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REVIEW

SYNTHESIS OF 1,2-DISUBSTITUTED POLYFLUOROBENZENES*

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During the past 25 years there has been a tremendous growth in the chemistry of polyfluoroaromatic compounds, the unique properties of which suggest their wide utility in various fields of modern technology. The scope of synthetic methods available at present allows the preparation of almost any polyfluoroaromatic compound. The general approaches and specific procedures are reported in monographs and reviews [1- 10].

This review is devoted to the synthesis of 1, 2-disubstituted polyfluorobenzenes, which, like their non-fluorinated analogues, are important intermediate products in routes to condensed aromatic and heterocyclic compounds. It is appropriate to classify methods for the preparation of 1,2-disubstituted polyfluorobenzenes into five principal groups.

1. METHODS BASED ON INTRODUCTION OF FLUORINE ATOMS TO THE AROMATIC RINGS OF COMPOUNDS o-C_6H_4XY

In 1960-61 Tatlow and his co-workers showed that their new method of synthesis of hexafluorobenzene by fluorination of benzene with transition metal fluorides [11] with subsequent catalytic defluorination of the resulting perfluoroalicyclic compounds is

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* Polyfluoroaromatic compounds containing non-fluorine substituents (including H) ortho to each other.

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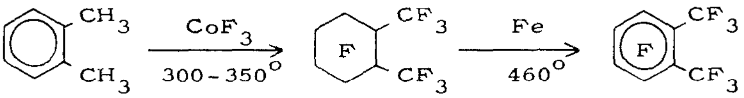
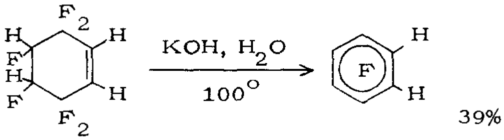
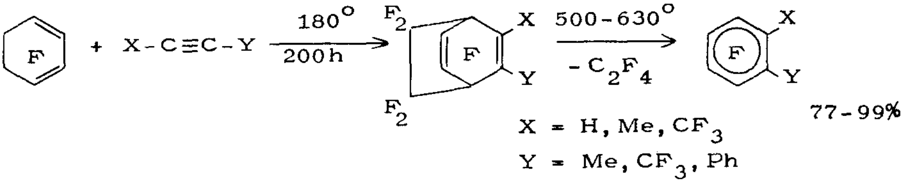
applicable to the synthesis of hexafluorobenzene homologues and partially fluorinated aromatic hydrocarbons, in particular perfluoro-o-xylene and 1,2,3,4-tetrafluorobenzene [12, 13].



The latter was obtained in 39% yield by dehydrofluorination of 4H/5H-3,3,4,5,6,6-hexafluorocyclohexene in the presence of an aqueous alkali [14].



One of the disadvantages of the method of fluorination - defluorination lies in the difficulty of isolation of individual compounds from the mixtures of products with similar properties. A modification of the method, proposed in 1969, involves the Diels-Alder reaction of perfluorocyclohexa-1,3-diene with acetylene derivatives and subsequent aromatisation by abstraction of the tetrafluoroethylene molecule [15].

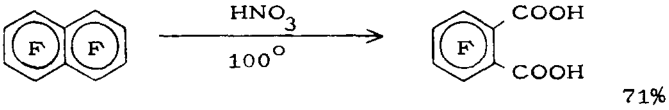


X = H, Me, CF_3
Y = Me, CF_3, Ph

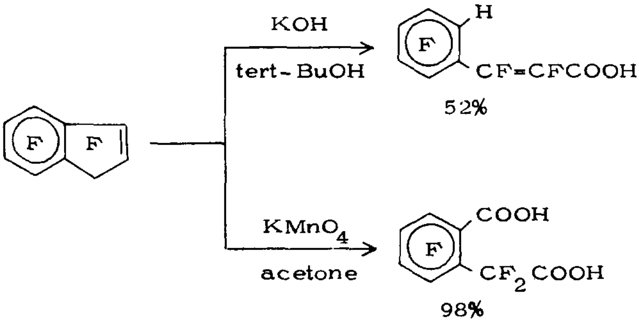
The process only succeeds when the groups X and Y are stable to thermolysis. An attempt to prepare diethyl tetrafluorophthalate by this method led to abstraction of the COOEt group in the second step. Better results were obtained by using a different approach, consisting in substitution of chlorine atoms in perchlorinated derivatives of phthalic acid with fluorine atoms in the presence of potassium fluoride [16-18].

2. METHODS BASED ON CLEAVAGE OF CONDENSED POLYFLUOROAROMATIC COMPOUNDS

There are a few examples of the preparation of ortho-substituted polyfluorobenzenes by cleavage of carbocyclic rings in condensed polyfluoroaromatic compounds. Reference [19] reports a synthesis of tetrafluorophthalic acid by oxidation of octafluoronaphthalene. In 1968 a more convenient variant of this reaction was suggested [20].



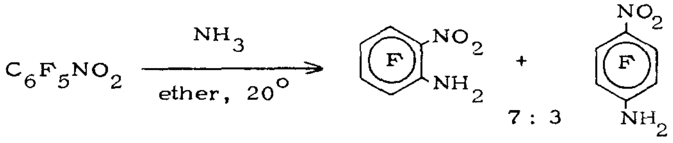
Soviet scientists report [21] very interesting reactions of alkaline and oxidative cleavage of perfluoroindene readily available from pentafluorophenol [22, 23]. These reactions smoothly give otherwise unavailable o-H-hexafluorocinnamic and hexafluorohomophthalic acids.



3. NUCLEOPHILIC SUBSTITUTION OF FLUORINE IN COMPOUNDS C_6F_5X

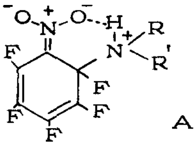
Nucleophilic substitution of fluorine is the principal method of introducing substituents directly into the polyfluorinated aromatic ring [24]. Substitution at the para-position predominates in the reactions of compounds of the type C_6F_5X with nucleophiles. The groups activating nucleophilic substitution, and a number of deactivating groups, are para-orientants. Strong electron donors (O^-, NH_2), which decrease the reaction rate by several orders, direct incoming nucleophiles into positions meta to substituent X. Yields of ortho-isomers usually do not exceed a few per cent.

When the character of the group X and the reaction conditions allow specific interaction with the nucleophilic reagent, significant or predominant substitution of ortho-fluorine takes place. The predominant ortho-orientation was first observed in reaction of pentafluoronitrobenzene with ammonia in ether [25].



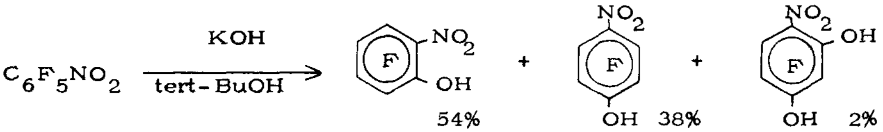
Currently there are many examples of the enhanced substitution of ortho-fluorine in compounds C_6F_5X by amino, alkylamino or arylamino groups (see Table 1). Most of the reactions listed in Table 1 may be used for the preparative synthesis of ortho-disubstituted tetrafluorobenzenes.

The most likely mechanism explaining [26] the predominant ortho-orientation, is considered to be hydrogen bonding between nucleophile and substituent X in a cyclic transition state of the type A [24]. This mechanism operates not only in reactions with amines



A

but also in reactions with other nucleophiles containing active hydrogen [38-40].



Increased yields of ortho-isomers are observed in cases when the substituent and the attacking molecule can form a donor-acceptor complex such as B.

TABLE 1

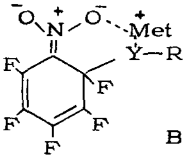
Reactions of C_6F_5X with amines

X	Nucleophile	Solvent	Yield of *ortho*-isomer in %, or *ortho*:*para* ratio	References
NO_2	NH_3	ether	51-58	25-27
-"-	$MeNH_2$	ether-ethanol	60	26
-"-	-"-	benzene	77:23	28
-"-	$PhNH_2$	ether	22	29
-"-	$p\text{-}MeC_6H_4NH_2$	benzene	71	30
NO	$MeNH_2$	ethanol	3 : 2	31
$-\underset{\substack{\downarrow \\ O}}{N}Y$	$RR'NH$	benzene	60-90 *	32
CHO	Me_2NH	ether	3 : 2	33
COOH	$MeNH_2$	ethanol	31	34
-"-	-"-	benzene	45 : 55	28
-"-	Me_2NH	-"-	47 : 53	28
COOEt	$MeNH_2$	-"-	35 : 65	28
COMe	-"-	-"-	36 : 64	28
-"-	$PhNH_2$**	dioxan	56	35
-"-	$ArNH_2$***	-"-	30 - 70	36
COPh	$PhNH_2$	$(i\text{-}C_5H_{11})_2O$	42	35
COC_6F_5	-"-	THF	46	35
SO_2Me	$MeNH_2$	benzene	58 : 42	28
$POPh_2$	-"-	benzene-ethanol	49	37
$PSPh_2$	-"-	-"-	46 : 54	37

*Yield of $2,6\text{-}(RR'N)_2C_6F_3N\frown Y$.

**In the presence of K_2CO_3.

***Ar = *m*- or *p*- MeC_6H_4; *o*-, *m*-, *p*- $MeOC_6H_4$; *p*-$Me_2NC_6H_4$; *p*- BrC_6H_4.
In the presence of K_2CO_3.



B

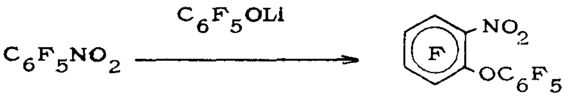
Examples of such reactions are given in Table 2.

TABLE 2

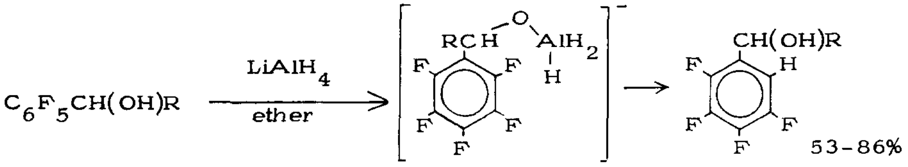
Reactions of C_6F_5X with ROMet and RSMet

X	Nucleophile	Solvent	Ortho : para ratio (by GLC)	References
COOEt	EtONa	ether-ethanol	97 : 3	28
SO_2Me	-"-	-"-	87 : 13	28
NO_2	-"-	-"-	55 : 45	28
-"-	C_6F_5OK	dioxan	89 : 11	41
-"-	NC_5F_4SK	ether	63 : 37	41
-"-	C_6F_5SK	-"-	68 : 32	38

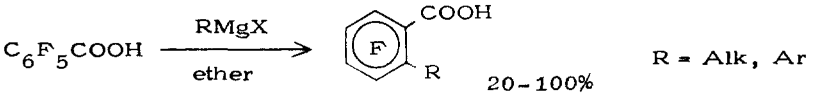
The highest yields of *ortho*-isomers obtained by substitution via transition states of type B are expected in non-polar solvents and with alkali metals possessing the highest complexing ability. Thus, the reaction of pentafluoronitrobenzene with lithium pentafluorophenoxide in dioxane, toluene or dichloroethane gives exclusively *ortho*-isomer [41].



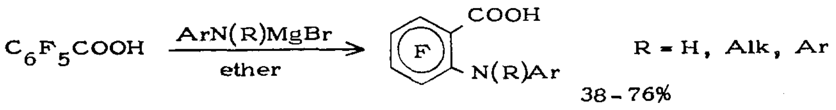
The reason for the unusually easy and selective substitution of *ortho*-fluorine by hydrogen in the reaction of polyfluorophenylcarbinols with $LiAlH_4$ was assumed to be the intermediate formation of a complex ion of type C, where the nucleophile is held near the reaction centre [42].



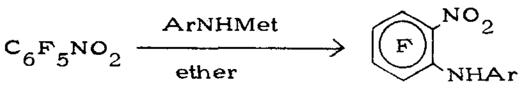
A mechanism involving formation of a cyclic transition state of type B has also been suggested for the substitution reactions of polyfluoroaromatic carbonyl compounds (pentafluorobenzoic acid, its ethers and polyfluorobenzophenones) with RMgX in ether, where ortho-fluorine is substituted by the Grignard reagent radical [43-47]. Preservation of the carbonyl-containing group seems to be caused by its low reactivity due to the steric influence of ortho-fluorine atoms. This reaction is the best method of preparation of rather unavailable o-alkyl- and o-aryltetrafluorobenzoic acids from pentafluorobenzoic acid [44-46].



Similar reactions have been reported for polyfluoroaromatic azomethine compounds [48, 49]. The reactions may be conducted with organolithium compounds [49, 50], or with halomagnezylamines, which are the Grignard reagent analogues in structure and reactivity [48, 51-54]. Reactions of polyfluorobenzoic acids with bromomagnezylanilines are useful as a preparative method for the synthesis of polyfluorinated arylanthranylic acids [55, 56].

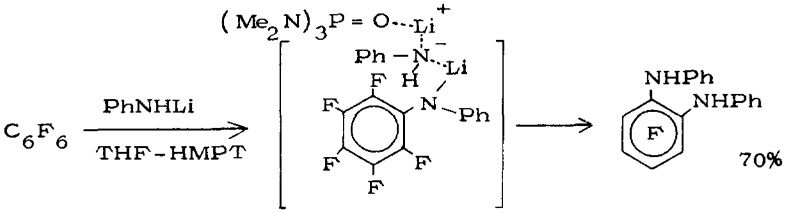


Substitution of ortho-fluorine in compounds C_6F_5X with arylamino groups may be carried out using lithium or sodium salts of aromatic amines [29].



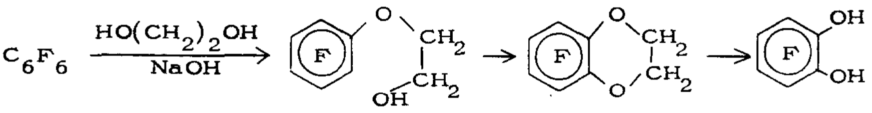
Met = Li, Na

The intermediate formation of a complex involving molecules of the reagent and the solvent seems to underlie Koppang's original synthesis of o-dianilinotetrafluorobenzene from hexafluorobenzene and PhNHLi in HMPT [57, 58].

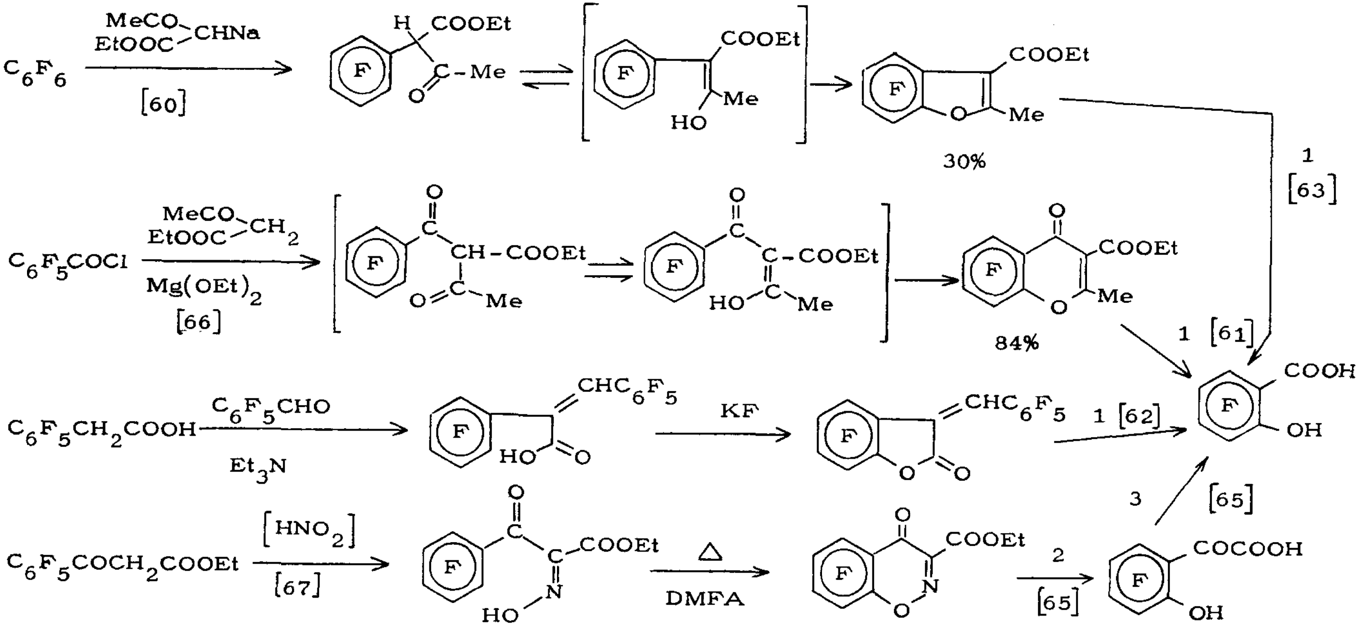


4. METHODS BASED ON THE INTRAMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTION

The first example of intramolecular nucleophilic substitution in polyfluoroaromatic compounds was obtained simultaneously in Great Britain and the U.S.S.R. by treatment of hexafluorobenzene with ethyleneglycol [59, 60].

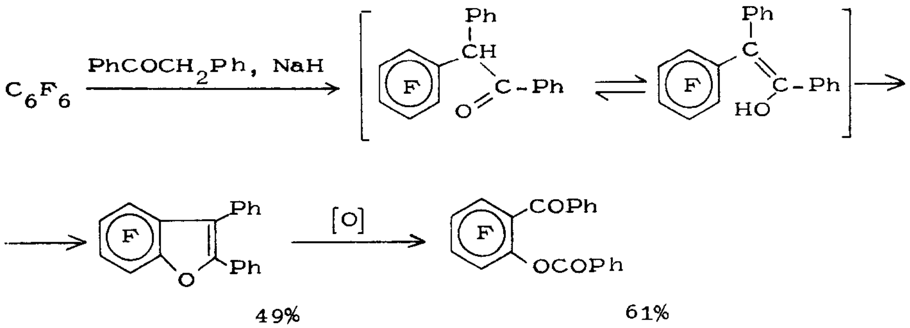


Scheme 1 represents the synthesis of tetrafluorosalicylic acid from oxygen-containing polyfluorobenzheterocycles - derivatives of chromone, oxazinone and cumaranone, through the intramolecular nucleophilic substitution reaction [61-65]. The preparative methods are those which involve one-step syntheses of benzheterocycles from available polyfluorinated aromatic compounds [60, 61, 63, 66].

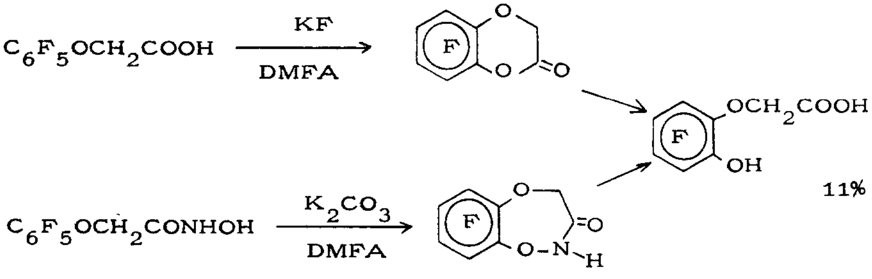


Scheme 1. Synthesis of tetrafluorosalicylic acid. Reagents: 1- $KMnO_4$, acetone; 2- HCl, H_2SO_4, MeCOOH; 3- K_2CO_3, H_2O.

The oxidative cleavage of 2,3-diphenyl-4,5,6,7-tetrafluorobenzofuran obtained from hexafluorobenzene [68] may be used for the synthesis of phenyl(2-benzoyl-3,4,5,6-tetrafluoro)benzoate [69].



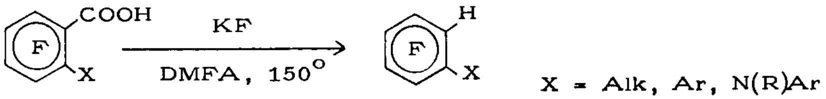
Reference [70] reports the one-step synthesis of ortho-disubstituted polyfluorobenzenes from compounds C_6F_5X in cases when the heterocycles formed by intramolecular nucleophilic substitution are unstable in the reaction conditions.



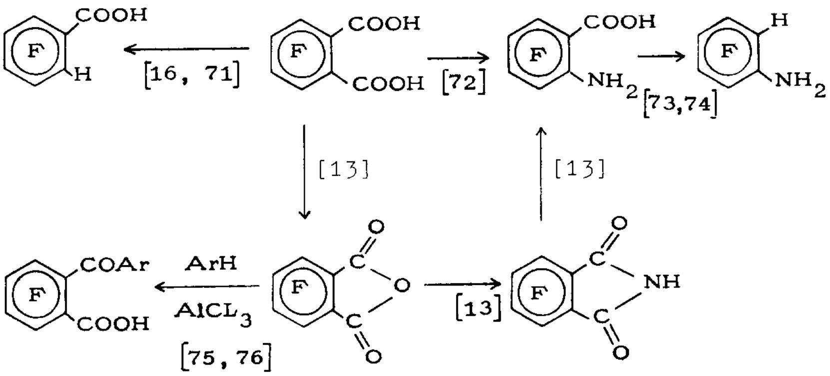
5. METHODS BASED ON CONVERSIONS OF FUNCTIONAL GROUPS IN COMPOUNDS C_6F_4XY

The most suitable starting compounds for synthesis of derivatives containing other groups are ortho-substituted polyfluorobenzoic acids and 1,2,3,4-tetrafluorobenzene.

Polyfluorinated aromatic acids are easily decarboxylated in basic media. The process is generally carried out by heating the acids in DMFA, sometimes in the presence of potassium carbonate of potassium fluoride [3]. Treatment in this way of ortho-alkyl- and ortho-aryltetrafluorobenzoic acids gave the otherwise inaccessible, partially fluorinated aromatic hydrocarbons [44, 45], and the reactions of polyfluoroarylanthranylic acids afforded diarylamines [52, 56].

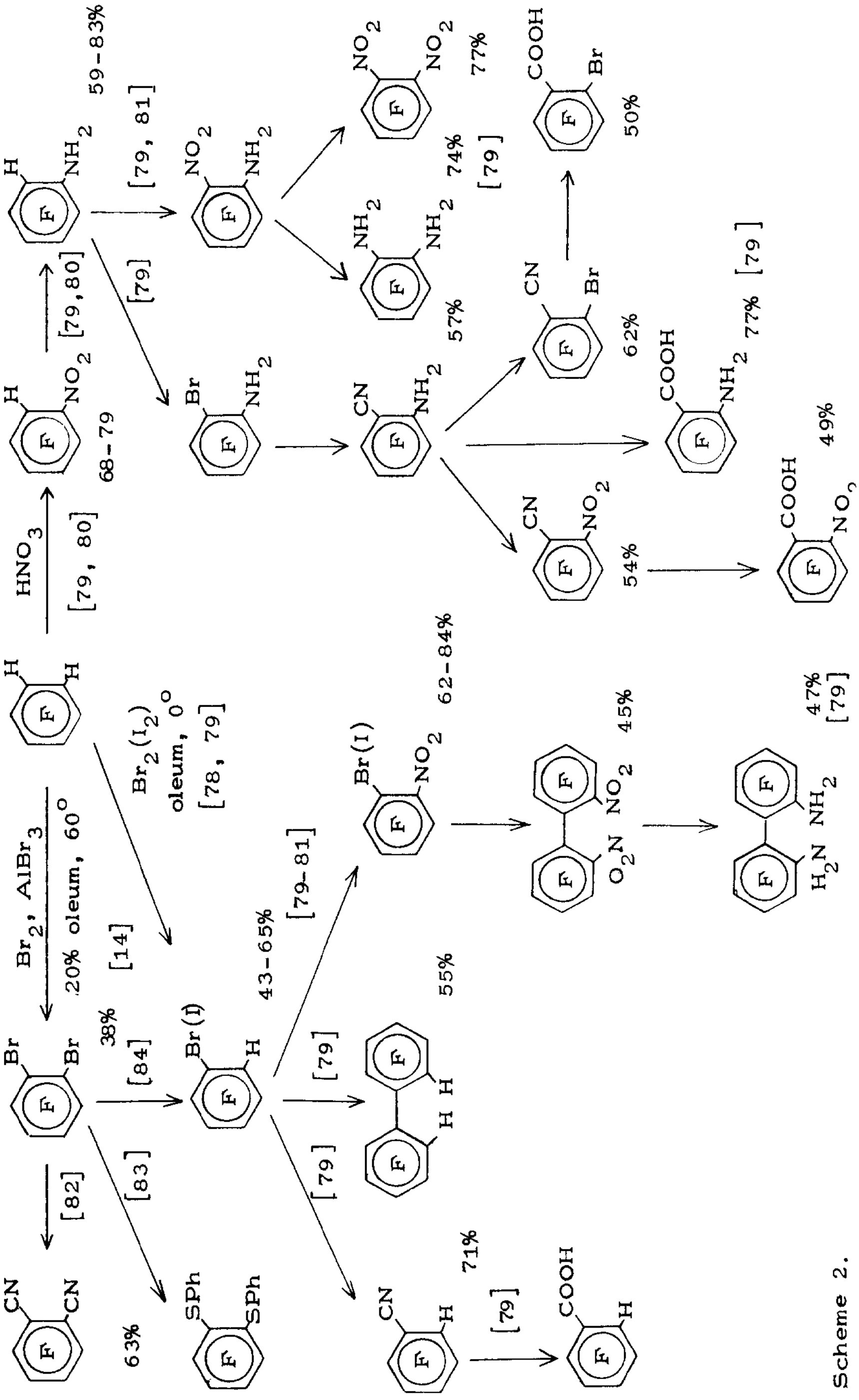


Heating of tetrafluorophthalic acid in DMFA leads to abstraction of one of the carboxyl groups and formation of 2,3,4,5-tetrafluorobenzoic acid [16, 71]. The following scheme shows transformations of tetrafluorophthalic acid used as a substrate for the preparation of a large number of ortho-disubstituted polyfluorobenzenes.



1,2,3,4-Tetrafluorobenzene can be utilized as a wide source of of ortho-disubstituted polyfluorobenzenes. Its synthetic uses fall into two main routes.

Partially fluorinated benzenes can undergo electrophilic substitution of hydrogen, unlike perfluoroaromatic compounds, the electrophilic attack of which leads to formation of addition products [77].

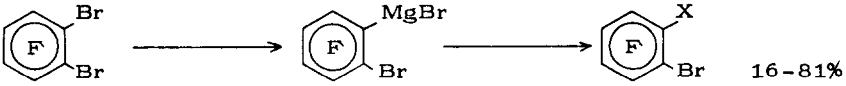

HNO$_3$
[79, 80]
68-79
[79,80]
59-83%
[79, 81]
[79]
74%
[79]
77%
57%
50%
62%
77%
[79]
49%
54%
Br$_2$, AlBr$_3$
20% oleum, 60°
[14]
Br$_2$(I$_2$)
oleum, 0°
[78, 79]
62-84%
45%
47%
[79]
38%
[84]
43-65%
[79-81]
55%
[79]
[82]
[83]
63%
[79]
71%
[79]
CN
SPh
Br(I)
H
NH$_2$
NO$_2$
COOH
Br
F

Scheme 2.

The deactivating effect of the fluorine atoms dictates more forcing conditions for such reactions. Examples of this approach are shown in Scheme 2.

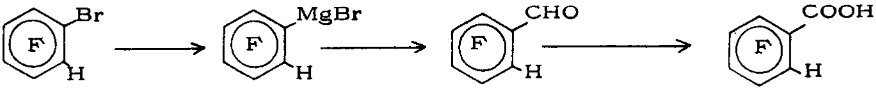
Bromination of 1,2,3,4-tetrafluorobenzene leads, depending on the conditions, to mono- or dibromo derivatives [14, 78, 79]. Nitration of 1,2,3,4-tetrafluorobenzene, or of 2,3,4,5-tetrafluorobromo(iodo)benzenes gives nitro-substituted derivatives in high yields [79-81]. Electrophilic substitution reactions of 1,2,3,4-tetrafluorobenzene with subsequent transformations of the products allow preparation of a wide range of 1,2-disubstituted polyfluorobenzenes. The major disadvantage of the method, especially in the cases of synthesis of ortho- substituted polyfluorobenzoic acids, is the multistep character of the reactions.

Carboxyl groups may be more conveniently introduced into polyfluoroaromatic rings by using organometallic reagents [2, 3]. Metallation of polyfluorobromo(iodo)benzenes or partially fluorinated benzenes with fluorine atoms ortho to hydrogen affords Grignard reagents [81, 85]. 1,2-Dibromotetrafluorobenzene reacts with magnesium in ether, ether-THF or in THF to give a monomagnesium derivative, further transformations of which yield various ortho-disubstituted derivatives of the type o-XC_6F_4Br [79, 86, 87].



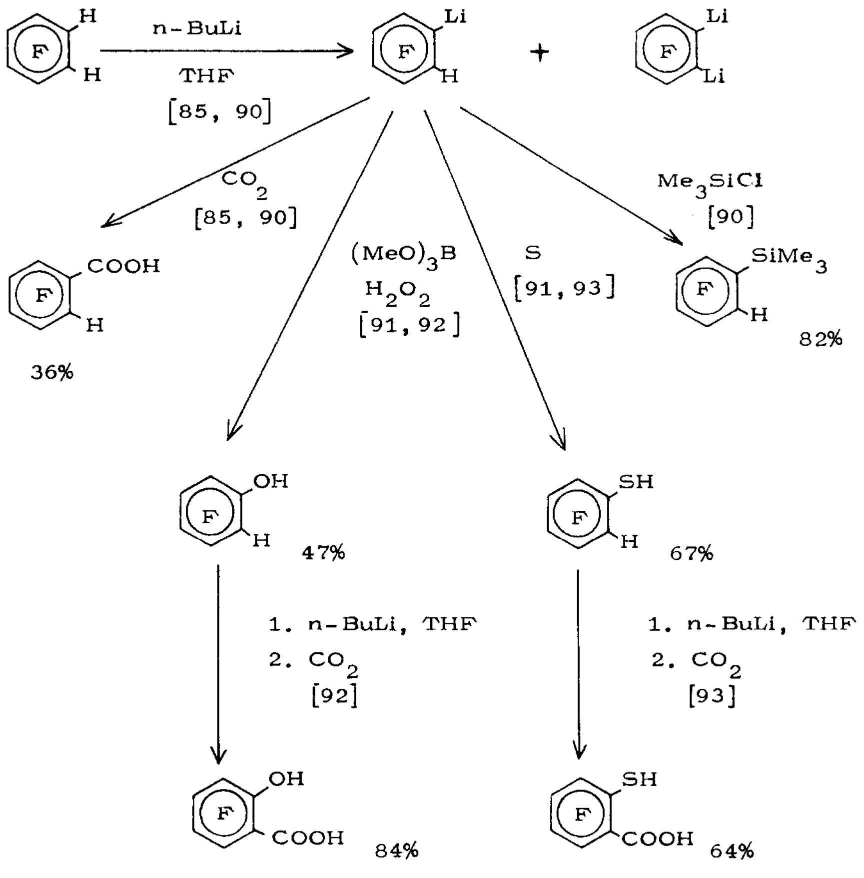
X = H, Me, COOH

A similar reaction of 2,3,4,5-tetrafluorobromobenzene has led to 2,3,4,5-tetrafluorobenzaldehyde further oxidized to the corresponding acid [79, 88].



1,2,3,4-Tetrafluorobenzene does not exchange hydrogen for metal when treated with EtMgBr or n-BuLi in ether [85, 89], but forms a mixture of mono- and dilithium derivatives with n-BuLi in

THF [85, 90]. Examples of the application of the latter reaction for the synthesis of polyfluorinated aromatic compounds are shown in Scheme 3. It should be noted that organolithium compounds and the corresponding carboxylic acids may be obtained from 2,3,4,5-tetrafluorosubstituted phenol [92], thiophenol [93], and aniline [79].



Scheme 3.

1,2-Dibromotetrafluorobenzene reacts with n-BuLi in hexane or ether-hexane to form the monolithium reagent which was the starting compound for the synthesis of the derivatives of sulphur, selenium, mercury, etc. [2, 86, 94-96]. With excess $TiCl_4$ ortho-bromotetrafluorophenyllithium yields o,o'-dibromooctafluorobiphenyl, which can be utilized as a source of a variety of o,o'-disubstituted octafluorobiphenyls [97-101], polyfluorinated derivatives of fluorene [84, 102], biphenylene [103] and dibenzothiophene [104, 105].

CONCLUSIONS

Thus it is clear that there are a multitude of approaches to the preparation of 1,2-disubstituted tetrafluorobenzenes. These compounds have attracted the attention of many chemists as important intermediates for the synthesis of otherwise difficultly accessible, synthetically useful and/or novel polyfluorinated heterocyclic systems. It is the authors' fervent hope that this review will be of assistance to further synthetic endeavours.

REFERENCES

1 J.C. Tatlow, Endeavour, 22 (1963) 89.

2 N.N. Vorozhtsov, Zh. Vses. Khim. Obshchest. im. D.I. Mendeleeva, 15 (1970) 52.

3 S.C. Cohen and A.G. Massey, Advances. in Fluor. Chem., 6 (1970) 83.

4 Synthesis of Fluororganic Compounds, I.L. Knunyants and G.G. Yakobson (eds.), Khimia Publishers, Moscow, (1973) 86.

5 Synthesis of Fluororganic Compounds, I.L. Knunyants and G.G. Yakobson (eds.), Khimia Publishers, Moscow, (1977) 37.

6 G.G. Yakobson and V.M. Vlasov, Synthesis, (1976) 652.

7 G.G. Yakobson and G.G. Furin, Synthesis, (1980) 345.

8 T.N. Gerasimova and E.P. Fokin, Uspekhi Khim., 49 (1980) 1057.

9 N. Ishikawa and Y. Kobayashi, Fluorine Compounds - Chemistry and Application, Kodonsha Scientific, 1979.

10 Reactivity of Polyfluoroaromatic Compounds, G.G. Yakobson (ed.), Nauka Publishers, Novosibirsk, 1983.

11 M. Stacey and J.C. Tatlow, Adv. Fluor. Chem., 1 (1960) 166.

12 P.L. Coe, C.R. Patrick and J.C. Tatlow, Tetrahedron, 9 (1960) 240.

13 B. Gething, C.R. Patrick and J.C. Tatlow, J. Chem. Soc., (1961) 1574.

14 E. Nield, R. Stephens and J. C. Tatlow, J. Chem. Soc., (1960) 3800.

15 L.P. Anderson, W.J. Feast and W.K.R. Musgrave, J. Chem. Soc. (C), (1969) 211.

16 G.G. Yakobson, V.N. Odinokov and N.N. Vorozhtsov, Zh. Obshch. Khim., 36 (1966) 139.

17 R.N. Haszeldine, British Pat. 1,026,290 (1966).

18 J.M. Birchall, R.N. Haszeldine and J.O. Morley, J. Chem. Soc. (C), (1970) 456.

19 G.G. Yakobson, V.D. Steingarts, N.N. Vorozhtsov, Zh. Vses. Khim. Obshchest. im. D.I. Mendeleeva, 9 (1964) 702.

20 P. Sartori and A. Golloh, Chem. Ber., 101 (1968) 2004.

21 V.M. Karpov, V.E. Platonov and G.G. Yakobson, Izv. Sibirsk. Otd. Akad. Nauk SSSR, (1974) N 2; Ser. Khim. Nauk, Issue 1, 124.

22 V.M. Karpov, V.E. Platonov and G.G. Yakobson, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 375.

23 V.M. Karpov, V.E. Platonov and G.G. Yakobson, Izv. Sibirsk. Otd. Akad. Nauk SSSR, (1977) N 4; Ser. Khim. Nauk, Issue 2, 129.

24 L.S. Kobrina, Fluor. Chem. Rev., 7 (1974) 1.

25 G.M. Brooke, J. Burdon and J.C. Tatlow, J. Chem. Soc., (1961) 802.

26 J.G. Allen, J. Burdon and J.C. Tatlow, J. Chem. Soc., (1965) 1045.

27 Reference 4, p. 201.

28 L.S. Kobrina, G.G. Furin and G.G. Yakobson, Zh. Org. Khim., 6 (1970) 512.

29 A.G. Hudson, A.E. Pedler and J.C. Tatlow, Tetrahedron, 26 (1970) 3791.

30 O.P. Sheremet, P.P. Rodionov and S.M. Shein, Izv. Sibirsk. Otd. Akad. Nauk SSSR, (1975) N 14; Ser. Khim. Nauk, Issue 6, 71.

31 J. Burdon and D.F. Thomas, Tetrahedron, 21 (1965) 2389.

32 M. Bellas, D. Price and H. Suschitzky, J. Chem. Soc. (C), (1967) 1249.

33 E.V. Aroskar, P.J.N. Brown, R.G. Plevey and R. Stephens, J. Chem. Soc. (C), (1968) 1569.

34 J. Burdon, W.B. Hollyhead and J.C. Tatlow, J. Chem. Soc., (1965) 6336.

35 T.N. Vasilevskaya, I.I. Baturina, M.I. Kollegova, T.N. Gerasimova and V.A. Barkhash, Zh. Org. Khim., 7 (1971) 1230.

36 T.N. Gerasimova, L.L. Gelumbovskaya, I.I. Baturina and E.P. Fokin, Izv. Sibirsk. Otd. Akad. Nauk SSSR, (1973) N 4; Ser. Khim. Nauk, Issue 2, 88.

37 J. Burdon, I.N. Rozhkov and G.M. Perry, J. Chem. Soc. (C), (1969) 2615.

38 G.G. Yakobson, G.G. Furin, L.S. Kobrina and N.N. Vorozhtsov, Zh. Obshch. Khim., 37 (1967) 1289.

39 J.M. Birchall, R.N. Haszeldine, J. Nikokavouras and E.S. Wilks, J. Chem. Soc. (C), (1971) 562.

40 Reference 4, p. 196.

41 L.S. Kobrina, G.G. Furin and G.G. Yakobson, Zh. Obshch. Khim., 38 (1968) 514.

42 T.N. Gerasimova, N.V. Semikolenova and E.P. Fokin, Zh. Org. Khim., 14 (1978) 100.

43 T.N. Gerasimova and I.I. Baturina, Zh. Org. Khim., 9 (1973) 639.

44 T.N.Gerasimova, I.I. Baturina, T.V. Fomenko, V.S.Chertok, V.F. Kollegov and E.P. Fokin, Zh. Org. Khim., 10 (1974) 2166.

45 T.N. Gerasimova, T.V. Fomenko and E.P. Fokin, Izv. Sibirsk. Otd. Nauk SSSR, (1975) N 12; Ser. Khim. Nauk, Issue 5, 100.

46 T.V. Fomenko, T.N. Gerasimova and E.P. Fokin, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1880.

47 T.N. Gerasimova, T.V. Fomenko and E.P. Fokin, Zh. Org. Khim., 13 (1977) 1562.

48 T.N. Gerasimova, N.V. Semikolenova and E.P. Fokin, Izv. Sibirsk. Otd. Akad. Nauk SSSR, (1977) N 4; Ser. Khim. Nauk, Issue 2, 142.

49 T. Sonoda, J. Inukai and H. Kobayashi, J. Fluor. Chem., 16 (1980) 529.

50 T.N. Gerasimova, L.N. Ogneva and E.P. Fokin, Izv. Sibirsk. Otd. Akad. Nauk SSSR, (1981) N 2; Ser. Khim. Nauk, Issue 1, 142.

51 T.N. Gerasimova and E.P. Fokin, Zh. Org. Khim., 9 (1973) 1758.

52 T.N. Gerasimova, N.V. Semikolenova, N.A. Orlova, T.V. Fomenko and E.P. Fokin, Izv. Sibirsk. Otd. Akad. Nauk SSSR, (1975) N 14; Ser. Khim. Nauk, Issue 6, 54.

53 N.A. Orlova, T.N. Gerasimova and E.P. Fokin, Izv. Sibirsk. Otd. Akad. Nauk SSSR, (1980) N 12; Ser. Khim. Nauk, Issue 5, 131.

54 N.A. Orlova, T.N. Gerasimova and E.P. Fokin, Zh. Org. Khim., 16 (1980) 1029.

55 T.N. Gerasimova and E.P. Fokin, USSR Pat. 490,797 (1977); Bullet. Izobret. (1975) N 41.

56 E.P. Fokin, T.N. Gerasimova, T.V. Fomenko and N.V. Semikolenova, Zh. Org. Khim., 14 (1978) 834.

57 R. Koppang, Acta Chem. Scand., 25 (1971) 3872.

58 R. Koppang, J. Organomet. Chem., 46 (1972) 193.

59 J. Burdon, V.A. Damodaran and J.C. Tatlow, J. Chem. Soc., (1964) 763.

60 G.G. Yakobson, T.D. Petrova, L.I. Kann, T.I. Savchenko, A.K. Petrov and N.N. Vorozhtsov, Dokl. Akad. Nauk SSSR, 158 (1964) 926.

61 A.T. Prudchenko, L.P. Vovdenko, V.A. Barkhash and N.N. Vorozhtsov, Khim. Geterotsikl. Soedin., (1968) 967.

62 V.P. Molosnova, V.A. Barkhash and N.N. Vorozhtsov, Zh. Org. Khim., 39 (1969) 1774.

63 T.D. Petrova, L.I. Kann, V.A. Barkhash and G.G. Yakobson, Khim. Geterotsikl. Soedin., (1969) 778.

64 V.M. Vlasov and G.G. Yakobson, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 893.

65 G.S. Shchegoleva, A.K. Petrov, V.A. Barkhash and N.N. Vorozhtsov, Khim. Geterotsikl., Issue 2 (1970) 278.

66 N.N. Vorozhtsov, V.A. Barkhash, A.T. Prudchenko and T.I. Khomenko, Dokl. Akad. Nauk SSSR, 164 (1965) 1046.

67 A.T. Prudchenko, G.S. Shchegoleva, V.A. Barkhash and N.N. Vorozhtsov, Zh. Obshch. Khim., 37 (1967) 2487.

68 Y. Inukai, T. Sonoda and H. Kobayashi, Bull. Chem. Soc. Japan, 52 (1979) 2657.

69 Y. Inukai, T. Sonoda and H. Kobayashi, Bull. Chem. Soc. Japan, 55 (1982) 337.

70 Y. Inukai, Y. Oono, T. Sonoda and H. Kobayashi, Bull. Chem. Soc. Japan, 54 (1981) 3447.

71 Reference 4, p. 170.

72 Reference 4, p. 175.

73 T.D. Petrova, V.P. Mamaev and G.G. Yakobson, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 679.

74 Reference 4, p. 191.

75 G.G. Yakobson, V.D. Steingarts, N.G. Kostina, O.I. Osina and N.N. Vorozhtsov, Zh. Obshch. Khim., 36 (1966) 142.

76 P.L. Coe, B.T. Croll and C.T. Patrick, Tetrahedron, 23 (1967) 505.

77 V.D. Steingarts and G.G. Yakobson, Zh. Vses. Khim. Obshchest. im. D.I. Mendeleeva, 15 (1970) 72.

78 J. Burdon, D.R. King and J.C. Tatlow, Tetrahedron, 22 (1966) 2541.

79 L.J. Belf, M.W. Buxton and J.F. Tilney-Bussett, Tetrahedron, 23 (1967) 4719.

80 P.L. Coe, A.E. Jukes and J.C. Tatlow, J. Chem. Soc. (C), (1966) 2323.

81 P.L. Coe and A.E. Jukes, Tetrahedron, 24 (1968) 5913.

82 L.J. Belf, M.W. Buxton and G. Fuller, J. Chem. Soc., (1965) 3372.

83 M.E. Peach and D.J. Sutherland, J. Fluor. Chem., 17 (1981) 225.

84 R.D. Chambers and D.J. Spring, J. Chem. Soc. (C), (1968) 2394.

85 R.J. Harper, E.J. Soloski and C. Tamborski, J. Org. Chem., 29 (1964) 2385.

86 D.E. Fenton, A.J. Park, D. Shaw and A.G. Massey, J. Organomet. Chem., 2 (1964) 437.

87 J.P.N. Brewer, J.F. Eckhard, H. Heaney and B.A. Marples, J. Chem. Soc. (C), (1968) 664.

88 M.D. Castle, R.G. Plevey and J.C. Tatlow, J. Chem. Soc. (C), (1968) 1225.

89 S.C. Cohen, D.E. Fenton, A.J. Tomlinson and A.G. Massey, J. Organomet. Chem., 6 (1966) 301.

90 C. Tamborski and E.J. Soloski, J. Organomet. Chem., 17 (1969) 185.

91 G.M. Brooke, B.S. Furniss, W.K.R. Musgrave and M.A. Quasem, Tetrahedron Lett., (1965) 2991.

92 G.M. Brooke and B.S.Furniss, J. Chem. Soc. (C), (1967) 869.

93 G.M. Brooke and M.A. Quasem, J. Chem. Soc. (C), (1967) 865.

94 R.D. Chambers, J.A. Cunningham and D.A. Pyke, Tetrahedron, 24 (1968) 2783.

95 S.C. Cohen and A.G. Massey, J. Organomet. Chem., 12 (1968) 341.

96 C. Tamborski and E.J. Soloski, J. Organomet. Chem., 10 (1967) 385.

97 S.C. Cohen and A.G. Massey, Chem. Commun., (1966) 457.

98 S.C. Cohen and A.G. Massey, Tetrahedron Lett., (1966) 4393.

99 S.C. Cohen and A.G. Massey, J. Organomet. Chem., 10 (1967) 471.

100 S.C. Cohen, D.E. Fenton, D. Shaw and A.G. Massey, J. Organomet. Chem., 8 (1967) 1.

101 S.C. Cohen, M.L.N. Reddy, D.M. Roe, A.J. Tomlinson and A.G. Massey, J. Organomet. Chem., 14 (1968) 241.

102 R. Filler and A.E. Fiebig, Chem. Commun., (1968) 606.

103 S.C. Cohen, D. Moore, R. Price and A.G. Massey, J. Organomet. Chem., 12 (1968) P 37.

104 R.D. Chambers and J.A. Cunningham, Chem. Commun., (1966) 469.

105 R.D. Chambers, J.A. Cunningham and D.J. Spring, Tetrahedron, 24 (1968) 3997.