163. Reactions of Alkenediazonium Salts. Part 1. 2,2-Diethoxyethenediazonium Hexachloroantimonate: A Diazonium, a Carbenium or an Oxonium Salt?

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(16.V.83)

Summary

Reactions of the title compound **1** with various nucleophiles have been studied. The salt behaves like an alkylating agent towards ethers, alcohols and water forming ethyl diazoacetate (**2**), which reacts further with excess of the nucleophile. A solvent cage mechanism accounting for the observed products is proposed. Thermal decomposition in inert solvents leads to the alkylation of the counter-ion, *i.e.* formation of chloroethane, and in anisole, alkylation and chlorination of the solvent are also observed.

With a standard coupling component, 2-naphtholate ion, no azo coupling reaction of **1** is observed, but instead 14-methyl-14*H*-dibenzo[*a,j*]xanthene (**17**) is formed. The products of the reaction with diethylamine are diethylcyanoformamide (**18**) and ethyl diethylcarbamate (**19**). None of the chemistry of salt **1** is explained by the intervention of vinyl cations expected to be formed in a heterolytic dediazoniation. The predominant pathways seem to involve reactions of an oxonium salt (alkylating properties) or, in the case of diethylamine, a carbenium salt (primary nucleophilic attack on the β-C-atom of **1**).

The free energy barrier to C=C rotation in **1** is estimated to be 75 to 77 kJ/mol (18.0 to 18.5 kcal/mol), a value which falls between those expected for a double and a single bond.

Introduction. – In the context of our investigations on the dediazoniation mechanism of aromatic diazonium ions[1]), comparisons with the reactivity of vinyldiazonium ions are interesting. Owing to their electronic similarity vinyldiazonium ions might be reagents for the formation of vinyl cations.

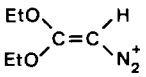
The unsubstituted vinyldiazonium ion, $H_2C{=}CH{-}N_2^+$, is not yet known. Therefore a theoretical study on the vinyldiazonium ion in the gas phase and in aqueous solution is a worthwhile undertaking. With others, we recently made such a study [2] for the gas phase by *ab initio* (STO-3G and 4-31G), and for solution by CNDO/2 methods. This investigation is a continuation of previous theoretical

[1]) See [1] and our preceding publications on the dediazoniation mechanism of arenediazonium salts.

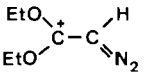
studies on the methyldiazonium [3] and the benzenediazonium ion [4] which were both verified by comparison with experimental data. The MO results for the vinyldiazonium ion indicate that its structural and energy characteristics are intermediate between those of the methyl and the benzene analogues, for example, with respect to the C–N bond length and the destabilization by solvent interaction.

Relatively few experimental data are available for reactions of substituted vinyldiazonium ions. They indicate ambient reactivities depending on substituents and reagents [5]; for example, 2-halo-substituted vinyldiazonium ions react with nucleophiles at C(2) before they lose N_2 in a dediazoniation [6].

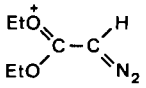
In this investigation we describe reactions of the 2,2-diethoxyethenediazonium ion (**1**) with various nucleophiles. The hexachloroantimonate of **1** was first synthesized by *Bott* [7] by ethylation of ethyl diazoacetate with triethyloxonium hexachloroantimonate. It can be considered as a representative of a new class of compounds, *i.e.* vinyldiazonium salts[2]) if structure **1a** is ascribed to it, or alternatively as a dialkoxycarbenium ion or an oxonium ion, represented by **1b** and **1c**, respectively. Structure **1a** seems to be supported by the high N=N stretching frequency as compared to ethyl diazoacetate [7], but no other chemical or physical indications are available. Compound **1** decomposes under the influence of various nucleophiles [5], but the decomposition products have so far not been elucidated.



1a



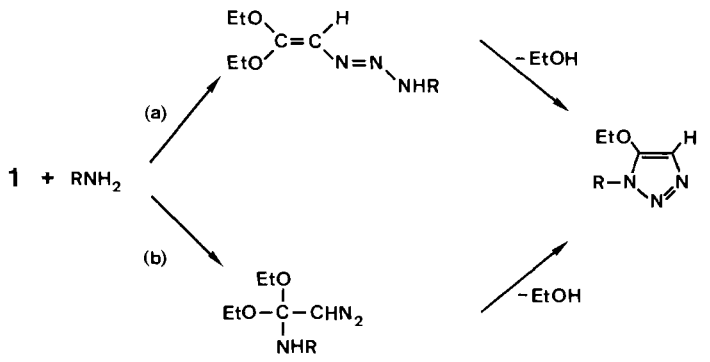
1b



1c

Saalfrank & Ackermann reported [9] [10] that **1** reacts with primary amines to give triazoles. This process might be a result of an initial *N*-azo-coupling reaction with the amine (characteristic of diazonium salts) with subsequent cyclization of the resulting triazene, or result from an attack of the amine at the β-C-atom with formation of a diazoalkane which cyclizes [10] *(Scheme 1)*.

Scheme 1



On the basis of these data it was interesting to study the reactions of **1** with simple nucleophiles (ethers, alcohols, water, anisole, 2-naphthol) and to use a secondary amine in a reaction analogous to that of Saalfrank & Ackermann, since

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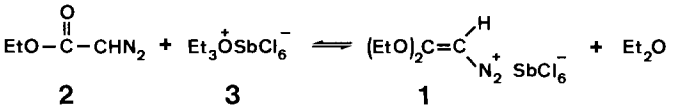
[2]) Formally **1** can also be considered as an analogue of ketene acetals [8], with an additional reaction site due to the presence of the diazonio group.

in this case the cyclization step of *Scheme 1* would not be possible. In addition, we present results on the free energy barrier to C=C rotation in **1** as investigated by variable temperature NMR measurements.

Results and Discussion. – *Reaction with Ethers.* We found that the synthesis of **1** from ethyl diazoacetate (**2**) and triethyloxonium hexachloroantimonate (**3**) required a large excess of **2** (much larger than in the original procedure [7]) to obtain a good yield of pure **1**, free of the triethyloxonium salt **3**. This suggested that an equilibrium may be involved. In fact, **1** reacts at room temperature with diethyl ether in 1,2-dichloroethane to yield triethyloxonium hexachloroantimonate (**3**) and ethyl diazoacetate (**2**), demonstrating that the equilibrium *(Scheme 2)* is established, and that **1** has properties of an alkylating agent which are even more pronounced when crown ethers are used. The formation of ethyl diazoacetate can be observed by IR spectroscopy immediately upon mixing of **1** with 18-crown-6 and 21-crown-7. Other unidentified products probably resulting from ring opening of the crown ethers were also formed. With 21-crown-7, the best complexing agent for diazonium salts [12], complexation of the diazonio group was also observed by IR.

Scheme 2

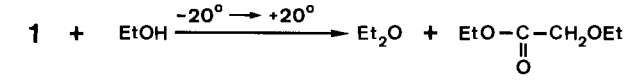


2 **3** **1**

Assuming that structures **1b** and **1c** contribute considerably to the properties of **1**, such behaviour is by no means surprising. Dialkoxycarbenium salts are much stronger alkylating agents than trialkoxyoxonium salts. Usually it is not possible to alkylate esters with trialkoxyoxonium salts [11].

Reactions with Alcohols and Water. Compound **1** decomposes in alcohols with vigorous N_2 evolution. When **1** was allowed to react with an excess of *ethanol* at low temperature, Et_2O and ethyl ethoxyacetate (**4**) were formed (GC/MS) *(Scheme 3)*. This result can be explained in terms of the alkylation of EtOH by **1** with the formation of Et_2O and ethyl diazoacetate (**2**), which reacts further with EtOH to form **4**, a normal product of the acidic diazoester solvolysis [13] [14].

Scheme 3



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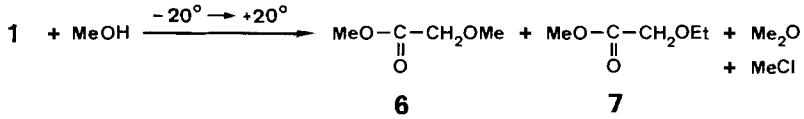
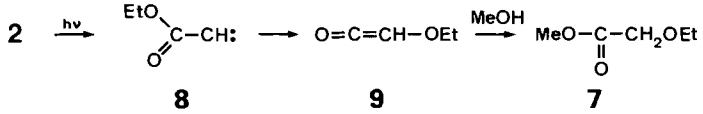
This simple picture becomes, however, more complicated if the analogous reaction of **1** with *methanol* is considered. In this case, one would expect the formation of ethyl methoxyacetate (**5**) and/or its transesterification product, methyl methoxyacetate (**6**). Compound **6** was indeed found, but instead of **5** methyl ethoxyacetate (**7**) was identified (GC/MS). Me_2O and CH_3Cl were also detected

(Scheme 4). The formation of rearranged compounds such as **7** from diazoesters is usually explained in terms of a carbene mechanism, in which a resulting ethoxycarbonyl carbene (**8**) undergoes a *Wolff* rearrangement forming a ketene **9** that solvolyzes to give **7** *(Scheme 5)*. Compound **7** was in fact observed in the photosolvolysis, but not in the acidic thermolysis of **2**.

Scheme 4

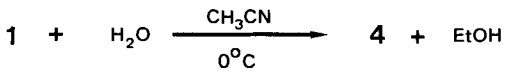


Scheme 5



The carbene mechanism is not involved in the acidic solvolysis of **2** [16] [17]. The main argument against the *Wolff* rearrangement is, however, the outcome of the hydrolysis of **1**. When **1** was allowed to react with *water* in acetonitrile, neither ethyl hydroxyacetate, the normal hydrolysis product, nor ethoxyacetic acid, the rearrangement product, were observed. Instead, ethyl ethoxyacetate (**4**) in addition to some EtOH was detected *(Scheme 6)*.

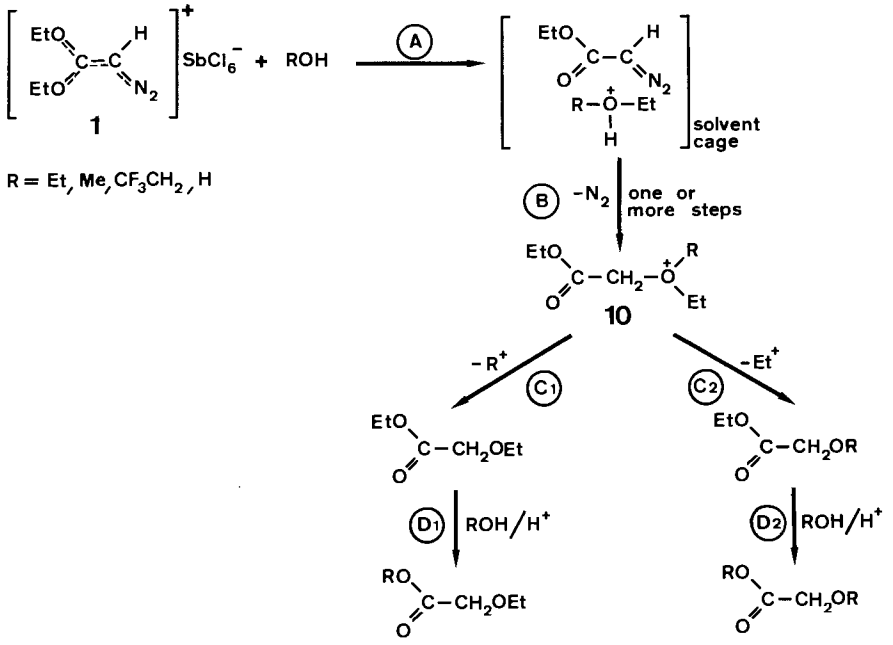
Scheme 6



The results of the ethanolysis, the methanolysis and the hydrolysis together support the following proposed unified mechanism *(Scheme 7)*. An alcohol molecule is alkylated within a solvent cage forming **2** and an oxonium ion $EtR\ddot{O}H$, still in the solvent cage. This complex, upon loss of a N_2-molecule, forms an oxonium salt **10**, which can give two alkoxyesters (routes C_1 and C_2). The analogous reaction of **2** with secondary oxonium salts (stages B and C) has been reported [18]. The loss of N_2 (stage B in *Scheme 7*) most likely involves more than one discrete reaction step. However, from the information available, it is impossible to reach any conclusion about their order, for example, whether initial proton transfer within the solvent cage is followed by dediazoniation to the carbenium ion, or whether a carbene is initially formed. Both pathways would eventually produce the oxonium ion **10**. Finally, in the last step (D), the alkoxyesters undergo a transesterification reaction under acidic conditions with the excess of solvent.

Depending on the identity of R, different products are expected. Thus, in the ethanolysis (R = Et), routes C_1 and C_2 are not distinguishable and ethyl ethoxyacetate (**4**) is formed. In the methanolysis (R = Me), methyl ethoxyacetate (**7**) and methyl methoxyacetate (**6**) are formed, respectively, by routes C_1 and C_2. In the

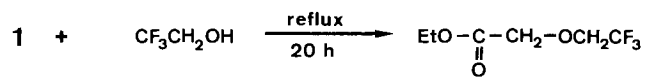
Scheme 7



hydrolysis (R = H), route C_1 is much more probable than route C_2, since loss of a proton from intermediate **10** is more favourable than loss of an ethyl cation.

The proposed mechanism is also supported by the reaction of **1** with *2,2,2-trifluoroethanol.* Trifluoroethanol is a very weak nucleophile, and the solution was refluxed for 20 h to achieve a complete decomposition. Only ethyl 2,2,2-trifluoroethoxyacetate (**11**) was detected *(Scheme 8).* With $R = CF_3CH_2$ *(Scheme 7)* route C_1 is less likely than C_2 owing to the instability of the trifluoroethyl cation relative to the ethyl cation. Trifluoroethanol is apparently not nucleophilic enough to bring about a transesterification.

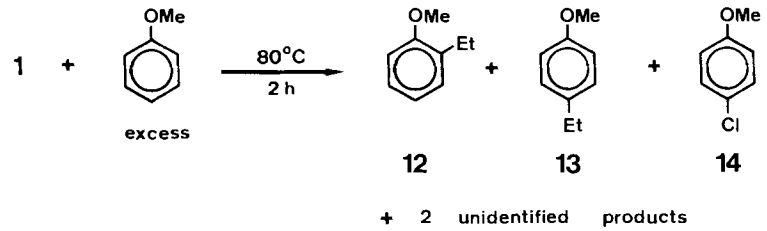
Scheme 8



11

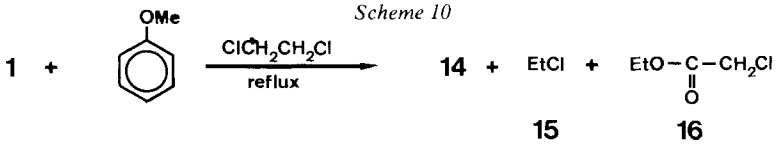
Reaction with Anisole and Thermal Decomposition. When **1** was dissolved in anisole and kept at 80° for 2 h, 2-ethylanisole (**12**), 4-ethylanisole (**13**) and 4-chloroanisole (**14**) were detected in the mixture (GC/MS) together with two other unidentified products (their peaks in the GC partially overlapped the anisole peak) *(Scheme 9).* Compounds **12** and **13** are further confirmation of the alkylating properties of **1**. Compound **14** can be explained as a result of anisole chlorination by $SbCl_5$, a strong chlorinating agent [19], formed during the course of the reaction.

Scheme 9

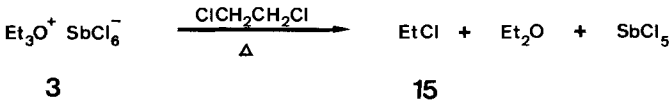


However, when equimolar amounts of **1** and anisole were refluxed in 1,2-dichloroethane, no alkylated anisole, but unreacted anisole, 4-chloroanisole (**14**), chloroethane (**15**) and ethyl chloroacetate (**16**) were found *(Scheme 10)*. Compounds **15** and **16** seem to be thermal decomposition products of **1**. Triethyloxonium hexachloroantimonate decomposes thermally forming chloroethane [20] *(Scheme 11)*. An analogous reaction of **1** would lead to chloroethane (**15**) and ethyl diazoacetate (**2**) *(Scheme 12)*, which would be further transformed to ethyl chloroacetate (**16**).

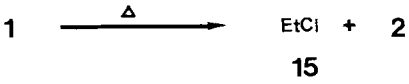
Scheme 10



Scheme 11

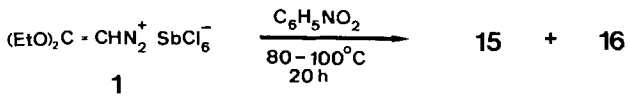


Scheme 12



To check whether the chlorine in **16** comes from the solvent rather than from $SbCl_6^-$, a thermal decomposition of **1** was carried out in nitrobenzene. Again **15** and **16** were detected in the mixture *(Scheme 13)*, the chlorine in **15** and **16** obviously coming from the counter-ion in **1**. The source of the additional proton in **16** is not clear. The most likely explanation seems to be traces of moisture producing HCl which would react with **2** *(Scheme 14)*.

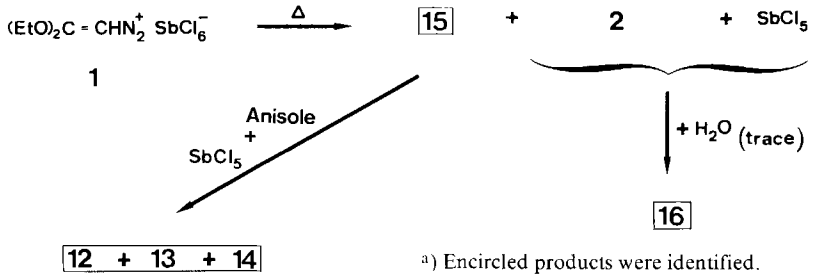
Scheme 13



Scheme 14

In the light of the above results, the formation of ethyl anisoles in the anisole solvent is most likely due to a *Friedel-Crafts* alkylation with chloroethane, the thermal decomposition product of **1**. The probable formation pathway of all the products identified is shown in *Scheme 15*.

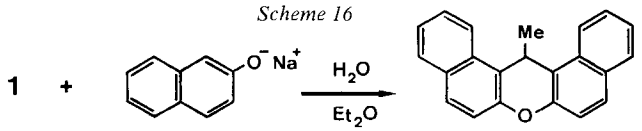
Scheme 15[a])



[a]) Encircled products were identified.

Reaction with Sodium 2-Naphtholate. In the hope that **1** would undergo a typical azo-coupling reaction, the salt was mixed with sodium 2-naphtholate in a two-phase H_2O/Et_2O system. After workup, besides unchanged 2-naphthol, 14-methyl-14*H*-dibenzo[*a,j*]xanthene was identified (comparison with an authentic sample) (**17**) *(Scheme 16)*. The pathway by which this could be formed is not clear. One possibility is that EtOH, which is liberated in the reaction (by alkylation of water), is oxidized by $SbCl_5$ to acetaldehyde or a derivative, which in turn then reacts with 2-naphthol to give **17**. Compound **17** is formed from 2-naphthol with acetaldehyde derivatives [21–23], acetylene [24] [25] or vinyl acetate [26].

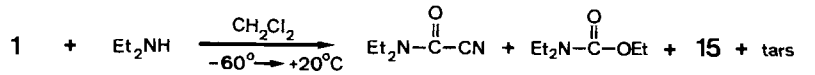
Scheme 16



17

Reaction with Diethylamine. As mentioned in the introduction, **1** gives a heterocyclic system when treated with primary amines. We decided to use a secondary amine in order to prevent the cyclization and see if the first step in the reaction is an *N*-azo-coupling. When treated with a threefold excess of Et_2NH in CH_2Cl_2 at low temperature, **1** gives a mixture whose main component is a tarry material having a strong band at 2075 cm^{-1}. No volatile products except the solvent could be detected by GC before workup. However, when the solution after workup (see *Exper. Part*) was analyzed by GC/MS, volatile products were found. The two major products were identified as the diethylamide of cyanoformic acid (**18**) and ethyl N,N-diethylcarbamate (**19**). Ethyl chloride (**15**) was also detected *(Scheme 17)*.

Scheme 17

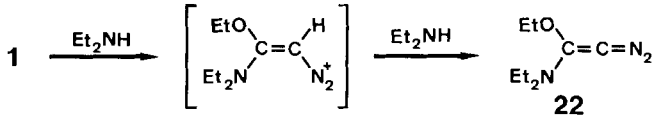


18 **19**

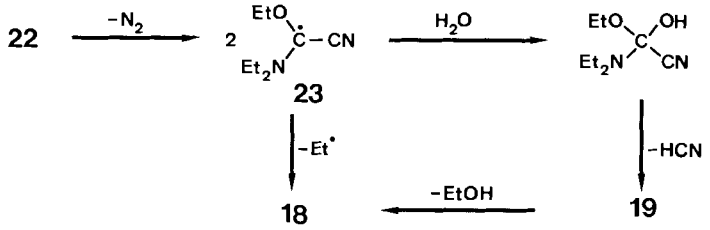
How can the formation of **18** and **19** be accounted for? Recently, it was suggested [27] that in the gas phase a rare species, diazoethene (**20**), can form acetonitrile radicals (**21**) by dimerization and loss of N_2 *(Scheme 18)*. If one molecule of Et_2NH substitutes[3]) an ethoxy group in **1** and another abstracts the vinylic proton, a diazoethene derivative **22** may be formed *(Scheme 19)*. The main reaction of this species would be polymerization leading to the tarry products observed. If, however, some **22** dimerizes as described [27], a cyano radical **23** can be formed to give **18** and **19** *(Scheme 20)*. Diazoethenes are very elusive species[4]) and except for [27], none of the groups reporting syntheses [29–32] observed the formation of nitriles. Therefore the proposed scheme should be considered more as a speculation than an indication about the mechanism, more so since the reaction took place in solution and not, as in the earlier study, in the gas phase [27].

Scheme 18

Scheme 19



Scheme 20



The first step in *Scheme 19* corresponds to a known reaction of ketene acetals [33] [34], for example **24**, *i.e.* nucleophilic substitution of alkoxide groups by NH_3, primary and secondary amines *(Scheme 21)*. Similar nucleophilic substitutions have also been observed with alkoxide ions [33]. Dicyanoketene cyclic acetals even act as alkylating agents towards amines, alkyl sulfides *etc.* [33] in a way similar to that demonstrated for reactions of salt **1** with water, alcohols and ethers. In addition, a variety of heterocyclic compounds such as pyrazoles, isoxazoles and pyrimidines

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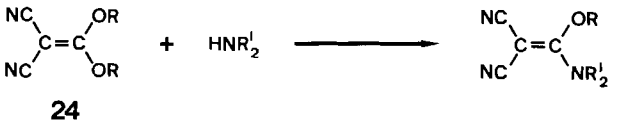
[3]) A nucleophilic attack by anisole and by MeOH on the β-C-atom of 2,2-dichloroethenediazonium salt, the most electrophilic vinyl diazonium salt synthesized, had been observed earlier by *Bott* [6], but chloride ion is a more likely leaving group than ethoxide.

[4]) As a matter of fact, the main purpose to try the reaction of **1** with amines [9] [10] by *Saalfrank*'s group was to obtain a diazoethene compound [28].

can be prepared in reactions of dicyanoketene acetals with certain N-bases [34]. Therefore the synthesis of heterocycles starting from **1** as described by *Saalfrank & Ackermann* [9] [10] is not characteristic for vinyl-diazonium ions, but is rather an additional example for the reactivity of certain ketene acetals. In view of this comparison, it seems more likely that the first step in this reaction is nucleophilic attack by the amine at the β-C-atom of **1** and not an *N*-azo-coupling reaction, *i.e.* pathway (b) rather than (a) in *Scheme 1*. A similar case of nucleophilic attack by piperidine at the β-C-atom of a mono β-alkoxyethenediazonium salt **25** was recently observed by *Bott* [35] *(Scheme 22)*. Interestingly, in this case the reaction stopped at the stage of the piperidinoethenediazonium salt (**26**).

Scheme 21



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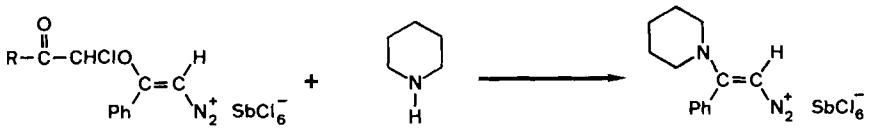
Scheme 22



25 **26**

All these examples indicate that in many reactions with nucleophiles the salt **1** reacts as a ketene acetal rather than as a diazonium salt.

A Variable-Temperature NMR Study of **1**. In the NMR spectrum of **1** the two ethyl groups appear separately. When the temperature increases, the signals coalesce. We have found perdeuterated nitrobenzene to be the most suitable solvent for the dynamic NMR study, since it has a relatively high boiling point and since the decomposition of **1** in it is so slow that it does not interfere with the measurements. In $C_6D_5NO_2$ the methylenes of the ethyl groups are already coalesced at r.t., but the methyl groups absorbed as two triplets separated by 22.15 Hz (at 90 MHz). The coalescence temperature was 350 ± 5 K, from which the rotation barrier was calculated [36] to be 75.3 to 77.4 kJ/mol (18.0 to 18.5 kcal/mol). This value compares very well with free energy barriers to C=C rotation for ketene acetals [37–39] and is characteristic of bonds with properties intermediate between a double and a single bond. In accordance with the corresponding difference in the NN stretching vibration frequencies [7], the C=C rotation barrier for **1** is higher than that for diazoesters [36].

Conclusions. – The reactivity of the title compound towards nucleophiles like ethers, alcohols, water and amines shows that **1** has properties of a dialkoxycarbenium salt, since it can alkylate the nucleophile and is prone to an attack at the β-C-atom. Similarly, the thermal decomposition pattern is typical for an oxonium salt. In reactions of **1** with amines a striking similarity with the reactivity of ketene

acetals was observed. The dynamic NMR study showed considerable single-bond character of the vinylic C=C bond. Although azo coupling with azide ions of certain vinyl diazonium short-lived intermediates produced from nitrosooxazolidones has been observed [40], no product which could be explained in terms of an azo coupling process in the reactions of **1** was found. Also no intervention of vinyl cation intermediates formed by dediazoniation of **1** could be demonstrated. It is therefore suggested that the reactivity of the title compound is represented better by the mesomeric structures **1b** and **1c** than by **1a**.

This conclusion is apparently in conflict with the MO results for the vinyldiazonium ion *in vacuo* and in solution [2]. These calculations indicate a partial negative charge for C(2) which is hardly consistent with reactions of nucleophiles at this C-atom. However, it must be emphasized that the charge distribution of the vinyldiazonium ion may be very different if the two H-atoms at C(2) are substituted by two ethoxy groups.

As mentioned earlier, no intervention of vinyl cation intermediates could be demonstrated in reactions of **1**. This is interesting, since the diazonio group is probably the best leaving group known, and one would expect even the relatively unstable primary vinyl cations to be accessible by heterolytic dediazoniation. Phenyl cations, which according to MO calculations have a stability comparable to that of primary vinyl cations [41], are easily formed this way. The answer to this problem may be the recent conclusion based on the comparison of thermodynamic and solvolysis data for vinyl systems with *ab initio* MO calculations [42], namely that the difficult formation of vinyl cations is not primarily due to their low stability, but to an unusually high kinetic barrier between vinyl derivatives and the corresponding ionic intermediates. This may be one of the reasons that **1**, with its capacity for ambident reactivity, first undergoes other reactions rather than straightforward dediazoniation.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. The authors thank Dr. *A. Stefani* for the GC/MS analyses, Dr. *G. Read* and Profs. *Z. Rappoport* and *P.J. Stang* for helpful discussions, and Prof. *J. Sandström* for sending us a manuscript before publication.

Experimental Part

General. M.P.'s and b.p.'s are not corrected. For IR a Beckman Acculab 4 was used. The NMR spectra were recorded on *Bruker WH-90* and *HY-90E* instruments. The MS were recorded on a *Hitachi Perkin-Elmer RMU-6L* mass spectrometer and for GC/MS analyses the same instrument was coupled to a *Perkin-Elmer 990* gas chromatograph. The GC/MS analyses were always preceded by a GC measurement on a *Varian Aerograph* Series *1400* instrument. All the unknowns in the different product mixtures were identified by comparison with authentic samples.

Preparation of the Reference Compounds. – *Ethyl diazoacetate* (**2**), *methyl methoxyacetate* (**6**), *ethyl methoxyacetate* (**5**), *4-chloroanisole* (**14**), and *ethyl chloracetate* (**16**) were purchased from *Fluka*. *Ethyl ethoxyacetate* (**4**) was prepared according to *Bruce & Coover* [43] and its identity was confirmed by NMR and IR. *Methyl ethoxyacetate* (**7**) was prepared by esterification of ethoxyacetic acid with MeOH in the presence of H_2SO_4, b.p. 138° ([44]: 148°) and its structure confirmed by IR and NMR. *2-Ethylanisole* (**12**) was prepared by methylation of 2-ethylphenol with $(CH_3)_2SO_4$ in aq. NaOH, b.p. 182–184° ([45]: 190–192°; [46]: 186–188°) and its structure confirmed by IR and NMR spectra. *4-Ethylanisole* (**13**) was prepared analogously from 4-ethylphenol, b.p. 190° ([46]: 196–197°; [45]:

199–200°) and its structure confirmed by IR and NMR spectra. *14-Methyl-14H-dibenzo*[a,j]*xanthene* (**17**) was prepared from 2-naphthol and acetaldehyde dimethylacetal by the procedure of *Delepine* [22], and its IR, NMR and mass spectra were consistent with its structure.

Ethyl Trifluoroethoxyacetate (**11**). To 1.1 g (0.047 mol) of Na in 20 ml of 2,2,2-trifluoroethanol, 5.3 g (0.043 mol) of ethyl chloroacetate were added. The mixture was stirred for 1 h at r.t. and refluxed for 3 h. Water (100 ml) was added and the mixture was extracted with Et_2O (2 × 50 ml), dried, distilled at atmospheric pressure and redistilled *in vacuo*, b.p. 42°/1 Torr. IR (film): 1760. NMR: 4.4 (*q*, *J* = 7.0, 2 H); 4.3 (*s*, 2 H); 4.0 (*q*, *J* = 8.9, 2 H); 1.3 ppm (*t*, *J* = 7.0, 3 H). MS: 166 (*M* − HF), 143, 139 (*M* − H − EtOH) 113 (*M* − EtO−C(=O)−), 83 (CF_3CH_2), 69 (CF_3).

Diethylcyanoformamide (**18**) was prepared [48] from *N,N*-diethyloxamide, and its structure was consistent with its IR, NMR and mass spectra. *N,N-diethyloxamide* was prepared from ethyl oxamate by refluxing with Et_2NH for 20 h with recrystallization from EtOH/hexane 1:3, m.p. 125–126° ([48]: 126–127°).

Ethyl Diethylcarbamate (**19**) was prepared by the procedure of *Lumière & Perrin* [49].

2,2-Diethoxyethenediazonium Hexachloroantimonate (**1**) was obtained according to *Bott* [7] except that a 6-fold excess of ethyl diazoacetate (**2**) was used and the mixture was refluxed from time to time to remove Et_2O. The crude product was additionally purified by dissolving it in a minimal amount of CH_2Cl_2 and precipitating with 100% AcOH [50]. The compound thus obtained was free of triethyloxonium hexachloroantimonate (IR bands at 800, 862 and 977 cm^{-1} were missing).

Reaction of **1** *with* Et_2O. To a solution of 20 mg of **1** in 1 ml of 1,2-dichloroethane was added 0.3 ml of Et_2O. The mixture was allowed to stand at r.t. overnight (16 h) and then CCl_4 was added. The precipitate formed showed the presence of strong bands at 800, 862 and 977 cm^{-1} in its IR spectrum (KBr pellet), characteristic of diethyloxonium hexachloroantimonate. Ethyldiazoacetate was detected in the filtrate by TLC.

IR Study of the Interaction of **1** *with Crown Ethers.* To a solution of 7.3 mg of **1** in 0.2 ml of 1,2-dichloroethane was added 4.5 mg of 18-crown-6 (molar ratio crown/**1** = 1.2) and the IR spectrum of the solution was measured immediately after mixing. By comparison with the IR spectrum of **2** in the same solvent the formation of **2** was detected, together with other unidentified bands.

21-Crown-7 behaved analogously (molar ratio crown/**1** = 2.8), but in this case a band which could be ascribed to complexed **1** was also observed.

Reaction of **1** *with EtOH.* To 50 mg of **1** 1 ml of precooled (−60°) EtOH was added and the temperature of the mixture allowed to increase slowly. At −20° the salt started to dissolve with gas evolution. Before r.t. was reached, complete dissolution was obtained and gas evolution ceased. Solid $NaHCO_3$ was then added and the mixture was analyzed by GC/MS on *Carbowax 4000* at 65°.

Reaction of **1** *with MeOH* was carried out in the same way as with EtOH.

Reaction of **1** *with* H_2O. To a solution of 50 mg of **1** in 1 ml of CH_3CN was added at 0° an amount of H_2O so as not to precipitate the salt. After the gas evolution had ceased, the mixture was quenched with $NaHCO_3$ and analyzed by GC/MS (*Carbowax 4000*, 65°).

Reaction of **1** *with* CF_3CH_2OH. A mixture of 50 mg of **1** and 2 ml CF_3CH_2OH was refluxed for 20 h, when all the salt had decomposed. Solid $NaHCO_3$ was added and the mixture analyzed by GC/MS (*Carbowax 4000*, 90°).

Reaction of **1** *with Anisole (without solvent).* A solution of 50 mg of **1** in 1 ml of anisole was maintained at 80° for 2 h during which time the sample became dark; CCl_4 was added and the resulting precipitate was filtered off. The eluate was stripped of CCl_4 and analyzed by GC/MS (*Carbowax 4000*, 100°). Owing to the strong anisole peak, not all the products could be separated.

Reaction of **1** *with Anisole in 1,2-Dichloroethane.* A solution of 48 mg (0.1 mmol) of **1** and 12.6 mg (0.117 mmol) of anisole in 1 ml of 1,2-dichloroethane was refluxed for 3 h and allowed to stand overnight at r.t. The mixture was then filtered through a short column packed with $NaHCO_3$ and analyzed by GC/MS (*Carbowax 4000*, 90°).

Thermal Decomposition of **1** *in Nitrobenzene.* A solution of 52 mg of **1** in 0.5 ml of nitrobenzene was kept overnight (20 h) at 80–90°; $NaHCO_3$ was added and the dark mixture was analyzed by GC/MS (*Carbowax 4000*, temp. program 60–150°, temp. increase rate 20°/min).

Reaction of **1** *with Sodium 2-Naphtholate.* To a solution of 0.15 g of 2-naphthol (1.07 mmol) in 20 ml of Et_2O was added 0.5 g of **1** (1.05 mmol). The mixture was cooled to 0° and 10 ml of cold 0.2N NaOH were added, followed by stirring for 40 min at 0° and for an additional 30 min at r.t. The ethereal

layer was separated and the aq. layer extracted with 30 ml of Et_2O. The combined ethereal solution was washed with H_2O, dried, partially stripped of solvent and applied to a *Merck PC 60 F_{254}* precoated TLC plate. The chromatogram was developed with $CHCl_3$. The product with R_f 0.65 was extracted from the plate with Et_2O and after evaporating the solvent the residue was sublimed at 0.01 Torr (bath temp. 120°). The substance obtained had IR, NMR and mass spectra identical with those of **17**. The other product (R_f 0.5) was 2-naphthol.

Reaction of **1** *with Et_2NH.* To a solution of 48 mg of **1** (0.1 mmol) in 0.5 ml of CH_2Cl_2, cooled to $-60°$, was added a cold solution of Et_2NH (25 mg, 0.29 mmol) in 0.5 ml CH_2Cl_2. The mixture turned yellow and was kept at $-60°$ for 1 h, subsequently being allowed to reach r.t. GC analysis showed no peak except that of the solvent. The solution was washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and analyzed by GC/MS (*Carbowax 4000*, program 60–120°, rate 20°/min). After stripping off the solvent the tarry residue showed a peak at 2075 cm^{-1} in IR (neat).

A Dynamic NMR Study of **1**. The NMR spectrum of **1** dissolved in $C_6D_5NO_2$ was recorded at different temperatures on a *Brucker WH-90* instrument. Two triplets at 1.690 and 1.565 ppm were observed for the two CH_3-groups. At 345 K two distinct, although very broad, triplets could still be seen, whereas at 335 K only one broad triplet was observed. Therefore, these two temperatures were taken as the lower and upper limits for the coalescence temp. and used for calculations separately. The barrier is considered to lie between the two calculated values.

The rate of rotation was calculated from the equation

$$k_{\text{coalesc.}} = \frac{\pi \Delta \nu}{\sqrt{2}} \quad (\Delta \nu = 12.15 \text{ Hz})$$

and the barrier $\Delta G^{\neq}$ was calculated from the *Eyring* equation, $k_{\text{coalesc.}} = \exp(-\Delta G^{\neq}/RT)$. This led to the conclusion that $\Delta G^{\neq} = 75.3$ to 77.4 kJ/mol (18.0 to 18.5 kcal/mol).

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