164. Reactions of Alkenediazonium Salts. Part 2. Methanolysis of 2,2(2′,2″-Biphenylylene)ethene-1-diazonium Hexachloroantimonate. A Rearrangement to 9-Methoxyphenanthrene[1])

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Summary

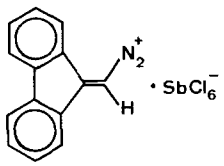
The title compound (**1**) reacts with excess methanol forming a rearranged product, 9-methoxyphenanthrene (**2**). 9-(Methoxymethylidene)fluorene (**4**) does not rearrange to give **2** under the same conditions. In deuterated methanol no labelled product is obtained, showing that the possible mechanism involves either the formation of a primary vinyl cation **5** rearranging to an aryl cation **6** or the formation of a β-alkoxycarbene (**12**), which rearranges to an arene. The results obtained are compared with previously reported reactions, which were postulated to proceed *via* a 2,2(2′,2″-biphenylylene)ethene-1-diazonium ion (**23**).

Introduction. – A comparison of vinyldiazonium ions and arenediazonium ions is interesting from the point of view of potential synthetic applications of vinyldiazonium salts as well as for mechanistic reasons. As relatively little is known about the reactivity of vinyldiazonium ions, we started experimental investigations [1] and, together with *Simonetta et al.* [2] theoretical studies.

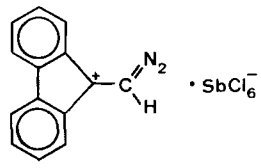
In the previous communication [1] we demonstrated that 2,2-diethoxyethenediazonium hexachloroantimonate reacted with various nucleophiles in a way consistent with dominant contribution from diazocarbenium and diazooxonium mesomeric structures. This manifested itself in the alkylating properties of the salt and in the reaction of a secondary amine at the β-C-atom. We were not able to find products consistent with either a primary dediazoniation or a nucleophilic addition to the β-N-atom of the diazonio group.

2,2(2′,2″-Biphenylylene)ethene-1-diazonium hexachloroantimonate (**1**) which was first synthesized by *Bott* [3], can be considered as a vinyldiazonium (**1a**) or a carbenium ion (**1b**), depending on the relative contributions of the different mesomeric structures. Compound **1** and similar compounds were postulated as intermediates in the solvolysis of nitrosooxazolidones [4–7], in the nitrosation of vinylamines [8] [9] and in the acidic decomposition of vinyltriazines [10]. A comparison of the solvolysis patterns of **1** and of the compounds mentioned should help to confirm or reject the intermadiacy of **1** in these reactions.

[1]) Part 1: [1].



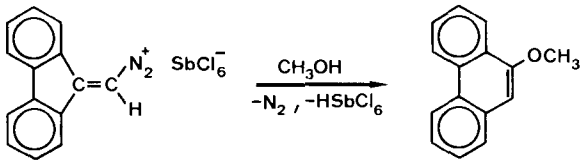
1a



1b

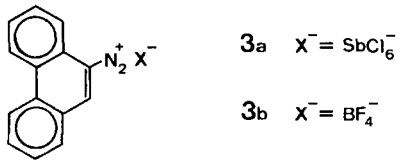
Results and Discussion. – When **1** was allowed to react with MeOH at low temperature, the only product separated from the reaction mixture was 9-methoxyphenanthrene (**2**) *(Scheme 1)*.

Scheme 1



1 **2**

This unexpected rearrangement prompted us to check whether **1** has the attributed structure, or whether it was the 9-phenanthrenediazonium cation (**3**), formed by rearrangement during the synthesis of **1**. 9-Phenanthrenediazonium tetrafluoroborate (**3b**) was prepared and was found to have properties characteristic of an arenediazonium salt and different from those of **1**.



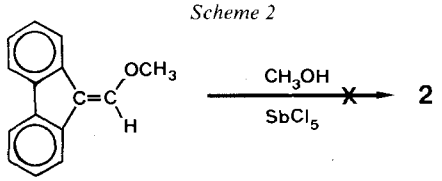
3a $X^- = SbCl_6^-$

3b $X^- = BF_4^-$

The non-rearranged product in the solvolysis of **1** in MeOH would be 9-(methoxymethylene)fluorene (**4**), which was found [4] [5] as a methanolysis product of the appropriate nitrosooxazolidone.

Derivatives of 9-(hydroxymethyl)fluorene can undergo a *Meerwein* rearrangement under strongly acidic conditions with the formation of phenanthrenes [11] [12]. It was, therefore, necessary to check whether or not **4** rearranges to **2** under the reaction conditions. Compound **4** was allowed to react with MeOH in the presence of an equimolar amount of $SbCl_5$ which simulated the reaction conditions. The mixture recovered did not contain **2** *(Scheme 2)*.

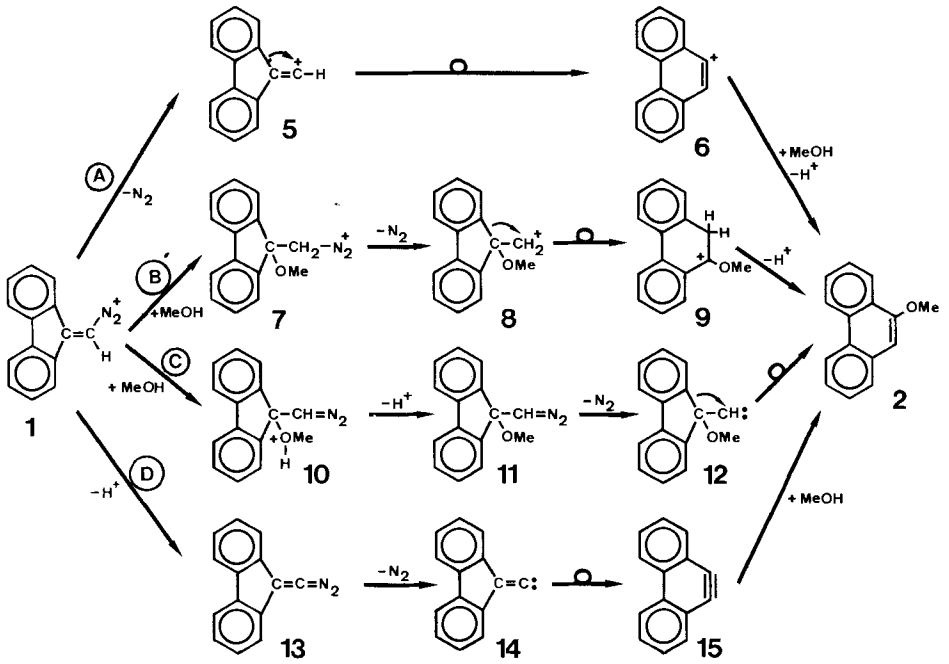
Scheme 2



4

Scheme 3 shows possible mechanisms which would account for the formation of the rearranged product. In mechanism B the addition of MeOH to the double bond, followed by dediazoniation gives a primary carbo-cation **8**, which then rearranges to a σ-complex **9**, while in mechanism D an unsaturated carbene **14** rearranges to give an aryne **15**. The common feature of these two mechanisms is that the H-atom at C(10) in the resulting phenanthrene would originate exclusively (mechanism D) or partially (mechanism B) from the solvent, a feature easily checked by using a deuterated solvent[2]).

Scheme 3



Before such an experiment could be carried out, however, it was necessary to check whether **2** would be labelled under the simulated reaction conditions. This control experiment was performed with the help of NMR spectroscopy and showed that there is no appreciable labelling of **2** in the $CD_3OD/SbCl_5$ system. Thus any deuteration of **1** in the deuterated solvent would be associated with the mechanism. Furthermore, there is no danger of 'washing off' the label during workup.

Compound **1** was allowed to react with CH_3OD and the product contained no label at C(10) or any other position, as shown by its NMR and mass spectra. Mechanisms B and D must therefore be rejected.

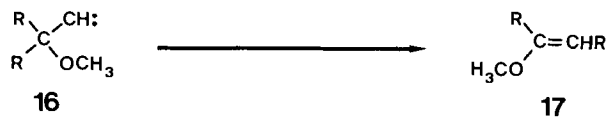
Of the remaining two mechanisms, A involves the formation of a primary vinyl cation **5** rearranging to an aryl cation **6**, both species of very high energy. In spite

[2]) The formation of deuterated products was observed in the solvolysis of nitrosooxazolidones [5].

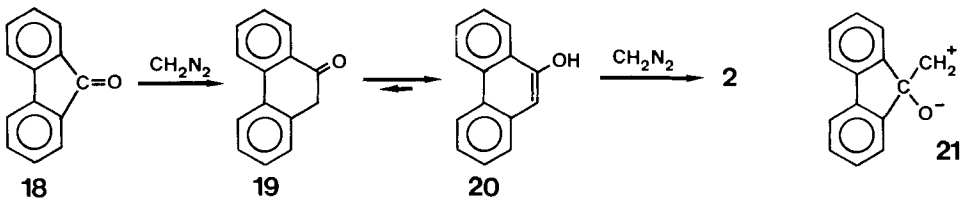
of this, path A cannot be rejected, since it is known that aryl cations are readily formed by dediazoniation of arenediazonium ions in solution [13–18] and since MO calculations seem to indicate that the stability of even the unsubstituted primary vinyl cation is roughly equal to that of the phenyl cation [19]. Furthermore, there are many precedents for aryl group migration leading to rearranged products in reactions proceeding *via* vinyl cations [20].

Mechanism C, on the other hand, involves nucleophilic attack by MeOH at the β-C-atom of **1**, followed by dediazoniation of the resulting diazo compound **11** to give a carbene **12**, which rearranges to **2**. β-Alkoxycarbenes **16** are known to rearrange in a similar manner to **17** [21] *(Scheme 4)*. The alkoxy substituent promotes the rearrangement. It is also known that aryl substituents show a higher tendency than alkyl to migrate to the electron-deficient carbene centre [22] [23]. Finally, fluorenone (**18**) reacts with diazoalkenes to form **2** [24] [25] *(Scheme 5)*. The first step in *Scheme 5* is a typical $5 \rightarrow 6$ ring enlargement, and similar reactions are believed [12] to proceed *via* a zwitter-ion **21**. Structure **21** differs from the carbene **12** in mechanism C only by the position of a proton. The mechanism of ring enlargements of ketones by diazoalkanes was not, however, studied in detail, and the possibility that there is a proton transfer from the carbo-cation to oxygen prior to the rearrangement cannot be excluded. In conclusion, the data available do not permit distinction between mechanism A and C.

Scheme 4



Scheme 5



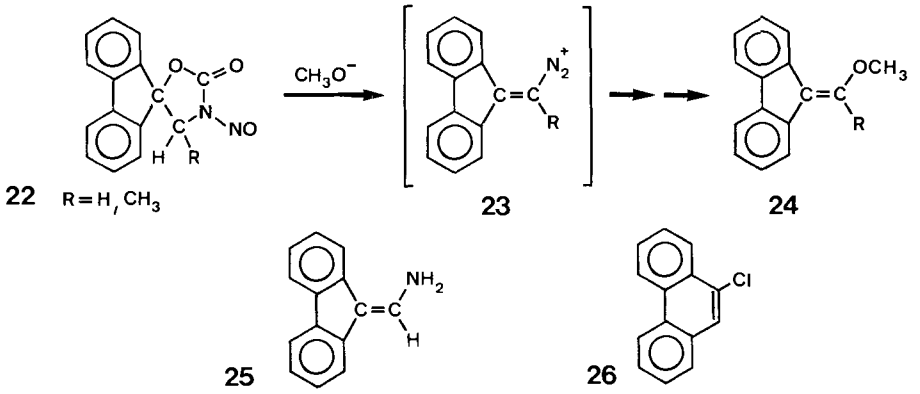
The possible intermediacy of vinyl cations or unsaturated carbenes during the decomposition of vinyl diazonium ions has been discussed by *Stang et al.* [26–28].

As mentioned earlier, *Newman et al.* [4] [5] studied the reaction of the *N*-nitrosooxazolidone (**22**) in MeOH with an equimolar quantity of NaOMe, as well as in EtOH in the presence of NaOEt. In all cases the corresponding unrearranged vinyl ether **24** was obtained as the major product *(Scheme 6)*. The authors postulate the reaction to proceed *via* the vinyldiazonium cation (**23**), followed by nucleophilic attack of the alkoxide ion at the β-C-atom and dediazoniation, similar to mechanism C in the *Scheme 3*. It can be questioned whether the reaction of nitrosooxazolidones [4] [5] really proceeds *via* vinyldiazonium ions **23**, since we have shown that the

vinyldiazonium salt **1**, upon methanolysis, yields only the rearranged product **2**. It is possible, however, that the reason for the different products formed are the different reaction conditions. The strongly basic alkoxide ion present in the experiments of *Newman et al.* may trap the reaction intermediate before rearrangement can occur, while under our acidic, non-nucleophilic conditions rearrangement can successfully compete and give **2** as the major product[3]).

In a study of the nitrosation of primary vinylamines [8], 5% of 9-chlorophenanthrene (**26**), *i.e.* a rearranged product, was obtained among other products when the amine **25** was allowed to react with nitrosyl chloride in dichloromethane.

Scheme 6



22 R = H, CH_3 **23** **24** **25** **26**

Since all the reactions mentioned [4] [5] [8] can be considered to proceed *via* the same diazonium ion **23**, the different products obtained indicate how sensitive is the decomposition of **23** towards changes in the conditions, and how close in energy the various reaction pathways probably are.

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Experimental Part

General. The melting points (m.p.) are uncorrected. The NMR spectra were measured on a *Bruker WH-90* instrument. The IR spectra were measured on a *Beckman-Acculab 4.* For MS a *Hitachi Perkin-Elmer RMU-6L* mass spectrometer was used. The UV measurements were performed on a *Beckman ACTA II.*

2,2(2',2''-Biphenylylene)ethene-1-diazonium hexachloroantimonate (**1**) was prepared according to [3]. *9-Methoxyphenanthrene* (**2**), m.p. 95°, was obtained by alkylation of 9-hydroxyphenanthrene with dimethyl sulfate in NaOH-solution [30] and its structure was confirmed by NMR, IR, UV and mass spectra. *9-(Methoxymethylene)-fluorene* (**4**) was prepared according to [31] by alkylation of formylfluorene [32] with $(CH_3)_2SO_4$. *Phenanthrene-9-diazonium tetrafluoroborate* (**3b**) was prepared by diazotization of 9-aminophenanthrene according to *Bavin & Dewar* [11] who, however, used it only as an intermediate and did not characterize it. Yellow substance, m.p. (dec)111–112°, IR 2263 cm^{-1}. It gives colour reactions with 2-naphthol, phenol and 9-aminophenanthrene.

Reaction of **1** *with MeOH.* Compound **1** (50 mg) was added to 1.5 ml of MeOH at −60° and the temperature allowed to increase slowly. At −20° **1** started to dissolve with vigorous gas evolution.

[3]) In a photochemical solvolysis of 2,2(2',2''-biphenylylene)-1-bromoethene in basic MeOH, a reaction which may proceed *via* the primary vinyl cation **5**, no rearrangement to **2** was observed [29]. This result parallels those of *Newman's* group [4] [5] which were also obtained in basic MeOH.

Before the mixture reached r.t. the gas evolution ceased. The mixture was quenched with solid $NaHCO_3$, 10 ml of H_2O was added and the mixture was extracted with CH_2Cl_2. The CH_2Cl_2-solution was dried ($MgSO_4$). TLC showed one spot. After the solvent had been removed, the residue was sublimed under reduced pressure (100°, 0.005 Torr). The sublimed substance had identical UV, IR, NMR, and mass spectra with 9-methoxyphenanthrene (**2**), but contained some impurities (m.p. lowered to 85°).

Reaction of **1** *with* CH_3OD was carried out exactly as with non-deuterated MeOH. The NMR and mass spectra of the obtained compound showed no label.

Attempted Isomerisation of **4** *to* **2**. To a solution of 100 mg (0.48 mmol) of **4** in 5 ml of MeOH was added 150 mg (0.5 mmol) of $SbCl_5$. The mixture was kept at $-60°$ for 1 h and was then allowed to reach r.t. After quenching with $NaHCO_3$ the mixture was worked up as in the case of the reaction of **1** with MeOH. TLC showed a mixture of compounds. The NMR spectrum of this mixture showed that none of its components was **2**.

Control NMR Experiment of Labelling of **2**. Compound **2** was dissolved in CD_3OD in an NMR tube and the NMR spectrum recorded. An equimolar amount of $SbCl_5$ in CD_3OD was then added and spectra were taken at intervals of 15 min. No noticeable H/D-exchange was observed after 30 min.

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