# FLUOROINDENES

## 7. REACTION OF OCTAFLUOROINDENE WITH TRIHALOACETATES*

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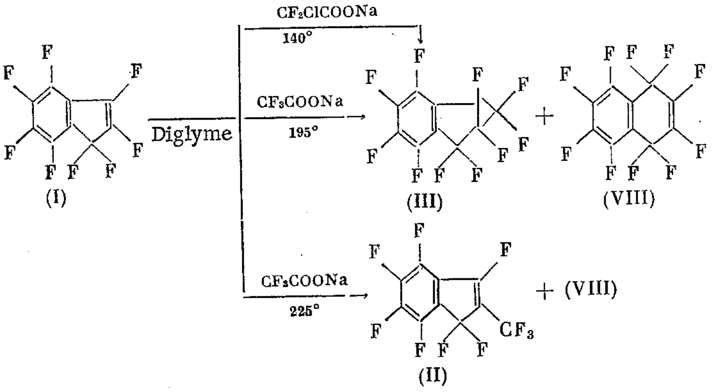
The reaction of octafluoroindene (I) with tetrafluoroethylene and hexafluoropropylene oxide as sources of difluorocarbene is known to afford perfluoro-2-methylindene (II) [2]. One mode of formation of the latter could be isomerization of the intermediate perfluoro-1,1a,6,6a-tetrahydrocycloprop[a]indene (III), the product of the cycloaddition of $:CF_2$ to (I) [2]. Reaction of indene with dihalocarbene (including $:CF_2$) sources, however, gives 2-halonaphthalenes via intermediate cyclopropane derivatives [3]. This difference in the behavior of indene and its perfluoro analog (I) led us to study the reaction of (I) with other $:CF_2$ sources and with $:CCl_2$ sources [4]. The present investigation concerned the reaction of (I) with $CF_3COONa$ (IV), $CF_2ClCOONa$ (V), and $CCl_3COONa$ (VI) in the absence of LiCl, and of $CCl_3COOCH_3$ (VII) in the presence of LiCl.

Reaction of (I) with salt (V) in diglyme at 140° affords the cyclopropane (III). Salt (IV) does not react under these conditions. At 195°, indene (I) and salt (IV) form (III), together with small amounts of perfluoro-1,4-dihydronaphthalene (VIII). Reaction of the indene (I) with salt (IV) in diglyme at 225° gives the methylindene (II) together with (VIII). The structures of (II), (III), and (VIII) were confirmed by comparison of their IR and $^{19}F$ NMR spectra with those of authentic samples.



Thus, the behavior of (I) in its reactions with salts (IV) and (V) in diglyme and with hexafluoropropylene oxide in the absence of a solvent [2] is similar. However, the effect of the solvent (diglyme) on the reaction of the indene (I) with salt (VI) is substantial.

Thus, reaction of (I) with (VI) in diglyme over the temperature range 80-140° gives 1-dichloromethyleneoctafluoroindan (IX) in addition to small amounts of 2-dichloromethyleneoctafluoroindan (X). The yields of (IX) and (X), calculated on (I) reacting, increase as the extent of reaction of the indene decreases, reaching 60-65 and 6-7%, respectively, at 15% reaction. The reaction of (I) with the methyl ester proceeds similarly in diglyme in the presence of LiCl and HMPA (cf. [5]).

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* For communication 6, see [1].

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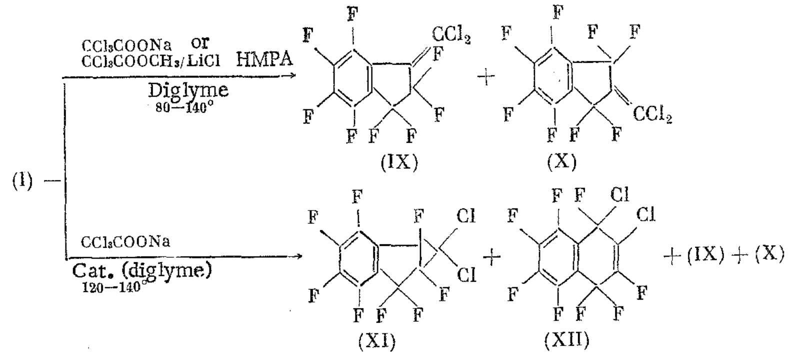
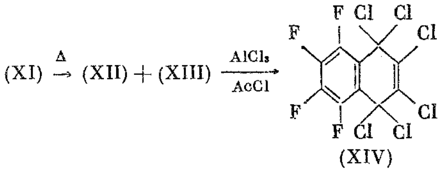


1,1-Dichloroperfluoro-1a,6a-dihydrocycloprop[a]indene (XI) was not found under these conditions. An attempt to obtain (XI) from the indene (I) and salt (VI) without the addition of a solvent was also unsuccessful, since in the absence of a solvent the salt (VI) failed to dissolve at 100-200°, and no reaction occurred.

When the indene (I) was reacted with salt (VI) in the presence of catalytic amounts of diglyme, we were able to obtain (XI), the product of the cycloaddition of $:CCl_2$ to indene (I). In addition to (XI), 1,2-dichloroperfluoro-1,4-dihydronaphthalene (XII) and the methyleneindans (IX) and (X) were obtained, together with unidentified compounds. The product ratios were temperature-dependent. At 120° the cyclopropane (XI) predominated, whereas at 140° the main product was the dihydronaphthalene (XII). The latter is probably formed from (XI) under the reaction conditions.

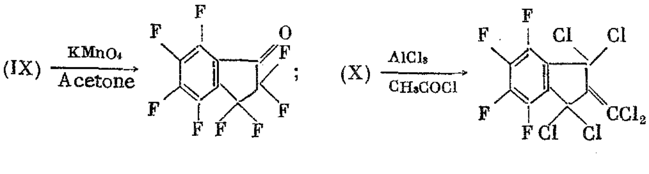
It was found that at 140°, in diglyme or in the absence of a solvent, (XI) was converted into a mixture of compounds, the principal product (~50%) being (XII). The mixture also appears to contain other isomeric dichloroperfluorodihydronaphthalenes (XIII) with chlorine atoms in the cyclohexadiene ring, since treatment of the mixture with $AlCl_3$ in AcCl afforded the known 1,1,2,3,4,4-hexachlorotetrafluoro-1,4-dihydronaphthalene (XIV) [6] in 80% yield. The methyleneindans (IX) and (X) were not found among the thermal degradation products from (XI).



Thus, the course of the isomerization of the cyclopropane (XI) into the dihydronaphthalene (XII) is markedly different from the behavior of its perfluorinated analog (III), which is converted to methylindene (II) [2]. Nevertheless, the behavior of (XI) on thermolysis is in agreement with the thermal conversion of the products of the cycloaddition of cyclocarbenes to indene to give 2-halonaphthalenes [3].

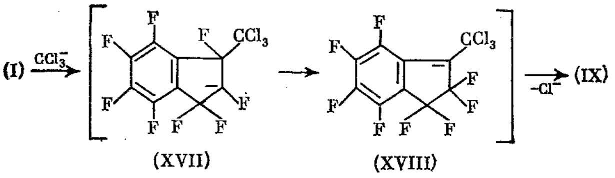
The structures of (IX)-(XII) were established from their elemental analyses, spectral features, and chemical reactions. Thus, the structure of the dihydronaphthalene (XII) was assigned on the basis of its conversion to (XIV) on treatment with $AlCl_3$, and also by comparison of its $^{19}F$ NMR spectrum with those of perfluoro-1,2- and perfluoro-1,4-dihydronaphthalenes [7], 1-chloroperfluoro-1,4-dihydronaphthalene [8], 1-chloro (XV) and 1,5-dichloroperfluoro-1,4-cyclohexadienes (XVI) [7]. The $^{19}F$ NMR spectrum of (XII) displayed signals at $\delta$ $-65.1$ ($2F^4$), $-61.7$ ($1F^1$), $-34.4$ [$1F^3$, t ($J_{F^3-F^4} = 23.5$ Hz) of doublets ($J_{F^1-F^3} = 7.5$ Hz), of multiplets], $-29.7$ (1F), $-25.0$ (1F), $-15.7$ (1F), and $-14.7$ ppm (1F). Similar constants have previously been observed in the $^{19}F$ NMR spectra of (XV) and (XVI) [7].

The oxidation of the methyleneindan (IX) with $KMnO_4$ in acetone to the known octafluoro-1-indanone [9], and the conversion of methyleneindan (X) on treatment with aluminum chloride into the known 2-dichloromethylene-1,1,3,3-tetrachlorotetrafluoroindan [1] confirm structures (IX) and (X), and eliminate the alternative structures, 3,4-dichloroperfluoro-1,2- and 2,3-dichloroperfluoro-1,4-dihydronaphthalene, respectively.



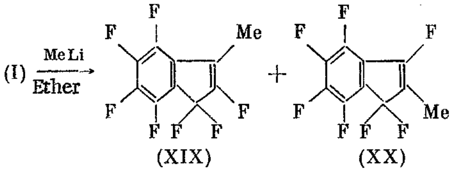
The course of the reaction of indene (I) with salt (VI) in diglyme, to give the methyleneindans (IX) and (X), may be formally regarded as proceeding via the intermediate cyclopropane (XI). However, this reaction route is excluded, at least at a temperature of 80°, since we have shown that at this temperature and under the reaction conditions, (XI) remains virtually unchanged. Also, the cyclopropane (XI) has not been found in the products of the reaction of (I) with (VI).

In view of these observations, a probable pathway for the formation of methyleneindan (IX) is reaction of the indene (I) with the $CCl_3^-$ anion to give the ion (XVII). The latter apparently isomerizes to the more stable anion (XVIII), which is stabilized by elimination of the $Cl^-$ anion. The formation of the methyleneindan (X) may be represented similarly



The proposed course of the reaction is not contradicted by information on orientations in the reactions of indene (I) with MeLi and other nucleophilic reagents [10, 11], and the possibility of the generation of the $CCl_3^-$ anion, which is capable of functioning as a nucleophile, on thermal decomposition of (VI) [4].

Reaction of (I) with MeLi in ether gives 3- and 2-methylheptafluoroindenes (XIX) and (XX) in a ratio of ~ 7 :1, respectively.



The structures of the methyleneindans (XIX) and (XX) were established by their elemental analyses and spectral features. It is noteworthy that the $^{19}F$ NMR spectrum of (XIX) displays doublet splitting of the F atoms in the $CF_2$ group with the F atom in the 2-position, with $J_{F1-F2}$ = 12-13 Hz, whereas the spectrum of (XX) displays no such constant (cf. [2, 11]). It has previously been reported that in the reaction of indene (I) with MeLi, one of the vinyl F atoms is replaced, but no orientation was given [12].

## EXPERIMENTAL

All reactions were carried out in an argon atmosphere. $^{19}F$ and $^{1}H$ NMR spectra were recorded on a Varian A-56/60A instrument at frequencies of 56.4 and 60 MHz, respectively, for solutions of the compounds in $CCl_4$ (11 mole %). Internal standard $C_6F_6$ and HMS (0.04 ppm from TMS). IR spectra were recorded on a UR-20 instrument in $CCl_4$. UV spectra were obtained on a Specord UV-VIS instrument in heptane. Mass spectra were obtained on an AEI MS 902 instrument. GLC analyses were carried out on an LKhM-7A chromatograph [50-270°, 4000 × 4 mm; a) SKTFV-803, b) SE-30, c) SKTFT-50 on Chromosorb W, 15 :100, He, 60 ml/min].

Perfluoro-2-methylindene (II), Perfluoro-1,1a,6,6a-tetrahydrocycloprop[a]indene (III), and Perfluoro-1,4-dihydronaphthalene (VIII). a) A mixture of 0.65 g of (I), 0.68 g of (IV), and 2 ml of diglyme was heated in a sealed ampul at 225°, then steam distilled to give 0.46 g of mixture (dried over $MgSO_4$) which contained according to GLC (a) and its $^{19}F$ NMR spectrum 69% of (I), 10% of (II), and 6% of (VIII).

b) Similarly, from a mixture of 1.0 g of (I), 1.05 g of (IV), and 1 ml of diglyme (195°, 5 h) there was obtained 0.87 g of a mixture of 80% of (I), 15% of (III), and 4% of (VIII).

c) To 1 g of (I) was added dropwise with stirring at 140° a solution of 1.15 g of salt (V) in 4 ml of diglyme, over 45 min. Stirring was continued at this temperature for a further 45 min, then steam distilled to give 0.8 g of a mixture (dried over $MgSO_4$) which contained, from GLC (b), 80% of (I) and 9% of (III) together with unidentified impurities. The IR and $^{19}F$ NMR spectra of the mixture displayed bands (signals) for (III) [2].

1- and 2-Dichloromethyleneoctafluoroindans (IX) and (X). To a stirred solution of 11 g of (I) in 10 ml of diglyme was added dropwise at 85° a solution of 7.8 g of (VI) in 35 ml of diglyme, over 2.5 h. The mixture was stirred at 85° for a further 0.5 h and steam distilled to give 11.23 g of a mixture (dried over $MgSO_4$) containing, according to GLC (a), 27% of (IX), 3% of (X), 44% of (I), 10% of $CCl_4$, and 5% of $CHCl_3$. Vacuum distillation of the mixture afforded a fraction (4.14 g), bp 110-119° (5 mm), which contained, according to GLC (b), 74% of (IX) and 7% of (X) together with unidentified impurities. Pure (IX) and (X) were isolated by preparative GLC (200°, SKTFV-803 on Celite, $N_2$).

Indan (IX). Found: C 35.34; Cl 20.81; F 44.39%; mol. wt. 342 (mass spectrum) $C_{10}Cl_2F_8$. Calculated: C 35.02; Cl 20.67; F 44.31%; mol. wt. 342 ($^{35}Cl$). The $^{19}F$ NMR spectrum contained six signals, at δ, ppm: −52.5 (2F), −47.7 (2F), −41.0 (1F), −22.5 (1F), −17.3 (1F), −14.7 (1F). The IR spectrum (ν, $cm^{-1}$): 1616 (C = C), 1647, 1525, 1507 (fluorinated aromatic ring), 1394. UV spectrum: $\lambda_{max}$ 268 nm (log ε 4.14).

Indan (X), mp 81-82° (from alcohol, in a sealed capillary). Found: $C_{10}Cl_2F_8$ (high-resolution mass spectrometry). The $^{19}F$ NMR spectrum contained three signals at δ, ppm: −72.2 (4F), −22.7 (2F), −17.6 (2F). IR spectrum (ν, $cm^{-1}$): 1625 (C = C), 1645, 1526, 1515 (fluorinated aromatic ring), 1407. UV spectrum, $\lambda_{max}$, nm (log ε): 252 (3.30, sh), 256 (3.23, sh), 267 (2.65, sh).

b) Similarly, from a solution of 11.4 g of (I) in 10 ml of diglyme and a solution of 1.63 g of (VI) in 15 ml of diglyme was obtained 11.8 g of a mixture which contained according to GLC (a), 12% of (IX) [~ 65% of reacted indene (I)], 1% (X), 80% (I), 1% of $CCl_4$, and 1% of $CHCl_3$.

c) To a stirred solution of 0.4 g of indene (I) and 0.15 g of (XI) in 0.6 ml of diglyme was added dropwise at 80° a solution of 0.29 g of (VI) in 0.8 ml of diglyme over 10 min. Stirring was continued at 80° for a further 15 min, then the mixture was steam distilled, to give 0.49 g of a mixture (dried over $MgSO_4$) containing, from its $^{19}F$ NMR spectrum, (I), (IX), and (XI) in molar proportions ~ 3 : 0.9 : 1, respectively. According to GLC (a), the mixture contained 15% of (IX), 2% of (X), 45% of (I), 7% of $CCl_4$, and 3% of $CHCl_3$. Compound (XI) was unstable under the conditions of the GLC analysis.

In a parallel experiment, 0.55 g of (I) in 0.6 ml of diglyme and a solution of 0.39 g of (VI) in 1.1 ml of diglyme in the absence of (XI) afforded 0.52 g of a mixture containing, according to GLC (a), 29% of (IX), 3% of (X), 46% of (I), 5% of $CCl_4$, and 3% of $CHCl_3$, together with unidentified impurities. The molar ratio of (I) to (IX) in the mixture was ~ 2 : 1 ($^{19}F$ NMR spectrum). The cyclopropane (XI) was not found.

d) To a stirred solution of 0.68 g of HMPA and 0.16 g of LiCl in 2 ml of diglyme was added at ~ 20° 0.5 g of (I) and 0.34 g of (VII). Stirring was continued for 0.5 h at 85°, and the mixture steam distilled to give 0.36 g of a mixture (dried over $MgSO_4$), containing, according to GLC (a) and the $^{19}F$ NMR spectrum, 33% of (IX), 3% of (X), and 47% of (I).

1,1-Dichloroperfluoro-1a,6a-dihydrocycloprop[a]indene (XI) and 1,2-Dichloroperfluoro-1,4-dihydronaphthalene (XII). To a stirred mixture of 33.6 g of (I) and 2.5 ml of diglyme was added portionwise at 130-140° 23.9 g of (VI) over 2 h 15 min. The mixture was stirred and heated for a further 10 min, then steam distilled to give 34.9 g of a mixture (dried over $MgSO_4$) which contained according to its $^{19}F$ NMR spectrum (I), (IX), (XI), and (XII) in a ratio of ~ 7 : 0.6 : 1 : 1.4, respectively. The mixture was then distilled in vacuo in a stream of argon to give 16.1 g of (I), bp 61° (20 mm). From the residues (28 g) from several experiments there was obtained 3.1 g of (XI), bp 55-58° ( ~ 1 mm). In addition, a fraction (14 g) was obtained, bp 58-62° (~ 1 mm), rich in (IX)-(XII). Compounds (IX) and (XII) were isolated in a slightly impure state by preparative GLC (175°, SKTN-1 on Celite, $N_2$). Compound (X) could only be obtained in admixture with (XII).

Compound (XI). Found: $C_{10}Cl_2F_8$ (high-resolution mass spectrometry). The $^{19}F$ NMR spectrum contained eight signals of equal intensity at δ, ppm: −74.9 and −42.5 (AB system, $J^{gem}_{F-F}$ = 275 Hz, F atoms in the five-membered ring), −24.1, −22.4, −17.7, −15.6 (F atoms in the aromatic ring), +43.2 and +50.5 ppm (F atoms in the three-membered ring). IR spectrum (ν, $cm^{-1}$): 1522 (fluorinated aromatic ring), 1423, 1402. UV spectrum: $\lambda_{max}$ 274 nm (log ε 2.98).

Compound (XII). Found: $C_{10}Cl_2F_8$ (high-resolution mass spectrometry). The $^{19}F$ NMR spectrum is given in the text. IR spectrum (ν, $cm^{-1}$): 1710 (C = C), 1640, 1530, 1503 (fluorinated aromatic ring), 1412, 1400.

b) To a stirred mixture of 4 g of (I) and 0.3 ml of diglyme was added in small portions at 118-120° 2.86 g of (VI) over 45 min. The mixture was stirred at this temperature for a further 1.5 h, then steam distilled. There was obtained 4.19 g of a mixture (dried over $MgSO_4$) which contained, from its $^{19}F$ NMR spectrum, 12% of (XI), 5% of (IX), 60% of (I), and 1% of (XII).

c) (XI) (0.87 g) was heated in a sealed ampul at 140° for 5 h, to give 0.87 g of a mixture containing, according to GLC (a), 51% of (XII) together with unidentified impurities. The methyleneindans (IX) and (X) were not found ($^{19}F$ NMR spectrum).

d) Heating (140°, 5.5 h) a solution of 0.15 g of (XI) in 0.2 g of diglyme gave a mixture, the $^{19}F$ NMR spectrum of which was virtually identical with that of the mixture obtained in the preceding experiment.

1,1,2,3,4,4-Hexachlorotetrafluoro-1,4-dihydronaphthalene (XIV). To a stirred solution of 0.39 g of $AlCl_3$ in 2 ml of AcCl was added dropwise at ~ 20° a solution of 0.25 g of the mixture obtained by thermolysis of (XI), in 1 ml of AcCl. The mixture was stirred at 50° for 6 h, and kept overnight. It was then poured on to ice, extracted with $CH_2Cl_2$, washed with a solution of $NaHCO_3$, dried over $MgSO_4$, and the solvent distilled off. The residue was transferred to a watchglass to give 0.29 g of solid containing, according to GLC (a) and the $^{19}F$ NMR spectrum, 85% of (XIV) [6].

2-Dichloromethylene-1,1,3,3-tetrachlorotetrafluoroindan. A mixture of 0.01 g of (X), 0.03 g of $AlCl_3$, and 0.15 ml of AcCl was heated in a sealed ampul for 6.5 h at 50°. It was worked up as in the preceding experiment to give 0.01 g of product which was identified by its IR spectrum [1].

Octafluoro-1-indanone. To a stirred solution of 0.2 g of (IX), 0.07 g of $NaHCO_3$, and 5 ml of acetone was added dropwise over 40 min at ~ 20° a solution of 0.18 g of $KMnO_4$ in 65 ml of acetone. The mixture was stirred at ~ 20° for a further 0.5 h, and the solvent distilled off. The residue was treated with a solution of $Na_2S_2O_3$, and acidified with sulfuric acid. The resulting solution was extracted with $CH_2Cl_2$, dried over $MgSO_4$, and the solvent distilled off to give 0.13 g of a mixture containing, according to its $^{19}F$ NMR spectrum, octafluoro-1-indanone [9] and (IX) in a ratio of ~ 5 :1. The IR spectra contained bands for these two compounds.

3- and 2-Methylpentafluoroindenes (XIX) and (XX). To a stirred solution of 5 g of (I) in 16 ml of abs. ether was added dropwise at 5° 20 ml of an ethereal solution of MeLi, obtained from 2.8 g of $CH_3I$, over 1 h. The mixture was stirred for a further 1 h, poured into 70 ml of 2% HCl, and extracted with ether. The extract was washed with $Na_2S_2O_3$ solution, dried over $MgSO_4$, and the solvent distilled off to give 4.6 g of a mixture containing, according to GLC (c), 58% of (I), 33% of (XIX), and 5% of (XX), which were separated by preparative GLC (150°, SKTFT-50 on Chromaton N-DMCS, $N_2$).

Compound (XIX). Found: C 46.82; H 1.27; F 51.76%. $C_{10}H_3F_7$. Calculated: C 46.89; H 1.18; F 51.93%. The PMR spectrum contained a single signal at 2.15 ppm. The $^{19}F$ NMR spectrum contained five signals at $\delta$, ppm: −36.9 (2 $F^1$), −22.2 (1F), −18.1 (1F), −13.5 (2F), −7.2 (1F). IR spectrum ($\nu$, $cm^{-1}$): 1705 (C = C), 1520, 1510, 1500 (fluorinated aromatic ring), 1440, 1403.

Compound (XX). Found: C 47.62; H 1.21%; mol. wt. 256 (mass spectrum). $C_{10}H_3F_7$. Calculated: C 46.89; H 1.18%; mol. wt. 256. The PMR spectrum contained a single signal at 1.91 ppm. The $^{19}F$ NMR spectrum contained six signals at $\delta$, ppm: −40.9 (2$F^1$), −31.9 (1F), −22.9 (1F), −16.3 (1F), −13.4 (1F), −8.9 (1F). IR spectrum ($\nu$, $cm^{-1}$): 1705 (C = C), 1520, 1510 (fluorinated aromatic ring), 1450.

## CONCLUSIONS

1. The influence of the solvent on the course of the reaction of octafluoroindene with sodium trichloroacetate has been shown. When the reaction is carried out in diglyme, the main product is 1-dichloromethyleneoctafluoroindan, whereas in the presence of catalytic amounts of diglyme, it is 1,1-dichloroperfluoro-1a,6a-dihydrocycloprop[*a*]indene. The latter compound is converted on thermolysis into 1,2-dichloroperfluoro-1,4-dihydronaphthalene.

2. Reaction of octafluoroindene with sodium difluorochloro- and trifluoroacetates in diglyme at 140-195° affords perfluoro-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, but at 225° perfluoro-2-methylindene is obtained.

3. Reaction of octafluoroindene with methyllithium results in the preferential replacement of the F atom in the 3 position, to form 3-methylheptafluoroindene.

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# SYNTHESIS AND SOME PROPERTIES OF 5-FLUORODINITROMETHYL- AND 5-DIFLUORONITROMETHYLTETRAZOLES

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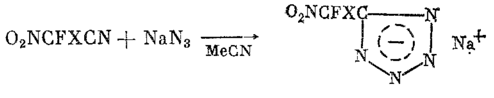
The presence of electron-accepting substituents in molecules containing nitrile groups significantly facilitates their interaction with salts of hydrazoic acid [1]. Thus, trifluoroacetonitrile reacts energetically with $NaN_3$ in acetonitrile [2].

It has been established by us in the present work that in spite of the high electron-accepting properties of the $O_2NCF_2$ and $(O_2N)_2CF$ groups the interaction of difluoronitroacetonitrile and fluorodinitroacetonitrile with $NaN_3$ is not as energetic under the same conditions as in the case of $CF_3CN$ [2]. The reaction proceeds at ~ 20°C and is accompanied by practically no exothermic effect

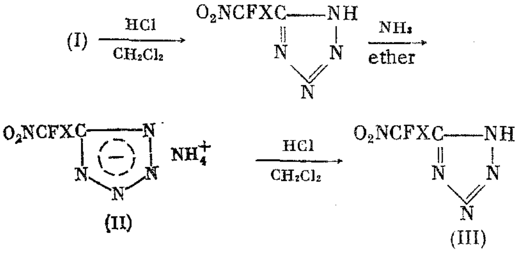


(I)

X = $NO_2$ (Ia), F (Ib).

The lower activity of the fluorodinitroacetonitriles and difluoronitroacetonitriles in comparison with trifluoroacetonitrile is probably explained by the screening of the nitro group oxygen atom by the nitrile group at which the primary attack by azide ion occurs.

Salts (Ia) and (Ib) were white crystalline, low-melting substances, extremely hygroscopic, and readily soluble in polar aprotic and protic solvents. The corresponding tetrazoles were obtained by treating a suspension of (Ia) or (Ib) in $CH_2Cl_2$ with dry HCl. Purification of the tetrazoles was effected by converting them into the readily crystallizable ammonium salts with subsequent acidification with dry HCl in anhydrous $CH_2Cl_2$ at ≤ − 10°



(II) (III)

X = $NO_2$ (IIa) and (IIIa), F (IIb) and (IIIb).

Compounds (IIIa) and (IIIb) were low-melting, hygroscopic, white crystalline substances.

On methylating (IIIa) and (IIIb) with diazomethane a mixture of the corresponding 1,5- and 2,5-disubstituted tetrazoles was formed.

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