Kurze Mitteilungen

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Synthesis of [9.10-b]-Phenanthrofuran *via* Ring Expansion of a Dichlorocyclopropane*

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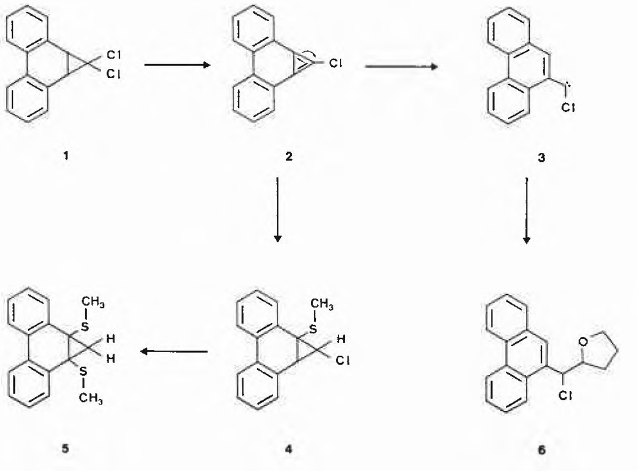
Abstract

Base-induced elimination of the dichlorocarbene adduct *8* of 9-methoxyphenanthrene (*7*) give rise to the formation of the phenanthrofuran *9*. A mechanism involving a cyclopropene-vinylcarbene rearrangement (*10-11*) followed by intramolecular insertion into the C-H bond of *11* is proposed for the transformation.

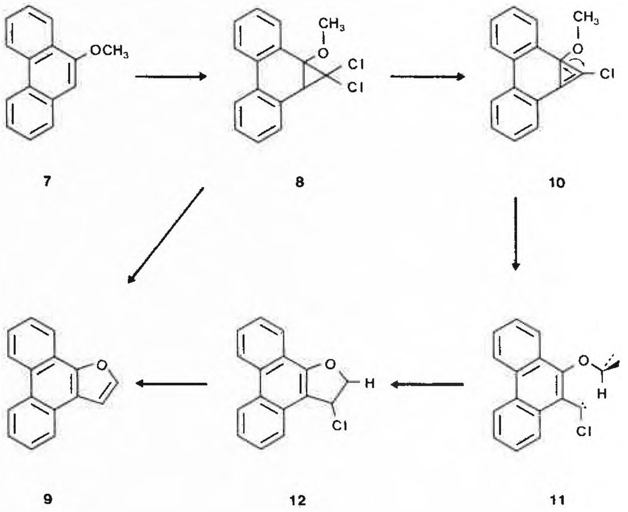
The dehydrohalogenation of the dichlorocarbene adduct **1** of phenanthrene has been investigared by *Billups* [1] and *Halton* [2] (Scheme 1). Reaction of **1** with *t*-BuOK leads to the chlorocyclopropene **2** which can be trapped if the reaction is carried out in the presence of methylmercaptide. The addition product **4** undergoes a second elimination of hydrogen chloride and subsequently a further addition of mercaptide to yield **5**. In the absence of mercaptide the chlorocylcopropene **2** rearranges to the vinylcarbene **3**. The latter is efficiently trapped giving the insertion product **6** by reaction with the solvent. The observation that rearrangement **2-3** occurs at o °C has been explained by release of steric strain and gain in resonance energy upon cyclopropene ring opening [1,3].

Scheme 1:



We wish to report that the cyclopropene-carbene rearrangement **2-3** can be exploited for a synthesis of [9,10-*b*]-phenanthrofuran. When the known dichlorocarbene adduct **8** (200 mg) [4] of 9-methoxyphenanthrene **7** [5] (Scheme 2) is reacted with 2 eq. of t-BuOK in tetrahydrofuran (30 min. at -50°, then slow warm-up to RT) in presence of crown ether (dicyclohexyl-18-crown 6, 20 mg) the furan **9** is formed in 80% yield. The structure of **9** follows from elemental analysis and spectral data, and is confirmed by comparison with the properties of **9** reported in the literature [6].

Scheme 2:



The formation of **9** from **7** is readily rationalized in terms of the mechanism of *Billups* and *Halton* [2] for the comportment of **1**. The intermediate methoxy-substituted chlorocarbene **11** is derived from the cyclopropene **10**. The key step consists in intramolecular carbene insertion of **11** into the C-H bond of the methoxy group to yield **12**, whereas the intermolecular insertion with the solvent does no longer occur. Finally, the furan **9** is formed by loss of HCl. An analogous furan formation *via* carbene insertion in the gas phase has recently been reported by *Engler* and

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Shechter [7]. Although the intermediacy of **2** and **3** during transformation of **1** is unequivocally established, the presence of the methoxy group could in principle favour other pathways in the case of **8**; conceivably, the carbene **11** could be formed directly from **8** rather than from **10** [1].

The transformation **7**-**9** represents a furan synthesis from a vinyl ether *via* carbene addition and ring expansion. We are investigating the generality of this sequence in the light of the recent observation [8] that even simple chlorocyclopropenes open to chlorocarbenes when appropriate conditions are found.

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References

1 *W.E. Billups, L.P. Lin* dand *W.Y. Chow*: J. Am. Chem. Soc. *96*, 4026 (1974); *W.E. Billups, L.E. Reed, E.W. Casserly* and *P. Lin*: J. Org. Chem. *46*, 1326 (1981).
2 *B. Halton* and *D.L. Officer*: Aust. J. Chem. *36*, 1167 (1983); *B. Halton* and *D.L. Officer*: Tetrahedron Lett. *22*, 3687 (1981).
3 *T.T. Coburn* and *W.M. Jones*: J. Am. Chem. Soc. *96*, 5218 (1974).
4 *R.G.R. Bacon* and *S.C. Rennison*: Chem. & Ind. *1966*, 812.
5 *W.E. Parham, D.A. Bolon* and *E.E. Schweizer*: J. Am. Chem. Soc. *83*, 603 (1961).
6 *A. Padwa* and *R. Hartmann*: J. Am. Chem. Soc. *88*, 3759 (1966).
7 *T.A. Engler* and *H. Shechter*: Tetrahedron Lett. *23*, 2715 (1982).
8 *J. Arct* and *B. Migaj*: Tetrahedron *37*, 953 (1981).