$Pt^{2.2}$–Pt one-dimensional chain).[11] However, it is much longer than the 2.466 Å reported for the Pt(III)–Pt(III) bond length in $K_2[Pt_2(SO_4)_4(H_2O)_2]$,[12] a binuclear complex, not a chain complex. It is also appreciably longer than the expected length of a covalent Pt–Pt single bond as found in $Pt_2(C_5H_5)_2(C_5H_5C_5H_4)$ [$Pt^{(I)}$–$Pt^{(I)}$ 2.58 Å],[13] $Pt_2S[P(C_6H_5)_3]_3$ [$Pt^{(I)}$–$Pt^{(I)}$ 2.65 Å],[14] and $[Pt_3(CO)_3(\mu\text{-}CO)_3]_n^{2-}$, $n = 2, 3$, or 5 [$Pt^{(0)}$–$Pt^{(0)}$ 2.66 Å].[15]

The above comparisons lend support to the formulation of PAB as a partial oxidation platinum chain complex. This is reinforced by the fact that R_2, R_3, and R_4 are approximate multiples of R_1 ($R_2/R_1 = \sim1.92$–4, $R_3/R_1 = \sim2.91$–3, $R_4/R_1 = \sim3.83$–4), suggesting the presence in PAB of entities consisting of at least four or five rather linearly bound platinum atoms. On the basis of R_1 and R_2, the angle between adjacent Pt–Pt bonds is 152°. This is significantly smaller than in α-PB (164°). With the assumption of a planar zigzag chain of five platinum atoms with an angle of 152° between adjacent bonds, and a bond length of 2.76 Å, the Pt–Pt distances in the chain are 2.76, 5.36, 8.07, and 10.72 Å. These are in reasonable agreement with the observed distances in view of the simple planar geometry assumed.

Peaks in the pair function distribution curve associated with Pt–Pt intermolecular distances are expected to be considerably broader in general than those associated with intramolecular distances because the latter should exhibit a more discrete series of values in the amorphous PAB. The nearest neighbor distance is the most likely to assume a narrow enough range of values so as to yield an observable peak. Here, this distance will be essentially equal to the chain diameter. The width of chains similar to those in α-PB, with bridging acetamido ligands, is about 10 Å. This distance can be accommodated by R_4. However, as seen above, R_4 fits well the estimated length of a pentanuclear platinum chain in PAB, and it is therefore more appropriately assigned only to the latter, although the assignment is not without some uncertainty.

It is of interest, from a practical point of view, to find out if it is possible to correlate in a simple, yet reasonably accurate, way a Pt–Pt distance with a maximum in the scattering curve. With the assumption that the scattering results solely from platinum atoms displaced by a distance d from one another, a simple relation for the scattering intensity is given by[16] eq 1 with $k = 4\pi \sin \theta/\lambda$.

$$I_{eu} \propto \frac{\sin (kd)}{kd} \tag{1}$$

The function $\sin (kd)/kd$ has the form of a strongly damped sine wave, with a maximum at $kd = 7.728$. Therefore, I_{eu} has a maximum at the scattering angle θ_{max} given by eq 2. Now, if

$$\theta_{max} = \sin^{-1}\left(\frac{7.728\lambda}{4\pi d}\right) \tag{2}$$

$d = 2.76$ Å and $\lambda = 1.54$ Å, $\theta_{max} = 20°$ from eq 2. A strong maximum is indeed observed on the experimental scattering curve for PAB in the region, namely, at 18°. Application of eq 2 in reverse results in the calculated Pt–Pt distance corresponding to $\theta_{max} = 18°$ being $d = 3.07$ Å. Although this number deviates appreciably (+0.31 Å) from the one given by the radial distribution, it is low enough to suggest significant Pt–Pt interaction. However, it indicates that eq 2 is not accurate enough for quantitative work in this type of system.[17]

In conclusion, this preliminary X-ray diffraction study of a platinum acetamide blue reveals the presence of platinum chains involving at least four or five metal atoms and a Pt–Pt bond length of 2.76 Å. The presence of platinum chains is consistent with the spectroscopic properties of PAB, and it is similar in this respect to α-PB. It is likely that PAB consists of a mixture of oligomers, with tetranuclear or pentanuclear chains accounting for a high enough proportion of the sample to be observable. Further information such as the proportion of each kind of chain can, in principle, be extracted from the scattering curve. However, our present data are not sufficiently extensive and precise to allow this in a reliable way. We hope to present a more detailed and complete study in the future. We feel it to be of interest to carry out X-ray studies of other blues, including other PAB samples, to determine the range of Pt–Pt bond distances and chain nuclearity in blues, and to correlate these with the spectroscopic and antitumor properties of blues.

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Interception of the Cope Chairlike Transition-State Product during the Tandem Cope–Claisen Rearrangement: A Route to an Ambrosanolide Synthon

Sir:

The preference for a chairlike transition state in the Cope and Claisen rearrangements of acyclic 1,5-dienyl systems is well-documented.[1,2] It has been demonstrated that a significant amount of product can arise from a boatlike transition state, particularly when one or both of the olefins are contained in a ring.[3] We present herein evidence that the Claisen rearrangement serves to trap the kinetically formed Cope rearrangement product during the tandem Cope–Claisen rearrangement.[4]

Thermolysis (377 °C, evacuated tube, 1.5 min) of vinyl ether **1b**, prepared by the method previously described,[4a] provided a 70:30 mixture of **4**/**5**. The diastereomeric ratio was found to be temperature dependent (306 °C, 0.5 h, 77:23; 257 °C, 5.6 h, 81:19) in contrast to the lack of selectivity and absence of temperature dependence in the rearrangement **1b** → **4**, **5** (secondary methyl = hydrogen).[4a] The 270-MHz ^1H NMR spectrum of the major component **4** revealed characteristic resonances at δ 9.67 (t, J = 3 Hz, CHO), 1.08 (s, R_3CCH_3), and 1.07 (d, J = 7 Hz, R_2CHCH_3) while the minor component **5** displayed resonances at δ 9.72 (t, J = 3 Hz, CHO), 1.31 (s, R_3CCH_3), and 1.10 (d, J = 7 Hz, R_2CHCH_3).

The stereochemistry of **4** was established by transformation (Scheme I) of a mixture of **4**/**5** (85:15) into a mixture of diketones **8**/**9** (80:20). The major diketone was found to be identical (270-MHz NMR) with a sample prepared from ketone **10**, which has been previously converted to damsinic acid **11**.[5,6]

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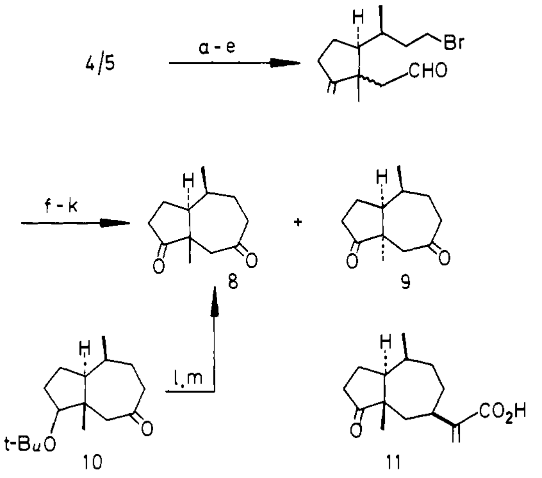
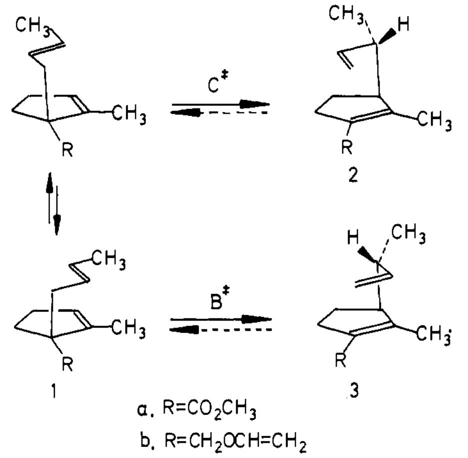
Scheme I[a]

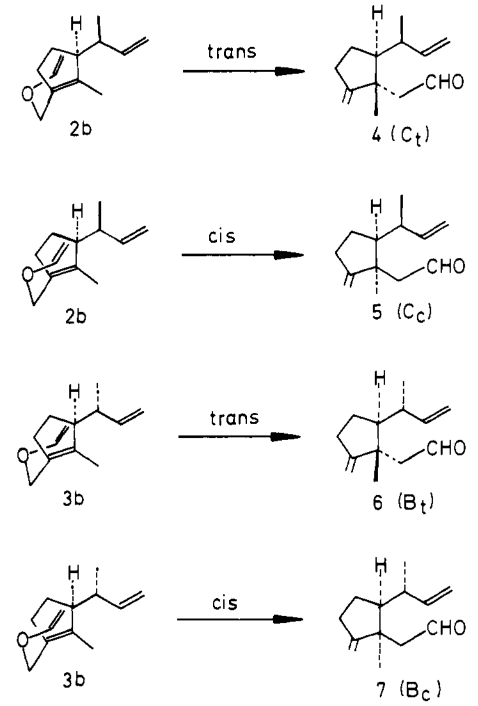


[a] (a) HC(OCH$_3$)$_3$, CH$_3$OH, p-TsOH; (b) (sia)$_2$BH; H$_2$O$_2$, NaOH;[10] (c) MsCl, Et$_3$N;[11] (d) LiBr, acetone; (e) H$_3$O$^+$; (f) KCN, HOAc, C$_2$H$_5$OH; (g) CH$_2$=CHOC$_2$H$_5$, p-TsOH; (h) LDA, THF;[12] (i) H$_3$O$^+$; (j) KOH, CH$_3$OH; (k) O$_3$; (l) CF$_3$CO$_2$H; (m) CrO$_3$·C$_5$H$_5$N·HCl.[13]

Scheme II



Scheme III



Thus, the lowest energy reaction pathway for the Cope rearrangement of **1b** proceeds through a chairlike transition state to produce **2b** (Scheme II) followed by Claisen rearrangement on the less hindered α face of the five-membered ring, giving rise to **4** (C_t),[7] having the butenyl and acetaldehyde chains in a trans arrangement (Scheme III).

The structure of the minor component **5** was established by deliberately generating Cope products derived from a boatlike transition state. To this end, ester **1a** was thermolyzed to produce a 60:40 equilibrium mixture of **1a**/(**2a** + **3a**). The ratio **2a**/**3a** was shown to decrease with time at a given temperature (266 °C, 0.5 h, 93:7; 263 °C, 2 h, 82:18; 266 °C, 4 h, 75:25; 235 °C, 6 h, 95:5) as witnessed by the increase of the high-field methyl doublet (270 MHz) at δ 0.83 (**3a**) relative to its counterpart at δ 1.06 (**2a**). A mixture of esters **1a**/(**2a** + **3a**) (60:40) was converted by successive LiAlH$_4$ reduction and vinylation to a mixture of vinyl ethers **1b**[8] (60%) and **2b** + **3b** (40%). A VPC collected sample of **2b** + **3b** (**2b**/**3b** = 79:21) was thermolyzed at 180 °C (14 h)[9] to effect Claisen rearrangement, providing an NMR (270 MHz) detectable mixture of three aldehydes in a ratio of 67:14:19 (integration of aldehyde protons). While the first two of these aldehydes were assignable to the previously observed thermolysis products **4** (C_t) and **5** (C_c), the third component [NMR (270 MHz) δ 9.64 (dd, J = 4, 2 Hz, CHO, singlet upon irradiation of CH_2CHO), 1.02 (s, R$_3$CCH$_3$), 0.99 (d, J = 7 Hz, R$_2$CHCH$_3$)] was ascribable to **6** (B_t), arising from **3b**. Therefore, the minor component of the Cope–Claisen rearrangement of **1b** must arise from a chairlike Cope rearrangement and a Claisen rearrangement cis to the butenyl side chain as represented in **5** (C_c).

If the rate of the Cope–Claisen rearrangement of **1b** were appreciable at 180 °C, the extrapolated (ln **4**/**5** vs. $1/T$) ratio **4**/**5** would be 88:12. If it is assumed that the same selectivity applies for the formation of **6** and **7** from **3b**, then the relative distribution of products should be **4** (C_t):**5** (C_c):**6** (B_t):**7** (B_c) or 70% (88 × 79):9% (12 × 79):18% (88 × 21):3% (12 × 21). The ratio **4**/**5**/**6** is in good agreement with the observed values. The component **7** (B_c) could not be detected.

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[7] This designation refers to the transition states required to form **4**. Thus, "C" refers to the chairlike transition state of the Cope rearrangement while the subscript "t" indicates trans arrangement of the acetaldehyde and butenyl groups in the product of the Claisen rearrangement.

[8] The Z isomer of **1b** was not detected.

[9] Thermolysis of a mixture of **2b** + **3b** (**2b**/**3b** = 82:18) for 3 h at 180 °C indicated 38% conversion to products **4**, **5**, and **6** with no sign of retro-Cope product **1b**.

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Total Synthesis of Pseudomonic Acid C: Application of the Alkoxyselenation Reaction in Organic Synthesis

Sir:

Pseudomonic acids A (**1a**) and B (**1b**) are antimicrobially active acidic substances produced by a strain of *Pseudomonas fluorescens* (NCIB 10586). The patent literature abounds with reports of the good activity in vitro of the major metabolite **1a** against