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REACTIONS OF 1,2-DICHLORO-3,3-DIFLUOROCYCLOPROPENE WITH POTASSIUM THIOCYANATE AND SODIUM ARYLSULFINATES. SYNTHESIS OF 1,2-DITHIOCYANO-3,3-DIFLUOROCYCLOPROPENE

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SUMMARY

The reaction of potassium thiocyanate with 1,2-dichloro-3,3-difluorocyclopropene in DMF leads to the formation of 1,2-dithiocyano-3,3-difluorocyclopropene. In contrast, the reaction of sodium arylsulfonates with 1,2-dichloro-3,3-difluorocyclopropene or tetrachlorocyclopropene gave (E)-1,2-bis(arylsulfonyl)ethene as the only product.

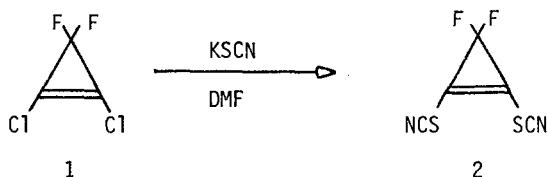
INTRODUCTION

The reaction of a variety of nucleophiles with halogenoperfluoroalkenes and halogenoperfluorocycloalkenes has been extensively investigated [1,2]. Similar investigations of fluorocyclopropenes have received considerable less attention. Since pioneering studies of West and co-workers [3-5] on fluorohalogenocyclopropenes only a limited number of papers dealing with chemistry of this class of compounds has been published. Thus, previous publications on the reactions of fluorohalogenocyclopropenes concerned mostly 1,2-dichloro-3,3-difluorocyclopropene. The nucleophilic substitution of this compound involved displacement of one or both chlorine atoms by iodine [6] or methoxy groups [7,8]. The reductive dechlorination of 1 and synthesis of 1-chloro-2-diisopropylamino-3,3-difluorocyclopropene has also been accomplished [9,10]. Other reports on the reactions of fluorohalogenocyclopropenes involve such nucleophilic reagents as fluoride [5] or amines [11].

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RESULTS AND DISCUSSION

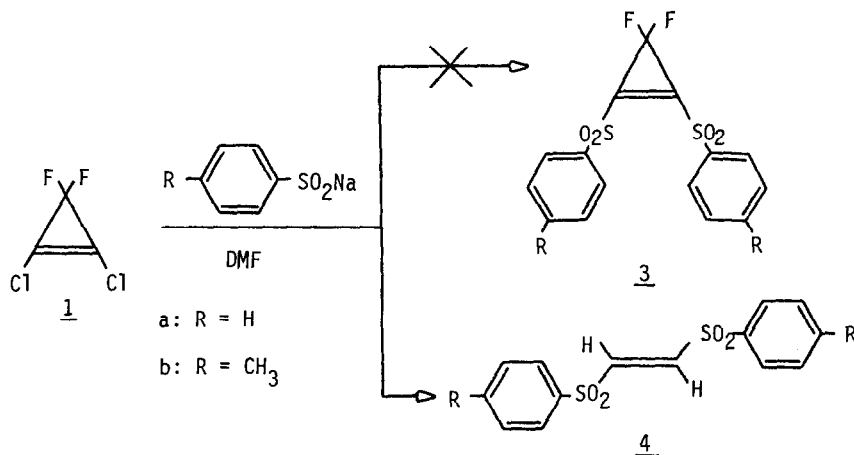
As a continuation of our studies on nucleophilic substitution of 1,2-dichloro-3,3-difluorocyclopropene we wish to report now the results of the reactions of 1 with potassium thiocyanate and sodium benzene- and p-toluenesulfonates. Addition of the DMF solution of potassium thiocyanate to the solution of 1 in DMF, stirring the solution at room temperature and then pouring the mixture into water gave a solid which was purified by sublimation under reduced pressure. Attempts to purify this product by recrystallization from a variety of solvents usually caused its total decomposition. Although the product was sufficiently stable to obtain spectral and analytical data it decomposed slowly during the course of a few weeks.



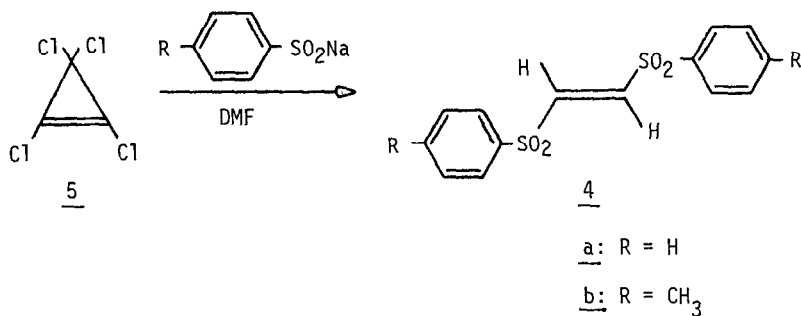
The structure of the sublimed solid (mp 113-114^o) was established on the basis of spectroscopic and analytical data. The ¹⁹F-NMR spectrum showed only a singlet resonance at -100.0 ppm. The position of this absorption is consistent with resonances of allylic fluorine atoms of the fluorocyclopropene system [5-7]. The IR spectrum revealed a strong band at 2180 cm⁻¹, (CN), a weak absorption of the double bond at 1714 cm⁻¹, and a strong, broad band at 1293 cm⁻¹ (CF₂). The pattern of this infrared spectrum was compatible with IR spectra of previously synthesized derivatives of difluorocyclopropene [6,8]. The fragmentation pattern of 2 in the mass spectrum further confirmed the structure of this compound. Weak molecular ions of 2 appeared at 190, 191 and 192 m/e units. The fragmentation pattern involved ions at 164 (M⁺ -CN); 132 (M⁺ -SCN); 140 (M⁺ - CF₂), and 171 (M⁺ -F) m/e units. All these spectral data support the expected structure of 2. We also found that the reaction of 1 and potassium thiocyanate was very sensitive to the change of conditions at which it was carried out. Even small prolongation of the reaction time often resulted in obtaining high-melting product which was very difficult to purify and gave none or traces of 2. However, in contrast to the successful preparation of 2 an attempt to extend this synthesis to other perfluorocycloalkenes failed.

Attempted reactions of potassium thiocyanate with 1,2-dichloroperfluorocyclobutene, 1,2-dichloroperfluorocyclopentene or 1-chloro-2-iodoperfluorocyclobutene failed to yield any of the desired products.

The reaction of 1,2-dichloro-3,3-difluorocyclopropene (1) with sodium salts of benzene - and p-toluenesulfonates in DMF gave unexpected products. Although the disubstituted cyclopropene 3 was expected to be unstable, good results with the synthesis of 1,2-dithiocyano-3,3-difluorocyclopropene (2) encouraged us to study reactions leading to 3. The reactions of 1 with sodium arylsulfonates were carried out in DMF at 13-16°C and the progress of the reaction was usually indicated by disappearance of slurry of sodium arylsulfonates from the reaction mixture. Isolation of the products was accomplished by pouring the DMF solution into water and filtration of the precipitated solids. However, spectral analysis of these solids revealed that (E)-1,2-bis(arylsulfonyl)ethene (4) was obtained in moderate yield instead of the cyclopropene 3.

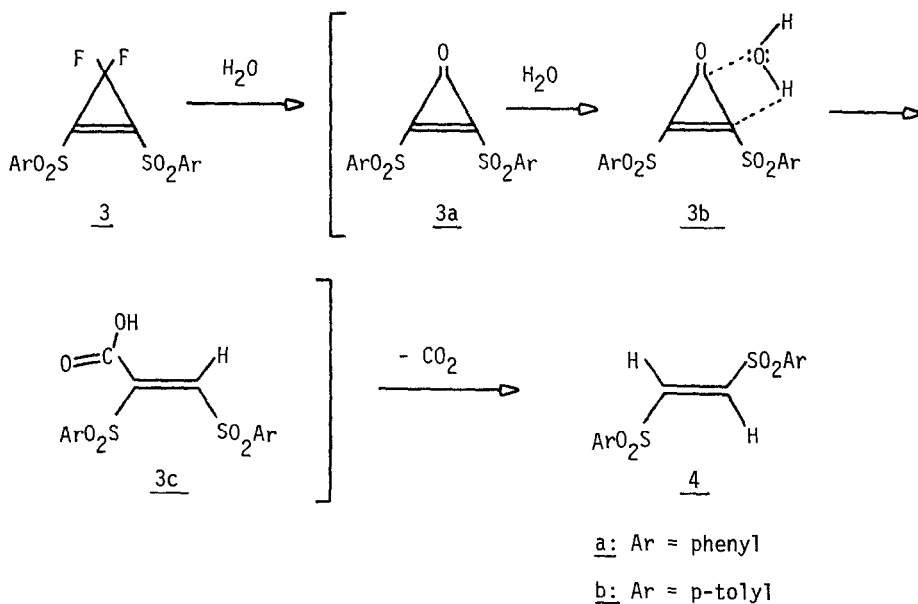


(E)-1,2-bis(phenylsulfonyl)ethene (4a) and (E)-1,2-bis(p-tolylsulfonyl)ethene (4b) gave in the mass spectrum strong molecular ions at 308 and 336 mass units, respectively. The fragmentation pattern in the mass spectra of these compounds was also compatible with the structure 4. ¹H-NMR spectrum of 4a revealed a singlet vinylic resonance at δ 7.16 ppm which was superimposed on a multiplet of aromatic protons. Aromatic protons of 4b appeared as a pair of doublets at δ 7.00 and 7.40 ppm and a vinylic resonance appeared as a singlet at δ 7.16 ppm. Furthermore, the values of melting points of these products correlate well with the literature data where the synthesis of 4a and 4b was accomplished by an unequivocal route [12,14].



The reaction of tetrachlorocyclopropene (5) with sodium arylsulfonates also gave compounds 4a and 4b with identical spectral properties as products obtained from 1 but yields did not exceed 10%.

The mechanism of ring opening of the cyclopropene system leading to the formation of trans-ethenes 4 remains unclear. Ring opening of intermediate product 3 associated with the addition-elimination stage may be a possible explanation.



West et al. [13] have reported a similar hydrolysis mechanism for arylhalogenocyclopropenes where the initial step was the attack of water on the geminal halogens to yield the isolatable arylcyclopropenones. Subsequent hydrolytic ring opening gave either the arylacrylic acid or the arylpropionic acid depending on whether the remaining vinylic halogen was chlorine or bromine.

In our case, the 1,2-bis(arylsulfonyl)acrylic acid (3c) intermediate should undergo rapid decarboxylation to yield the more stable (E)-1,2-bis(arylsulfonyl)ethene (4).

EXPERIMENTAL

All melting points are uncorrected. Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colorado. ^{19}F -NMR were obtained on a Varian 56/60 with fluorotrichloromethane as an internal standard. ^1H -NMR spectra were obtained on a Perkin Elmer R-12A using TMS as an internal standard. The mass spectra were obtained on a DuPont 21-491 instrument and IR spectra were obtained on a Beckman IR-8 spectrometer. Sodium benzene sulfinate and sodium p-toluenesulfinate dihydrate (Aldrich Chemical Co.) was used as received.

1,2-Dithiocyano-3,3-difluorocyclopropene, (nc) (2)

A solution of potassium thiocyanate (1.34g, 13.8 mmol) in dimethylformamide (15 ml) was slowly added dropwise during a period of 10 min. to the stirred solution of 1,2-dichloro-3,3-difluorocyclopropene (1.0g, 6.9 mmol) in DMF (5 ml). The temperature was maintained at 18-20°C and after 15 min. the dark solution was poured into water. The precipitated yellow-brown solid was filtered off, washed with water, dried and purified by repeated sublimations under vacuum (0.01 mm Hg) to afford 280 mg (21%) of 2 as colorless crystals; mp 113-114°C.

IR(KBr) 2325, 2180 s, 1714, 1647, 1293 s, 1105 s, 1068 s, 855 s, 764 cm^{-1} .
 ^{19}F -NMR (CDCl_3) -100.0 ppm (s, CF_2) - upfield from F-11 (CCl_3F);
 MS (70eV) 192, 191, 190 (M^+), 171, 164, 140, 132 (base peak), 106, 100, 87, 82, and 74 mass units.

Calcd. for $\text{C}_5\text{F}_2\text{N}_2\text{S}_2$ (190.19) : C 31.57; F 19.98; N 14.73; S 33.72

Found : C 31.82; F 19.26; N 14.17; S 33.96

The reaction of 1,2-dichloro-3,3-difluorocyclopropene (1) with sodium benzenesulfinate (1:2 ratio)

A solution of 1 (1.0g, 6.9 mmol) in DMF (5 ml) was placed in a 100 ml flask equipped with magnetic stirring bar, a thermometer, and addition funnel. The solution was cooled to 14°C and a slurry of sodium benzenesulfinate (2.3g, 13.8 mmol) in DMF (20 ml) was slowly added. The mixture was stirred at 14°C for one hour and at room temperature for an additional three hours. The solution was poured into water (200 ml) and precipitated solid was filtered off, washed with water, dried, sublimed under reduced pressure and recrystallized from ethanol to yield 1.3g (61%) of 4a as colorless crystals; mp 224°C (lit., [12] mp 229°C).

The reaction of tetrachlorocyclopropene (5) with sodium benzenesulfinate (1:2 ratio)

A slurry of sodium benzenesulfinate (2.7 g, 16.8 mmol) in DMF (15 ml) was added to the stirred and cooled (15°C) solution of tetrachlorocyclopropene (1.5g, 8.4 mmol) in DMF (5 ml). The clear solution was stirred at room temperature for three hours and then poured into water (200 ml). The precipitated solid was left standing overnight and was then filtered on a Büchner funnel, washed with water, dried, sublimed in vacuo and recrystallized from ethanol to afford 240 mg (9%) of 4a as colorless crystals, mp 229-230°C (lit., [12] mp 229°C).

Ethenes 4a obtained from 1 or 5 had identical spectral properties: IR (KBr) 3095, 3058, 3020 s, 1785, 1573, 1440, 1310 s, 1170 s, 1132 s, 1072 s, 996, 967 s cm⁻¹; ¹H-NMR (CF₃COOH/TMS) δ 7.60-7.26 (m, H_{arom}), 7.16 ppm (s, H_{vinyl}ic); MS (70eV) 310, 309, 308 (M⁺, base peak), 276, 250, 244, 218, 186, 167, 155, 141, 125, and 109 mass units.

The reaction of 1,2-dichloro-3,3-difluorocyclopropene (1) with sodium p-toluenesulfinate (1:2 ratio)

A slurry of sodium p-toluenesulfinate dihydrate (2.9 g, 13.8 mmol) in DMF (20 ml) was added slowly to the stirred and cooled (13-16°C) solution of 1 (1.0g, 6.9 mmol) in DMF (5 ml). The slurry disappeared immediately producing a clear solution. After additional 25 min. of stirring the solution was poured into water (150 ml). The precipitated solid was isolated and purified in usual manner to give 1.0g (43%) of 4b as colorless crystals, mp 231°C (from ethanol), (Lit., [14] mp 229.5-230°C).

The reaction of tetrachlorocyclopropene (5) with sodium p-toluenesulfinate (1:2 ratio)

A slurry of sodium p-toluenesulfinate dihydrate (3.6g, 16.8 mmol) in DMF (20 ml) was added to cooled (15°C) and stirred solution of 5 (1.5g, 8.4 mmol) in DMF (5 ml). The clear solution was stirred for two hours at room temperature and then poured into water (200 ml). After standing overnight, the precipitated colorless solid was isolated and purified in a usual manner. Recrystallization from ethanol afforded 210 mg (7%) of 4b as colorless crystals; mp 231°C (lit., [14] mp 229.5-230°C).

Ethenes 4b obtained from 1 or 5 showed the same spectral properties: IR (KBr) 3040, 2320, 1582, 1315 s, 1290 s, 1155 s, 1130 s, 1070 s, 1010, 930 s cm⁻¹; ¹H-NMR (CF₃COOH/TMS) δ 7.40 (d, H_{arom}, J = 9 Hz), 7.16 (s, H_{vinyllic}), 7.00 (d, H_{arom}, J = 9 Hz), 2.03 ppm (s, -CH₃); MS (70eV) 338, 337, 336 (M⁺, base peak), 321, 304, 272, 208, 181, 155, 139, 116, and 107 mass units.

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