In sum, the cyanine borates are unique compounds whose irradiation leads to intra-ion-pair electron transfer from a nonvertical excited state and to subsequent formation of reactive free radicals.

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Registry No. 1a, 113352-39-9; **1b**, 113352-41-3; **1c**, 113352-42-4; **1d**, 113378-60-2; poly(butylacrylate), 9003-49-0.

Palladium-Catalyzed Polyene Cyclizations of Dienyl Aryl Iodides

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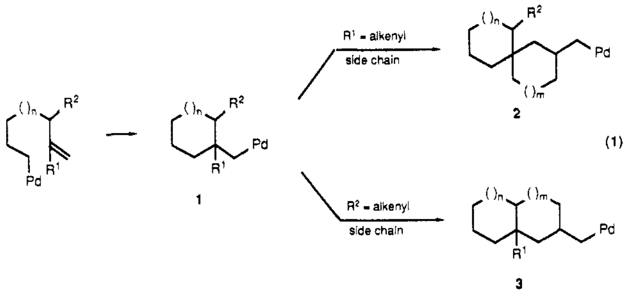
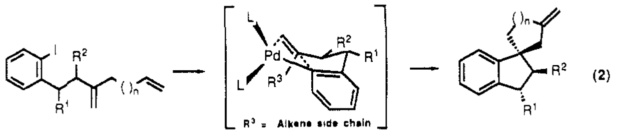
Metal-catalyzed additions of carbon fragments to alkenes have found wide application in organic synthesis.[2] The utility of this chemistry would be greatly expanded if the newly created carbon–metal bond could be routinely transformed to a new carbon–carbon bond. In this communication, we report that (σ-alkyl)palladium intermediates **1**, produced by intramolecular Heck cyclization,[3,4] can be efficiently captured by neighboring double bonds to give bis-cyclization products of either spiro **2** or fused **3** geometry (see eq 1).[5,6] Since the regiochemistry for the reaction of organopalladium intermediates with alkenes can be opposite to that of related radical or carbonium ion intermediates,[7] palladium-catalyzed polyene cyclizations hold exciting potential for organic synthesis.



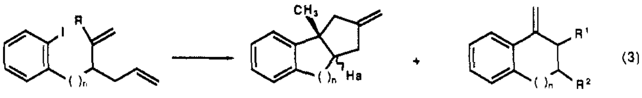
By using Heck reaction conditions we recently described,[4e] dienyl aryl iodide **4**[8] was cyclized in acetonitrile at room temperature in the presence of 1 mol% of $Pd(OAc)_2$, 4 mol% of Ph_3P, and 1 equiv of Ag_2CO_3 to afford tricyclic alkene **8**[9] in 86% yield (see eq 2). The initially formed bicyclic (σ-alkyl)palladium intermediate can be trapped also by insertion into a 4-pentenyl side chain as demonstrated by cyclization of **5** under identical conditions at 70 °C to afford **9**[9] in 85% yield. Useful levels of relative asymmetric induction at the newly formed quaternary center were observed in cyclizations of diene substrates containing a stereogenic center in the chain connecting the aromatic ring with the exocyclic double bond. Thus, cyclization[10] of **6** proceeded in 81% yield with 13:1 diastereoselectivity to provide **10**[9] as the major stereoisomer, while **7** was cyclized[10] (73% yield, 6.5:1 diastereoselectivity) to afford **11**[9] as the predominant product. Suprafacial insertion[3,11] of an initially formed (aryl)palladium intermediate via a conformation which places the substituents in favored pseudoequatorial positions (see eq 2) provides a rationale for the observed diastereoselectivities.[12] It merits note that the facility of these transformations and the lack of isomerization of the exocyclic double bond of tricyclic alkene products **8–11** provide a dramatic illustration of the advantages[4e,13] of employing a Ag(I) additive in alkenyl palladations.



4 $R^1 = R^2 = H$; $n = 1$
5 $R^1 = R^2 = H$; $n = 2$
6 $R^1 = CH_3$, $R^2 = H$; $n = 1$
7 $R^1 = H$; $R^2 = CH_3$; $n = 1$

8 86%
9 85%
10 81%
11 73%

Bis-cyclizations in the fused mode were examined with substrates **12–14** (see eq 3). Cyclization[10] of **12** yielded, as the major products, tetralin **17**[9] and tricycle **15**[9] in a 1.5:1 ratio, respectively.[14]



12 $R = CH_3$; $n = 1$
13 $R = CH_3$; $n = 2$
14 $R = H$; $n = 1$

15 $n = 1$; β Ha
16 $n = 2$; α Ha
18 $n = 2$; β Ha

17 $R^1 = H$, $R^2 = C(CH_3)=CH_2$; $n = 1$
19 $R^1 = CH_2CH=CH_2$, $R^2 = H$; $n = 0$

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[1] NIH NRSA Postdoctoral Fellow (GM-11332), 1986–1987. American Cancer Society Postdoctoral Fellow (PF-3066), 1987–1988.

[2] See, e.g.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: 1987, Chapters 6 and 17.

[3] (a) Davison, S. F.; Maitlis, P. M. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. L., de Jonge, C. R. H. I., Ed.; Plenum Press: New York, 1986; pp 482–488. (b) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985. (c) Trost, B. M. In *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 8, pp 867–874. (d) Heck, R. F. *Org. React.* (*NY*) **1982**, *27*, 345.

[4] Recent publications, not reviewed in ref 3, include the following: (a) Negishi, E.-I.; Tour, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (b) Kasahara, A.; Izumi, T.; Murakami, S.; Yanai, H.; Takatori, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 927. (c) Mori, M.; Kanda, N.; Ban, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1375. (d) Grigg, R.; Sridharan, V.; Stevenson, P.; Worakan, T. J. *J. Chem. Soc., Chem. Commun.* **1986**, *1697*. (e) Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4130. (f) Larock, R. C.; Babu, S. *Tetrahedron Lett.* **1987**, *28*, 5291.

[5] There are, to the best of our knowledge, no reported examples[3,4] of Heck-type polyene cyclizations. There are a few important reports[6] of the intramolecular trapping by alkenes of (σ-alkyl)palladium intermediates generated in other fashions.

[6] (a) Trost, B. M.; Burgess, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1084. (b) Hegedus, L. S.; Allen, G. F.; Olsen, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 3583. (c) Danishefsky, S.; Taniyama, E. *Tetrahedron Lett.* **1983**, *24*, 15. (d) Fugami, K.; Oshima, K.; Utimoto, K. *Ibid.* **1987**, *28*, 809.

[7] Giese, B. *Radicals in Organic Synthesis*: *Formation of Carbon–Carbon Bonds*; Academic: London, 1986; Chapter 4. Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, Chapter 5.

[8] Prepared from 2-(chloromethyl)-1-iodobenzene, allyl bromide, and ethyl acetoacetate by using conventional alkylation and Wittig chemistry. Other cyclization substrates[9] were prepared in related fashions.

[9] New compounds showed IR, 500 MHz ^1H NMR, ^{13}C NMR, and mass spectra in accord with their assigned structures. Molecular composition was determined by high resolution MS or elemental analysis, while isomer ratios were determined by capillary GC analysis. Stereochemistry was typically assigned on the basis of NOE studies.

[10] Cyclizations were conducted with 1 mol% of $Pd(OAc)_2$, 4 mol% of Ph_3P, and 1 equiv of Ag_2CO_3 in CH_3CN (~0.1 M) at room temperature for 2–8 h, unless noted otherwise.

[11] For a recent theoretical study of the insertion of the Pd–H bond and leading references, see: Fujimoto, H.; Yamasaki, T. *J. Am. Chem. Soc.* **1986**, *108*, 578.

[12] The R_3 side chain may occupy one of the ligand sites on Pd. Coordination of the second double bond during the first insertion step does *not* appear possible for the bis-cyclizations reported in eq 4. These and other mechanistic and stereochemical issues will be discussed in more detail in a subsequent full account of this work.

[13] (a) For example, the cyclization of **4** was complete at room temperature within 3 h in the presence of 1 equiv of Ag_2CO_3. An identical cyclization conducted with Et_3N in place of Ag_2CO_3 required 24 h for completion and provided **8** together with 10% of two endocyclic alkene isomers. (b) The effect of Ag(I) additives on the rate of Heck arylations was originally described by Hallberg and co-workers, see, e.g.: Andersson, C.-M.; Karabelas, K.; Hallberg, A.; Anderson, C. *J. Org. Chem.* **1985**, *50*, 3891.

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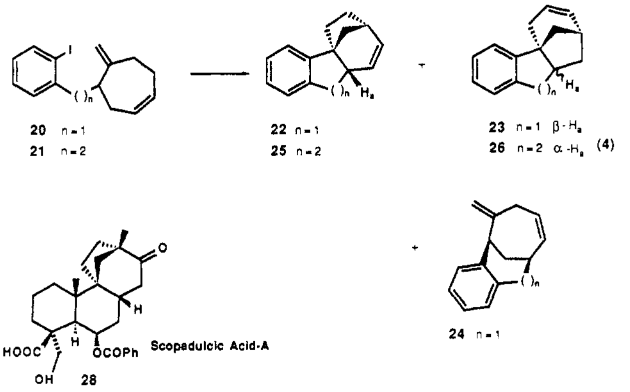
Initial insertion of the (aryl)palladium intermediate with the terminal vinyl group, which leads to monocyclization, was less important when this competing process would lead to the formation of a seven-membered ring. Thus, cyclization of **13** at 70 °C for 9 h proceeded to provide the angular tricycles $\mathbf{16}^{9,15}$ and $\mathbf{18}^{9,15}$ in a 1.3:1 ratio, respectively, and 67% yield (76% based on consumed **13**). It was key to the success of the bis-cyclization reaction that insertion of the proximal double bond provided a (σ-alkyl)palladium intermediate which could not decompose by simple β-hydrogen insertion. This limitation is clearly seen in the cyclization of **14** which afforded $\mathbf{19}^{9}$ as the sole product.

The power of this chemistry for quickly assembling complex polycyclic systems is well-illustrated by cyclizations of the cyclic dienyl aryl iodides **20** and **21** (see eq 4). Cyclization[10] of **20** provided a 1.2:1 mixture of tetracycle $\mathbf{22}^{9}$ and tricycle $\mathbf{24}$,[9] which were isolated after silica gel chromatography in yields of 43% and 25%, respectively. Ozonolysis of **22** provided a dialdehyde which showed a doublet for each aldehydic hydrogen, thus ruling out a tetracycle with the alternate bicyclo[3.2.1]octene partial skeleton (e.g., **23**).[16] That the bridgehead hydrogen H_a was β to the one-carbon bridge was established by NOE spectroscopy.[17] Initial insertion into the ring double bond was less prevalent in the cyclization of **21** (at 83 °C for 10 h) which proceeded in 90% yield to provide **25** and **26** in a ratio of 1.3:1, respectively.[18] Stereochemical assignments for **25** and **26** were based on relating, by NOE effects,[17] the angular hydrogen H_a with the cis related bridge of the bicyclooctene ring system. Tetracycles **25** and **26** contain carbon skeletons found in several diterpene natural products,[19,20] e.g., aphidicolin,[19a] stemodin,[19b] and the scopadulcic acids.[20] The conversion of **21** → **25** and **26** represents the first one-step construction of these ring systems from a bicyclic precursor.



In conclusion, the results described here provide the first demonstration that palladium-catalyzed alkene arylations can be accomplished in a tandem sense to form two rings. The high yields observed in many of these bis-cyclizations suggest that palladium-catalyzed polyene cyclizations that form more than two rings should be possible. We are actively exploring this possibility as well as the scope and total synthesis applications of the bis-cyclizations documented in this preliminary account.

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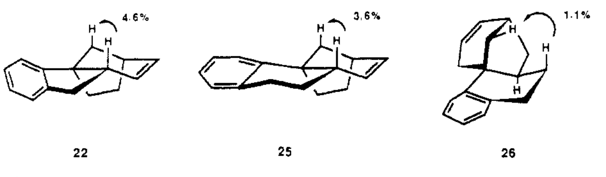
(14) The crude yield was 96%. Small amounts of deiodinated **12** (7%) and what is provisionally assigned as the trans isomer of **15** (8%) were also isolated by preparative GC.

(15) Stereochemistry was assigned in analogy with Orrell et al. (Orrell, K. G.; Packer, R. A.; Sik, V.; Whitehurst, J. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 117).

(16) Tetracycle **22** was contaminated with $\sim$10% of what is believed to be the alternative bicyclo[3.2.1]octene tetracyclic **23**. A triplet and doublet were observed for the CHO hydrogens of this minor product after ozonolytic cleavage.

(17) Key NOE's are shown below. ^{1}H NMR assignments were based on extensive 1- and 2-D NMR experiments.



(18) Also isolated by preparative GC was 8% of deiodinated **21**.

(19) For recent synthetic accomplishments and leading references, see: (a) Holton, R. A.; Kennedy, R. M.; Kim, H.-B.; Krafft, M. E. *J. Am. Chem. Soc.* **1987**, *109*, 1597. (b) White, J. D.; Somers, T. C. *Ibid.* **1987**, *109*, 4424.

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Microwave Spectrum of Uracil

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Biological systems are based on macromolecules stemming from a limited number of small molecules, notably 20 amino acids, five nitrogen heterocycles, and several pentoses and hexoses. Though small, these molecules are difficult to vaporize without extensive decomposition, and so detailed structural information about them has almost always been based on X-ray crystallographic studies rather than high-resolution vapor phase spectroscopic measurements. Hitherto the only species for which spectroscopic information has been obtained are urea[1] and glycine,[2] while gas-phase electron diffraction studies[3] and fluorescence spectra[4] have recently been reported for uracil. We now report the detection and analysis of the microwave spectrum of uracil, from which some limited structural information can be derived for comparison with results derived from crystallographic[5,6] and electron diffraction studies.[3]

Preliminary studies of the vaporization of uracil[7] had revealed that vaporization without decomposition was possible under carefully controlled conditions and provided a vapor pressure curve and heat of sublimation. An attempt to observe the microwave spectrum in a conventional Stark-modulated spectrometer incorporating a P-band cell in a thermal enclosure heated to 200 °C, a technique that had been successful for a microwave spectral study of urea,[1] produced marginal results,[7] inadequate for a definitive assignment of the spectrum. We have now developed a Stark-modulated spectrometer for microwave measurements on a seeded supersonic nozzle expanded beam of uracil in argon. The CW beam plume passes between parallel plates that produce the Stark field, the microwave beam, collimated with Teflon lenses, passing transversely between the plates to the detector. The microwave spectrum of the heterocycle has been observed at adequate S/N in the vicinity of 60 GHz, lines of S/N up to 10 or more being recorded with a time constant of 1 s. Table I gives the spectroscopic parameters derived from 65 assigned lines.

From the inertial defect it is apparent that uracil is essentially planar in the gas phase, in contrast to its structure in the crystal[6] (the electron diffraction study[3] could not detect small deviations from molecular planarity). Presumably lattice forces are responsible for the very small distortion observed in the latter.

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(2) Brown, R. D.; Godfrey, P. D.; Storey, J. W. V.; Bassez, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 547-548. Suenram, R. D.; Lovas, F. J. *J. Mol. Spectrosc.* **1978**, *72*, 372-382. Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1980**, *102*, 7180-7184.

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(4) Fujii, M.; Tamura, T.; Mikami, N.; Ito, M. *Chem. Phys. Lett.* **1986**, *126*, 583-587.

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(7) Porter, A. P. Ph. D. Thesis, Monash University, 1979.