluorescence interference and was further complicated by photolysis.[8]

We describe here the first application of near-infrared-excited Fourier transform (FT) Raman spectroscopy[9] to study photolabile organocobalt compounds. By using near-IR excitation at 1.064 μm, this new technique precludes electronic transitions and thus completely eliminates fluorescence interference and Co–C bond photolysis, problems encountered with visible laser excitations. As a result, high-quality FT-Raman spectra have been obtained for coenzyme B_{12} itself and for a number of organocobalt B_{12} models[10] of the type $LCo(DH)_2R$ (where L = neutral axial ligand, R = alkyl axial ligand) both in the solid state and in solution. Although interpretation of the B_{12} coenzyme spectrum requires additional studies, the nonresonant FT-Raman spectra of the models provide particularly rich information about the Co–C bond and allow several important issues concerning this organometallic bond to be addressed, such as conclusive identification of the Co–C stretching frequency, the trans ligand influence, and the environmental effect.

Figure 1 depicts FT-Raman spectra of $pyCo(DH)_2CH_3$ (py = pyridine) and its deuterated derivative, $pyCo(DH)_2CD_3$, obtained in the solid state. Three isotopically sensitive lines are detected. The symmetric stretching and deformation modes of the axial

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0002-7863/89/1511-9256$01.50/0