the damage arises from a direct reaction between a benzenoid diradical and DNA or through the intermediacy of other species.

In summary, compounds in the enediyne antibiotic manifold with demonstrated independent propensity for both Bergman cycloaromatization and DNA cleavage have been synthesized. Qualitatively, a direct relationship between the proclivities of these two processes has been demonstrated. Further experiments in this area are in progress.

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**Supplementary Material Available:** Experimental procedures and documentations of this work (3 pages). Ordering information is given on any current masthead page.

## A Simple Highly Stereospecific Preparation of Vinylphosphonium Salts: Palladium-Catalyzed Vinylation of Triphenylphosphine via Vinyl Triflates

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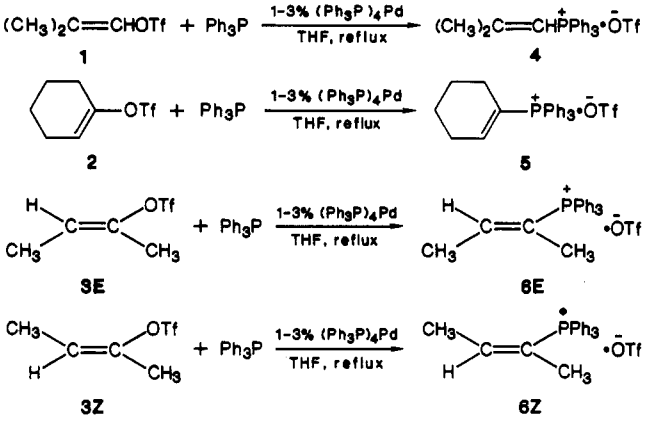
*Summary:* Interaction of vinyl triflates with $Ph_3P$ in the presence of 1–3% $(Ph_3P)_4Pd$ results in vinylphosphonium salts in 62–89% isolated yields. The reaction is stereospecific, thereby providing a simple means to either (*E*)- or (*Z*)-vinylphosphonium salts.

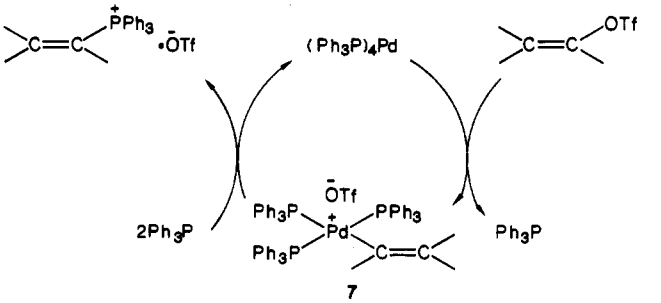
*Sir:* Vinylphosphonium salts are valuable synthetic reagents commonly used in cycloadditions, Michael additions, and the synthesis of heterocyclic systems.[1-7] In spite of their importance, there are no known methods for the preparation of stereodefined isomeric vinylphosphonium salts. Current methods of preparation include additions to alkynylphosphonium salts,[8] reaction of allyl bromides with triphenylphosphine, and subsequent base-catalyzed prototropic rearrangement to the vinyl compound,[9] as well as the high-temperature nickel-catalyzed fusion reaction of vinyl bromides with triphenylphosphine.[10] However, all these procedures result either in mixtures of stereoisomers or the exclusive formation of *E* isomers.[8,11] Hence, in this paper we report our preliminary results for the stereospecific preparation of vinylphosphonium salts via a simple new procedure employing vinyl triflates.

Interaction of the readily available[12] vinyl triflates **1–3** with a 5% excess of $Ph_3P$ in refluxing THF in the presence of catalytic (1–3 mol %) $(Ph_3P)_4Pd$ results in the corresponding vinylphosphonium triflates **4–6** in 62–89% isolated yields as shown in Scheme I.

**Scheme I**




**Scheme II**




Phosphonium salts **4–6** are stable, crystalline, albeit slightly hygroscopic, solids that are fully characterized[13] by spectral means as summarized in Table I.

As the data show the reaction is applicable to the formation of cyclic as well as acyclic vinylphosphonium salts. Particularly noteworthy is the fact that the reaction is

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(13) Compounds **4** and **5** gave satisfactory elemental analyses and **6E** and **6Z** gave correct HRMS.

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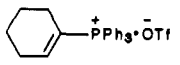
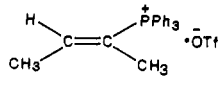
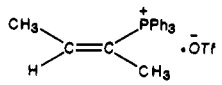
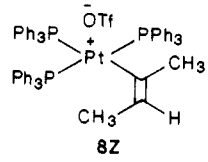
**Table I. Physical and Spectral Data for Vinylphosphonium Triflates 4–6**

| compd | % yield | mp, °C | IR,[a] cm$^{-1}$ | $^{31}$P,[b] δ | $^{1}$H,[c] δ | $^{13}$C,[d] δ |
|---|---|---|---|---|---|---|
| $(CH_3)_2C{=}CHPPh_3{\cdot}OTf$ **4** | 71 | 188–190 | 3070 w, 3003 w, 1610 s, 1585 vw, 1480 m, 1435 s, 1265 s, 1140 s, 1103 s, 1027 s, 740 s, 714 s, 688 s, 630 s | 11.7 | 1.70 (dd, $^{4}J_{PH}$ = 2.6 Hz, $^{3}J_{HH}$ = 1.0 Hz, 3 H), 2.32 (m, 3 H), 6.18 (d, $^{2}J_{PH}$ = 23 Hz, 1 H), 7.5–7.8 (aromatics, 15 H) | 24.7 (d, $^{3}J_{PC}$ = 7.6 Hz), 29.8 (d, $^{3}J_{PC}$ = 19 Hz), 102.7 (d, $^{1}J_{PC}$ = 90 Hz), vinyl, 119.4 (d, $^{1}J_{PC}$ = 90 Hz), 130.6 (d, $^{3}J_{PC}$ = 13 Hz), 133.3 (d, $^{2}J_{PC}$ = 11 Hz), 135.0 (d, $^{4}J_{PC}$ = 3.1 Hz), 172.4(d, $^{2}J_{PC}$ = 1.4 Hz) |
|  **5** | 89 | 246–247 | 3060 w, 2941 w, 1612 m, 1481 m, 1434 m, 1270 s, 1221 s, 1190 s, 1104 s, 1029 s, 993 m, 749 s, 720 s, 689 s, 632 s | 23.8 | 1.75 (m, 4 H), 2.18 (m, 2 H), 2.45 (m, 2 H), 6.71 (dm, $^{3}J_{PH}$ = 23 Hz, 1 H), 7.5–7.85 (aromatics, 15 H) | 20.3 (s), 21.9 (d, $J_{PC}$ = 8.4 Hz), 26.4 (d, $J_{PC}$ = 8.5 Hz), 27.8 (d, $J_{PC}$ = 15 Hz), 116.7 (d, $^{1}J_{PC}$ = 89 Hz), 118.7 (d, $^{1}J_{PC}$ = 78 Hz), 130.5 (d, $^{3}J_{PC}$ = 13 Hz), 134.0 (d, $^{2}J_{PC}$ = 9.7 Hz), 135.3 (s), 155.9 (d, $^{2}J_{PC}$ = 7.8 Hz) |
|  **6E** | 73 | 131–132 | 3064 w, 3011 w, 1614 m, 1438 s, 1268 vs, 1225 m, 1147 s, 1109 s, 1031 s, 997 m, 753 s, 745 s, 719 s, 691 s, 636 vs | 27.5 | 2.05 (m, 6 H), 6.50 (m, 1 H), 7.50–7.90 (aromatics, 15 H) | 15.3 (d, $J_{PC}$ = 12 Hz), 16.5 (d, $J_{PC}$ = 17 Hz), 116.5 (d, $^{1}J_{PC}$ = 81 Hz), 117.1 (d, $^{1}J_{PC}$ = 89 Hz), 130.6 (d, $^{3}J_{PC}$ = 13 Hz), 134.1 (d, $^{2}J_{PC}$ = 10 Hz), 135.3 (d, $^{4}J_{PC}$ = 3.2 Hz), 154.5 (d, $^{2}J_{PC}$ = 11 Hz) |
|  **6Z** | 62 | 178–179 | 3067 w, 1626 m, 1443 s, 1271 s, 1222 s, 1172 s, 1147 s, 1108 s, 1029 s, 997 s, 846 m, 758 s, 723 s, 702 s, 637 s | 18.3 | 1.54 (m, 3 H), 1.95 (dt, $^{3}J_{PH}$ = 14.3 Hz, $^{4}J_{HH}$ = 1.5 Hz, 3 H), 7.27 (dqq, $^{3}J_{PH}$ = 36.7 Hz, $^{3}J_{HH}$ = 6.1 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1 H), 7.50–7.90 (aromatics, 15 H) | 19.9 (d, $^{3}J_{PC}$ = 9.1 Hz), 24.1 (d, $^{2}J_{PC}$ = 13.6 Hz), 114.7 (d, $^{1}J_{PC}$ = 74 Hz) vinyl, 117.9 (d, $^{1}J_{PC}$ = 87 Hz), 130.7 (d, $^{3}J_{PC}$ = 12.7 Hz), 133.8 (d, $^{2}J_{PC}$ = 10.2 Hz), 135.2 (d, $^{4}J_{PC}$ = 3.0 Hz), 153.2 (d, $^{2}J_{PC}$ = 7.9 Hz) vinyl |

[a] KBr pellet. [b] $CDCl_3$ referenced to external 85% $H_3PO_4$. [c] $CDCl_3$ referenced to residual $CHCl_3$. [d] $CDCl_3$ referenced to $CDCl_3$ triplet.

stereospecific: (*E*)-2-butenyl triflate, **3E**, gives exclusively (*E*)-2-butenylphosphonium triflate, **6E**, whereas the *Z* isomer, **3Z**, yields the isomeric **6Z**.[14]

A likely mechanism for this novel reaction is shown in Scheme II. Oxidative addition of the vinyl triflate to the catalyst results in complex **7** that upon reductive elimination (and added phosphine) results in the "coupled" vinylphosphonium salt and regenerates the Pd(0) catalyst. Stille[15] and Scott proposed oxidative addition of vinyl triflates to Pd(0) as the first step in the vinylic cross-coupling reaction. By substitution of platinum for palladium we have recently isolated and reported the single-crystal X-ray structure of **8Z** the platinum analogue of the proposed oxidative addition intermediate **7**.[16]



**8Z**

In summary, we have developed a simple high-yield method for the stereospecific formation of vinylphosphonium salts via the Pd(0)-catalyzed reaction of readily available vinyl triflates with triphenylphosphine.

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(14) Vinyl triflate **3E** gave **6E** in greater than 99% isomeric purity whereas **3Z** gave a 94/6 mixture of **6Z**/**6E** as determined by $^{31}$P and $^{1}$H NMR.

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