Trihalogenmethanesulfenyl chlorides: preparation and use (part 2).

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2.2. Investigation of Ruhr-Universitat Bochum

For many years experts of the University have been studying different properties of DiCl and DiF as well as compounds produced with their use. It has been determined that (the) reactivity of S-Cl bond in the row of $Cl_{3-n}F_nCSCl$ (n=0-3) increases along with increase of n (80,90), effect of the nature of acid-binding agent on the reaction of DiCl with compounds of different classes has been investigated. Thus, the reaction with a heterocyclic compound, furan, takes place only in the presence of pyridine (83). Individual reactions of DiCl and DiF were studied also, for example with sodium acetate and silver trifluoracetate (68,85).

Sulfenylacetates produced allow to introduce sulfenyl group under soft conditions into thiophene for example. Also, a mechanism of hydrolysis of DiCl and DiF with a number of compounds and further conversions of the substances produced were studied:

1. with AgSCN (69,73)
2. with uracyl and mercaptouracyl (70,72). Similar sulfenyl substituted compounds were not decribed earlier. Pyridines were used as acid-bonding agents
3. with heterocycles
    a. adenine (76)
    b. pyrroles (78,82,91). Sulfenyl substituted compounds produced were studied for agrobiological activity. Synthesis was carried out in the presence of $C_4F_9SO_3H$ as a catalyst. The reaction medium influences the result of the synthesis. Interaction in ether gives a mixture of isomers while interaction in $CFCl_3$ results in substitution to position 2
    c. thiophene. Treatment of $ClCF_2SCl$ is carried out in the presence of a catalyst,F_3CSO_3H, the product produced is oxidized with H_2O_2 to form $–(O)_2$-$CCClF_2$ (92). $SnCl_4$ may be used as a catalyst also (77)
    d. furan. The reaction takes place in the presence of Lewis acids in a low yield (35%) in the presence of pyridine
4. Olefins. F_3CSO_3H is an effective catalyst for addition of DiCl and DiF to olefins also (cyclohexen, allylbromide, vinyl bromide) (87)
5. Selenium-containing compounds (81,89)
6. Dichlorophosphines (79)

7. Norborene. Norborene easily reacted with DiF and DiCl even in the absence of catalyst or solvent via skeletal rearrangement to give nortricyclanes (86)
8. Cyanamides. Cyanamides and substituted cyanamides form NN'bis(sulfenyl)chloroformamides (75)
9. There was shown a route to form sulfenylpyrazoles by condensation of ketones $RCOCH_2COCH_3$ (R=CH_3, C_2H_5-O) with DiCl or DiF to give $Cl_{3-n}F_nCSCH(COR)COCH_3$ and its following cyclization with phenylhydrazine to form pyrazole. Reaction of DiCl with diethyl malonates followed by cyclization with substituted hydrazine to the appropriate pyrazoles was carried out in a similar way (74,80).
10. Ammonia. It is possible to form bis- and tris(sulfenyl)amines by consecutive substitution of "H" for sulfenyl group(71).

2.3. BASF AG development

To produce effective fungicides, a reaction of interaction of N-containing compounds with DiCl in the presence of pyridine was used.

The following derivatives were used as N-containing compounds:

1. Anilides

   a)benzoanilides (93)

   b)formanilides (95)

2. methylimidazolcarboxamides (100)
3. hydantoin (94,97,98)
4. diurethane (96)
5. triazole (99)

2.4. Ciba-Geigy development

To produce active compounds the following substituted compounds were used:

1.pyrroles. Sulfenyl pyrroles produced are used as fungicides (103). Sulfenyl pyrroles woth different substituents are good wood preservatives, antifouling agents, bactericides, fungicides, algicides)(104).

2. acetamides. Sulfenyl substituents are microbicides (102)

3. imidazoles. N-sulfenyl substituted are bactericides and fungicides (101)

2.5. Development of other companies.

Bioactive compounds as plant protection have been produced by a similar technology in a number of other countries using the following derivatives as the second component of the reaction:

1.pyrazoles. Sulfenyl derivatives of pyrazoles are used in pesticidal compositions (108,109)

2. imidazoles. Compounds with sulfenyl group at position 4 are used as pesticide (110). N-sulfenyl substituted derivatives possess microbiocidic activity (105).

3. uraciles. Sulfenyl-substituted derivatives of uracile are applied in bactericidal and fungicidal compositions (106,107)

4. hydrazines. N'-sulfenyl substituted are used as insecticides (112)

Investigation of chemical properties of DiF and DiCl has been carried out by many countries. In South Korea trifluoroacetoxytrihalogenmethylmercaptanes were synthesized by interaction of DiCl with F_3CCO_2Ag (113), earlier similar products had been produced (68).

Prague Institute of Chemical Technology studied reactions of dichloromethanesulfinic acid with a number of compounds including DiCl which forms S-ethers with the mentioned acid (114).

At Univercitat Saarlandes the following fluorine-containing substances: CF_2ClSF, CF_2ClSF_3, CF_3SF_5, CF_3SF_3 (115) were synthesized by interaction of DiF with AgF_2, the reaction of DiF with HgF_2 (116) was studied also.

At Berginshe Universitat a research on production of polymerizable fungicides were conducted. N-(sulfenyl)-N-(4-met-hacryloyloxyphenyl) formamide was formed (117).

At Sheffield University interaction of DiF and DiCl with $(Si(CH_3)_3\text{-}O)_2POH$ and $(CH(CH_3)_2\text{-}O)_2POH$ resulted in formation of phosphorotioates (118), interaction of DiF and DiCl with $[(CH(CH_3)_2O)_2PO]_2CH\text{-}Me$ (where Me=Li,Na, CH_3) gave $[(CH_3CH_2CHO)_2PO]_2C{=}S(H)CCl_nF_{3-n}$ (119).

Conclusions

1. Dichlorofluoromethanesulfenyl chloride and chlorodifluoromethanesulfenyl chloride are used as one of initial components in synthesis of biologically active compounds to protect plants, and dichlorofluoromethanesulfenyl chloride exhibits the most activity.
2. With the purpose to get the most effective compounds, interaction of dichlorofluoromethanesulfenyl chloride with different compounds particularly with N-containing heterocycles was investigated.
3. German company BAYER AG is a leader in developments of bioactive compounds. They have developed a technology to produce dichloromethanesulfenyl chloride and parameters of processes of its interaction with different compounds. The developments of the company have been patented in Germany as well in other countries.
4. A wide scope of research on reactions using dichlorofluoro- and chlorofluoromethanesulfenyl chlorides has been carried out by Ruhr-Universitat Bochum.

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