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Alkoxycarbenium Ions

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The method of synthesis, NMR spectra, and chemical properties of alkoxycarbenium ions are examined and the influence of the medium, temperature, and the structure of the ions on their stability are discussed.
The bibliography includes 99 references.

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I. INTRODUCTION

Alkoxycarbenium ions are intermediate in the reactions of organic compounds of many classes: acetals, α-halogenoethers, vinyl ethers, unsaturated ketones, etc. In many respects they determine the reactivity of these compounds and the mode of their reactions. The interest in these compounds is therefore entirely legitimate; since the 1960s, a considerable number of original communications, reflecting particular aspects of the chemistry of alkoxycarbenium ions, have appeared in the literature. Particularly marked progress in this field has been achieved in connection with the development of NMR spectroscopy and the practical applications of the results of research into superacids, which permit the generation of various cations, including alkoxycarbenium ions, and the investigation of their properties under "long life" conditions.

The majority of the reviews and monographs[1-5] devoted to the chemistry of oxonium and in particular alkoxycarbenium ions were published more than ten years ago and reflect inadequately the present advances in this field. In addition, the reviews hardly describe the work of Soviet investigators.

The present review deals with the methods of synthesis of alkoxycarbenium ions, their structure and chemical properties, and the mode of their reactions as a function of the structure of the ions, the reaction conditions, and the character of the nucleophile.

II. METHODS OF SYNTHESIS OF ALKOXYCARBENIUM IONS

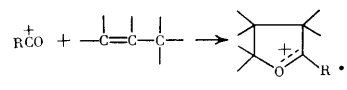
The methods of synthesis of alkoxycarbenium ions are fairly varied. In terms of the principles underlying the synthesis, the methods can be divided into seven groups:

1. Alkylation of the carbonyl group:

$$\rangle C{=}O + R^+ \rightarrow \rangle C^{+}\!\cdots\!OR\ .$$

Cyclic alkoxycarbenium ions are mainly obtained by this procedure as a result of the intramolecular alkylation of the carbonyl groups of aldehydes and ketones containing other functional groups.

2. Acylation of olefins and cyclopropanes:



3. Protonation of vinyl ethers:

$$-\overset{|}{C}{=}\overset{|}{C}{-}OR + H^+ \rightarrow -\overset{|}{C}H-\overset{|}{C}^{+}\!\cdots\!OR\ .$$

4. Abstraction of the halide anion from α-halogenoethers:

$$R_2C(X)-OR' \xrightarrow{-X^-} R_2C^{+}\!\cdots\!OR';\quad X=Cl,\ Br,\ I\ .$$

5. Abstraction of the alkoxy-group from acetals by protic or aprotic acids:

$$ROCOR \xrightarrow{+H^+} ROC^{+}OR \xrightarrow{-ROH} -C^{+}\!\cdots\!OR\ .$$

6. The formation of the carbenium centre at a site in the molecule remote from the oxygen atom with subsequent hydride or alkyl shift:

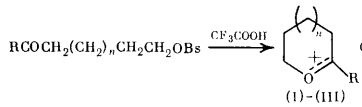
$$-\overset{+}{C}-\left(-\overset{|}{C}-\right)_n-\overset{|}{C}R-OR' \longrightarrow -\overset{|}{C}R-\left(-\overset{|}{C}-\right)_n-\overset{|}{C}^{+}\!\cdots\!OR';\quad n=0,\ 1;\quad R=H,\ Alk\ .$$

7. Isomerisation of oxenium ions:

$$-\overset{|}{C}R-\overset{+}{O} \longrightarrow -\overset{|}{C}^{+}\!\cdots\!OR\ .$$

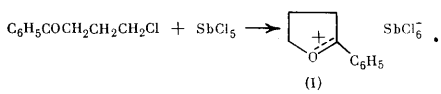
1. Alkylation of the Carbonyl Group

The intramolecular alkylation methods differ in the procedure used to generate the alkyl cation attacking the carbonyl group. The solvolysis of brosylates or the elmination of a halogen are the most convenient for the generation of primary alkyl cations. Thus, when the brosylates of γ- and δ-hydroxyketones are dissolved in trifluoroacetic or formic acid, five- and six-membered cyclic alkoxycarbenium ions (I)–(III) are formed:[6,7]

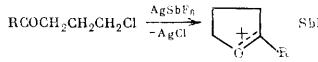


(I) $n=0$, $R=C_6H_5$; (II) $n=0$, $R=CH_3$;
(III) $n=1$, $R=C_6H_5$; OBs = p-$BrC_6H_4SO_2O$.

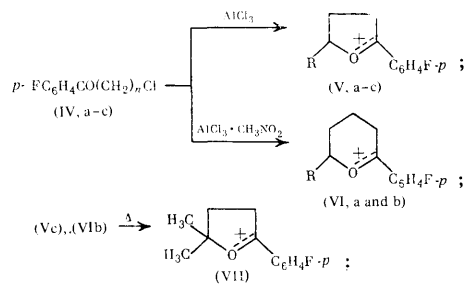
Unambiguous evidence supporting the formation of the ion (I) is provided by the identity of the ^1H NMR spectrum with that of a solution of the salt obtained by treating γ-chlorobutyrophenone with antimony pentachloride in SO_2 or acetonitrile:[7]



The chloride ion can also be removed by treatment with silver salts:[8]



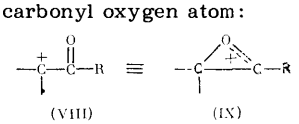
Analogous ions are formed on interaction of ω-chlorophenones (IV, a–c) with aluminium chloride.[9,10] It is of interest that, on treatment with free $AlCl_3$, only the five-membered cyclic ion (Vb) is formed from the ketone (IVb), while on treatment with the complex $AlCl_3.CH_3NO_2$, a mixture of five-membered (V, b and c) and six-membered (VI, a and b) cyclic alkoxycarbonium ions is formed with the five-membered ions predominating. On heating, the ions (Vc) and (VIb) are converted into the more stable ion (VII):



(IV): $n = 3$ (a), 4 (b), 5 (c); (V), (VI): R = H (a), CH_3 (b), C_2H_5 (c).

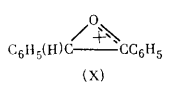
Thus five-membered cyclic alkoxycarbenium ions are more stable than the six-membered ions.

Three- and four-membered cyclic alkoxycarbenium ions are apparently unstable. It has been suggested[11] that α-acylcarbenium ions can have the cyclic structure as a result of the interaction of a vacant orbital with the unshared electron pairs of the carbonyl oxygen atom:



(VIII) (IX)

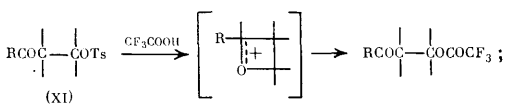
Quantum-chemical calculations have shown[12] that structure (IX) should be more stable than structure (VIII). At −75 °C signals due to the first representative of three-membered cyclic alkoxycarbenium ions (X) were detected in ^1H and ^{13}C NMR spectra:[12]



(X)

α-Acylcarbenium ions have been in many instances suggested as intermediates.[8,11–17]

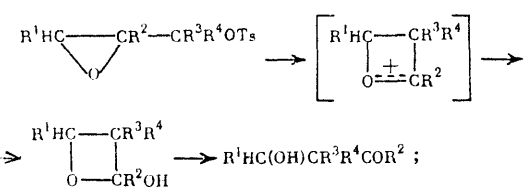
The formation of four-membered cyclic alkoxycarbenium ions has been postulated in a number of studies.[18–21] In particular, their formation is indicated by the results of the solvolysis of compounds of type (XI) in trifluoroacetic acid:[18,19]



(XI)

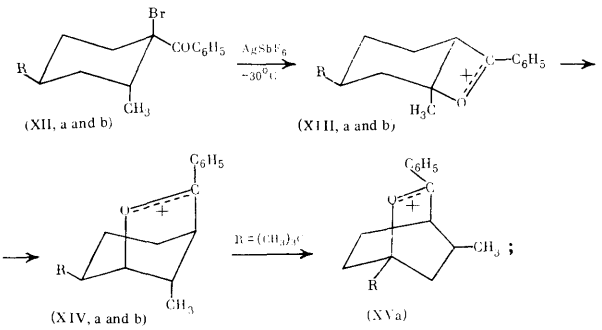
R = p-$CH_3OC_6H_4$, p-$NO_2C_6H_4$, C_6H_5, CH_3.

The study of the kinetics and stereochemistry of the products of the solvolysis of oxiranylmethyl toluene-*p*-sulphonates also led to the conclusion that such ions are formed:[20]



R^1–R^4 = H, CH_3.

Four-membered cyclic alkoxycarbenium ions were first detected by NMR after the elimination of the bromide anion from α-bromoketones.[12,13] The ions (XIII, a and b) were detected following the interaction of the ketones (XII, a and b) with $AgSbF_6$ at −30 °C:

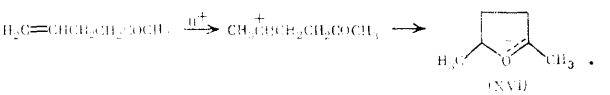


(XII)–(XV): R = $(CH_3)_3C$ (a), H (b).

When the temperature is raised to 25 °C, the ions (XIII, a and b) isomerise to the more stable five-membered ions (XIV, a and b), and t-butyl-substituted ions (XIVa) can isomerise in their turn to the six-membered ions (XVa).

When the reaction is carried out at room temperature, five- and six-membered cyclic alkoxycarbenium ions are formed immediately.[14–16]

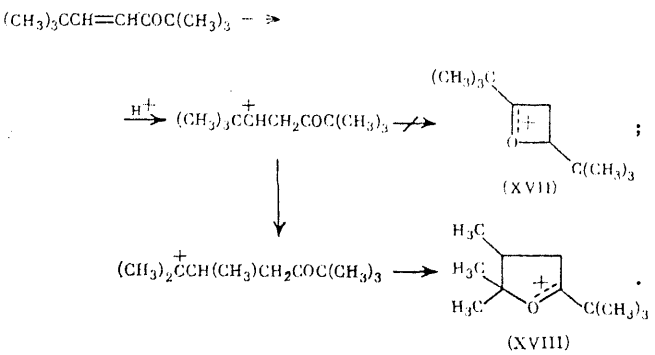
The most convenient method of synthesis of cyclic alkoxycarbenium ions involves the protonation of unsaturated ketones. When the protonation leads to the formation of a carbenium centre in the γ- or δ-position relative to the carbonyl group, the cations cyclise and give rise to five- and six-membered cyclic ions respectively,[22–32] for example:



(XVII)

The cyclisation takes place under the influence of both various superacids[22,27–30] and also weaker acids such as HBF_4,[31] $HClO_4$,[32] concentrated sulphuric acid,[23,24] and dilute sulphuric acid.[25] This method of synthesis has been used to determine the heats of formation of alkoxycarbenium ions.[23,24]

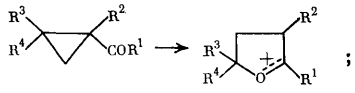
If the protonation leads to the formation of a carbenium centre in the β-position relative to the carbonyl group, the corresponding four-membered alkoxycarbenium ions (XVII) are not formed and instead a rearrangement takes place (provided that it is feasible), which leads to the formation of five-membered cyclic alkoxycarbenium ions (XVIII).[31–33]



(XVII)

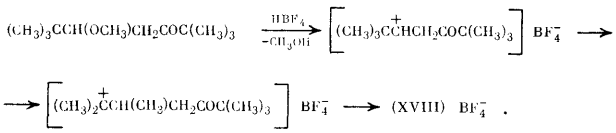
(XVIII)

Cyclic alkoxycarbenium ions are also formed on protonation of cyclopropryl ketones in 75–96% H_2SO_4:[34,35]

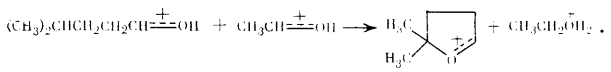


R^1–R^4 = H, CH_3, C_6H_5, cyclo-C_3H_5.

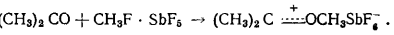
In some cases the abstraction of the alkoxy-group by strong acids has been used to generate the alkyl cation alkylating the carbonyl group:[31]



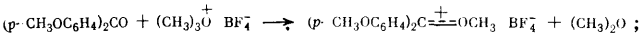
The carbenium centre attacking the carbonyl group can be created also by abstracting a hydride ion from the γ- and δ-positions relative to the carbonyl group. Thus, when 4-methylvaleraldehyde reacts with acetaldehyde in the 9 : 1 HF–SbF_5 system, the protonated acetaldehyde acts as the acceptor of the hydride ion. The dication formed from the protonated 4-methylvaleraldehyde abstracts a proton from the oxygen atom and is converted into a cyclic ion:[36]

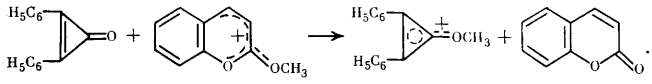


The ethanol formed is protoned in this medium. Only aromatic carbonyl compound readily undergo intermolecular alkylation. The majority of aliphatic aldehydes and ketones undergo the aldol condensation under alkylation conditions,[1,37] but, on treatment with $CH_3F.SbF_5$ in SO_2 at −78 °C, it is possible to methylate also aliphatic ketones:[38]



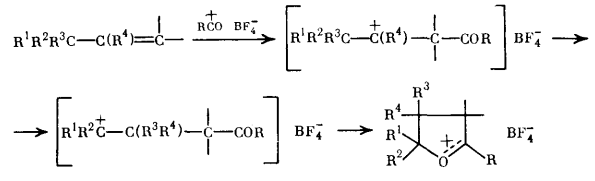
Trialkyloxonium or dialkoxycarbenium ions are used frequently as alkylating agents for the intermolecular alkylation of aromatic carbonyl compounds:[39]



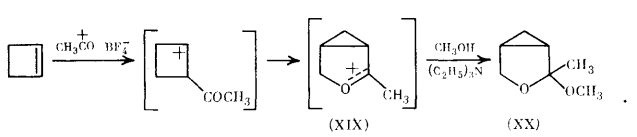


2. Acylation of Olefins and Cyclopropanes

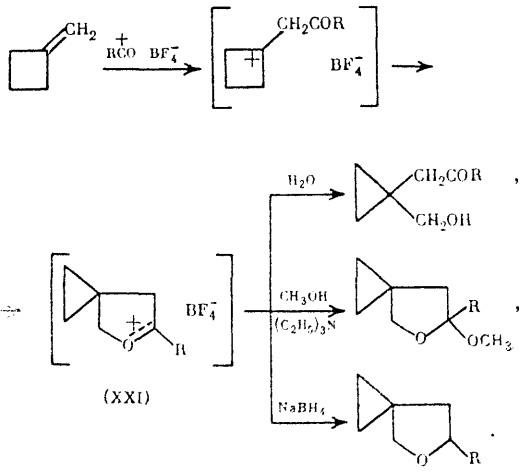
A novel method for the simultaneous introduction of the carbonyl group and the generation of the carbonium ion leading to the formation of cyclic alkoxycarbenium ions involves the acylation of olefins:[40–46]



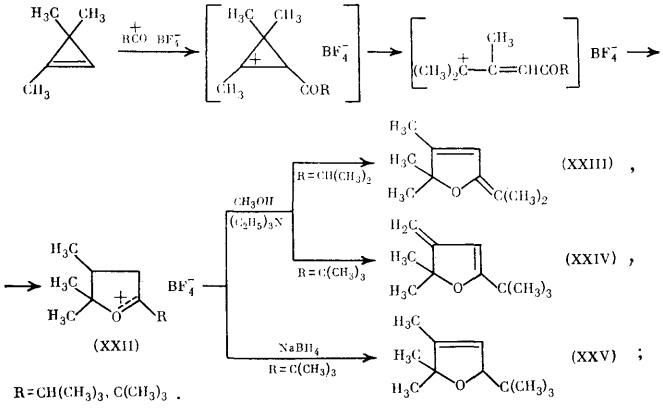
Both acylic and cyclic olefins enter into this reaction.[40–42] After the addition of the acyl cation, a 1,2-hydride or 1,2-alkyl shift and cyclisation take place. In the acylation of cyclobutene the ring contracts and the bicyclic cation (XIX) is formed.[43] Its treatment with a methanol solution of triethylamine leads to the formation of the acetal (XX):



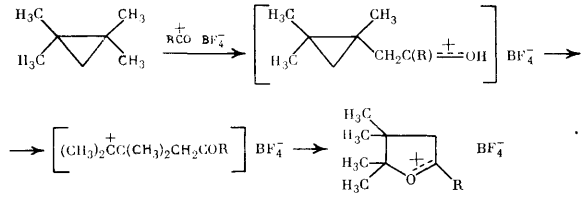
In the acylation of methylenecyclobutane cyclic alkoxycarbenium ions are formed only when pivaloyl and isobutyryl tetrafluoroborates are used.[44,45] Ring contraction also takes place in this instance. The formation of the alkoxycarbenium ion (XXI) has been confirmed by its subsequent reactions:



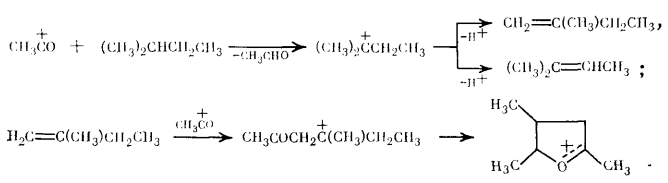
Alkoxycarbenium ions (XXII) of the dihydrofuran series are formed on acylation of 1,3,3-trimethylcyclopropene with pivaloyl or isobutyryl tetrafluoroborate:[46]



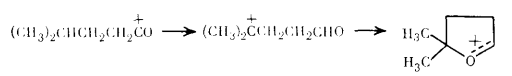
Analogous results have been obtained also on acylation of cyclopropanes.[47] The reaction of acyl cations with 1,1,2,2-tetramethylcyclopropane is somewhat unusual. Using tracer atoms, it has been shown that the ring is not attacked directly by the acyl cation; the authors proposed the following reaction mechanism:[47]



Cyclic alkoxycarbenium ions can be obtained by the reaction of acylcations with alkanes containing a tertiary carbon atom. The acyl cation then abstracts a hydride ion and is reduced to an aldehyde. The tertiary alkyl cation formed is converted into an olefin, which reacts with yet another acyl cation to form an alkoxycarbenium ion:[48]

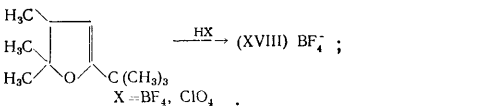


An example of an intramolecular reaction of this kind is provided by the isomerisation of acyl cations to alkoxycarbenium ions in superacid media:[36,49]

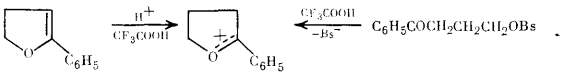


3. Protonation of Vinyl Ethers

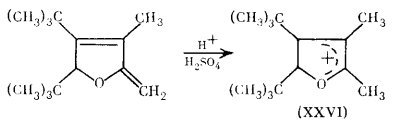
Alkoxycarbenium ions can be obtained by protonating vinyl ethers. Thus, when 2-t-butyl-4,5,5-trimethyl-4,5-dihydrofuran is mixed in the cold with an ethereal solution of HBF_4[31] or with $HClO_4$,[32] the salt of the corresponding cation (XVIII) is formed:



The addition of a proton on dissolution of 2-phenyl-4,5-dihydrofuran in trifluoroacetic acid has been used to identify the ion (I) formed on solvolysis of γ-hydroxybutyrophenone brosylate in trifluoroacetic acid:[6,7]

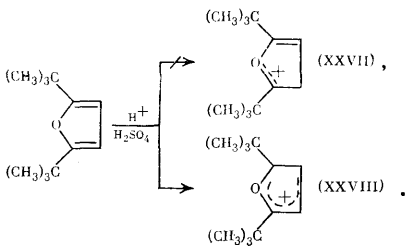


When 4,5-di-t-butyl-3-methyl-2-methylene-2,5-dihydrofuran is dissolved in sulphuric acid, the ion (XXVI), where the positive charge is distributed over four atoms, is formed:[50]



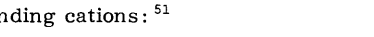
(XXVI)

It is remarkable that only the more stable ion (XXVIII) is formed when 2,5-di-t-butylforan, whose protonation can result in the formation of the two ions (XXVII) and (XXVIII):[50]

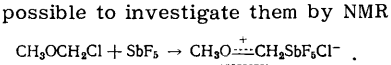


4. Abstraction of a Halide Anion from α-Halogenoethers

α-Halogenoalkyl ethers are themselves incapable of ionising with elimination of a halide anion. The ionisation is promoted by the binding of the halide, for example, in a complex anion on treatment with certain metal polyhalides. Antimony pentachloride or pentafluoride is most frequently used for this purpose. Thus the interaction of α-chloroethers with $SbCl_5$ at −75 °C results in the formation of hexachloroantimonates of the corresponding cations:[51]

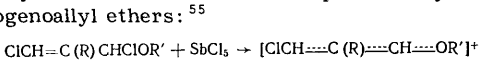


When α-halogenoethers are treated with a solution of SbF_5 in SO_2, the alkoxycarbenium ions formed remain in solution, which makes it possible to investigate them by NMR:[52–54]

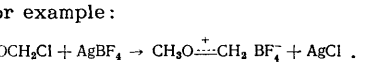


(XXIX)

Alkoxycarbenium ions are formed particularly readily from α-halogenoallyl ethers:[55]

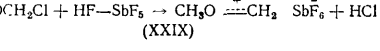


A convenient method for the synthesis of alkoxycarbenium ions from α-halogenoethers involves treatment of the latter with silver salts such as $AgSbF_6$, $AgBF_4$, or $AgOSO_2C_6H_2(NO_2)_3$,[56–61] for example:



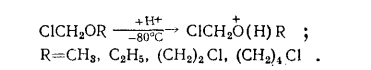
(XXIX)

The halide anions can also be bound by protonation on treatment with strong acids. For example, when chloromethyl methyl ether is treated with a mixture of HF and SbF_5, methoxycarbenium hexafluoroantimonate (XXIX) is formed in quantitative yield:[62]



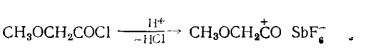
(XXIX)

Interesting results have been obtained in the study of this reaction by ^1H NMR in the HSO_3F–SbF_5–SO_2 system at low temperatures.[63] When α-halogenoethers are dissolved in this mixture at −80 °C, the oxygen atom is protonated with the consequent formation of oxonium ions:



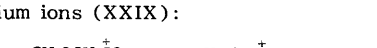
On raising the temperature to −60 °C, the oxonium ions slowly split off HCl and are converted into alkoxycarbenium ions:

The formation of alkoxycarbenium ions from alkoxyacetic acid chlorides can also be regarded as an application of this method. When methoxyacetic acid chloride is dissolved in the HF–SbF_5 mixture at −60 °C, the oxocarbenium ion (XXX) is formed:[62]



(XXX)

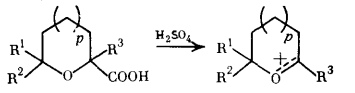
On raising the temperature, the ion (XXX) slowly splits off a molcule of carbon monoxide and is converted into the methoxycarbenium ions (XXIX):



(XXIX)

Decarboxylation of carboxylic α-alkoxyacids also constitutes a procedure closely resembling the above method. Thus, when tetrahydrofuran- and tetrahydropyran-2-carboxylic acids are

dissolved in 96% H_2SO_4, the carboxy-group is split off and five- and six-membered cyclic alkoxycarbenium ions are formed respectively:[64]



$R^1-R^3 = H, CH_3$; $p = 0, 1$.

The six-membered ions are in equilibrium with the isomeric five-membered ions.

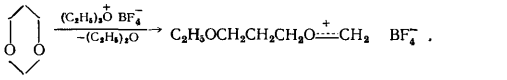
5. The Synthesis of Alkoxycarbenium Ions from Acetals

Like α-chloroethers, acetals are extremely convenient precursors for the generation of alkoxycarbenium ions. The alkoxy-group is a much more powerful nucleophile than the halide anion and its elimination from the acetal molecule therefore requires preliminary electrophilic attack on the oxygen atom.

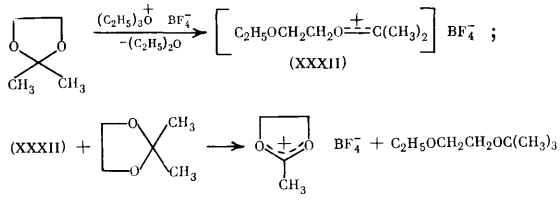
One of the first method described in the literature for the preparation of alkoxycarbenium ions and acetals involves treatment of the latter by trialkyloxonium salts:[65]

$$(CH_3)_3CC(CH_3)(OCH_3)_2 \xrightarrow[-2(CH_3)_2O]{(CH_3)_2\overset{+}{O}BF_4^-} (CH_3)_3CC(CH_3)\overset{+}{=}OCH_3BF_4^- .$$

Under the influence of trialkyloxonium salts, the ring in cyclic acetals is cleaved, which entails the formation of alkoxycarbenium ions:[66-68]



When cyclic ketals are treated with trialkyloxonium salts, cyclic dioxolenium ions (XXXI) are formed. It has been suggested[69] that acyclic alkoxycarbenium ions (XXXII) are formed initially and then abstract an alkyl anion from a second ketal molecule, for example:



(XXXII)

(XXXII) + $\rightarrow$ $BF_4^- + C_2H_5OCH_2CH_2OC(CH_3)_3$.

(XXXI)

The same reactions take place when cyclic ketals are treated with other electrophiles, such as dialkoxycarbenium ions, Lewis acids, and RHal–$AgBF_4$ mixtures.[69]

BF_3 or $SbCl_5$ are most often used as the Lewis acids.[70] Thus, when BF_3 interacts with benzaldehyde dimethyl acetal, salts (tetrafluoroborates) are formed. The mechanism of their formation can be described schematically as follows:[70]

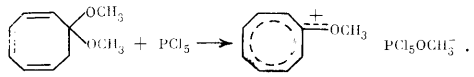
$$C_6H_5CH(OCH_3)_2 + BF_3 \rightarrow \underset{\text{(XXXIII)}}{C_6H_5CH\overset{+}{=}OCH_3} \quad BF_3OCH_3^- ;$$

$$3BF_3OCH_3^- + BF_3 \rightarrow 3BF_4^- + B(OCH_3)_3 .$$

The anion $BF_3OCH_3^-$ formed initially is unstable and its interaction with the excess BF_3 converts it into the stable anion BF_4^-, which reacts with the cation (XXXIII) to form the salt $C_6H_5\overset{+}{C}H{-}OCH_3BF_4^-$, which is insoluble in the reaction mixture.

It is noteworthy that, when this reaction is carried out in $CDCl_3$ as the solvent, the anion $BF_3OCH_3^-$ does not disproportionate and the salt remains in solution, which makes it possible to investigate this reaction by ^1H NMR.[71,72] The introduction of electron-accepting groups in the *para*-position in the benzene ring reduces the reactivity of the acetal and *p*-nitrobenzaldehyde dimethyl acetal does not react with BF_3 at all.[72]

Weaker Lewis acids have also been used to obtain more stable alkoxycarbenium ions. Thus treatment of a solution of 7,7-dimethoxycyclo-octa-1,3,5-triene in liquid SO_2 with PCl_5 or $SOCl_2$ at −20 °C results in the formation of the 1-methoxycyclo-octatrienylium ion:[73]



Molecular bromine can also be used as the electrophile for the abstraction of the alkoxy-group.[74,75] When 2,2-dimethoxypropane reacts with bromine in SO_2 at −60 °C, the methoxydimethylcarbenium ion (XXXIV) is formed:

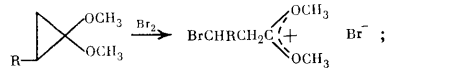
$$(CH_3)_2C(OCH_3)_2 + Br_2 \rightarrow \underset{\text{(XXXIV)}}{(CH_3)_2C\overset{+}{=}OCH_3}\ Br^- + CH_3OBr .$$

Benzaldehyde, acetophenone, benzophenone, cyclohexanone, cycloheptanone, and cyclobutanone dimethyl acetals behave analogously.[75]

The ions formed from acetaldehyde and formaldehyde acetals are unstable under these conditions and, having combined with the Br^- counterion, are converted into the corresponding α-bromoethers:

$$RCH(OCH_3)_2 \xrightarrow[-CH_3OBr]{Br_2} [RCH\overset{+}{=}OCH_3]Br^- \rightarrow RCHBrOCH_3 ;$$
$$R = H,\ CH_3 .$$

In cyclopropanone dimethyl acetals, the cyclopropane ring is more reactive in relation to bromine, which leads to the formation of β-bromoethyldimethoxycarbenium ions:[75]



$R = H, C_6H_5$.

The simplest method of synthesis of alkoxycarbenium ions from acetals involves treatment of the latter with strong acids. This method is also convenient because in this instance the ions are in solution and can be investigated by ^1H NMR. Depending on the stability of the alkoxycarbenium ions, acids of different strengths must be used for their generation. For example, the simplest alkoxycarbenium ion, namely the methoxycarbenium ion, has been obtained in an acid as strong as the equimolar mixture of HSO_3F and SbF_5 diluted with liquid SO_2 to reduce its viscosity:[54]

$$CH_2(OCH_3)_2 \xrightarrow[HSO_3F-SbF_5]{2H^+} \underset{\text{(XXIX)}}{CH_2\overset{+}{=}OCH_3} + CH_3\overset{+}{O}H_2 .$$

The methanol split off is protonated in this medium. At −60 °C there is almost no proton exchange with the medium. The splitting of the signal due to the methyl group of the protonated methanol into a triplet is observed in ^1H NMR spectrum (as a consequence of the spin–spin coupling with the protons of the $\overset{+}{O}H_2$ groups), which permits an unambiguous assignment of the signals of the methyl groups of methanol and methoxycarbenium.

The presence of substituents at the acetal carbon atom increases the stability of the ions formed from the acetals and they become stable in less acid media. Thus the methoxydimethylcarbenium ion (XXXIV) can be obtained at room temperature in 30% oleum:[76]

$$(CH_3)_2C(OCH_3)_2 \xrightarrow[H_2SO_4-SO_3]{H^+} \underset{\text{(XXXIV)}}{(CH_3)_2C\overset{+}{=}OCH_3} + CH_3OH .$$

The alkoxycarbenium ions derived from ketone and benzaldehyde acetals at −60 °C can be obtained even on treatment with HBr:[74]

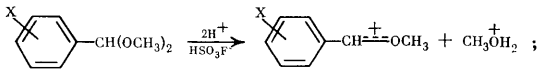
$$RR^1C(OCH_3)_2 \xrightarrow[-60°C]{HBr} RR^1C^{+}{-}OCH_3 + CH_3\overset{+}{O}H_2 \ ;$$
$$R=R^1=CH_3;\quad R=R^1=C_6H_5;\quad R=H,\ R^1=C_6H_5;\quad R=CH_3,\ R^1=C_6H_5 \ .$$

Under these conditions, the methanol is also present in the protonated form.

HSO_3F is most often employed to obtain alkoxycarbenium ions from acetals. The possibility of the generation and the stability of alkoxycarbenium ions in HSO_3F depend on the structure of the acetal and temperature. The dissolution of ketals even at room temperature leads to the formation of alkoxycarbenium ions:[77]

$$C_6H_5C(CH_3)(OCH_3)_2 \xrightarrow[HSO_3F]{2H^+} C_6H_5C(CH_3)^{+}{-}OCH_3 + CH_3\overset{+}{O}H_2 \ .$$

As in the $HSO_3F-SbF_5-SO_2$ mixture, methanol is present in the protonated form, as shown by the identity of the chemical shifts of the signals of the methyl protons in the two media. However, owing to the rapid proton exchange with the medium, there is no splitting of the signal into a triplet. The protonated methanol is therefore a convenient internal standard. The dimethyl acetals of substituted benzaldehydes give rise to alkoxycarbenium ions on dissolution in HSO_3F at −60 °C:[71,72,78]



X = H, 4-CH_3, 4-OCH_3, 4-Cl, 4-Br, 4-F, 3-F, 2-CH_3, 2-OCH_3, 4-NO_2 .

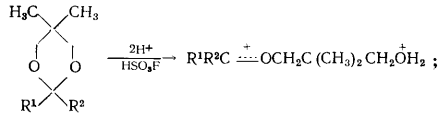
It was noted above that the corresponding ion cannot be obtained from the dimethyl acetal of *p*-nitrobenzaldehyde on treatment with BF_3. In HSO_3F this ion is formed readily.

Furthermore, the corresponding dications $CH_3O^{+}{=}CHC_6H_4.CH^{+}{=}OCH_3$ have been obtained from the bis(dimethyl acetals) of *o*-, *m*-, and *p*-phthaladehydes.[72,78] All the ions obtained are stable when the temperature is raised to 36 °C. The dissolution of the acetals of aliphatic aldehydes in HSO_3F at −70 °C results in the formation of alkoxycarbenium ions, whose stability depends on temperature:[79-81]

$$RCH(OR^1)_2 \xrightarrow[HSO_3F]{2H^+} RCH^{+}{-}OR^1 + R^1\overset{+}{O}H_2 \ ;$$
$$R=H,\ CH_3,\ C_2H_5;\ R^1=CH_3,\ C_2H_5,\ C_3H_7,\ CH(CH_3)_2 \ .$$

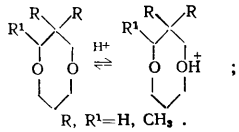
When R = alkyl, the ions are fairly stable at room temperature and appreciable changes in the ^1H NMR spectrum are observed only over a period of 2–3 h. When R = H, the ions are stable in the range between −70° and −30 °C.

The behaviour of cyclic acetals and ketals in HSO_3F does not differ from that of their acyclic analogues. At −70 °C the ring is opened, which entails the formation of the corresponding dications,[82,83] for example:



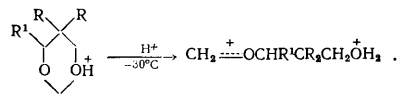
$R^1=R^2=CH_3;\quad R^1=H,\ R^2=C_6H_5$.

In their response to treatment with HSO_3F, cyclic formals differ from all the acetals described previously. The point is that the formation of alkoxycarbenium ions from acetals is a two-stage process. In the first stage the acetal is protonated with formation of an oxonium ion. The alkoxycarbenium ion is formed after the subsequent elimination of an alcohol molecule from the oxonium ion. However, when the acetals described previously were allowed to react with acids, the intermediate oxonium ions were not detected. Only on dissolution in HSO_3F of certain cyclic formaldehyde acetals at −70 °C was it possible to detect oxonium ions by ^1H NMR:[83,84]



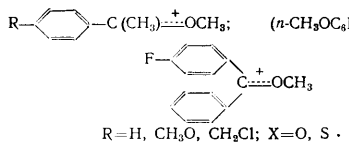
R, R^1=H, CH_3 .

The ^1H NMR spectrum indicates the retention of the ring at temperatures between −70 °C and −40 °C, although the signal of the oxonium proton is not observed as a consequence of the rapid proton exchange.[84] Above −40 °C, ring opening takes place:



However, the alkoxycarbenium ions formed are unstable and rapidly undergo further reactions.[84]

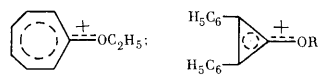
In less acidic media the alkoxycarbenium ions derived from acetals can be obtained and detected only in exceptional cases. Thus in solution in 96–100% H_2SO_4 the following ions derived from the corresponding acetals were detected by ^1H NMR at room temperature:[85]



R = H, CH_3O, CH_2Cl; X = O, S .

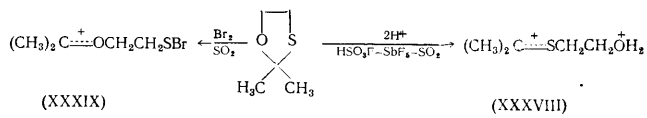
In more dilute H_2SO_4 solutions the formation of alkoxycarbenium ions from acetals cannot be detected by NMR.[85]

The ions (XXXV)–(XXXVII) have been detected by ultraviolet spectroscopy under conditions where the rate of their formation exceeds the rate of their hydrolysis:[86]



(XXXV) (XXXVI): R = CH_3; (XXXVII): R = C_2H_5 .

In the presence of various heteroatoms in the acetal molecule the direction of attack depends on the nature of the attacking reagent. Thus, when 2,2-dimethyloxathiolan is dissolved in the $HSO_3F-SbF_3-SO_2$ mixture at −60 °C, the alkylthiocarbenium ion (XXXVIII) is formed, while the interaction with bromine in SO_2 at −80 °C leads to the alkoxycarbenium ion (XXXIX):[87]



(XXXIX) (XXXVIII)

The authors[87] explained these results by the lower basicity but greater nucleophilicity of the sulphur atom compared with the oxygen atom.

6. Rearrangement of Oxygen-containing Carbenium Ions

When a positive charge is generated in the molecules of ethers on a carbon atom not adjoining the oxygen atom, a rearrangement leading to alkoxycarbenium ions is frequently

observed. For example, when 2-halogeno-3-methoxy-2,3-dimethylbutane is dissolved in the SbF_5-SO_2 or $HSO_3F-SbF_5-SO_2$ mixture at −60 °C, the t-butylmethoxymethylcarbenium ion is produced:[88]

$$(CH_3)_2CXC(CH_3)_2OCH_3 \xrightarrow[-SbF_4X]{SbF_5} [(CH_3)_2\overset{+}{C}C(CH_3)_2OCH_3] \rightarrow (CH_3)_3CC(CH_3)=\overset{+}{O}CH_3;$$
X=Cl, Br, I.

The dissolution of alkoxyalcohols in the $HSO_3F-SbF_5-SO_2$ mixture at −60 °C leads to oxonium dications. On raising the temperature, some of them are dehydrated with formation of alkoxycarbenium ions,[53] for example:

$$CH_3OCH_2CH(CH_3)OH \xrightarrow[-60°C]{2H^+} CH_3\overset{+}{O}(H)CH_2CH(CH_3)\overset{+}{O}H_2 \xrightarrow[-10°C]{-H_2O,\ -H^+} \longrightarrow CH_3O\overset{+}{=}CHCH_2CH_3;$$

$$C_2H_5O(CH_2)_3OH \xrightarrow[-60°C]{2H^+} C_2H_5\overset{+}{O}(H)(CH_2)_3\overset{+}{O}H_2 \xrightarrow[0°C]{-H_2O,\ -H^+} C_2H_5O\overset{+}{=}CHCH_2CH_3.$$

7. Isomerisation of Oxenium Ions

The isomerisation of unstable oxenium ions formed in certain reactions constitutes a fairly unusual method for the formation of alkoxycarbenium ions. Thus, when t-alkyl hydroperoxides are dissolved in superacids, alkoxydialkylcarbenium ions (XXXIV) are formed:[89,90]

$$(CH_3)_3COOH \xrightarrow{H^+} [(CH_3)_3C\overset{+}{O}OH_2] \xrightarrow[-H_2O]{} [(CH_3)_3C-\overset{+}{O}] \rightarrow (CH_3)_2C=\overset{+}{O}CH_3.$$
(XXXIV)

The formation of alkoxycarbenium ions via the isomerisation of intermediate oxenium ions has been observed in the oxidation with ozone in superacids of stable t-alkyl cations,[91] branched hydrocarbons,[92,93] and alcohols,[94] in the oxidation of hydrocarbons in superacids with hydrogen peroxide,[93,95] and on dissolution of t-alkyl esters of peracids in superacids.[96]

III. THE STRUCTURE AND PROPERTIES OF ALKOXYCARBENIUM IONS

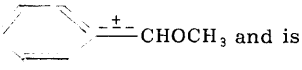
It follows from the analysis of the methods of synthesis of alkoxycarbenium ions presented above that almost all these ions are stable at low temperatures in weakly nucleophilic media such as HSO_3F and $HSO_3F-SbF_5-SO_2$. With increase of temperature and of the nucleophilicity of the medium, the stability of the alkoxycarbenium ions falls. The cyclic ions are more stable than the acyclic ions; many cyclic alkoxycarbenium ions exist at room temperature in H_3SO_4 [23,24] and in trifluoroacetic acid in the absence of trifluoroacetate anions.[6,7]

The stability of acyclic alkoxycarbenium ions depends to a large extent on the presence of electron-donating substituents at the carbenium carbon atom. Alkoxycarbenium ions without substituents at the carbenium centre are stable in HSO_3F only at temperatures not exceeding −30 °C, while their methyl-substituted analogues are stable even at room temperature.[44,45,49] Electron-accepting substituents destabilise alkoxycarbenium ions. Thus the methoxy-4-*p*-nitrophenylcarbenium ion is not formed from the corresponding acetal on treatment with BF_3, although the dimethyl acetals of other substituted benzaldehydes are converted into methoxyarylcarbenium ions under the same conditions.[71,72] The use of a less nucleophilic medium (HSO_3F), which tends to increase the stability of the ions, makes it possible to obtain not only the nitrophenyl-substituted cation but also the dications.[72,78]

Protons at the carbenium carbon atom give rise to signals in the ^1H NMR spectra of alkoxycarbenium ions in a very low field (Table 1), which indicates their carbenium character. This is also indicated by the downfield shift of the signals of the α-protons of the substituents at the carbenium centre. The chemical shifts of the benzyl protons in the ^1H NMR spectra of aryl-substituted alkoxycarbenium ions depend on the positions and character of the substituents (Table 2) and are better correlated with the δ^+ constants of the substituents ($\delta_{H_\alpha} = 0.588\delta^+ + 9.078$, $r = 0.972$) [72] than with the σ constants ($r = 0.852$), which is a consequence of the carbenium character of the ions.

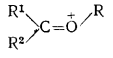
The substitution of the chemical shifts for the benzyl protons in the *meta*- and *para*-dications in the correlation expression made it possible to determine the σ^+ constants for the substituent $-CH=\overset{+}{O}CH_3$ ($\sigma_m^+ = 0.916$; $\sigma_p^+ = 1.074$).[72] It follows from these values that the $-CH=\overset{+}{O}CH_3$ group is a stronger electron acceptor than the nitro-group.

The carbenium centre is conjugated with the aromatic ring, which hinders rotation about the partially double bond



and is manifested by some non-equivalence of the protons in the aromatic ring in the *para*-substituted ions.[71]

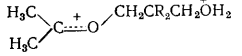
On the other hand, alkoxycarbenium ions also have some oxonium character, which is indicated, for example, by the correlation between the chemical shift of the protons of the methoxy-groups and the σ^+ constants of the substituents in aryl-substituted alkoxycarbenium ions.[72] In the oxonium form of the ions the bond between the oxygen and the carbon should be double:



This leads to the non-equivalence of the substituents R^1 and R^2 (when $R^1 = R^2$) and the existence of two isomers of the ions for $R^1 \neq R^2$. The chemical shifts of the methylene protons in the ^1H NMR spectrum of the methoxycarbenium ion (XXIX) at −60 °C differ by 0.12 p.p.m. In addition, these protons interact with one another, the corresponding constant being $J = 20.79$ Hz, and with the protons of the methoxy-group, the corresponding constants being $J = 0.83$ and 0.97 Hz. An analogous fact has been established also for the chloromethoxycarbenium ion (XL) (Table 1).[54]

Recent analysis of the ^{17}O NMR spectra showed that the degree of π-bonding in the methoxydimethylcarbenium ion (XXXIV) is ~60%.[38]

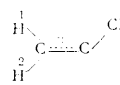
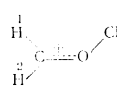
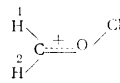
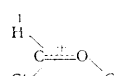
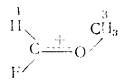
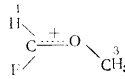
The partially double bond is retained even at room temperature. Thus the chemical shifts of the signals of the methyl groups at the carbenium centre in the ^{13}C NMR spectrum of the ion (XLIa) are different at −60 °C (32.6 and 27.8 p.p.m.),[94] while for the analogous ion (XLIb) the difference is maintained even at room temperature (32.6 and 28.4 p.p.m.):[82]



(XLI, a and b)
R=H (a), CH_3 (b).

The majority of the alkoxycarbenium ions with different substituents at the carbenium carbon atom exist only in the form of one isomer, which can be explained by the difference between the thermodynamic stabilities of the two isomers.[53] However, the simplest ions, such as the chloromethoxycarbenium ions (XLII) and the fluoromethoxycarbenium ion (XLIII), each form two isomers, which have different ^1H NMR spectra (Table 1). The isomers have been identified on the assumption that the *cis*-allyl constant is higher than the *trans*-constant. The ratio of the isomers (XLIIa) and (XLIIb) is 81 : 19, while that of (XLIIIa) and (XLIIIb) is 70 : 30.[52]

Table 1. Characteristics of the ^1H NMR spectra of alkoxycarbenium ions in superacids.

Ion	Solvent	T, °C	δ, p.p.m.*; multiplicity (J, Hz) H¹	H²	H³	Refs.
 (XXIX)	A	−75	9.13; s	9.13; s	5.14; s	[79]
	B	−60	9.66	9.78	5.59	[54]
	C	−60	9.70; d.qr (20.8; 0.9)	9.82; d.qr (20.8; 1.0)	5.63; d.d (0.9; 1.0)	[54]
 (XL)	C	−60	10.06; d.t (18.4; 1.1)	9.99; d.t (18.4; 1.5)	7.02; d.d (1.5; 1.1)	[54]
 (XLIIa)	C	−60	10.90; qr (1.2)	—	5.60 d (1.2)	[52]
 (XLIIb)	C	−60	10.66; qr (0.7)	—	5.72 d (0.7)	[52]
 (XLIIIa)	C	−60	9.76; d.qr (98.0; 1.2)	—	5.46; d (1.2)	[52]
 (XLIIIb)	C	−60	9.86; d.qn (98.0; 0.7)	—	5.64; t (0.7)	[52]
$CH_2\overset{+}{=}OCH_2CH_3$ (XLVII)	A	−75	9.34; s	5.54; qr (7.0)	1.71; t (7.0)	[79]
$CH_2\overset{+}{=}OCH(CH_3)_2$	A	−75	9.25; s	5.78; sp (6.2)	1.65; d (6.2)	[79]
$CH_3CH\overset{+}{=}OCH_3$ (XLIX)	A	−75	9.49; qr (3.5)	2.95; d (3.5)	5.00; s	[79]
	B	−60	9.50 qr.qr (4.0; 0.8)	3.20; d.qr (4.0; 0.8)	5.30; qn (0.8)	[53]
$(CH_3)_2C\overset{+}{=}OCH_3$ (XXXIV)	A	−45	—	2.78; s	4.87; s	[80]
	B	−60	—	3.18; s	5.00; s	[53]
	D	20	—	3.4; s	5.3; s	[76]
$CH_3CH\overset{+}{=}OCH_2CH_3$ (LI)	A**	−75	9.54; qr (3.5)	2.94; d (3.5)	5.36; qr (7.0)	[79]
	B***	−60	9.85; qr (4.0)	3.07; d (4.0)	5.55; qr (7.0)	[53]
$CH_3CH_2CH\overset{+}{=}OCH_3$ (L)	B****	−60	9.90; m	3.60; qr (7.0)	1.25; t (7.0)	[53]
$CH_3CH_2CH\overset{+}{=}OCH_2CH_2$	B*****	−60	9.95; m	3.52; qr (6.5)	1.10; t (6.5)	[53]

Notation. Solvent: A = HSO_3F; B = HSO_3F–SbF_5–SO_2; C = SbF_5–SO_2; D = H_2SO_4–SO_3 (30%). Multiplicity: s = singlet; d = doublet; t = triplet; qr = quartet; qn = quintet; sp = septet; m = multiplet.

*The values of δ in H_2SO_3F have been determined relative to the internal standard CH_2Cl_2 (δ = 5.33 p.p.m.) and have been recalculated relative to TMS; in the remaining cases the recalculation has been relative to an external TMS standard.

**The parameters 1.67; t (7.0) correspond to the signal of the H^4 proton.

***The parameters 1.70; t (7.0) correspond to the signal of the H^4 proton.

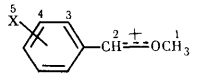
The carbenium and oxonium characters of alkoxycarbenium ions determine their dual reactivity. In most cases, alkoxycarbenium ions react as carbenium ions. For example, the interaction of a solution of the methoxycarbenium ion (XXIX) in the SbF_5–SO_2 mixture with methanol in the presence of K_2CO_3 at −78 °C results in the formation of dimethoxymethane:[52]

$$\underset{\text{(XXIX)}}{CH_2\overset{+}{=}OCH_3} + CH_3OH \xrightarrow[-H^+]{} CH_3OCH_2OCH_3 .$$

An analogous formation of an acetal takes place when a salt of the alkoxycarbenium ion (XLIV) is treated with sodium ethoxide in benzene:[55]

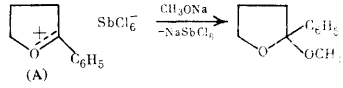
$$\underset{\text{(XLIX)}}{[ClCH\overset{+}{=}C(CH_3)\overset{+}{=}CHOC_2H_5]^+ SbCl_6^-} \xrightarrow[-NaSbCl_6]{C_2H_5ONa} ClCH=C(CH_3)-CH(OC_2H_5)_2 .$$

Table 2. The chemical shifts (δ, p.p.m.) in the ^1H NMR spectra of aryl-substituted alkoxycarbenium ions in HSO_3F at 34 °C (relative to a TMS external standard).[72]



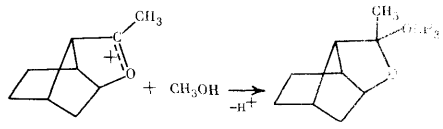
X	H¹	H₂	H³	H⁴	H⁵
H	4.78	9.13	—	—	—
p-CH_3	4.71	8.96	8.00	7.44	2.40
p-OCH_3	4.51	8.57	7.94	7.02	3.90
p-Cl	4.71	9.12	8.08	7.56	—
p-Br	4.78	9.13	7.93	7.77	—
p-F	4.78	9.07	—	—	—
p-NO_2	5.01	9.55	8.36	8.36	—
m-F	4.88	9.25	—	—	—
o-CH_3	4.79	9.26	—	—	2.56
o-OCH_3	4.61	9.31	—	—	3.90
o-$CH\overset{3+}{=}OCH_3$	5.16	9.85	—	—	—
m-$CH\overset{+}{=}OCH_3$	5.07	9.62	—	—	—
p-$CH\overset{+}{=}OCH_3$	5.12	9.71	8.44	8.44	—

On treatment with alkoxide anions, cyclic alkoxycarbenium ions also give rise to acetals. When 2-phenyl-2-tetrahydrofurylium hexachloroantimonate was treated with sodium methoxide in methanol, 2-methoxy-2-phenyltetrahydrofuran was obtained:[7]



(A)

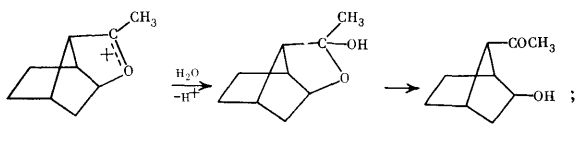
In many cases acetals are formed also when alkoxycarbenium salts are treated with alcohols:[40]

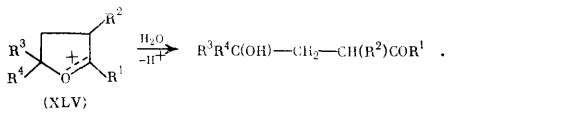


****The parameters 5.30; s correspond to the signal of the H^4 proton.

*****The parameters 5.51; qr (7.0) correspond to the signal of the H^4 proton and the parameters 1.70; t (7.0) correspond to that of the H^5 proton.

Alkoxycarbenium ions react with water also as carbenium ions. The reaction products are unstable hemiacetals, which are then converted into carbonyl compounds:[40,41]

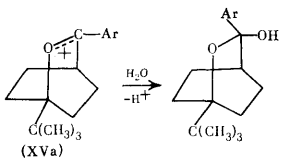




(XLV)

When solutions of alkoxycarbenium ions (XLV) are poured into an aqueous solution of NaOH, γ-hydroxycarbonyl compounds are produced.[34,35]

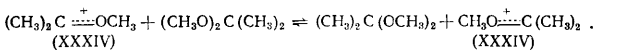
In some cases, hemiacetals have been isolated and characterised:[17]



(XVa)

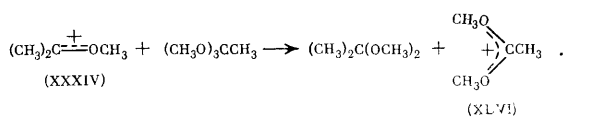
The rate of hydrolysis of alkoxycarbenium ions varies within wide limits depending on their structure.[85]

Alkoxycarbenium ions can react also with weaker nucleophiles such as acetals and orthoesters. Thus, it was noted above that, when acetals are treated with an excess of bromine in SO_2 at −60 °C, alkoxycarbenium ions are formed. In the presence of a deficiency of bromine, the chemical shifts observed in the ^1H NMR spectrum assume intermediate values between those of the acetal and the ion; within the limits of the bromine : acetal ratios from 0 to 1, they vary linearly with the bromine content, but, on further increase of the latter, remain unchanged, which shows that the following rapid equilibrium exists in solution even at −60 °C:[74]



(XXXIV) (XXXIV)

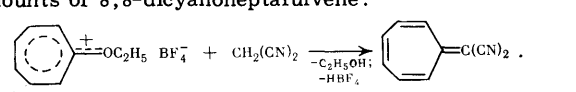
The interaction of the same ion (XXXIV) with methyl orthoacetate leads irreversibly to the formation of the more stable dimethoxymethylcarbenium ion (XLVI) and an acetal:[74]



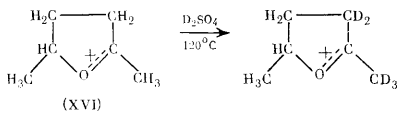
(XXXIV) (XLVI)

The methoxycarbenium ion adds smoothly to double and triple bonds in various compounds.[56–61]

Alkoxycarbenium ions can react with compounds containing an activated methylene group. For example, ethoxytropylium tetrafluoroborate reacts with malonodinitrile in the presence of bases, and together with tropone, gives rise to considerable amounts of 8,8-dicyanoheptafulvene:[97]



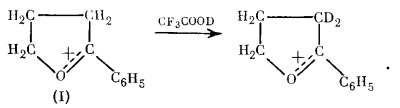
Like other carbenium ions, alkoxycarbenium ions can be stabilised by splitting off a proton from the β-position. Experiments with deuterated sulphuric acid established that the hydrogen atom in the β-positions relative to the carbenium centre in the 2,5-dimethyl-2-tetrahydrofuryl cation (XVI) are substituted by deuterium at 120 °C:[25]



(XVI)

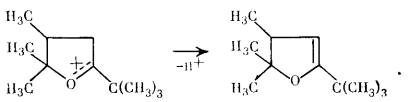
In the analogous cations (XLV) in solution in 96% D_2SO_4 the H–D exchange takes place at 70–100 °C, but is hardly observed at 25 °C. However, on reducing the D_2SO_4 concentration to 80%, the exchange proceeds at an appreciable rate also at 30 °C.[34] Such exchange is effected via deprotonation with the intermediate formation of vinyl ether and its subsequent deuteration.

In a less acidic medium (trifluoroacetic acid) deuterium exchange is observed even at room temperature:[6,7]

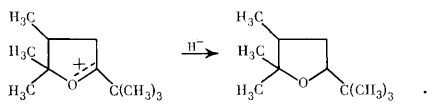


(I)

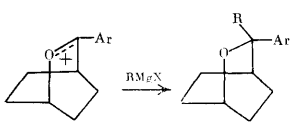
The deprotonation of sterically hindered alkoxycarbenium ions with formation of vinyl ethers becomes the dominant pathway even in reactions such as hydrolysis[32] or interaction with an alkoxide anion:[31,32]



On treatment with hydride ion donors[17,40,41,47] or on catalytic hydrogenation in the presence of Pd/C,[32] alkoxycarbenium ions are reduced to ethers:

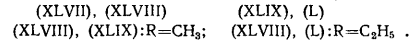


On treatment with Grignard reagents, alkoxycarbenium ions are alkylated:[17]



Under suitable conditions, alkoxycarbenium ions can abstract on alkyl anion from cyclic ketals. It has been suggested that this reaction is responsible for the formation of cyclic dialkoxycarbenium ions (XXXI) on treatment of cyclic ketals with trialkyloxonium salts[69] (see the scheme above).

The most striking manifestation of the carbenium character of alkoxycarbenium ions is their capacity for isomerisation. When ethoxycarbenium hexachloroantimonate (XLVII) and propoxycarbenium hexachloroantimonate (XLVIII) were dissolved in water, considerable amounts of methanol and acetaldehyde or propionaldehyde were formed apparently as a result of the isomerisation of the ions (XLVII) and (XLVIII) via the 1,3-hydride shift to the methoxymethylcarbenium ion (XLIX) or the ethylmethoxycarbenium ion (L), together with the hydrolysis products—formaldehyde and ethyl or propyl alcohol:[98]



(XLVII), (XLVIII) (XLIX), (L)

(XLVIII), (XLIX): R=CH_3; (XLVIII), (L): R=C_2H_5 .

The study of the behaviour of the alkoxycarbenium ions obtained by dissolving formaldehyde acetals in HSO_3F at −70 °C[80,81] showed that ethoxy- and propoxycarbenium ions are stable in HSO_3F up to −30 °C. At higher temperatures signals due to the presence in solution of methanol and also

of the ions (XLIX) and $CH_3CH{=}\overset{+}{O}CH_2CH_3$ (LI) or (L) and $C_2H_5CH{=}\overset{+}{O}C_3H_7$ (LII) appear in the ^1H NMR spectra.

The characteristic signal of the fragment $CH_3O{=}\overset{+}{C}-$ has been detected also in the ^1H NMR spectra of the cyclic formaldehyde acetals in HSO_3F at temperatures above −30 °C.[83]

The ion (XLIX) could be formed from the ion (XLVII) not only via an internal 1,3-hydride shift but also as a result of intermolecular hydride transfer. The abstraction of a hydride ion from the ethyl alcohol present in solution should lead to the formation of ethyl methyl ether and protonated acetaldehyde:

$$\underset{\text{(XLVII)}}{CH_2{=}\overset{+}{O}CH_2CH_3} + CH_3CH_2OH \rightarrow CH_3OCH_2CH_3 + CH_3CH{=}\overset{+}{O}H .$$

Next, the transfer of the hydride ion from the α-position in the ethyl group of ethyl methyl ether to the protonated acetaldehyde or the ethoxycarbenium ion would lead to the methoxymethylcarbenium ion and ethyl alcohol or ethyl methyl ether:

$$CH_3OCH_2CH_3 + CH_3CH{=}\overset{+}{O}H \rightarrow \underset{\text{(XLIX)}}{CH_3O{=}\overset{+}{C}HCH_3} + CH_3CH_2OH ;$$

$$CH_3OCH_2CH_3 + \underset{\text{(XLVII)}}{CH_3CH_2O{=}\overset{+}{C}H_2} \rightarrow \underset{\text{(XLIX)}}{CH_3O{=}\overset{+}{C}HCH_3} + CH_3CH_2OCH_3 .$$

However, specially formulated experiments showed that under these conditions diethyl ether does not react with protonated acetaldehyde or the methoxycarbenium ion:[81]

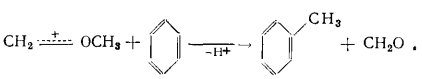
$$CH_3CH_2OCH_2CH_3 + CH_3CH{=}\overset{+}{O}H \not\rightarrow \underset{\text{(LI)}}{CH_3CH_2O{=}\overset{+}{C}HCH_3} + CH_3CH_2OH ;$$

$$CH_3CH_2OCH_2CH_3 + \underset{\text{(XXIX)}}{H_2C{=}\overset{+}{O}CH_3} \not\rightarrow \underset{\text{(LI)}}{CH_3CH_2O{=}\overset{+}{C}HCH_3} + CH_3OCH_3 .$$

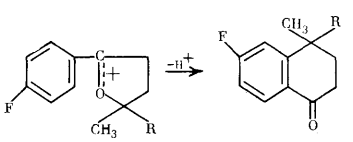
On this basis, it was concluded that the ion (XLVII) is converted directly into (XLIX) via an internal 1,3-hydride shift.[81]

Whereas the 1,3-hydride shift in the ethoxycarbenium ion leads to an energy gain since the ion (XLIX) is more stable to the extent of 46 kJ mol^{-1} than the ion (XLVII),[99] the analogous process in the methoxycarbenium ion is degenerate. The study of the temperature-induced changes in the ^1H NMR spectra and experiments with deuterated dimethoxymethane species showed that the 1,3-hydride shift in the methoxycarbenium ions takes place at 40 °C.[81]

Alkoxycarbenium ions can react as oxonium ions, splitting off an alkyl cation or transferring it to nucleophiles. Thus a methoxycarbenium salt methylates aromatic hydrocarbons:[62]

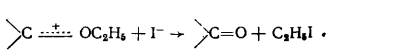


An example of the intramolecular alkylation of an aromatic ring can be provided by the conversion of the ions (Vb) and (VII) into the corresponding tetralones:[9]

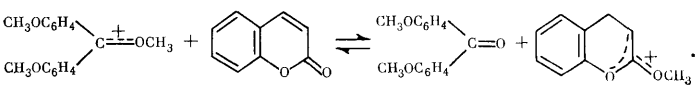


R = H (Vb), CH_3 (VII)

The interaction of alkoxycarbenium ions with iodides results in the alkylation of the iodide ion:[37]



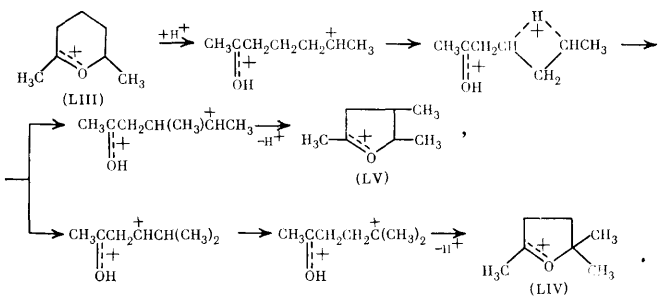
Alkoxycarbenium ions can alkylate also certain oxygen-containing compounds. For example, the interaction of the methoxydi(*p*-methoxyphenyl)carbenium ion with coumarin leads to the formation of an equilibrium mixture:[39]



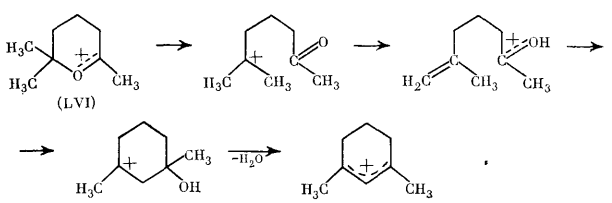
The possibility of the reaction of alkoxycarbenium ions as oxonium ions depends also on the strength of the nucleophile. For example, the cyclic 2-phenyl-2-tetrahydrofuryl cation is stable in trifluoroacetic acid. When sodium trifluoroacetate is added to the solution, the cation reacts with the trifluoroacetate ion to form γ-trifluoroacetoxybutyrophenone:[6]

$$\text{(A)} + CF_3COO^- \rightarrow C_6H_5COCH_2CH_2CH_2OCOCF_3 .$$

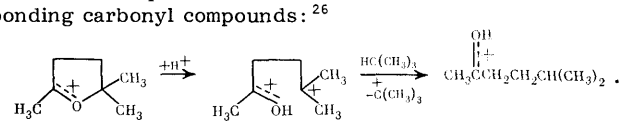
In the absence of nucleophiles the oxonium character of alkoxycarbenium ions is manifested by the possibility of their dealkylation. Thus the ion (LIII), which is stable in superacids at room temperature, is converted into a mixture of the ions (LIV) and (LV) on heating to 100 °C. It has been suggested[28] that this reaction proceeds in accordance with the following scheme:



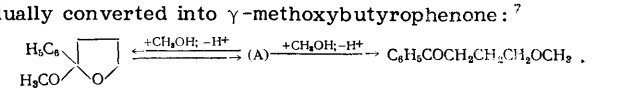
The 6,6-dimethyl-substituted analogue (LVI) is still less stable. In 96% H_2SO_4 the ring is opened in the course of 5 min even at room temperature and a series of reactions lead ultimately to the cyclic allyl cation:[84]



Five-membered cyclic alkoxycarbenium ions without substituents at the carbenium centre undergo an analogous dehydration.[49] In superacid media cyclic alkoxycarbenium ions can abstract a hydride ion from hydrocarbons such as isobutane or isopentane and can be reduced to the corresponding carbonyl compounds:[26]

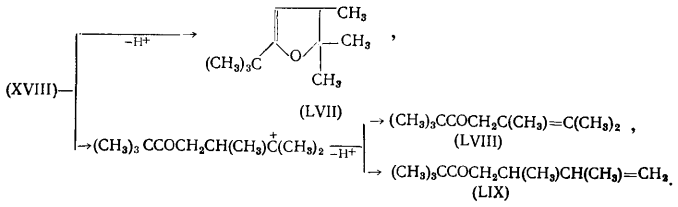


In certain cases the carbenium and oxonium properties of alkoxycarbenium ions are manifested simultaneously. In the reaction of the ion (A) with methanol, the product formed initially is 2-methoxy-2-phenyltetrahydrofuran, which is gradually converted into γ-methoxybutyrophenone:[7]



Such behaviour is due to the fact that in an acid medium the first reaction is reversible and its rate is higher than that of the second reaction. In the initial instant the main product is therefore 2-methoxy-2-phenyltetrahydrofuran—the product of the reaction occurring under the conditions of kinetic control. After a time, the product resulting from thermodynamic control, namely γ-methoxybutyrophenone, accumulates in the mixture.

Three products, compounds (LVII), (LVIII), and (LIX) in the proportions 9 : 2 : 3, have been obtained on heating a mixture of 2-t-butyl-4,5,5-trimethyl-2-tetrahydrofurylium tetrafluoroborate with potassium t-butoxide: [31]



The formation of the first proton (LVII) is due to the carbenium character of the initial ion, while the formation of the other two products (LVIII) and (LIX), is due to its oxonium character.

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Thus alkoxycarbenium ions have now been transformed from hypothetical intermediates into entirely real objects available for study by physical methods. Nevertheless, one cannot claim that these ions have been adequately investigated. The study of alkoxycarbenium ions by modern methods such as ^{1}H, ^{13}C, and ^{17}O NMR, ion-cyclotron resonance, and quantum-chemical calculations will yield more detailed information about their structure and properties, which will in its turn enable chemists to predict their reactivity and to control appropriately the reactions in which they are formed.

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