ON THE EFFECT OF RING SIZE IN THE CYCLIZATION OF CARBONYL AND VINYL RADICALS ONTO ALKENES

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It is demonstrated that carbonyl and vinyl radicals cyclise readily onto alkynes when the product is a five membered ring but not when the product is a six membered ring; a transition state model is proposed to explain these observations.

The formation of functionalised five and six membered ring systems by cyclization of vinyl radicals onto alkenes¹ and of alkyl radicals onto alkynes² has been widely exploited in recent years. The vinyl radical cyclizations can be subdivided into two classes; those in which the π system of the vinyl radical is exocyclic to the ring formed a-g and those in which it is endocyclic to the ring formed^{la, g}. For clarity we will call these variations $(\pi - exo)$ and $(\pi - endo)$ type cyclizations respectively. The formation of rings by cyclization of vinyl or carbonyl radicals onto alkynes is much less common and we report here the results of our exploratory work in this area and propose a model for the transition state of such reactions which is consistent with the results observed.

A recent paper by Bachi demonstrated³ that α -alkylidene- γ -lactones (2) can be prepared in high yield by the reaction of selenocarbonates $(\underline{1})$ with tri-n-butyltin hydride and azo isobutyronitrile (AIBN). This reaction is an example of a 5-(π -exo)-exo-dig radical process. Encouraged by this result we attempted the cyclization of the selenol ester $(3)^{4,5}$ under similar conditions but were unable to find any evidence for the formation of the expected product (4) of a 6-(π -exo)-exo-dig process in the complex reaction mixture. The predominant modes of reaction involved reduction of the selenol ester to the corresponding aldehyde and hydrostannylation of the triple bond. Similarly tin hydride/AIBN reduction of the vinyl bromide (5) gave none of the expected $6-(\pi-exo)-exo-dig$ product (7) or of any related product but only reduction

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2896

product (<u>6</u>) in 70%⁶ isolated yield. Evidently the $6-(\underline{\pi}-\underline{exo})-\underline{exo}-\underline{dig}$ process is not a favoured reaction mode. Tin hydride/AIBN treatment of the vinyl bromide (<u>8</u>) gave the diene (<u>10</u>) in 20% isolated yield and the reduction product (<u>9</u>) in 41% yield, demonstrating that the $6-(\underline{\pi}-\underline{endo})-\underline{exo}-\underline{dig}$ process is favourable. The selenol ester (<u>11</u>), gave the cyclohexanone (<u>13</u>) and the aldehyde (<u>12</u>) in 32 and 55% yields respectively;⁷ the $6-(\underline{\pi}-\underline{exo})-\underline{exo}-\underline{trig}$ process is therefore favourable. The vinyl bromide (<u>14</u>) gave products (<u>15</u>) and (<u>16</u>) in 12 and 61% isolated yields respectively on treatment with tin hydride and AIBN.⁸ Both products result from the favourable $5-(\underline{\pi}-\underline{exo})-\underline{exo}-\underline{trig}$ radical cyclization; (<u>16</u>) being the result of subsequent hydrostannylation.

The above results are best explained in terms of two postulates. The first criterion for cyclization onto an alkyne is that the incoming radical must approach along the correct vector, <u>ie</u> at an angle of <u>ca</u> 120[°] with the axis of the single bond from the alkyne.⁹ The second criterion, we suggest, is that the π systems of the attacking radical and of the alkyne be as near co-planar as possible in the transition state bearing in mind the diene or enone nature of the products. The transition states for the $6-(\underline{\pi}-\underline{\text{exo}})-\underline{\text{exo}}-\underline{\text{dig}}$; $6-(\underline{\pi}-\underline{\text{endo}})-\underline{\text{exo}}-\underline{\text{dig}}$ and $5-(\underline{\pi}-\underline{\text{exo}})-\underline{\text{exo}}-\underline{\text{dig}}$ cyclizations are then represented by $(\underline{17}) + (\underline{18})$; $(\underline{19}) + (\underline{20})$ and $(\underline{21}) + (\underline{22})$ respectively.from which it can be seen that in agreement with the experimental findings the latter two are relatively strain free and readily accessible but the former is subject to considerable steric strain and is therefore largely inaccessible.

We have not studied the $5-(\underline{\pi}-\underline{endo})-\underline{exo}-\underline{dig}$ system but predict, on the basis of molecular models that the transition state will be relatively strain free and the reaction favourable. The cyclization of aryl radicals onto 2-(3'-acetylenic) linkages as in $(\underline{23}) \rightarrow (\underline{24})^{10}$ can be construed as either an example of $5-(\underline{\pi}-\underline{endo})-\underline{exo}-\underline{dig}$ or $5-(\underline{\pi}-\underline{exo})-\underline{exo}-\underline{dig}$.

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7







 $\frac{11}{12}, X = SePh$ $\frac{12}{12}, X = H$













<u>17</u>

H



<u>18</u>

 $6-(\underline{\pi}-\underline{exo})-\underline{exo}-\underline{dig}$ $x = 0, \ CR_2$



<u>19</u> $6-(\pi-\text{endo})-\text{exo}-\text{dig}$ <u>20</u>



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- 5. All new products gave satisfactory spectroscopic and microanalytical and/or high resolution mass data.
- 6. Yields quoted in this paper are for slow addition of Bu₃SnH/AIBN to the substrate in benzene at reflux. In every case photochemically initiated reactions at room temperature gave comparable results.
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