The *cis*-Cyclo-oct-4-enyl Radical is Reluctant to Rearrange

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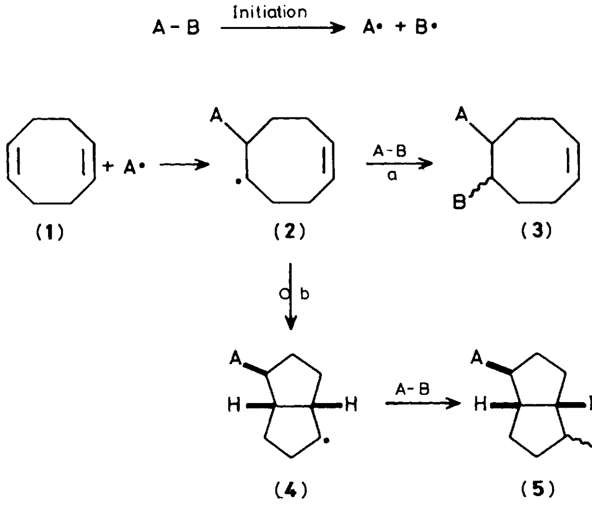
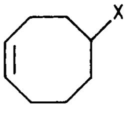
The *cis*-cyclo-oct-4-enyl radical, generated both photochemically and thermally from the *O*-acyl thiohydroxamate (**9**) is efficiently trapped by (**9**), tetrachloromethane, 1,1-diethylpropanethiol, and oxygen.

The reaction of a compound A–B with *cis,cis*-cyclo-octa-1,5-diene (**1**) under radical conditions typically leads either to a simple addition product (**3**) (Scheme 1, path a) or to a product (**5**) resulting from transannular cyclisation of the intermediate radical (**2**) to radical (**4**) (Scheme 1, path b).

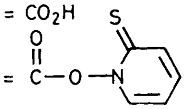
The product distribution thus depends upon the relative rates of chain transfer and transannular cyclisation of the substituted cyclo-oct-4-enyl radical (**2**). In this manner the reagents A–B (Scheme 1) fall into two distinct groups. One group, comprising thiols,[1a] thiolacids,[1a] trimethylstannane,[1b] and hydrogen bromide,[1c] is capable of rapidly quenching alkyl radicals by hydrogen transfer and leads to the substituted cyclo-octenes (**3**). The second group, made up of tetrachloromethane,[2a] trichloromethane,[2a] *N*-t-butylformamide,[2a,b] and



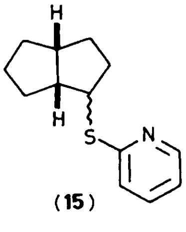
Scheme 1



(6) X = Br
(7) X = CN
(8) X = CO_2H



(9) X =
(10) X = 2-pyridylthio
(11) X = cyclo-oct-4-enyl
(12) X = Cl
(13) X = H
(14) X = OOH



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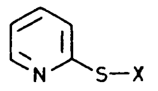
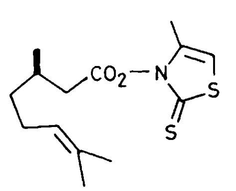


(16) X = CCl_3
(17) X = $SCEt_3$
(18) X = 2-pyridylthio



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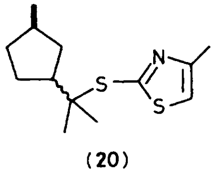
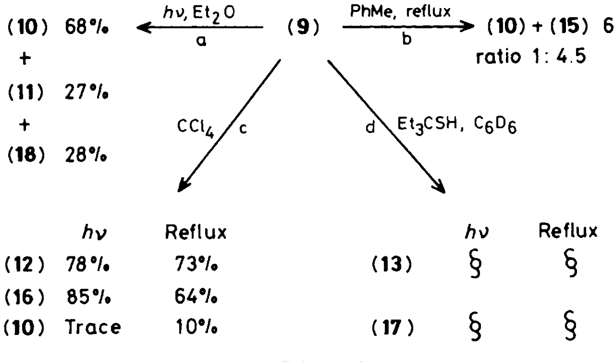


(20)

diethylphosphate,[2b] quenches alkyl radicals less rapidly and so leads to the bicyclo[3.3.0]octane products (5). Closer inspection reveals an additional factor: those radicals (2) that follow path a (Scheme 1) can be considered to be stabilised by a β-heteroatom[3] and so to be less prone to cyclisation (the inclusion of diethylphosphate in the second group is an obvious exception). More recently various annelated cyclo-oct-4-enyl radicals have been shown to rearrange to linear tri-[4a] and tetra-quinanes[4b] in the presence of the efficient hydrogen donor tri-n-butylstannane. This shows that rates of chain transfer cannot be the only factor involved and suggests that rates of transannular cyclisation may be significantly affected by ring substituents and/or conformational effects. We present here the results of our study on the chemistry of the parent cyclo-oct-4-enyl radical which show that in the absence of ring substituents the transannular cyclisation is a relatively slow process.



Scheme 2

Experience[5] led us to choose the *O*-acyl thiohydroxamate (9) as a clean, convenient, and above all versatile source of the cyclo-oct-4-enyl radical. 5-Bromocyclo-octene[6] (6) was converted into the nitrile (7) which was hydrolysed to give the acid (8)[7] in an overall yield of 80%. This acid was transformed by reaction of the derived acyl chloride with *N*-hydroxypyridine-2-thione and pyridine in diethyl ether into the stable yellow crystalline ester† (9) in an isolated yield of 60%.

Ester (9) was allowed to take part in free radical chain reactions (Scheme 2) with itself (paths a and b), with tetrachloromethane (path c),‡ and with 1,1-diethylpropanethiol[8] (path d), under both photochemical and thermal conditions.

In all reactions but one, the only cyclo-octene-derived products observed were those from trapping of the unrearranged cyclo-oct-4-enyl radical. Not surprisingly, therefore, photolysis of (9) in diethyl ether solution in the presence of oxygen and 1,1-diethylpropanethiol led to the hydroperoxide (14)[10] which could be isolated in 45% yield on a 1 mmol scale. The only conditions under which transannular cyclisation competed effectively with chain transfer involved the thermal decomposition of (9) in toluene at reflux.

Comparison of the above results with the observation[11] that the *O*-acyl thiohydroxamate (19) leads exclusively to the cyclopentylmethyl sulphide (20) on photolysis in diethyl ether at room temperature indicates that the rearrangement of the cyclo-oct-4-enyl radical into the bicyclo[3.3.0]octan-2-yl radical is significantly slower than the 5-*exo–trig*[12] cyclisation of a hept-5-enyl radical[3,13] under similar conditions.

We conclude that the rate of transannular cyclisation of the parent cyclo-oct-4-enyl radical is relatively slow but that it can be significantly accelerated by the addition of ring substituents, an effect which is analogous to that found for the hex-5-enyl–cyclopentylmethyl system.[3] However, cyclo-oct-4-

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† All new compounds gave spectroscopic and analytical data consistent with their assigned structures.

‡ The formation of sulphide (10) as a byproduct in tetrachloromethane at reflux can probably be attributed to a residual cage mechanism.[9]

§ Bicyclo[3.3.0]octane was absent from the crude product mixture as shown by ^1H and ^{13}C n.m.r. spectroscopy.

enyl radicals that bear certain heteroatoms β to the radical centre do not readily rearrange, presumably owing to β-stabilisation. Finally, examination of molecular models leads to the prediction that *trans*-cyclo-oct-4-enyl radicals will undergo transannular cyclisations much more readily than the *cis* isomers considered here.

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