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The Chemistry of Trialkyloxonium Fluoroborates

V.G.Granik, B.M.Pyatin, and R.G.Glushkov

The preparation and the chemical properties of trialkyloxonium fluoroborates—highly effective alkylating agents—are surveyed. Special attention is paid to the *O*-alkylation of organic compounds (ethers, epoxides, oxo- and hydroxy-derivatives, *N*-oxides, etc.). The bibliography contains 104 references.

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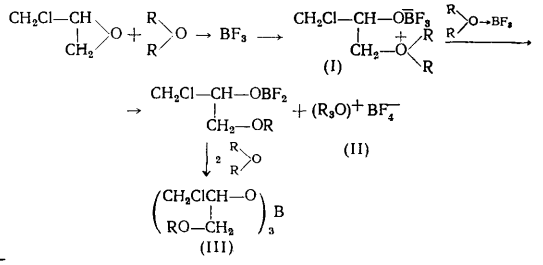
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I. INTRODUCTION

The discovery in 1937 by Meerwein and his coworkers[1] of a new class of highly effective alkylating agents—trialkyloxonium salts—considerably extended the field of application of alkylation reactions in organic chemistry. In the course of the investigation of tertiary oxonium salts methods were developed for the preparation of hitherto unknown classes of organic compounds, such as acetals of amides, lactams, and lactones, azidinium salts, etc. New and more effective procedures were found for obtaining known types of compounds (e.g. imidic esters, orthoesters, lactimidic esters, etc.). Among the large number of trialkyloxonium salts which have now been obtained, trimethyloxonium and triethyloxonium fluoroborates have found the widest use in preparative organic chemistry. A considerable number of interesting investigations have been made during recent years on the use of these alkylating agents for the preparation of complicated organic compounds, the results of which do not appear in Meerwein's brief review[2] of the chemistry of various types of oxonium salts. The present Review summarises available information on the synthetic application of trialkyloxonium fluoroborates, primarily the trimethyloxonium and triethyloxonium salts†.

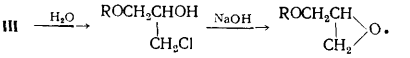
II. PREPARATION OF TRIALKYLOXONIUM FLUOROBORATES

The most widely used method for preparing trialkyloxonium fluoroborates is based on the reaction between 2-chloromethyloxiran and the appropriate ether complex of boron trifluoride in excess of the ether[1,4]:



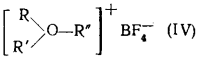
† The Review does not include information on triaryloxonium salts[3], nor on the applications of trialkyloxonium salts in the chemistry of macromolecular compounds.

The above mechanism is supported by the isolation of intermediate inner salts of type (I: R = CH_3, C_2H_5), and the fact that (I: R = C_2H_5) gives triethyloxonium fluoroborate (II: R = C_2H_5) with diethyl ether and its boron trifluoride complex. The boric esters formed in this reaction can be converted into 2-alkoxymethyloxirans:

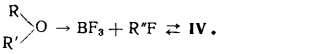


The latter in turn are able to give trialkyloxonium fluoroborates[5].

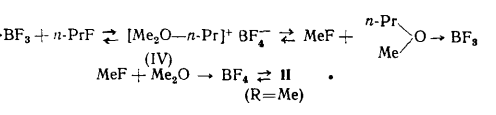
The above method can be used to prepare trimethyloxonium and triethyloxonium fluoroborates (II: R = CH_3, C_2H_5). However, when R = n-C_3H_7, the yield of (II) does not exceed 30%, and oxonium salts containing higher alkyl radicals could not be obtained at all. Furthermore, it is evident from the above scheme that this method cannot be used to prepare unsymmetrical oxonium salts of the type



Such oxonium salts can in principle be obtained by the reaction of alkyl fluorides with the ether complexes of boron trifluoride[3]:



Thus the corresponding oxonium salts are obtained in satisfactory yields by keeping the reactants in a sealed tube for a long time. The compounds (II: R = C_2H_5), (IV: R = R′ = CH_3; R″ = C_2H_5), and (IV: R = R′ = C_2H_5; R″ = CH_3) have been prepared by this method. However, the method is not universally applicable to the preparation of salts of type (IV). For example, reaction between the dimethyl ether complex of boron trifluoride and propyl fluoride yields merely (II: R = CH_3) instead of the expected (IV: R = R′ = CH_3; R″ = n-C_3H_7):

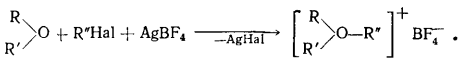


Evidently formation of the more symmetrical cation is energetically more favourable in this reaction. The above scheme agrees well with the easier elimination of methyl rather than other alkyls from the cations (see

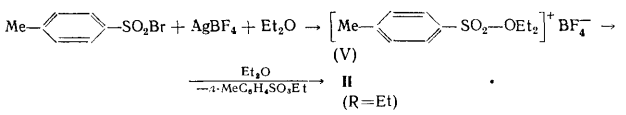
Section III). The formation of (II: R = CH_3) is seen to be based on a series of reversible reactions. The decomposition of triethyloxonium fluoroborate when heated above the melting point provides evidence that oxonium salts are in equilibrium with the alkyl halides and the ether complexes of boron trifluoride: the diethyl ether complex and ethyl fluoride were isolated in high yields[1].

Although the above method enables various oxonium salts (including unsymmetrical salts) to be obtained, the considerable duration of the process (several months) and the relatively low yields make it unsuitable for practical preparations.

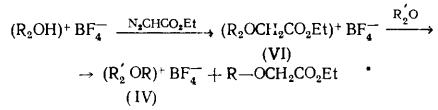
Trialkyloxonium fluoroborates can be prepared more conveniently by the reaction of alkyl halides with ethers in the presence of silver fluoroborate[6,7]:



This reaction can be used to obtain not only trialkyloxonium but also mixed acylalkyloxonium salts. For example, treatment of a mixture of ether and silver tetrafluoroborate with toluene-*p*-sulphonyl bromide at −70°C gives the corresponding oxonium salt (V), from which triethyloxonium fluoroborate (II: R = C_2H_5) is obtained on further reaction with ether[8]:



Trialkyloxonium fluoroborates can be prepared also by the reaction of dialkyloxonium fluoroborates with diazomethane or with ethyl diazoacetate[9]



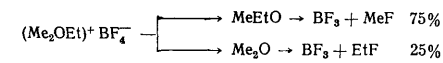
The oxonium salt (VI) formed in the first stage of the reaction is further alkylated by an ether molecule to give the tertiary oxonium salt (IV).

The reaction of a trialkyloxonium fluoroborate with an ether, which is discussed in Section IIIA, 1, provides another method for the preparation of trialkyloxonium fluoroborates.

III. PROPERTIES AND REACTIONS OF TRIALKYLOXONIUM FLUOROBORATES

Trialkyloxonium fluoroborates, like ammonium salts, are typical ionic compounds, whose solutions in anhydrous sulphur dioxide are electrically conducting[4]. They are readily soluble in polar solvents such as nitrobenzene, nitromethane, anhydrous sulphur dioxide, etc. Their solubility in less polar solvents is determined by the length of the alkyl radicals: "loading" the hydrophobic alkyl radicals produces an increase in solubility in these solvents, so that e.g. (II: R = C_2H_5) dissolves well in dichloromethane, whereas (II: R = CH_3) is almost insoluble. All the lower oxonium fluoroborates are solids which melt with decomposition; their melting points fall regularly with increase in length of the alkyl[1,4].

A characteristic property of tertiary oxonium salts is their dissociation at high temperatures with the separation of ether complexes of boron trifluoride and alkyl fluorides. Methyl is detached more readily than other alkyl radicals. For example, the decomposition of ethyldimethyloxonium fluoroborate when heated above 120°C occurs as follows[1]:

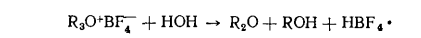


Trialkyloxonium salts decompose not only at high temperature but also when their solutions are allowed to stand. In particular, triethyloxonium fluoroborate is unstable in solution, decomposing comparatively readily into diethyl ether, boron trifluoride, and ethyl fluoride[10]. Decomposition is accelerated by the addition of ethers to the solutions[10].

A. *O*-ALKYLATION BY TRIALKYLOXONIUM FLUOROBORATES

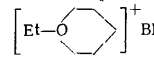
1. Reactions with Hydroxylated Compounds, Ethers, and Epoxides

The simplest and most thoroughly studied reaction of this type is the hydrolysis of tertiary oxonium salts[1]:

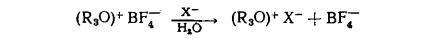


Hydrolysis is accompanied by the formation of an alcohol and an ether, so that the electrical conductivity of the solutions falls gradually[4]. Table 1 gives the rate of hydrolysis of several salts, determined from the variation in the conductivity of aqueous solutions[4]. The results show that "loading" the alkyl radicals, as well as including positively charged oxygen in a ring, leads to considerable stabilisation of tertiary oxonium salts towards water.

Table 1. Times (min) for complete hydrolysis (at 18°C).

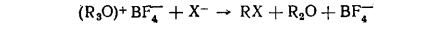
$(Me_3O)^+BF_4^-$	8
$(Et_3O)^+BF_4^-$	80
$(n\text{-}Pr)_3O^+BF_4^-$	120
	220

The relatively low rate of hydrolysis enables ion exchange to be effective with the formation of water-insoluble oxonium salts containing complex anions[4]:



where R = CH_3, C_2H_5; X = $AuCl_4$, $SnCl_4$, HgI_3, $SbCl_6$, etc. Double decomposition of (II: R = C_2H_5) with sodium tri-iodomercurate can be used for the quantitative determination of triethyloxonium fluoroborate[4]. Similarly, the reaction of (II: R = CH_3, C_2H_5) with 2,4,6-trinitrobenzenesulphonic acid yields the corresponding trinitrobenzenesulphonates, which also serve as alkylating agents[11].

When nucleophilic agents other than the hydroxide ion are present in aqueous solution, two competing processes—hydrolysis of the salts and formation of RX



may occur. Table 2 gives the yields of ethylation products obtained when various anions react with triethyloxonium fluoroborate in water[3]. It is evident that the yields of alkylation products usually increase with increase in the polarisability of the anion[4].

Trialkyloxonium fluoroborates react with hydroxylated compounds such as alcohols, phenols, and carboxylic acids with formation of the corresponding *O*-alkyl derivatives[1,2] (a reaction similar to hydrolysis or the ethylation of anions):

$$(R_3O)^+ BF_4^- + R'OH \rightarrow RO_2 + HBF_4 + R'OR \ .$$

Use of the sodio-derivatives of the hydroxylated compounds (i.e. alkylation of the anion $R'O^-$) increases the yields of alkylated products owing to the considerable increase in electron density on the oxygen atom[1,2].

Table 2.

X⁻	F⁻	Cl⁻	Br⁻	I⁻	CNS⁻	CN⁻
Yield of C_2H_5X, %	trace	12	23	53	64	55

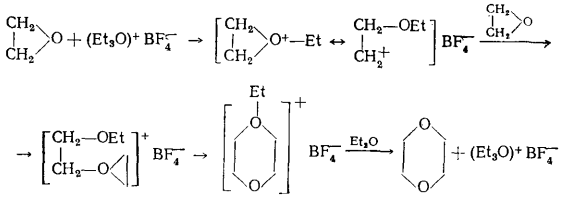
The alkylation of alcohols, phenols, and carboxylic acids does not in all cases, of course, require the use of such strong alkylating agents as trialkyloxonium salts. However, where mild conditions are necessary (e.g. in stereospecific synthesis) or when other methods of alkylation give low yields of the desired products, the application of tertiary oxonium salts acquires considerable preparative value. For example, triethyloxonium fluoroborate is employed for the ethylation of chloroalkanols[1,2] (these compounds cannot be alkylated in alkaline medium[1,2] owing to the elimination of hydrogen chloride with formation of an epoxide) and for the alkylation of (+) (*S*)-pinacolyl alcohol[12].

The alkylation of ethers occupies a special position among the reactions of trialkyloxonium fluoroborates, since it results in new oxonium salts[2]:

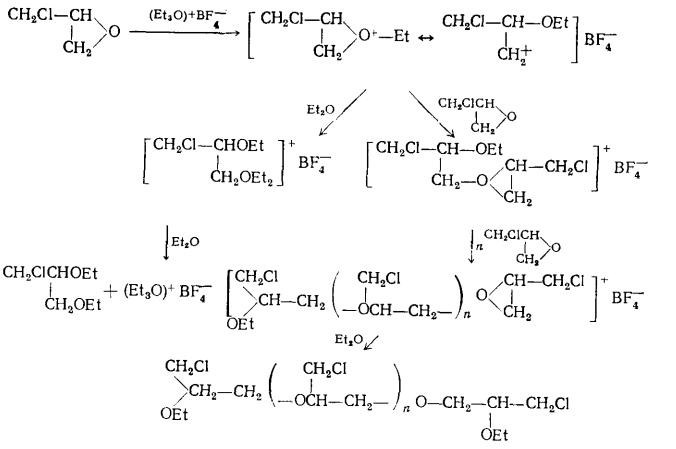
$$(R_3O)^+ BF_4^- + R'_2O \rightleftarrows (R'_2OR)^+ BF_4^- + R_2O \ .$$

As the reaction between oxonium salts and ethers is reversible, the yield of newly formed fluoroborates depends both on the stability of initial and final salts and on their solubility in the reaction medium. In the reaction of (II: R = C_2H_5) with dimethyl ether, for example, a 92% yield of (II: R = CH_3) is formed, whereas in the reaction of the same salt with oxan the yield of ethyloxanium fluoroborate is only 52%.

The first stage in the reaction of trialkyloxonium fluoroborates with epoxides[13] resembles their reaction with ethers. However, the subsequent reactions of the resulting oxonium compounds depend on the structure of the initial epoxide. Thus dioxan has been isolated as final product of the reaction of triethyloxonium fluoroborate with oxiran in ether[13]:



With chloromethyloxiran reaction can occur in two ways[13]:



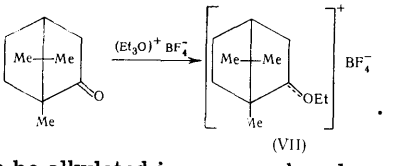
products of different degrees of polymerisation being formed depending on the reaction conditions.

2. Reactions with Carbonyl Compounds

A detailed study of reactions of this type enabled Meerwein et al.[14] to arrange carbonyl compounds in the following sequence according to their capacity for alkylation by oxonium salts: aldehydes < ketones < esters < lactones < acid amides < lactams. This sequence will be adopted in the present survey.

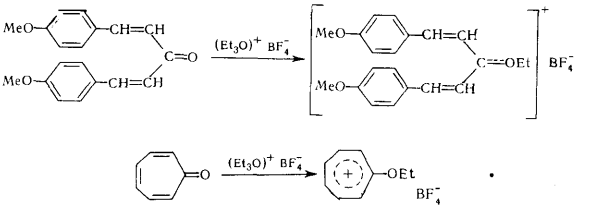
(*a*) Alkylation of aldehydes, ketones, and carboxylic esters

The reaction of aldehydes and ketones with tertiary oxonium salts yields only aldol condensation products[2]: owing to the low basicity of these compounds, they do not usually undergo *O*-alkylation. In some cases, nevertheless, alicyclic ketones are alkylated, and camphor, for example, gives the corresponding fluoroborate (VII) in 78% yield[1]:



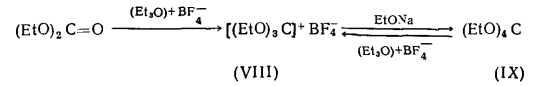
(VII)

The ability to be alkylated increases sharply on passing from simple to $\alpha\beta$-unsaturated ketones, as a consequence of the considerable stabilisation of the resulting cation. Quantitative yields are obtained, for example, in the reactions of triethyloxonium fluoroborate with di-*p*-methoxystyryl ketone[1] and with tropone[15]:



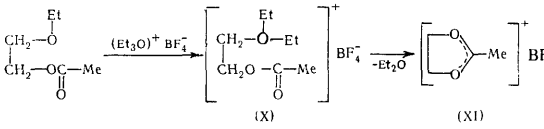
In esters, as in saturated aldehydes and ketones, the electron density on the carbonyl is usually insufficient for

alkylation by oxonium salts[2]. When, however, the resulting cation is largely stabilised by conjugation, as e.g. in the ethylation of carbonic ester, it is possible to obtain the corresponding fluoroborate salt (VIII)[16], whose structure has been proved by conversion into tetraethoxymethane (IX):



(VIII) (IX)

Alkylation of ethers occurs appreciably more readily than that of carbonyl compounds. When the molecule contains both functions, e.g. 2-ethoxyethyl acetate, the first stage is *O*-alkylation of the ether[14]:

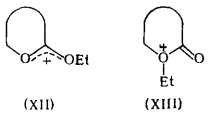


(X) (XI)

The resulting cation (X) is stabilised by elimination of a molecule of ether with the formation of 2-methyl-1,3-dioxolenium fluoroborate (XI).

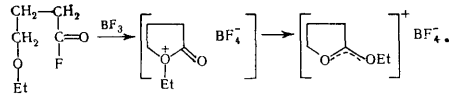
(*b*) Alkylation of lactones

Trialkyloxonium fluoroborates alkylate lactones solely at the carbonyl oxygen[16]. The explanation of such selectivity is that the resulting cation (XII) is stabilised by conjugation, unlike the cation (XIII), which might have been obtained by alkylation of the cyclic oxygen atom.

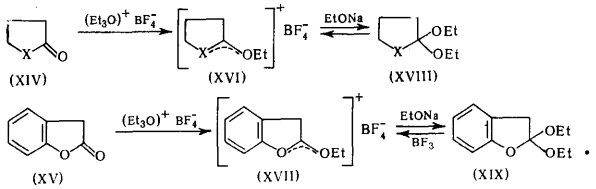


(XII) (XIII)

If, however, only cations of type (XIII) can be formed, they immediately pass into stabilised cations of type (XII)[16]:



Examples of the reaction of triethyloxonium fluoroborate with lactones are provided by the alkylation of compounds (XIV: X = O, S) and phthalide (XV)[17]:

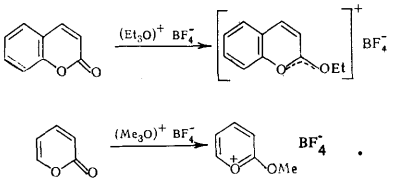


(XIV) (XVI) (XVIII)

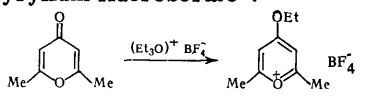
(XV) (XVII) (XIX)

Treatment of the salts (XVI) and (XVII) with sodium ethoxide converts them into lactone acetals (XVIII) and (XIX)[16].

Lactones which can form fluoroborates with stable cations are especially readily alkylated[1,18]:

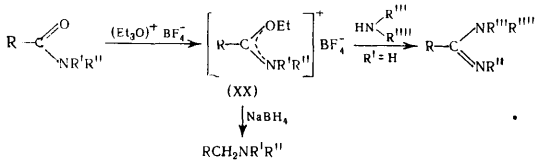


Similarly, the action of triethyloxonium fluoroborate on 2,6-dimethyl-4-pyrone readily forms the stable 4-ethoxy-2,6-dimethylpyrylium fluoroborate[1]:



(*c*) *O*-Alkylation of amides

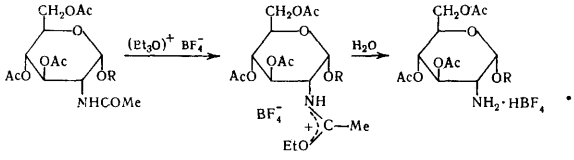
The reaction of trialkyloxonium fluoroborates with compounds containing an amide function is one of the most promising for synthetic purposes. It is sufficient to note that this reaction has opened up a new pathway for the preparation of such important and extremely reactive compounds as imidic and lactimidic esters[18]. Several members of a new class of organic compounds—amide and lactam acetals—have also been synthesised[19-21]. Meerwein first accomplished the reaction of trialkyloxonium fluoroborates with amides and lactams in the case of acetamide[1], and subsequently extended the reaction to a large number of diverse compounds containing an amide function[16,20]. The salts of imidic esters formed by alkylation are easily converted by amines into amidines[22]:



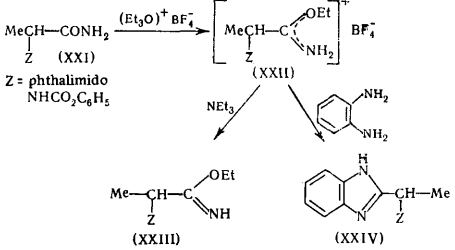
(XX)

Fluoroborates of imidic esters (XX) can be reduced by sodium tetrahydroborate under mild conditions to give high yields of the corresponding amines[23]. Since amides are usually reduced by means of the considerably less selective lithium tetrahydroaluminate, the new method shows great promise for the preparation of various amines, including polyfunctional compounds, which are difficult to obtain by other methods.

The availability of salts of type (XX) also provides opportunities for the selective detachment of *N*-acyl groups under exceptionally mild conditions, for salts of imidic esters are easily hydrolysed by water. This has been utilised for removing a protective *N*-acetyl group while preserving acetoxy-groups[24]:

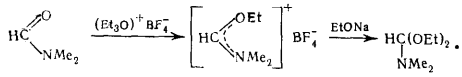


In substituted alaninamides (XXI) only the carbamoyl group is affected by triethyloxonium fluoroborate, in spite of the simultaneous presence of a phthalimido- or a phenoxycarbonylamino-group. The structure of the resulting fluoroborates (XXII) was proved by converting them into imidic esters (XXIII) and substituted benzimidazoles (XXIV)[25]:

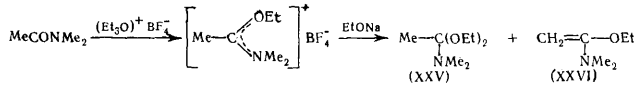


(XXI) (XXII) (XXIII) (XXIV)

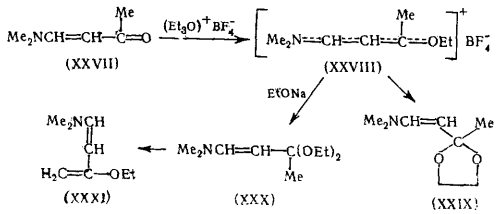
The reaction of trialkyloxonium fluoroborates with *NN*-disubstituted amides yields, after treatment of the intermediate fluoroborates with sodium ethoxide, the corresponding amide acetals: e.g.[20]



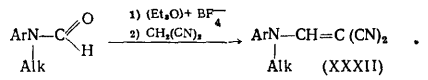
The alkylation of *NN*-dimethylacetamide with (II: R = C_2H_5) produces a fluoroborate salt, treatment of which with sodium ethoxide gives a mixture of the corresponding acetal (XXV) and the "*ON*-keten-acetal" 1-ethoxyvinyldimethylamine (XXVI)[20]:



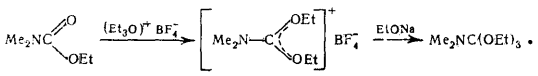
Alkylation of the vinylogue (XXVII) of *NN*-dimethylacetamide proceeds similarly. If the resulting fluoroborate (XXVIII) is decomposed with sodium glycollate, a stable cyclic acetal, *NN*-dimethyl-2-2'-methyldioxolan-2'-ylvinylamine (XXIX), is formed[20]. Reaction of (XXVIII) with sodium ethoxide gives an unstable diethyl acetal (XXX), vacuum distillation of which is accompanied by elimination of a molecule of alcohol with formation of the corresponding "keten-acetal" (XXXI)[20]:



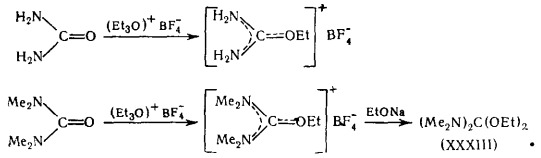
Amide acetals react very vigorously with various nucleophilic reagents[21]. It is not usually necessary to isolate the amide acetal (as in the preparation of amidines from amides—see above), and the intermediate fluoroborate salts can be used for further syntheses[25-27]. For example, *N''*-alkylanilinomethylenemalononitriles (XXXII) have been synthesised by the reaction of *N*-alkyl-*N*-arylformamides with trialkyloxonium fluoroborates followed by treatment with malononitrile in the presence of triethylamine[27]:



Urethanes and urea derivatives react similarly to amides with trialkyloxonium salts[4,20]. Thus triethyloxonium fluoroborate and ethyl *NN*-dimethylcarbamate give the corresponding salt, which is further converted by sodium ethoxide into orthocarbonic dimethylamide—a stable compound which is not hydrolysed under normal conditions[20]:

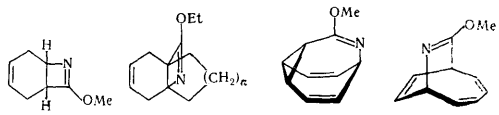


Similarly, the alkylation of urea[4] yields the fluoroborate of *O*-ethylisourea, and that of tetramethylurea the corresponding salt, from which diethoxy-*NNN'N'*-tetramethylmethylenediamine (XXXIII) was prepared by the action of sodium ethoxide[20]:

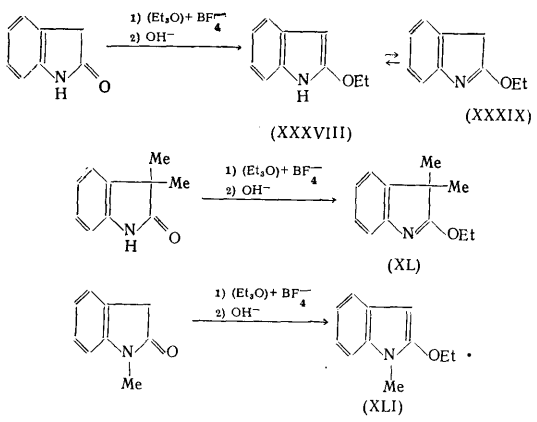


The reaction of trialkyloxonium fluoroborates with cyclic amides (lactams) has found wide application in organic synthesis. The resulting *O*-alkylated lactams have been starting materials for a large number of heterocycles, including members of novel heterocyclic systems[19].

The alkylation of simple lactams—2-oxopyrrolidine, 2-oxopiperidine, ϵ-caprolactam—by trialkyloxonium salts followed by treatment of the resulting fluoroborates with alkaline reagents gives high yields of the corresponding lactimidic esters[19,28,29]. This method has been used also to prepare lactimidic esters of phthalimidine[30], 1,2,3,4-tetrahydro-2-oxoquinoline[31,32], 3,5,7-trimethyl-2-oxoazepine[33], 2,3,4,5-tetrahydro-10-methyl-1-oxoazepino[3,4-*b*]indole[34], and also more complicated bi- and tri-cyclic lactams (XXXIV)–(XXXVII)[35-37].

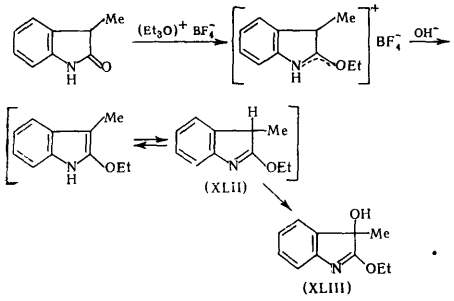


Interesting results have been obtained for the alkylation of oxindole and its derivatives with triethyloxonium fluoroborate[38-40]. Oxindole itself yields 2-ethoxyindole (XXXVIII), which on sublimation is converted into the lactimidic ester (XXXIX). The tautomeric equilibrium between (XXXVIII) and (XXXIX) in solution is demonstrated by comparing their infrared and proton magnetic resonance spectra with those of a model imine (XL) and a model enamine (XLI)[38]:



Comparison of the ionisation constants and also spectral data for the lactimidic esters of 3-substituted and 3,3-disubstituted 2-oxopiperidines (prepared from the corresponding lactams and triethyloxonium fluoroborate) indicate that such tautomerism is probably a general feature of lactimidic esters[41]. When 3-methyloxindole was alkylated with triethyloxonium fluoroborate, the product isolated was

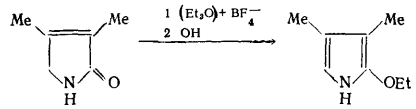
not the lactimidic ester (XLII) but (unlike what occurs with oxindole and 3,3-dimethyloxindole) an oxidation product, 2-ethoxy-3-hydroxy-3-methylindole (XLIII)[40]:



(XLII)

(XLIII)

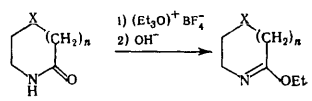
The alkylation of 3,4-dimethyl-2-oxopyrroline (XLIV) with triethyloxonium fluoroborate does not yield the corresponding lactimidic ester but a 2-ethoxypyrrole derivative (XLV):



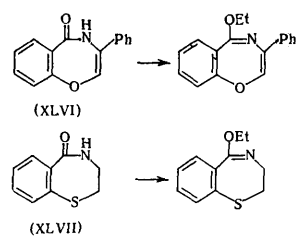
(XLIV) (XLV)

Migration of the double bonds probably occurs with formation of the stable aromatic ring[42].

Lactams containing a second heteroatom in the ring are alkylated selectively at the lactam carbonyl. Alkaline treatment of the products yields the corresponding lactimidic esters[18,32,43-48]:



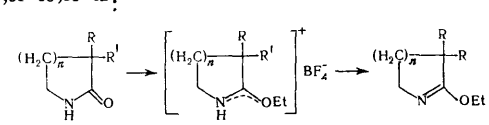
where $n = 1$, 2 and X = O, S, N.CO.CH$_3$. The corresponding lactimidic esters are obtained also from bicyclic lactams (XLVI) and (XLVII)[49,50]:



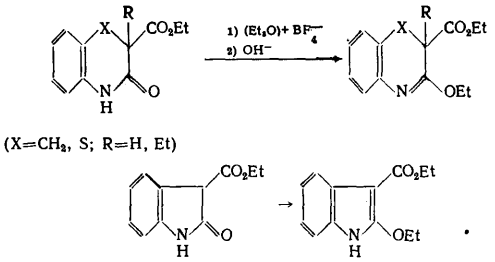
(XLVI)

(XLVII)

A considerable amount of work has been done on the alkylation of compounds containing other functional groups in addition to the lactam group[39,41,47,51-65]. In particular, the alkylation of a series of simple 3-mono- and 3,3-disubstituted lactams has been studied in connection with the synthesis of fused pyrimidine systems from lactimidic esters[41,51-56,58-62]:

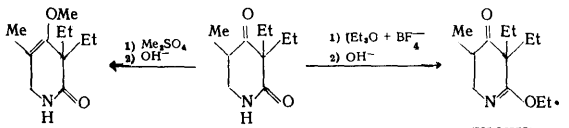


where with $n = 1$: R = COOC$_2$H$_5$ and R′ = H; with $n = 2$: R = H, C$_2$H$_5$, C$_6$H$_5$, Cl, Br, CH$_3$, OC$_2$H$_5$ and R′ = H, COOC$_2$H$_5$; and with $n = 3$: R = COOC$_2$H$_5$, CN and R′ = H. It was established that alkylation occurs selectively at the lactam carbonyl, the functional substituents remaining unaffected. The alkylation of benzo-derivatives of 3-ethoxycarbonyl-lactams proceeds similarly[39,47,63,66]:



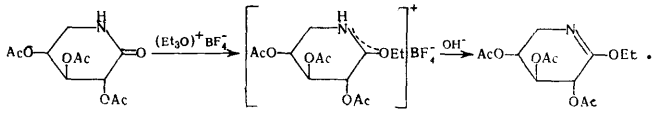
(X=CH$_2$, S; R=H, Et)

Alkylation of 3,3-diethyl-5-methyl-2,4-dioxopiperidine by triethyloxonium fluoroborate goes smoothly to the corresponding lactimidic ester (XLVIII)[51]. It is interesting that, with dimethyl sulphate as alkylating agent, the 4-carbonyl is alkylated with formation of the lactam (XLIX)[51]:

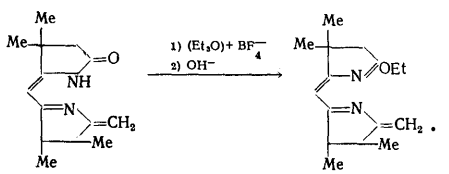


(XLIX) (XLVIII)

The mild conditions under which alkylation by tertiary oxonium salts takes place makes this method almost irreplaceable when the lactam ring contains such functional substituents as the acetoxy-group[57]:

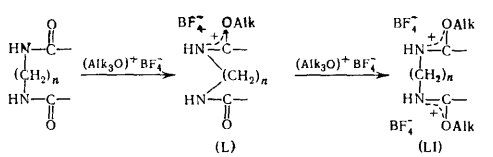


The great readiness of tertiary oxonium salts to alkylate a lactam carbonyl has been used for the preparation of intermediate products in the synthesis of corrin derivatives[64]:



Results have been published for the alkylation of compounds containing two amide functions. For example, triethyloxonium fluoroborate gives lower yields than usual of the lactimidic esters from 1-acetyl-3-oxopiperazine and its methyl 2-carboxylate[44,45,56], and also from ethyl 1-benzoyl-1,2,3,4-tetrahydro-3-oxoquinoxaline-2-carboxylate[47]. Together with the isolation of considerable quantities of the initial lactams, this can be explained by the simultaneous alkylation of the $N_{(4)}$-carbonyls.

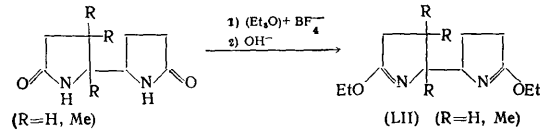
Examination of the scheme of alkylation of compounds containing two (or more) amide carbonyls reveals that, after the first amide group has been alkylated, attack by the alkylating agent on the second amide carbonyl is impeded by the electron-accepting action of the positively charged group in (L):



(L) (LI)

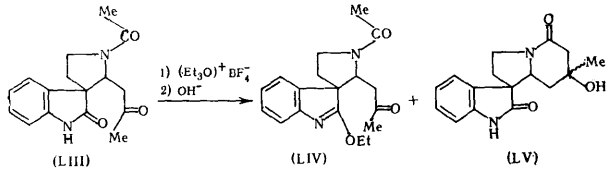
It is quite clear that this effect is weakened by large values of n, so that the decrease in electron density on the second amide carbonyl is insufficient to prevent formation of the dication (LI). As n becomes smaller, the electron density on this carbonyl decreases, and electrophilic attack by the alkylating agent will consequently be hindered.

The above principles can be illustrated by published results. Derivatives of 5,5'-dioxo-2,2'-bipyrrolidinyl react with triethyloxonium fluoroborate[6] to give high yields of bislactimidic esters (LII)[67,68]:



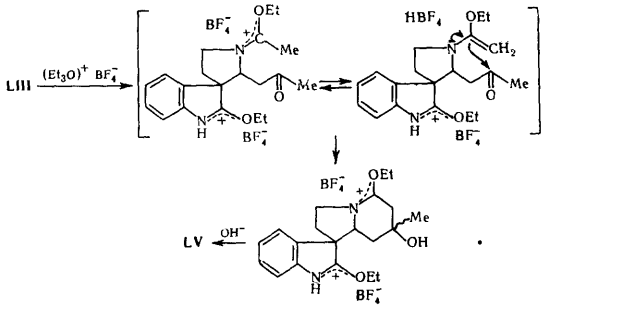
(R=H, Me) (LII) (R=H, Me)

Alkylation of the spiro-compound (LIII) with the same agent gave not only the corresponding lactimidic ester (LIV) but also a tetracyclic compound (LV)[69]:

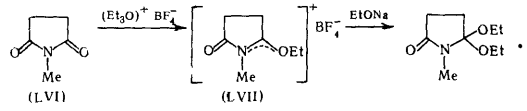


(LIII) (LIV) (LV)

Formation of the latter was regarded[70] as a consequence of alkylation of both amide groups:



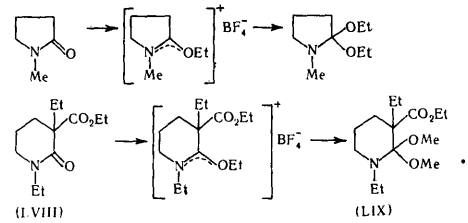
Nevertheless, only one carbonyl group is involved in the alkylation of N-methylsuccinimide (LVI) by triethyloxonium fluoroborate[71]:



(LVI) (LVII)

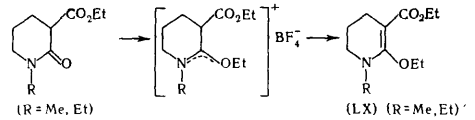
Indeed, it is difficult to imagine that under normal conditions the cation (LVII) could undergo further alkylation at the second carbonyl.

As in the alkylation of N-methylsuccinimide, the reaction of trialkyloxonium fluoroborates with N-substituted lactams yields lactam acetals after treatment with bases[2,20]. The examples of the N-methyl-2-oxo-derivatives of pyrrolidine, quinoline, benzoxazole, and benzothiazole show that this is probably a general method for the preparation of lactam acetals which are unsubstituted in position 3 of the ring[20]. The alkylation of a 3,3-disubstituted N-methyl-2-oxopiperidine (LVIII) also goes smoothly with formation of the corresponding acetal (LIX)[61]:

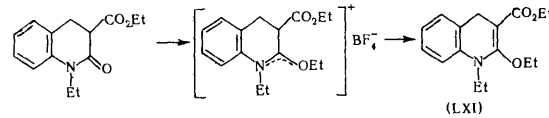


(LVIII) (LIX)

However, lactams containing a 3-ethoxycarbonyl group give enamines (LX) and (LXI)[59,63]—cyclic analogues of "*ON*-keten-acetals" (see beginning of this subsection)—as final products:

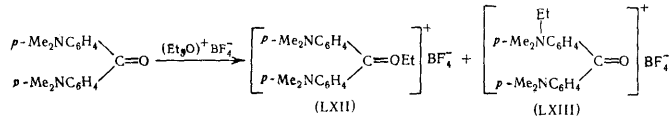


(R = Me, Et) (LX) (R = Me, Et)



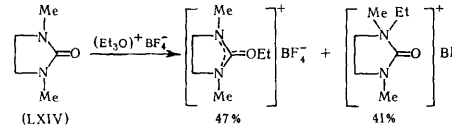
(LXI)

The results discussed above show that trialkyloxonium fluoroborates are excellent alkylating agents for the preparation of O-alkyl derivatives of amides, lactams, and related compounds, especially with respect to selectivity: when a lactam molecule contains several active groups, it is usually only the amide carbonyl that undergoes alkylation. However, examples are known in which alkylation by tertiary oxonium salts takes place ambiguously. Thus Michler's ketone yields not only the O-ethyl derivative (LXII) but also the isomeric N-alkyl compound (LXIII)[20]:



(LXII) (LXIII)

1,3-Dimethyl-2-oxoimidazolidine (LXIV) also gives a mixture of O- and N-alkylated products[20]:

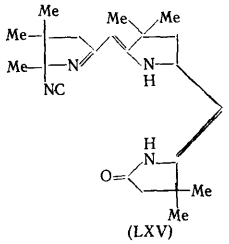


(LXIV) 47% 41%

It should be noted that triethyloxonium fluoroborate acts on the benzo-derivative of (LXIV) unambiguously with the formation of 2-ethoxy-1,3-dimethylbenzimidazolium fluoroborate[20].

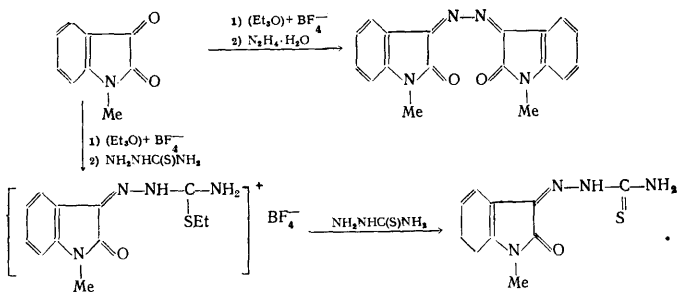
Until recently no cases were known of the N-alkylation of lactams by tertiary oxonium salts. However, it has

been reported recently that the reaction of the tricyclic lactam

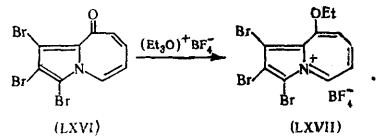


(LXV)

proceeds ambiguously to give a mixture of *N*- and *O*-isomers[72]. Treatment with hydrazine hydrate or thiosemicarbazide of the reaction mixture obtained from *N*-methylisatin and triethyloxonium fluoroborate yields the azine and the thiosemicarbazone of *N*-methylisatin[65]:



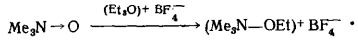
In concluding this subsection we must note a reaction which is closely related to the alkylation of lactams and their vinylogues—the action of triethyloxonium fluoroborate on the dicyclic oxoazepine (LXVI), resulting in the formation of an ethoxyazonia-azulene fluoroborate (LXVII)[73]:



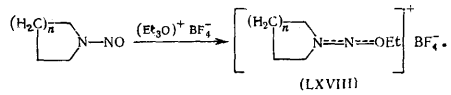
(LXVI) (LXVII)

3. Other *O*-Alkylations

Another reaction of tertiary oxonium salts is the *O*-alkylation of *N*-oxides[4] and *N*-nitroso-compounds[74]:

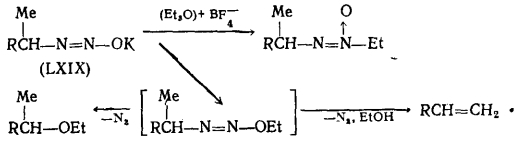


Investigation of the alkylation of *N*-nitrosoazacycloalkanes led to a new class of organic compounds—*O*-alkylnitrosoimmonium salts (LXVIII)[74]:



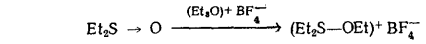
(LXVIII)

The alkylation of compounds containing nitrogen–oxygen bonds does not always occur unambiguously. Thus the reaction of triethyloxonium fluoroborate with diazoates (LXIX) yields not only *O*-alkylated products but also *N*-alkyl derivatives[75]:



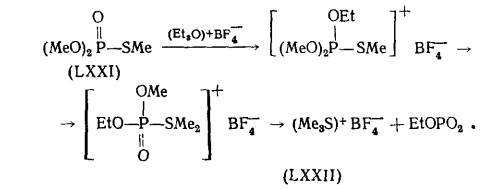
(LXIX)

As with *N*-oxides the alkylation of compounds containing an *S*-oxide group takes place at the oxygen atom with the formation of high yields of *S*-alkoxysulphonium salts (LXX)[4]:



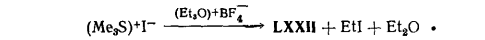
(LXX)

Interaction of the thioester (LXXI) with triethyloxonium fluoroborate gives trimethylsulphonium fluoroborate (LXXII). This process of alkylation was represented by the scheme[76]



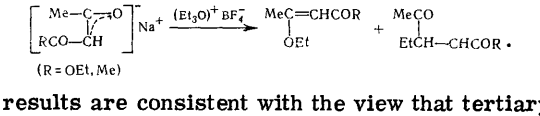
(LXXI) (LXXII)

The structure of the salt (LXXII) was proved[76] by its preparation from trimethylsulphonium iodide and triethyloxonium fluoroborate:



B. REACTIONS OF TRIALKYLOXONIUM FLUOROBORATES WITH AMBIDENT ANIONS

The molecules of ambident anions react with strongly electrophilic reagents mainly at the site of highest electron density[77,78]. This explains why the action of triethyloxonium fluoroborate on the sodium derivatives of acetoacetic ester‡ and penta-2,4-dione yields considerably greater proportions of *O*-alkylated products than when alkyl halides are used[79]. It is important to note that the reaction was conducted under heterogeneous conditions, which usually favour *C*-alkylation[80]:



(R = OEt, Me)

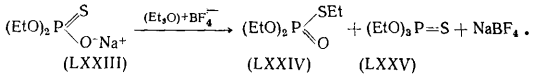
These results are consistent with the view that tertiary oxonium salts are considerably more strongly electrophilic than are alkyl halides.

Another study of the alkylation of metal derivatives of acetoacetic ester in hexamethylphosphoramide and in dimethyl sulphoxide has established that the use of triethyloxonium fluoroborate gives no higher yields of *O*-alkyl derivatives than are obtained with dialkyl sulphates, although the latter are considerably less electrophilic[81].

‡ The reaction of triethyloxonium fluoroborate with sodium acetoacetic ester had been accomplished earlier[1], but only the *C*-isomer had then been isolated (in 47% yield).

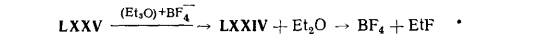
This anomaly was explained[81,82] on the assumption that the alkylating agent was not the tertiary salt but its reaction product with the solvent. This hypothesis is supported by the increased yields of *O*-ethyl derivatives obtained when the alkylation is conducted in a mixture of hexamethylphosphoramide and dichloromethane, and also by the ability of triethyloxonium fluoroborate to ethylate dimethyl sulphoxide[4].

Comparison of results for the alkylation of dialkyl phosphorothionate anions (LXXIII) by various alkylating agents, including triethyloxonium fluoroborate[83], also indicates the tendency of this reagent to attack at the site of highest electron density. Indeed, whereas the alkylation of (LXXIII) by alkyl halides and esters of mineral acids produces solely the *S*-derivatives (LXXIV), when the oxonium salt is used (LXXIV) is accompanied by the *O*-isomer (LXXV) in 8% yield:

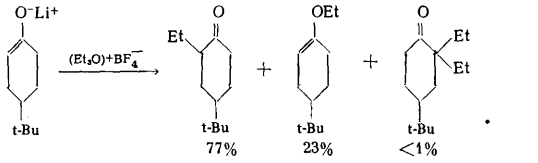


(LXXIII) (LXXIV) (LXXV)

Since in the presence of triethyloxonium fluoroborate the *O*-isomer (LXXV) is partly converted into the *S*-isomer (LXXIV), the actual yield of the former may even be rather higher than the above value[83]:

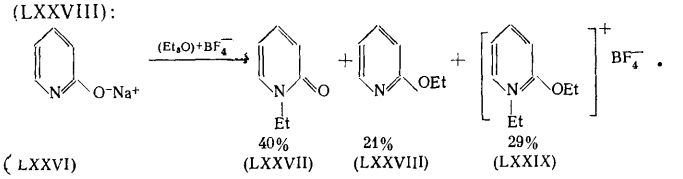


Similarly, when triethyloxonium fluoroborate acts on the enolate anion [of 4-t-butylcyclohexanone], *C*-alkylation is accompanied by *O*-alkylation, whereas with methyl iodide as alkylating agent no *O*-alkylation products are found[84]:



77% 23% <1%

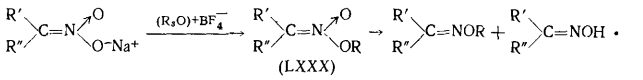
Results for treatment of the sodium salt of 2-hydroxypyridine (LXXVI) with triethyloxonium fluoroborate also support the principle that the more electrophilic alkylating agents show a greater tendency to *O*-alkylation. With alkyl halides this compound is alkylated at the nitrogen atom[85], the method being used most frequently for the preparation of 1-alkyl-1,2-dihydro-2-oxopyridine derivatives. On the other hand, when the tertiary oxonium salt is used, the *N*-ethyl derivative (LXXVII) is accompanied by a quite considerable quantity of 2-ethoxypyridine (LXXVIII)[85]. Another product is the *ON*-diethyl derivative (LXXIX), which results from further alkylation of the monoethylated compounds (LXXVII) and (LXXVIII):



(LXXVI) 40% (LXXVII) 21% (LXXVIII) 29% (LXXIX)

The salt (LXXIX) also is an alkylating agent and capable of alkylating the initial compound (LXXVI)[85]. However, since it is less strongly electrophilic than triethyloxonium fluoroborate, it produces the *O*-ethyl derivative (LXXVIII) in considerably smaller yield (up to 9%), and the yield of the *N*-isomer (LXXVII) increases correspondingly (to 79%).

A fairly detailed investigation has been made of the alkylation of the sodium salts of nitroalkanes by trialkyloxonium fluoroborates[5,86,87]. The primary products are esters of the *aci*-nitro-derivatives (LXXX)[87], which are then converted into oximes and their ethers:

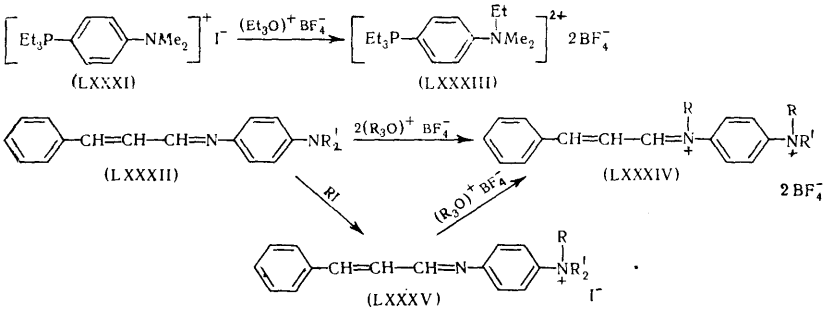


(LXXX)

It should be noted that triethyloxonium fluoroborate always gives higher yields than does the trimethyloxonium salt. Since alkylation is conducted in aqueous medium[4], this difference is probably due to the greater tendency of methyl derivatives to be hydrolysed.

C. *N*-, *P*-, AND *S*-ALKYLATION BY TRIALKYLOXONIUM FLUOROBORATES

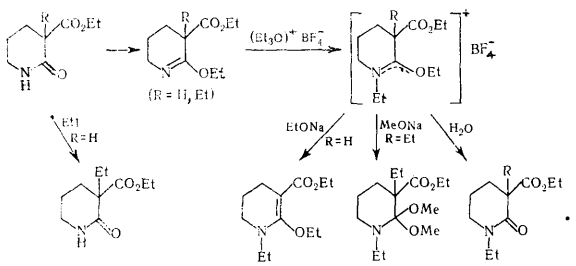
Oxonium salts have not found wide application for the alkylation of amines, since such strongly electrophilic reagents are not needed for this purpose. However, they can be usefully applied to the alkylation of compounds containing also strongly electron-accepting substituents, which weaken the nucleophilic character of the amino-group. Examples are provided by the alkylation of *p*-dimethylaminophenyltriethylphosphonium iodide (LXXXI)[88] and the cinnamylideneaniline derivative (LXXXII)[89], which yield the bivalent salts (LXXXIII) and (LXXXIV). The latter salt can be prepared in stages, in the first of which alkyl halides can be used to obtain the ammonium salt (LXXXV), but a trialkyloxonium fluoroborate is needed for the second stage[88]:



(LXXXI) (LXXXIII) (LXXXII) (LXXXIV) (LXXXV)

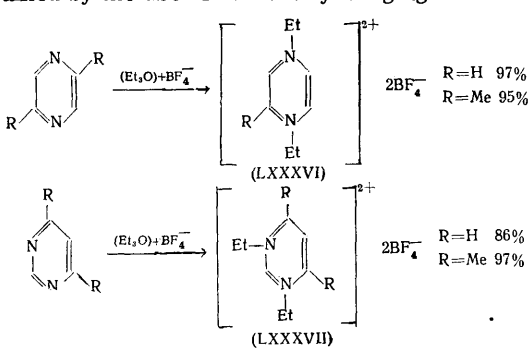
The strongly electrophilic character of trialkyloxonium salts enables several reactions to be accomplished that cannot be effected by other alkylating agents. Considerable interest therefore attaches to the use by Wittig et al. of trimethyloxonium fluoroborate for the quaternisation under mild conditions of sterically hindered amines such as e.g. *cis*- and *trans*-*N*-methyl-12-aza-1,2:3,4:7,8:9,10-tetrabenzocyclotrideca-1,3,5,7,9-pentaenes[90]. Furthermore, the reactions of a series of saturated heterocycles with tertiary oxonium salts reveal that not only axial but also equatorial isomers undergo alkylation, which is not observed with ethyl iodide[91].

Triethyloxonium fluoroborate has been successfully used to alkylate lactimidic esters of 2-oxopiperidines and 1,2,3,4-tetrahydro-2-oxoquinolines[59-61,63]. It is significant that this reaction takes place even when position 3 of the lactam ring is occupied by an electron-accepting substituent, and direct introduction of an *N*-alkyl group into the lactam cannot be achieved. Isolation of the intermediate fluoroborates then enables them to be used directly for preparing the corresponding α-alkoxy-enamines and acetals of the lactam[61]: e.g.

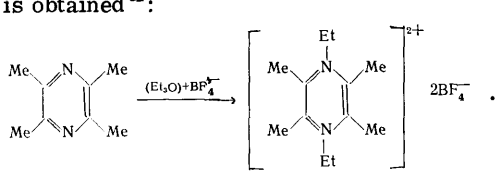


The above scheme shows that the use of tertiary oxonium salts makes possible the *N*-alkylation of compounds containing C=N double bonds.

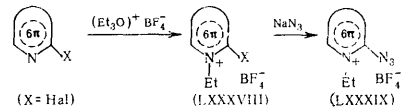
Heteroaromatic compounds similarly undergo smooth alkylation. Thus triethyloxonium fluoroborate acts on pyridine to give the *N*-ethylpyridinium salt[1], and pyrazine and pyrimidine derivatives yield the corresponding diquaternary salts (LXXXVI) and (LXXXVII), which cannot be obtained by the use of other alkylating agents[92]:



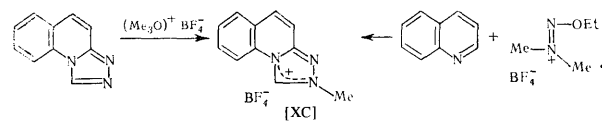
The yields of diquaternary salts decrease sharply when methyl groups are present in the $\alpha\alpha$-positions relative to the cyclic nitrogen atoms[92], and e.g. in the case of 2,3,5,6-tetramethylpyrazine only a 6% yield of the alkylation product is obtained[92]:



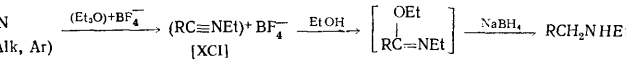
The alkylation of derivatives of thiazole, benzothiazole, naphtho[2,1-*d*]thiazole, benzoselenazole, benzimidazole, pyridine, isoquinoline, and 1,2,4-triazole also yields the corresponding fluoroborates (LXXXVIII), from which members of a new class of organic compounds—azidinium salts (LXXXIX)—have been prepared by reaction with sodium azide[93]:



Methylation of triazolo[4,3-*a*]quinoline with trimethyloxonium fluoroborate yields the corresponding fluoroborate (XC), whose structure has been proved by synthesis from quinoline and 2-ethoxy-1,1-dimethyldiazenium fluoroborate[94]:

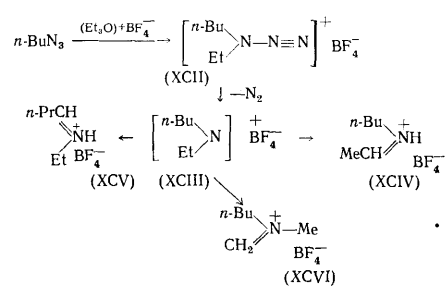


Trialkyloxonium fluoroborates act on nitriles to form nitrilium salts (XCI)[28,95,96], which on reduction with alcoholic sodium tetrahydroborate yield secondary amines[96]:



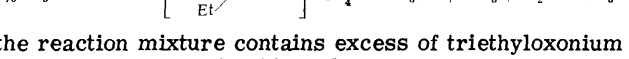
It should be noted that nitriles themselves are not reduced by alkali-metal tetrahydroborates.

Alkyl azides also undergo alkylation by triethyloxonium fluoroborate. With butyl azide, for example, the fluoroborate (XCII) is probably formed initially[97], and is then converted into a new salt (XCIII). The latter yields fluoroborates of Schiff bases (XCIV) and (XCV) together with an isomerisation product (XCVI):

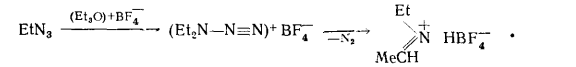


These compounds have not themselves been isolated, but their intermediate formation has been deduced from the presence of the corresponding amines and aldehydes after hydrolysis of the reaction mass[97].

The alkylation of triphenylsilyl azide proceeds rather differently, for the intermediate fluoroborate (which likewise was not isolated) undergoes cleavage without the evolution of nitrogen[98]:



If the reaction mixture contains excess of triethyloxonium fluoroborate, the ethyl azide undergoes further alkylation with the formation of ethylethylideneammonium fluoroborate[98]:



Tervalent phosphorus compounds react similarly to nitrogen-containing compounds, with the formation of quaternary phosphonium salts[88,99]:

$$PR_3 \xrightarrow{(Et_3O)^+BF_4^-} (EtPR_3)^+BF_4^-$$

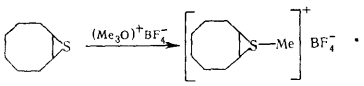
where R = OCH_3, OC_6H_5, $OCH_2CH_2C_6H_5$.

A considerable number of papers have been published on the *S*-alkylation of sulphur-containing compounds. Diethyl sulphide[4] and dimethyl disulphide[11] yield the corresponding sulphonium fluoroborates:

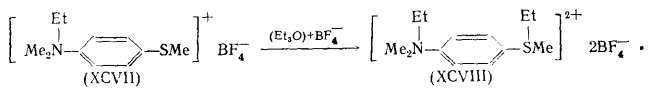
$$Et_2S \xrightarrow{(Et_3O)^+BF_4^-} (Et_3S)^+ BF_4^-$$

$$Me{-}S{-}S{-}Me \xrightarrow{(Me_3O)^+BF_4^-} (Me{-}S{-}SMe_2)^+ BF_4^-.$$

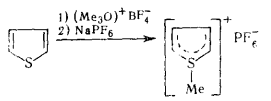
The alkylation of cyclo-octene sulphide occurs similarly[11]:



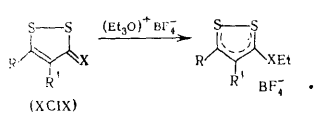
S-Alkylation takes place even when the sulphur atom is considerably depleted of electrons. Thus triethyloxonium fluoroborate acts smoothly on a *para*-substituted methyl phenyl sulphide (XCVII) containing in the ring such a strong electron acceptor as an ammonium group, with formation of a sulphonio-ammonium salt (XCVIII)[88]:



Even thiophen, in which the lone pair of the sulphur atom forms part of an aromatic sextet, has been alkylated[100]:

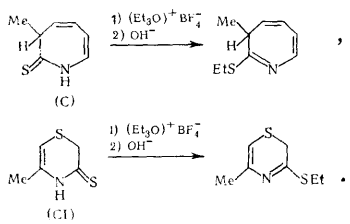


Thiocarbonyl compounds undergo alkylation by oxonium salts extremely readily. Thus the compounds (XCIX: X = S) give almost quantitative yields of the corresponding fluoroborates[101]:



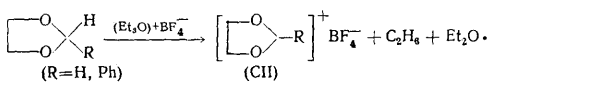
Appreciably lower yields of alkylation products are usually obtained when X = O[101].

Several examples have been described of the alkylation by triethyloxonium fluoroborate of thiolactams, e.g. thiocaprolactam[30], an azepinethione (C)[33], and a thiazinethione (CI)[102]. In all cases the final reaction products are the corresponding thiolactimidic esters:



D. TRIETHYLOXONIUM FLUOROBORATE AS ACCEPTOR OF THE HYDRIDE ION

Triethyloxonium fluoroborate can act not only as an alkylating agent but also as a hydride-ion acceptor[10,103,104]. It reacts with hydride-ion donors, e.g. dioxolan derivatives, to form carbonium ions (CII), ethane, and diethyl ether[10,103]:



It has also been reported[104] that triethyloxonium fluoroborate can act in this way with lithium tetrahydroaluminate and sodium tetrahydroborate.

The results surveyed in the present Review show that study of the chemistry of trialkyloxonium fluoroborates has proved extremely fruitful from both synthetic and theoretical points of view. The great reactivity of these salts, together with the relative simplicity of their preparation, makes them valuable starting materials for the synthesis of various organic compounds.

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Ordzhonikidze All-Union Research Institute
of Pharmaceutical Chemistry, Moscow