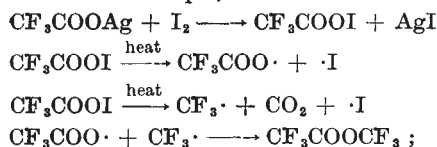# RECENT ADVANCES IN ORGANIC FLUORINE CHEMISTRY

By Dr. R. N. HASZELDINE

University Chemical Laboratory, Cambridge

THE preparation of fluoroiodides has enabled many routes of interest in synthetic organic fluorine chemistry to be developed.

Perfluoro esters and lactones. A method for the preparation of fluoroiodides by the interaction of iodine and heavy metal salts of fluoro mono- and di-basic acids has been described in earlier communications[1,2]. Thus $CF_3[CF_2]_nCOOAg$ and $AgOOC[CF_2]_nCOOAg$ with halogens yield $CF_3[CF_2]_nX$ and $X[CF_2]_nX$ (X = Cl, Br, I). The compounds of general formula $X[CF_2]_nX$ (n even) can also be obtained via polymerization of tetrafluoroethylene with iodine (X = I) followed by reaction with bromine or chlorine (X = Br or Cl)[3]. Other products from these reactions are now being identified. Thus, the interaction of iodine and the silver salt of trifluoroacetic acid or of heptafluorobutyric acid can be made to yield small amounts of trifluoromethyl-trifluoroacetate CF_3COOCF_3, and heptafluoropropyl-heptafluorobutyrate $C_3F_7COOC_3F_7$. These compounds, the first completely fluorinated esters to be reported, are believed to arise by a free radical mechanism : for example,

$$CF_3COOAg + I_2 \longrightarrow CF_3COOI + AgI$$
$$CF_3COOI \xrightarrow{heat} CF_3COO \cdot + \cdot I$$
$$CF_3COOI \xrightarrow{heat} CF_3 \cdot + CO_2 + \cdot I$$
$$CF_3COO \cdot + CF_3 \cdot \longrightarrow CF_3COOCF_3 ;$$

rather than by the simple ionic mechanism analogous to that which can be postulated to explain ester formation from hydrocarbon acids :

$$CH_3COOAg \xrightarrow{I_2} CH_3COOI \rightarrow CH_3I$$
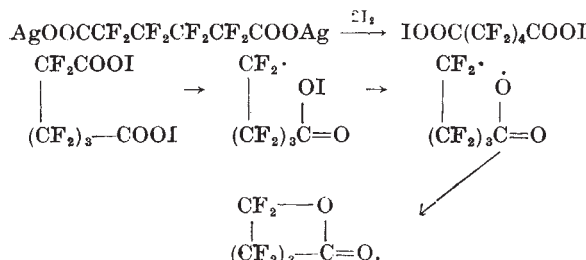$$CH_3COOAg + CH_3I \rightarrow CH_3COOCH_3 + AgI.$$
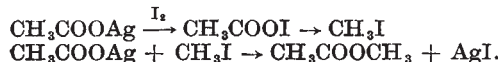
Heterolytic fission of the carbon–iodine bond in CF_3I under the conditions of the reaction is considered unlikely (cf. ref. 4). The properties of these volatile fluoro-esters, which have boiling points near those of the corresponding fluorocarbons, are being investigated.

The silver salts of dibasic acids react with iodine to give perfluorinated lactones as well as fluoroiodides. Thus silver perfluoroglutarate and perfluoroadipate yield
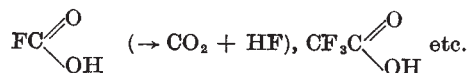
$$\overline{OCF_2CF_2CF_2CO} \text{ and } \overline{OCF_2CF_2CF_2CF_2CO},$$
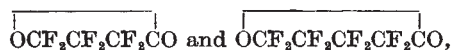
and again a radical rather than an ionic mechanism is preferred :

$$AgOOCCF_2CF_2CF_2CF_2COOAg \xrightarrow{2I_2} IOOC(CF_2)_4COOI$$

Although quite stable in a vacuum system, treatment of these lactones with aqueous reagents opens up the lactone rings to give transient compounds containing the $—CF_2OH$ group. These primary hydroxy fluorine compounds are unstable in aqueous media, and the quantitative loss of two fluorine atoms as fluoride ion can be demonstrated :
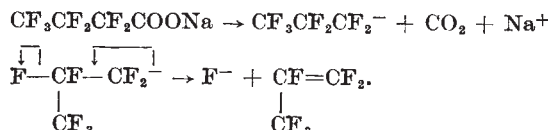
$$HOOC—(CF_2)_3—CF_2OH \rightarrow HOOC—(CF_2)_3—C{\underset{\textstyle OH}{\overset{\textstyle O}{\big\langle}}} + 2F$$
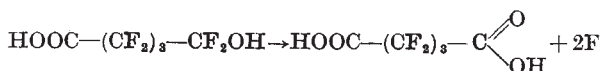
The dibasic fluoro-acid containing one less CF_2 group than the original acid is thus obtained. This indicates that the still unknown primary carbinols CF_3OH, C_2F_5OH, etc., would decompose in aqueous solution to give

$$FC{\underset{\textstyle OH}{\overset{\textstyle O}{\big\langle}}} \;(\rightarrow CO_2 + HF), \; CF_3C{\underset{\textstyle OH}{\overset{\textstyle O}{\big\langle}}} \; etc.$$

The stability of such primary fluoro-carbinols in non-aqueous media is still a matter for conjecture, however, and it may be possible to prepare these compounds from the perfluorinated esters or lactones.

Perfluoro olefins. Sodium trifluoroacetate reacts with iodine on heating to give CF_3I[2]. Sodium heptafluorobutyrate, however, yields C_3F_7I in relatively poor yield and the main product is $CF_3CF=CF_2$, the formation of which can be visualized as proceeding by an elimination of the type :
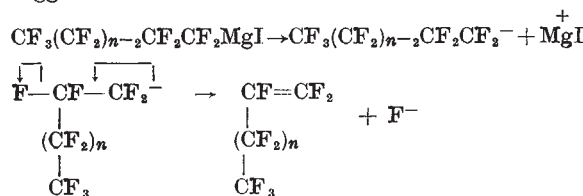
$$CF_3CF_2CF_2COONa \rightarrow CF_3CF_2CF_2^- + CO_2 + Na^+$$

$$F{-}\overset{\downarrow}{CF}{-}\overset{\downarrow}{CF_2}{-} \rightarrow F^- + CF=CF_2.$$
$$\underset{\textstyle CF_3}{|} \qquad\qquad \underset{\textstyle CF_3}{|}$$

Heptafluoroiodopropane, prepared from CF_3I and tetrafluoroethylene or from C_3F_7COOAg, can be converted into $CF_3CF=CF_2$ by means of zinc, and the olefin can also be prepared by the thermal dehydrofluorination of the C_3F_7H obtained from C_3F_7COOH by decarboxylation. Oxidation of the fluoro-olefin gives the acid containing two fewer CF_2 groups than originally, so that one can descend the homologous fluoro-acid series as well as ascend it by fluoroiodide reactions[1,3].

Perfluoro alkyl Grignard reagents. As reported earlier[3], the fluoroiodides $CF_3[CF_2]_nI$ yield Grignard reagents $CF_3[CF_2]_nMgI$. The essential technique for the Grignard preparation is to carry out the reaction in a completely anhydrous solvent such as an ether of suitable boiling point, with a high solvent to fluoroiodide ratio, slight excess of magnesium and operating at a temperature below $-30°$ C. ; $-50°$ to $-80°$ C. has been found convenient once the reaction has been initiated at room temperature, or at $-40°$ C. in the case of fluoroiodides with $n \geqslant 1$. Once Grignard formation has occurred, the temperature can be allowed to rise to $0°$ C. without appreciable decomposition and the compound to be treated can be added at some convenient temperature $-60°$ to $0°$ C. Alternatively, the compound to be
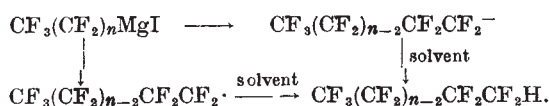
treated can be added after Grignard formation has been initiated and the temperature lowered, so that it is present during Grignard formation and reacts immediately. Yields of up to 65 per cent of the Grignard reagent have been obtained when $n > 1$.

The reactions so far investigated indicate that in the main the fluoro Grignard reagents react like hydrocarbon Grignard reagents. Compounds containing active hydrogen yield $CF_3[CF_2]_nH$; carbon dioxide yields $CF_3[CF_2]_nCOOH$, thus providing a simple method for fluoro-acid formation from longer-chain fluoroiodides (cf. ref. 1). The reactions of CF_3MgI, C_3F_7MgI and in certain instances C_2F_5MgI, with HCHO, CH_3CHO, CH_3COCH_3, C_2H_5CHO, $C_2H_5COC_2H_5$, CF_3COCH_3 and C_6H_5CHO have been found to proceed normally to give the carbinols; appreciable reduction occurs during these reactions, and the nature of the side reactions has not been completely determined. Ketones have been prepared by reaction with CH_3CN, CH_3COCl and C_6H_5COCl; the reactions with CF_3COCl or CF_3CN provide simple syntheses of perfluoro-ketones such as CF_3COCF_3, $CF_3COC_2F_5$ or $CF_3COC_3F_7$.

Elimination reactions of fluorine compounds. Decomposition of the Grignard reagent $CF_3[CF_2]_nMgI$, for example during its formation or on standing, yields $CF_3[CF_2]_nH$, $CF_3[CF_2]_{n-2}CF=CF_2$, MgF_2, MgI_2 and small amounts of the fluorocarbon $CF_3(CF_2)_{2n}CF_3$. The polymerization of the olefin, formed by the suggested elimination mechanism,

$$CF_3(CF_2)_{n-2}CF_2CF_2MgI \rightarrow CF_3(CF_2)_{n-2}CF_2CF_2{}^- + \overset{+}{MgI}$$

$$\overset{\downarrow\sqcap}{F}-CF-\overset{\downarrow\overline{\sqcap}}{CF_2}{}^- \rightarrow CF=CF_2 + F^-$$
$$\underset{CF_3}{\overset{\mid}{(CF_2)_n}} \qquad \underset{CF_3}{\overset{\mid}{(CF_2)_n}}$$

would account for the formation of polymeric material isolated under non-optimum conditions of Grignard formation and reaction. The formation of $CF_3(CF_2)_nH$ could involve an ionic or free radical mechanism:

$$CF_3(CF_2)_nMgI \longrightarrow CF_3(CF_2)_{n-2}CF_2CF_2{}^-$$
$$\downarrow \qquad\qquad\qquad \downarrow \text{solvent}$$
$$CF_3(CF_2)_{n-2}CF_2CF_2\cdot \xrightarrow{\text{solvent}} CF_3(CF_2)_{n-2}CF_2CF_2H.$$
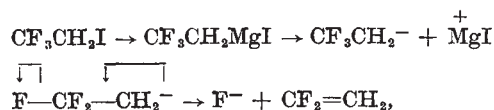
It is known that free perfluoroalkyl radicals will abstract hydrogen from solvents at room temperature[5]. The formation of the fluorocarbon $CF_3(CF_2)_{2n}CF_3$ thus probably occurs by a bimolecular reaction
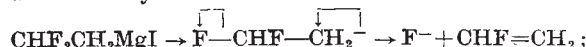
$$CF_3(CF_2)_{n-2}CF_2CF_2MgI + CF_3(CF_2)_nI \rightarrow$$
$$CF_3(CF_2)_{2n}CF_3 + MgI_2$$
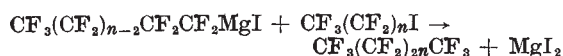
rather than by combination of really 'free' radicals.

The observations in the literature[6,7] that the reactions of CF_3CH_2I or CHF_2CH_2I with magnesium in ether lead to olefin formation and not to Grignard formation may be reinterpreted on the above basis:

$$CF_3CH_2I \rightarrow CF_3CH_2MgI \rightarrow CF_3CH_2{}^- + \overset{+}{MgI}$$

$$\overset{\downarrow\sqcap}{F}-\overset{\overline{\sqcap}}{CF_2}-CH_2{}^- \rightarrow F^- + CF_2=CH_2,$$

and similarly

$$CHF_2CH_2MgI \rightarrow \overset{\downarrow\sqcap}{F}-CHF-\overset{\overline{\sqcap}}{CH_2}{}^- \rightarrow F^- + CHF=CH_2;$$
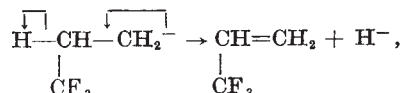
that is, Grignard formation does occur but is followed by decomposition under the unfavourable reaction conditions employed. The reaction of CHF_2CH_2Br with sodium or potassium[6] to give $CHF=CH_2$ can be similarly interpreted. There are indications that the application of the techniques used for the preparation of Grignard reagents from perfluoroalkyl iodides leads to the successful preparation of similar reagents from the dihydro fluoroalkyl halides CF_3CH_2I and CF_3CH_2Br. The carbon–iodine bond in CF_3CH_2I can be broken homolytically to give the $CF_3CH_2\cdot$ radical; the mercurial CH_3CH_2HgI has been prepared.

Application of the silver salt technique[1,2] to CF_3CH_2COOH, a compound prepared by the sequence

$$CF_3CH_2CH_2I \rightarrow CF_3CH_2CH_2OH \rightarrow CF_3CH_2COOH,$$

yields, by reaction with the appropriate halogen, CF_3CH_2I or CF_3CH_2Br.

It is noteworthy that olefin formation occurs only in fluorohalides which have a β-fluorine atom. Thus $CF_3CH_2CH_2I$[8] gives $CF_3CH_2CH_2MgI$, which reacts normally with many functional groups. Olefin formation from this Grignard is unlikely to involve

$$\overset{\downarrow\sqcap}{H}-CH-\overset{\downarrow\overline{\sqcap}}{CH_2}{}^- \rightarrow CH=CH_2 + H^-,$$
$$\underset{CF_3}{\overset{\mid}{}} \qquad\qquad \underset{CF_3}{\overset{\mid}{}}$$

and the $CF_3CH=CH_2$ obtained on heating the Grignard to $100°$ C. or during certain reactions, for example, with copper or with silver or cuprous halides to produce $CF_3(CH_2)_4CF_3$, is almost certainly formed by free radical disproportionation of two $CF_3CH_2CH_2$ radicals:

$$2CF_3CH_2CH_2\cdot \rightarrow CF_3CH_2CH_3 + CF_3CH=CH_2.$$

The presence of $CF_3CH_2CH_3$ can be demonstrated. Radical reactions to give olefin formation from, say, CF_3CH_2I or $CF_3(CF_2)_2MgI$ are unlikely, since they would involve homolytic fission of a C—F bond. Thus, it may well be that an important reaction of a fluorocarbanion will be to undergo an elimination reaction with expulsion of a β-fluorine atom as fluoride ion. Whereas olefin formation does not occur during Grignard formation from $CF_3CH_2CH_2I$, this fluoroiodide, like other fluoro-halo compounds containing the $CF_3(CF_2)_nCHCX$ unit, readily undergoes dehydrohalogenation with alcoholic alkali. The removal of β-hydrogen as a proton will clearly be facilitated by the electronegative β-$CF_3(CF_2)_n$ group tending to make the β-hydrogen atom relatively more acidic[10], for example,

$$OH^-\overset{\downarrow\sqcap}{\mid}H-CH-\overset{\downarrow\overline{\sqcap}}{CH_2}-\overset{\downarrow}{X} \rightarrow H_2O + X^- + CH=CH_2$$
$$\underset{CF_3}{\overset{\downarrow}{}} \qquad\qquad\qquad\qquad \underset{CF_3}{\overset{\mid}{}}$$
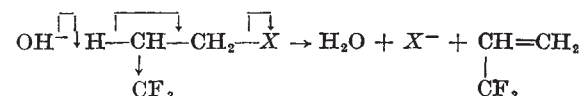
Perfluoroalkyl nitroso and nitro compounds. Other reactions under investigation are designed to produce further perfluoro compounds containing functional groups. The synthesis of perfluoroalkyl nitroso and nitro compounds is reported for the first time. Representative members of perfluoroalkyl iodides and di-iodides have been converted into the monomeric blue nitroso compounds, for example, $CF_3(CF_2)_nNO$, and into the nitro compounds, for example, $CF_3(CF_2)_nNO_2$. The reduction of these compounds to the corresponding amines is being attempted.

Perfluoro carbinols. The preparation of the carbinols $CF_3(CF_2)_nOH$, $[CF_3(CF_2)_n]_2CHOH$ and $[CF_3(CF_2)_n]_3COH$ by interaction of the perfluoroalkyl Grignard reagents with suitable reagents such as oxygen, perfluoroaldehydes (such as CF_3CHO), perfluoroketones (such as CF_3COCF_3), alkyl perfluoroacetates (such as CF_3COOEt), etc., is believed to have yielded, in specific examples, $(CF_3)_2CHOH$ and $(CF_3)_3COH$, the first completely fluorinated secondary and tertiary alcohols.

Zinc and cadmium perfluoroalkyls. Solutions of zinc and cadmium perfluoroalkyls have been prepared from the perfluoroalkyl iodides CF_3I and C_3F_7I, and as in the case of the Grignard reagents it is noticed that trifluoroiodomethane is the least reactive fluoroiodide. These new organometallic compounds also appear to react like their hydrocarbon analogues, though less readily, and may well prove advantageous (for example, in ketone preparation from acyl chlorides) in avoiding side-reactions found with the Grignard reagents.

Perfluoro acids. Application of the general method for the preparation of fluoro-acids from fluoroiodides has resulted in the synthesis of C_3F_7COOH [*], C_4F_9COOH, $C_5F_{11}COOH$, $C_6F_{13}COOH$, $C_7F_{15}COOH$, $C_8F_{17}COOH$, $C_9F_{19}COOH$ and $C_{11}F_{23}COOH$; derivatives and reactions of these long-chain acids have been examined. The use of the Grignard reagent provides a simpler method for converting fluoroiodides to fluoro-acids. Thus, while it is possible to apply the technique outlined earlier to perfluoroalkyl di-iodides $I[CF_2]_nI$ and hence obtain perfluoro dibasic acids $HOOC[CF_2]_nCOOH$, it is more convenient to prepare the di-Grignard reagent $IMg[CF_2]_nMgI$ ($n > 2$), since this reacts normally with carbon dioxide to give the required acid; reactions of the di-Grignard reagents with other functional groups are being investigated. Monohydro perfluoro acids of general formula $H(CF_2CF_2)_nCOOH$ have been prepared from the monohydro fluoroiodides $H(CF_2CF_2)_nI$ and also by the action of CH_3OH with C_2F_4 under free-radical conditions, isolation of the alcohols $H(CF_2CF_2)_nCH_2OH$, and oxidation of these to the acids.

The reaction of metallic sodium with ethyl trifluoroacetate in ethereal solution yields a mixture of products among which trifluoroacetoacetic ester and trifluoroethanol have been identified. The nature of high-boiling material formed during the reaction is being investigated. The expected diketone $CF_3COCOCF_3$, and the acyloin $CF_3CHOHCOCF_3$, are not formed under the conditions used, and the mechanism of this reaction is clearly of interest.

A perfluoro cyclic acid has been synthesized by the following route. The interaction of hexaiodobenzene and iodine pentafluoride yields, among other products, perfluoro cyclohexyl iodide $C_6F_{11}I$. This iodide yields a Grignard reagent $C_6F_{11}MgI$ which with carbon dioxide gives perfluoro cyclohexane carboxylic acid $C_6F_{11}COOH$ and perfluorocyclohexene C_6F_{10}, the latter arising by decomposition of the acid in aqueous media. It is of interest that the Grignard formation is again accompanied by olefin and by hydrocompound formation (see following reaction scheme). The acid may be converted into the chloride, bromide, or iodide by application of the silver salt reaction, while fluorination of the iodide yields perfluorocyclohexane. Preliminary examination indicates that $C_6F_{11}I$ shows many of the reactions associated with the perfluoroalkyl iodides. The perfluorocyclohexyl radical $C_6F_{11}\cdot$ is formed on heating or on exposure
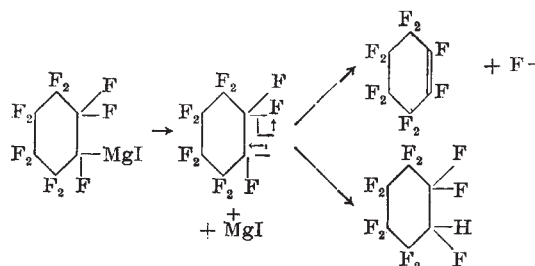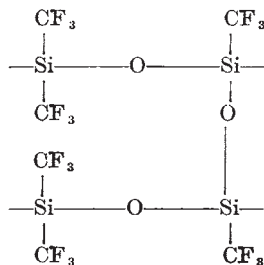

to ultra-violet radiation, and will add to unsaturated compounds. Acetylene, for example, yields $C_6F_{11}CH=CHI$, oxidation of which gives perfluorocyclohexene C_6F_{10} and only small yields of $C_6F_{11}COOH$. The oxidation product of perfluorocyclohexene, that is, perfluoro adipic acid, is also formed in substantial amount.

Infra-red spectra of fluorine compounds. The infra-red spectra of many compounds derived from fluoroacids and fluoroiodides have been taken and will be published in full later. Wave-lengths 'characteristic' of functional groups in fluorine compounds are tentatively assigned in the accompanying table, and may need revision as more samples become available. R_F denotes $CF_3, C_2F_5 \ldots$ etc., or C_6F_{11}; the third column of the table gives the values for corresponding hydrocarbons.

R_FCOOH	5·60–5·65	5·85
R_FCOOEt } R_FCOOMe }	5·6	5·7–5·8
R_FCOONa } R_FCOOK }	5·9	6·15–6·4
R_FCOOAg	6·15–6·20	
R_FCONH_2	5·70–5·85 6·10–6·15	two bands 6·0–6·2
R_FCOCH_2—	5·65	5·9–6·0
R_FCOR_F	5·55	5·9–6·0
$R_FCO{>}0$ $R_FCO{>}0$	5·3, 5·5	5·36–5·48 5·6–5·7
R_FCHO	5·6–5·7	5·8–5·9
R_FCOF	5·3	
R_FCOCl	5·4–5·5	5·52–5·54
R_FCN	4·45	4·3–5·3
$R_FC{\equiv}CH$	4·6–4·7 for C≡C 3·01 for C—H	4·6–4·7 2·95
R_FCH_2OH	2·99 for OH	c. 3·0
$R_FCH(OH)_F$	3·03 for OH	
R_FI	c. 13·5–14·5	
R_FBr	c. 13·0–13·5	
R_FCl	c. 12·8	
$R_FCH=CH_2$	5·99 10·2, 10·4	6·08 10·1, 11·0
$R_FCH=CHCl$	6·06 10·7	
$R_FCH=CHBr$	6·08 10·7	
$R_FCH=CHI$	6·15–6·20 10·55–10·65	
$R_FCBr=CH_2$	6·1 10·7, 11·9	6·1 11·2
$R_FCH=CHCH_3$ *trans*	5·90 10·4	6·0 10·36
$R_FCH=CHCF_3$ *trans*	10·4	10·36
$R_FCH=CHCF_3$ *cis*	5·95	6·02
$R_FCH=CHCOOH$ *trans*	5·85 6·00 10·28	5·85 6·05 10·30
C_6F_{10} cyclic	5·76	
$R_FCF=CF_2$	5·57	
$R_FCF=CFR$	5·78	

Perfluoroalkyl silicon compounds. It would clearly be of interest if the stability and inertness of fluorocarbons could be combined with the valuable properties of silicones, that is, if fluoro-silicones could be produced. From what is now known of perfluoroalkyl organo-metallic and -metalloidal compounds, it is not at all certain that perfluoro silicones will be

resistant to hydrolysis. Two routes have been followed to prepare perfluoro-silicon compounds for examination. In the first, the perfluoroalkyl Grignard reagents have been found to react with $SiCl_4$ to yield a mixture of products from which $(CF_3)_2SiCl_2$, for example, has been isolated ; other compounds such as $Si(CF_3)_4$, CF_3SiCl_3, etc., are undoubtedly present. In the second instance, the interaction of fluoro-iodides and silicon–copper has been found to yield fluoroalkyl silicon compounds together with dispro-portionation products. From such compounds it may well be possible to prepare silicones of the type

$$
\begin{array}{ccc}
CF_3 & & CF_3 \\
| & & | \\
-Si & -O- & Si- \\
| & & | \\
CF_3 & & O \\
& & | \\
CF_3 & & | \\
| & & | \\
-Si & -O- & Si- \\
| & & | \\
CF_3 & & CF_3
\end{array}
$$

Even if such polymeric compounds cannot be obtained or should they prove unstable, perfluoro silicon compounds of a different and more suitable type might become possible. Furthermore, it should be emphasized that although fluoroiodides have been used for much of the work described in this and earlier communications, it is distinctly possible that fluorobromo compounds might undergo many similar reactions. There are indications that perfluoroalkyl bromides yield Grignard reagents $CF_3(CF_2)_nMgBr$, and that they can undergo free-radical reactions involving addition to olefins[11].

As the chemistry of fluorine and its organic com-pounds progresses, it becomes increasingly evident that a vast new field of study is being opened up, a field of chemistry that will eventually considerably supplement the more established field based on hydrocarbon chemistry. [Aug. 24.

[1] Haszeldine, Nature, 166, 192 (1950).
[2] Haszeldine, J. Chem. Soc., 584 (1951).
[3] Haszeldine, Nature, 167, 139 (1951)
[4] Banus, Emeléus and Haszeldine, J. Chem. Soc., 60 (1951).
[5] Banus, Emeléus, and Haszeldine, J. Chem. Soc., 3041 (1950).
[6] Henne, J. Amer. Chem. Soc., 60, 2275 (1938).
[7] Gilman and Jones, J. Amer. Chem. Soc., 65, 2037 (1943).
[8] Haszeldine, J. Chem. Soc., 2856 (1949).
[9] Haszeldine, J. Cnem. Soc., 2789 (1950).
[10] Haszeldine, J. Chem. Soc., 2495 (1951).
[11] Steele and Haszeldine (unpublished).

LECTOTYPES IN MYCOLOGY : A TAXONOMIC PROPOSAL

By E. J. H. CORNER

Botany School, Cambridge

I WISH to direct the attention of taxonomists to a procedure which is becoming common, at least in the nomenclature of Basidiomycetes. It is the method of proposing types (lectotypes) for genera of more than one species. Such typification is, of course, the goal of generic nomenclature, and the need for it in Basidiomycetes is great, where many highly artificial, untypified assemblages must be combed into homogeneous genera. Typification by a lecto-type, however, amounts to generic emendation, inasmuch as species which do not qualify with the lectotype must be excluded. Emendation implies generic and specific revision, comprehensive enough to satisfy modern standards of classification. The scientific approach would be first to revise the genus and its allies, so as to obtain a clear insight into the relationships of the species, and then, in the resultant monograph, to consider lectotypes with the utmost caution in view of the facts that knowledge is always imperfect and that a lectotype once accepted cannot be changed. Unfortunately, the procedure of which I complain proposes the lectotypes first by reference to early (and, scientifically, elementary) publications, without basic revision, without re-definition of genera, even without personal acquaintance with the organisms concerned, and leaves to posterity the real task of evaluating the proposals by study of the species[1-5]. The cart is put before the horse, and, to change the metaphor, the botanist is left in the dark, because fundamental knowledge of the structure of these fungi, on which better classification depends, is so dim. As it is easier to consult libraries than it is to become personally acquainted in microscopic detail with a large number of species, this procedure is becoming a popular expedient to the detriment of mycology. Genera, of course, are not dictated, but are discerned from the study of species.

I will give two examples of the disconcerting con-sequences of this procedure. They are drawn from the Clavariaceæ and result from the publication of my monograph, which was reviewed in Nature[6]. Many more could be cited, especially from the Polyporaceæ. In fact, there must be so many instances of this procedure among cryptogams generally that I hope my proposal will call for approval at the next International Botanical Congress.

Lachnocladium Lév. was described with seven species, none designated as the type. By 1940, it had 113 specific names and was clearly heterogeneous. L. furcellatum (Fr.) Lév., as one of the seven, was then proposed as the lectotype, without anything more being known about it than was published in 1830 : indeed, none of the original species had been re-described ; scarcely any of the whole genus had been described with any exactitude, and there was no attempt to revise the tropical 'clavarias' which are the content of the genus[1,2,4]. In the meantime, I was working on my monograph of the whole family, for the express purpose of modernizing descriptions and discovering generic limits. I interpreted Lachno-cladium on L. brasiliense Lév., another of the seven, because it represented the largest tropical group of species that required generic differentiation, while conforming with the original diagnosis, and because type-material was available in Kew and Paris. In consequence, the genus became the most distinctive and, taxonomically, the most important among all the clavarioid fungi, instead of being the nondescript receptacle for all 'tough' clavarias from the tropics. I deliberately avoided L. furcellatum because it was based on three collections (Brazil, Guinea, Bourbon), which were then as inaccessible to me as they had been to others. Now, six years later, through the kindness of Dr. Seth Lundell, of the Institute of Systematic Botany at Uppsala, I have been able to examine the only original collection of L. furcellatum that there is in the Friesian herbarium, namely, the Brazilian collection of Beyrich's. It does not belong