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THE FORMATION AND DECOMPOSITION OF 1,1-DICHLORO-1*H*-CYCLOPROPA[ℓ]PHENANTHRENE[1]

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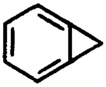
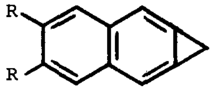
Summary: *Selenoxide elimination from (8) delivers 1,1-dichloro-1*H*-cyclopropa[ℓ]phenanthrene (9) which is converted into the ester (11) upon reaction with methanol. The intervention of (9) is supported by labelling studies.*

The strained and highly distorted cycloproparenes[2] result from the fusion of a three-membered carbocyclic ring with a benzenoid nucleus. Cyclopropabenzene (1)[3] and cyclopropa[*b*]naphthalene (2)[4] are surprisingly stable, readily available materials while cyclopropa[*b*]anthracene (3)[5] and its derivatives[6] have only recently become available. By way of comparison cyclopropa[*a*]naphthalene (4)[7] decomposes explosively on melting, and all prior attempts to generate the 1*H*-cyclopropa[ℓ]phenanthrene ring-system (5) have failed.[8-11] These observations could be taken to imply that enhanced olefinic character in the bridge bond [bond 1a,7b of (4) and bond 1a,9b of (5)] results in a decrease in the stability of the cycloproparene. Undaunted by such a prospect, we have continued to pursue the 1*H*-cyclopropa[ℓ]phenanthrene ring-system[9,10] and we now provide the first definitive evidence for its formation.

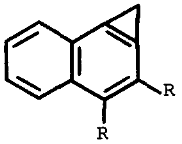


(1)



(2) R = H

(3) R = benzo-fusion



(4) R = H

(5) R = benzo-fusion

Previous studies[8,9] have shown that certain dihydrocyclopropa[ℓ]phenanthrenes, *e.g.* (6) (Scheme), serve as progenitors for bicyclohepta-2,4,6-trienes, e.g. (12). However, the aromatization of such compounds does not occur[2] and the observed products are formed by way of the corresponding ring-opened arylcarbene, e.g. (13) (Scheme).[8,9] Nevertheless, the introduction of unsaturation into a preformed ring-system provides the method of choice for cycloproparene synthesis.[2] Hence the present study has involved the *syn*-elimination of the elements of phenylselenenic acid between the 1a- and 9b-positions of the dichlorodihydrocyclopropa[ℓ]phenanthrene (8), a substrate from which selenoxide elimination can occur in one direction only.

The necessary selenide (7) was obtained from the addition of dichlorocarbene to the known 9-phenylselenophenanthrene.[12] Interestingly, the addition of carbenes to activated olefins is well established,[13] but relatively little emphasis has been given to analogous activated aromatics. In the present case a 35% yield of (7)[14] is obtained using the phase transfer method. Oxidation of (7) with *m*-chloroperbenzoic acid affords the selenoxide (8) which was used without further purification.[15,16] As expected,[15] stirring a solution of the selenoxide (8) at ambient temperature is sufficient to effect elimination as evidenced by the precipitation of phenylseleninic acid. When this is allowed to occur under standard conditions (with t-butylhydroperoxide added to oxidize the "PhSeOH" formed initially)[15] much decomposition is evident and only complex mixtures of organic products are isolated in low yield. However, when the elimination is allowed to occur in the presence of methanol (but in the absence of t-butylhydroperoxide) methyl phenanthrene-9-carboxylate (11)[17] is obtained in 65% yield. We take this result as evidence for the formation of 1,1-dichloro-1*H*-cyclopropa[ℓ]phenanthrene (9) (Scheme) by selenoxide elimination from (8) since isolable 1,1-dihalocyclopropa-benzene and -naphthalene homologues are known[18] to deliver carboxylate esters in alcoholic media. Thus ionization of (9) leads to cation (10)[19] (Scheme) which upon sequential capture and solvolysis by methanol affords ester (11) by way of 9-trimethoxymethylphenanthrene.[18]

Support for this claim has been derived from complementary labelling experiments. Decomposition of the selenoxide (8) in MeOD leads to (11) with 76% deuterium incorporation[20] at C10. On the other hand, when the label is incorporated into the substrate[21] and the decomposition of (8) (enriched with 60% deuterium at C9b) is allowed to occur in MeOH ester (11) is produced with 17% deuterium at C10. These experiments are consistent in showing that ∿75% of the C9b-*H(D)* is lost in the conversion of (8) into (11). Consequently the major pathway to (11) cannot involve nucleophilic attack of methanol at C1 with concomitant cleavage of the three-membered ring and ejection of phenylselenoxide. Moreover, the major route requires the intervention of a species of sufficient reactivity to incorporate D(H) at what becomes C10 of ester (11). Taken with the known[15] facility for *syn*-selenoxide elimination and the behaviour[18] of 1,1-dihalocycloproparenes, the present results argue convincingly for the formation of 1,1-dichlrocyclopropa[ℓ]phenanthrene (9) as the reactive molecule involved. Attempts to 'trap' (9) with various dienes have thus far failed.

Acknowledgments:

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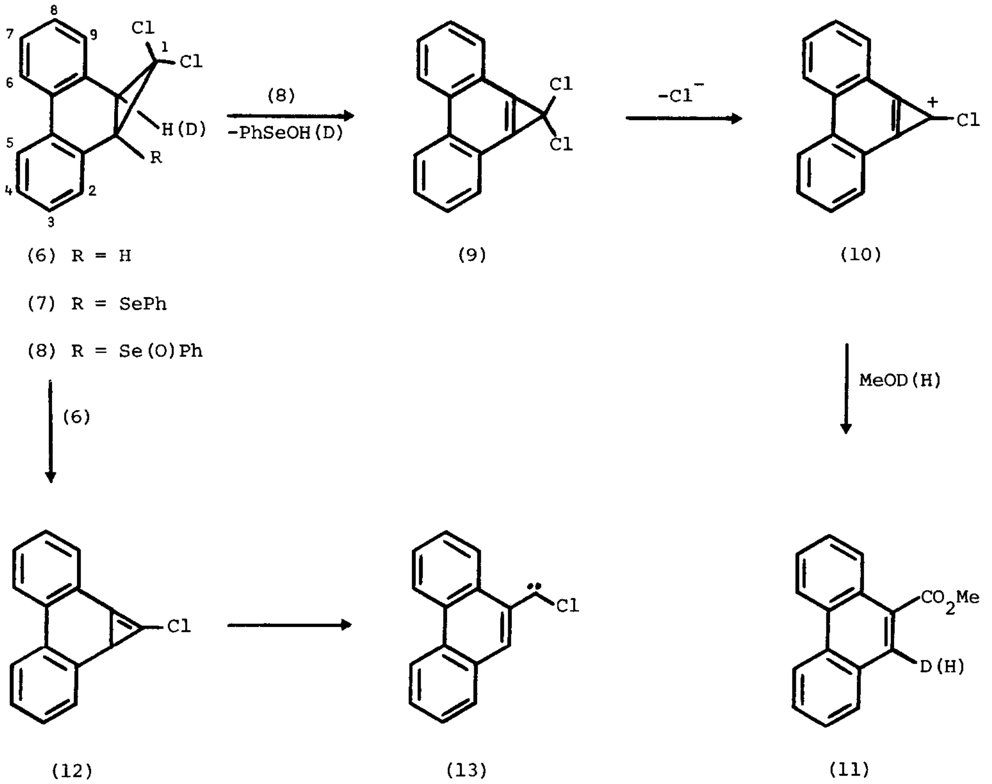

SCHEME

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16. In one experiment the organic phase was concentrated after standard work-up and the H-1 n.m.r. spectrum recorded before decomposition set in. The proton at C-9b was moved downfield from 3.49 ppm in (7) to 4.21 ppm in (8).

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20. The deuterium level was determined by n.m.r. integration of the proton at 8.4 ppm and from analysis of the mass spectrum of the compound.

21. Halogen-lithium exchange of 9-bromophenanthrene followed by quenching in D_2O delivers 9-[^{2}H]-phenanthrene. Bromination-dehydrobromination of this compound provides 9-bromophenanthrene with 60% deuterium label at C10. This latter compound provides (7) with 60% deuterium incorporation at C9b by the usual sequence - see ref.12. It has not proved possible to obtain (7) fully labelled at C9b by other routes.

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