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Simple synthesis of 1,1-bis(trifluoromethyl)cyclopropanes

Viacheslav A. Petrov [a,*], Will Marshall [b]

[a] DuPont Central Research and Development[1], Experimental Station, PO Box 80500, Wilmington, DE 19880-0500, United States
[b] DuPont Corporate Center for Analytical Sciences, Experimental Station, PO Box 80500, Wilmington, DE 19880-0500, United States

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ABSTRACT

A new, simple synthesis of 1,1-bis(trifluoromethyl)cyclopropanes has been discovered. It is based on the reaction of readily available 2,2-bis(trifluoromethyl)thietanes with tertiary phosphines in a polar solvent, which leads to an unusual desulfurization process, resulting in the formation of 1,1-bis(trifluoromethyl)-2-alkoxy cyclopropanes. The process of the corresponding thietanes appears to be sensitive to the steric volume of the atom connected to carbon in α-position to sulfur.

1. Introduction

Trifluoromethylated cyclopropanes were originally prepared by the reaction of activated fluoroolefins with diazomethane [1,2], followed by thermal or photochemical decomposition of the pyrazoline intermediate. Although quite versatile, this method has limited application due to the hazardous nature of diazomethane. Later, trifluoromethyl-containing diazirines were introduced, serving as a source of the corresponding carbene, which can be added across the double bond (see Ref. [3,4]). Metal-catalyzed reactions of fluorinated diazoalkanes with olefins used for diastereo- and enantio-selective synthesis of trifluoromethylated cyclopropanes have been developed in recent years [5]. Other methods include the reaction of sulfonium ylides with fluorinated olefins [6] and a synthesis involving optically active 2-trifluoromethyl oxirane [7]. Most of these methods are limited to the synthesis of cyclopropanes containing only one CF_3 group. The reaction of cyclopropane carboxylic acids with SF_4 developed by the Dmowski and the Yagupol'ski research groups is probably the most general method for the preparation of trifluoromethylated cyclopropanes, including compounds carrying multiple CF_3-groups [8–10], although the necessity to handle gaseous, corrosive and toxic sulfur tetrafluoride severely limits this method. More details on the synthesis and reaction of trifluoromethylated cyclopropanes can be found in a comprehensive and detailed review published recently [11].

In this study we report an unprecedented and simple method for the preparation of 1,1-bis(trifluoromethyl)cyclopropanes, which bear a substituent in the 2-position. The process involves the reaction of 2,2-bis(trifluoromethyl)4-R-thietanes (R = OAlk, NR_2) with tertiary phosphines, leading to a high yield of the corresponding cyclopropanes.

2. Results and discussion

Hydrocarbon sulfides are not reactive towards tertiary phosphines, and can be prepared by the reaction of di-[12,13], or tri-[14] sulfides with $(R_2N)_3P$ at ambient or elevated temperature. Popkova reported a similar process for partially fluorinated disulfides [15], which has been also adopted for the synthesis of polyfluoroalkyl thiiranes [16]. The desulfurization process was also used in a high yield synthesis of non-fluorinated thietanes from 1,2- dithiolanes [17,18], since hydrocarbon thietanes are stable under the reaction conditions and do not undergo further desulfurization.

Lately, we have been studying the reactivity of hexafluorothioacetone [19–23] towards different olefinic systems, and have developed a simple synthesis of a variety of 2,2-bis(trifluoromethyl)thietanes, and 1,2- and 1,3-dithiolanes [22,23]. 2,2-Bis(trifluoromethyl)thietanes have interesting reactivity and are able not only to react with strong acids [24] and oxidizing agents

* Corresponding author. Tel.: +1 302695 1958; fax: +1 302695 8281.
E-mail address: viacheslav.a.petrov@usa.dupont.com (V.A. Petrov).
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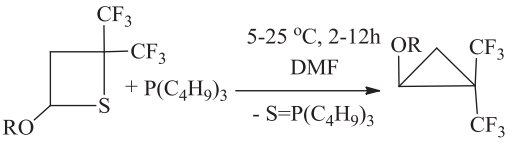
[21], but also show an unusual reactivity towards nucleophilic reagents [25–27], and undergo ring-expansion reactions in the presence of sulfur/metal fluoride catalysts [22,25] or activated aluminum powder [21]. Accumulated experimental data suggest that the sulfur atom in 2,2-bistrifluoromethyl-4-alkoxythietanes bears a significant positive charge, which makes 2,2-bis(trifluoromethyl)thietanes unique and distinctly different from its hydrocarbon counterparts.

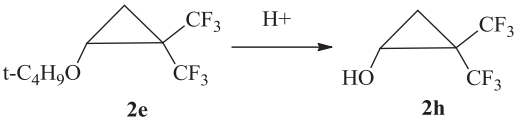
In this study, it was found that 2,2-bis(trifluoromethyl)-4-alkoxythietanes **1a–g** exhibit unusual and unexpected reactivity towards tertiary phosphines. Indeed, the addition of **1a–g** to a solution of $P(C_4H_9\text{–}n)_3$ results in an exothermic reaction with the formation of a 1:1 mixture of the corresponding cyclopropane **2a–g** and $S{=}P(C_4H_9\text{–}n)_3$ (Eq.(1)).



1a	**R=C_2H_5**	**2a**, 86 %
1b	**R=*n*-C_3H_7**	**2b**, 71%
1c	**R=*i*-C_3H_7**	**2c**, 75-81%
1d	**R=*n*-C_4H_9**	**2d**, 90%
1e	**R=*t*-C_4H_9**	**2e**, 70%
1f	**R=*c*-C_6H_{11}**	**2f**, 65%
1g	**R=$ClCH_2CH_2$**	**2g**, 89%

(1)

The reaction is exceptionally clean and the corresponding cyclopropanes of ~97–99% purity were isolated after vacuum transfer of the product into a cold trap under dynamic vacuum, followed by water wash to remove residual solvent. The addition of $P(C_4H_9\text{–}n)_3$ should be carried out at sub-ambient temperature, since the reaction is exothermic and at elevated temperatures (>30–40 °C) it may produce by-products derived from a ring-expansion process. Cyclopropane **2e**, prepared using this protocol, was found to be acid-sensitive. Despite the fact that the desulfurization process led to clean formation of **2e** (NMR), drying of this material over $MgSO_4$, resulted in its partial conversion into alcohol **2h**, (Eq. (2)). The product was isolated as a mixture of **2e** and **2h**.

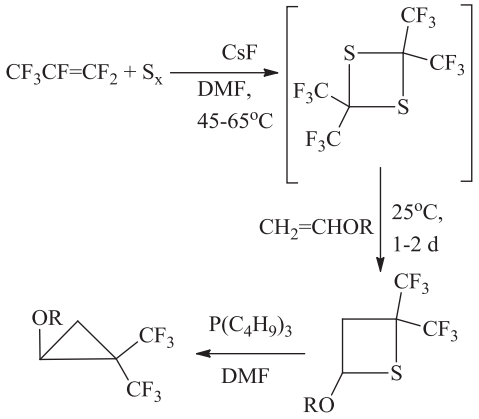


2e **2h**

(2)

The desulfurization process is sensitive to both solvent polarity and the nucleophilicity of the phosphine. For example, in THF the reaction of **1d** and $P(C_4H_9\text{–}n)_3$ was very slow (~20% conversion after 1 month at 25 °C). Using **1a**, it was also demonstrated that triphenylphosphine was much less active in this process (4 months (THF) and 1 week (DMF), respectively at 25 °C to reach >95% conversion), while both $[(CH_3)_2N]_3P$ and $[(C_2H_5)_2N]_3P$ have very high reactivity, reacting rapidly and exothermically with either **1a** or **b** and producing the corresponding cyclopropanes quantitatively (NMR experiments).

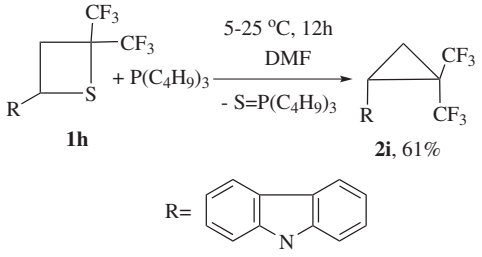
We also demonstrated that compounds **2a–d** can be prepared in 65–75% yield in a one-pot process, starting with hexafluoropropene, sulfur and vinyl ether (or cyclic dimer of HFTA and vinyl ether), followed by the treatment of the generated *in situ* thietane by $P(C_4H_9\text{–}n)_3$ (Eq. (3)).



(3)

2a, 75 %
2b, 72%
2c, 65%
2d, 68%

It should be pointed out that the ring contraction of thietanes has some generality and can be used for the preparation of 1,1-bis(trifluoromethyl)cyclopropanes bearing other substituents in position 2. For example, the treatment of thietane **1h** by $P(C_4H_9\text{–}n)_3$ led to **2i**, isolated in 61% yield after crystallization (Eq. (4))



1h **2i**, 61%

(4)

The structure of **2i** was confirmed by single crystal X-ray diffraction (Fig. 1).

^{19}F NMR spectra of all cyclopropanes exhibit two quartets (J = ~7 Hz). In ^{13}C NMR spectra of all cyclopropanes **2a–h** the resonances of the carbon bearing two CF_3 groups (septet, J = ~30–34 Hz) are significantly shifted upfield relative the corresponding signals in the thietanes **1a–g** (δ = ~30 ppm vs. δ = ~46 ppm).

The NMR spectrum of cyclopropane **2i** has some peculiarities. While the ^{19}F spectrum is similar to spectra of other cyclopropanes, the ^{1}H spectrum exhibits 8 (instead of the expected 4) aromatic resonances for the carbazole substituent. Similarly, the ^{13}C spectrum contains 12 resonances for aromatic carbons, along with 5 signals for the cyclopropane and CF_3 groups. All these data indicate restricted rotation of the carbazole unit around the C–C bond on the NMR time scale (probably due to strong steric interaction with CF_3 substituent, located on same side of cyclopropane ring). This hypothesis is also consistent with single crystal X-ray diffraction data. Indeed, the distance between the fluorine of the CF_3 group pointed towards the nitrogen of the carbazole (F1 and N1) is only 2.790 Å, while "half-length" of the carbazole fragment (the distance N1-H8(H10)) is 4.491 Å and clearly is long enough to prevent free rotation around the C–N bond.

The IR spectra of the new cyclopropanes all exhibit a band at ~1450 cm^{-1}, which is not present in IR spectra of the starting thietanes. Mass spectra typically exhibit a parent ion (see Tables 1 and 2).

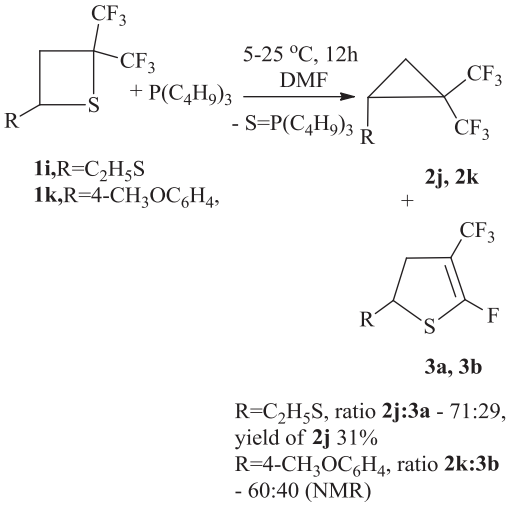
The ring contraction process seems to be sensitive to the size of the substituent on the thietane ring. For example, the reaction of

Table 1
Preparation of 1,1-bis(trifluoromethyl)cyclopropanes from thietanes.

Entry no.	Compound no.	Yield (%)	b.p. °C (mmHg); (m.p. °C)	MS
1	**2a**	86	110–111	222(M^+, $C_7H_8F_6O^+$)
2	**2b**	71	128–129	236(M^+, $C_8H_{10}F_6O^+$)
3	**2c**[a]	75–81	124–125	236(M^+, $C_8H_{10}F_6O^+$)
4	**2d**	90[b]	148–149[c]	250(M^+, $C_9H_{12}F_6O^+$)
5	**2e**	70[d]	–	235[$(M^-CH_3)^+$, $C_8H_9F_6O^+$]
6	**2f**	65	192–193[c]	276(M^+, $C_{11}H_{14}F_6O^+$)
7	**2g**	89	–	257(M^+, $C_7H_7ClF_6O^+$)
8	**2h**	–	–	194(M^+, $C_5H_4F_6O^+$)
9	**2i**	61	136–137	343 (M^+, $C_{17}H_{11}F_6N^+$)
10	**2j**	30	30–32/0.7[e]	238(M^+, $C_7H_8F_6S^+$)
11	**2k**	Quant.		

[a] Purity 97%, contaminated by DMF, 3%.
[b] Crude, purity 98%.
[c] Sivoloboff method.
[d] Calc. yield.
[e] Crude, purity 97%, Sivoloboff method.

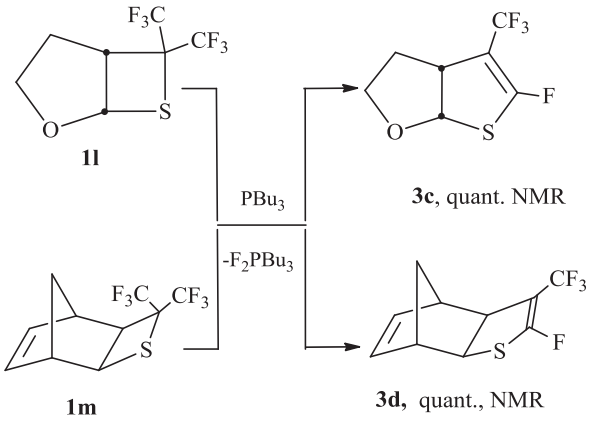
thietane **1i** bearing a 4-C_2H_5S– substituent results in the formation of a mixture of cyclopropane **2j** and dihydrothiophene **3a** [21].



(5)

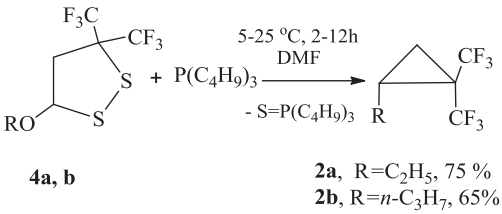
Cyclopropane **2j** was isolated in this reaction in 31% yield. The NMR analysis of the crude reaction mixture revealed the presence of $F_2P(C_4H_9\text{–}n)_3$, which was likely the byproduct of a ring expansion process.

While the cyclopropane **2j** is still the major product in the reaction of **1i**, polycyclic thietanes **1l** and **1m** under the same reaction conditions produced exclusively the corresponding dihydrothiophenes **3c** [21] and **3d** [21] (Eq. (6)), while the formation of the cyclopropanes was not observed.



(6)

It should also be pointed out that 1,2-dihydrothiolanes are also react with PBu_3. For example, the addition of **4a** or **b** to a two-fold excess the phosphine solution in DMF resulted in rapid formation of cyclopropanes **2a** and **b** in 65–75% yield (Eq. (7)).



(7)

NMR monitoring of the reaction mixture of **4a** and PBu_3 (ratio 1:1), revealed the formation of approximately equal amounts of the cyclopropane **2a** and the thietane **1a**, while the addition of

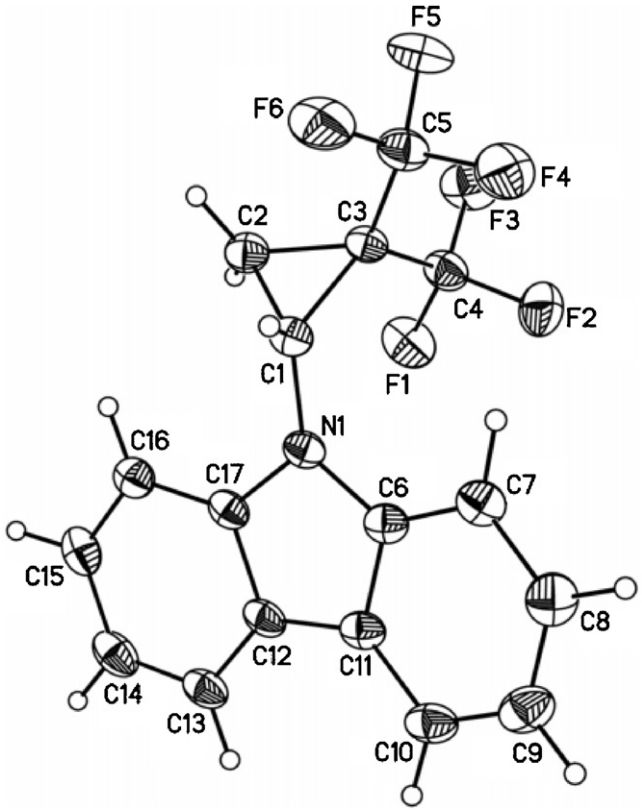


Fig. 1. Crystal structure of **2i** with thermal ellipsoids drawn to the 30% probability level.

Table 2
NMR[a] and IR data for 1,1-bis(trifluoromethyl)cyclopropanes.

Entry no.	Compound no.	^{1}H NMR (δ, ppm, J, Hz)	^{19}F NMR(δ, ppm, J, Hz)	^{13}C NMR (δ, ppm, J, Hz)	IR (cm^{-1})
1	**2a**	1.22(3H,t, 7.1), 1.44(1H, tq, 7.8, 2.1), 1.71(1H,ddq, 7.8, 5.3, 1.2), 3.67(2H, qd, 7.1, 1.2), 3.78(1H,m, 2.2),	−61.04 (3F, qt, 7.3, 2.4), −66.59 (3F, qd, 7.3, 1.2)	10.05, 10.80, 27.70(sept., 33.5), 55.53(q, 3.5), 64.36, 120.35(q, 274), 120.56(q, 274)	1453
2	**2b**	0.92(3H, t, J=7.4), 1.44 (1H, tq 7.6, 2.4), 1.60(2H, sext., 7.4) 3.34 (1H, m), 3.56 (1H, d, 12.2), 1.72(1H, ddq, 7.8, 5.3, 1.3), 3.57(2H, m), 3.78(1H, m, 2.4)	−60.90 (3F, qt, 7.0, 2.3), −66.55 (3F, qd, 7.0, 1.3)	10.25, 13.50, 22.52, 30.52 (sept., 34), 58.34, 73.73 122.86(q, 274), 123.03(q, 274)	
3	**2c**	1.19(3H, d, 6.2), 1.23(3H, d, 6.2), 1.43(1H, tq, 7.8, 2.0), 1.68(1H, ddm, 7.8, 6.3), 3.80(1H, sept., 6.2), 3.83(1H, m, 2.6)	−60.0 (3F, qt, 7.1, 2.0), −66.52 (3F, qd, 7.1, 1.1)	13.51, 21.20, 21.87, 30.57 (sept., 33), 56.53, 73.78, 122.90(q, 273), 123.00(q, 273)	1459
4	**2d**	0.92(3H,t, 7.3), 1.36(2H,m), 1.42(1H, td, 7.7, 2.2), 1.57(2H, m), 1.70(1H,ddq, 7.7, 5.4, 1.1), 3.60(2H,m), 3.77(1H,m), 1.28 (9H, s), 1.41 (1H, t, J=5.8), 1.60 (1H, t, J=5.8), 3.80 (1H, m)	−60.97 (3F, qt, 7.0, 1.3), −66.92 (3F, qd, 7.0, 1.3)	13.50, 13.60, 18.97, 30.51(sept., 31), 31.36, 58.65, 80.00 122.82(q, 274), 123.00(q, 274)	1455
5	**2e**	1.30–1.94 (12H), 3.48(1H,m), 3.88(1H,m)	−60.89 (3F, qq, 7.0, 1.9), −66.37 (3F, q, 7.0)		1452
6	**2f**	1.50(1H, tq, 8.0, 2.2), 1.79(1H, ddq, 8.0, 5.2, 1.2), 3.62(2H, m), 3.83(1H, m), 3.89(1H,m, 2.6), 3.93(1H, m, 5.4)	−60.89(3F, q,m, 6.8, 1.8), −66.45(3F, q)	13.5, 30.77(sept., 33.5), 41.92, 58.580, 71.76, 122.61(q,274), 122.18(q, 274)	1450
7	**2g**	1.60(2H), 4.10(1H,m), 7.80(1H,br.s)	−60.88(3F,qt, 7.2, 2.0), −66.61(qd, 7.2, 1.4)		
8	**2h**	2.33(1H,t, 7.5), 2.60(1H, t, 7.0), 4.12(1H, tq, 7.8, 2.2), 7.29(2H,m), 7.49(4H,m), 8.07(2H,m)	−60.68(3F, qq, 6.9, 2.0), −66.42(3F, q, 6.7)	13.91, 31.47(sept. 33.80):34.14(q, 3.0), 109.33, 109.83, 120.11, 120.22, 120.66, 120.75, 122.62(q, 280), 123.01(q, 280), 123.53, 124.01, 126.00, 126.55, 140.19, 141.00	
9	**2i**		−62.59(3F, q, 7.1), −66.22(3F, q, 7.1)		
10	**2j**	1.32(3H,t, 7.1), 1.50(1H,m), 1.66(1H,m), 2.70(3H,m)	−60.81 (3F, qt, 7.3, 1.9), −67.03 (3F, qd, 7.3, 1.3)		
11	**2k**[b]		−61.64(3F,q, 6.7), −67.42(3F,q, 6.7)		

[a] in $CDCl_3$ solvent.
[b] Compound **3b** was characterized in the reaction mixture by ^{19}F NMR δ = −61.11(3F,d, 17.5 HZ), −106.60 (1F, qt, 17.5, 4.7 HZ) ppm.

Scheme 1.

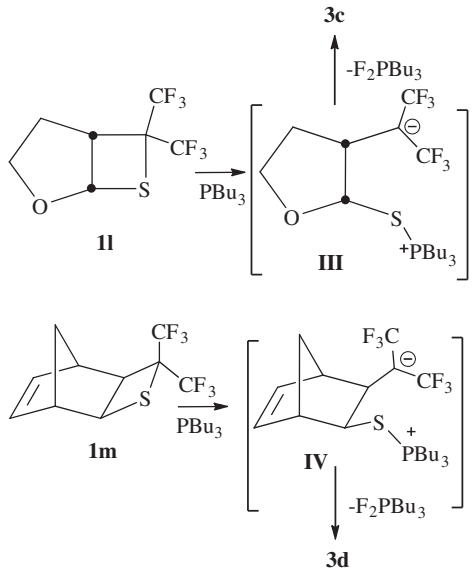
second mole of the phosphine led to complete conversion to **2a**, indicating that the thietane was an intermediate in this process.

We believe that the mechanism of the reaction responsible for the conversion of thietanes into cyclopropanes involves nucleophilic attack of phosphine on an electropositive atom of sulfur of the thietane ring, leading to intermediate **I** (Scheme 1).

Path A involves intramolecular attack of the $(CF_3)_2C$ carbanion on the carbon bearing an excellent leaving group (–S–PBu_3), leading to nucleophilic cyclization with the formation of cyclopropane **2** and S=PBu_3. It should be pointed out that the order of the reactivity of tertiary phosphines with thietanes **2** ($Ph_3P \ll Bu_3P$, $(R_2N)_3P$) is in good agreement with the nucleophilic nature of this step. The fact that more basic, but less nucleophilic, triethylamine was found to be inert in the reaction with thietane **2a** under similar conditions also supports this mechanism. Path **B** involves the migration of fluoride ion from a CF_3 group to phosphorous with the formation of alkene-containing fluorophosphorane **II** and intramolecular cyclization with the formation of dihydrothiophene **3** and F_2PBu_3.

The balance between the two reaction pathways seems to depend on the steric volume of the substituent at the carbon bearing sulfur in intermediate **I**. Since substituent R in the alkoxy group of thietanes **2a–g** does not affect the outcome of the reaction at all (in all cases cyclopropanes formed exclusively), one can assume that the size of the atom directly connected to this carbon is more important than the steric volume of the whole substituent. Indeed, in the reaction of thietanes with PBu_3 having relatively small atoms, such as oxygen or nitrogen (van der Waals radii 1.52 and 1.55 Å [28], compounds **1a–g** and **1h**, respectively), the corresponding cyclopropanes **2a–g** and **2h** were formed predominantly. In the case of **1h**, the crude product contained ~5% of the corresponding dihydrothiophene (by NMR). In the case of thietanes **1i** and **1k**, which contain larger S or C atoms in same position (van der Waals radii 1.80 and 1.70 Å [28], respectively), the reaction results in the formation of appreciable amounts of the dihydrothiophenes **3a** and **b** (Eq. (5)).

The exclusive formation of dihydrothiophenes **3c** and 3**d** is probably the result of the rigid structure of both starting materials. Indeed, both **1l** and **1m** exist exclusively as *cis*- [19] and *exo*- [22] isomers, respectively, which means that both intermediate **III** and



Scheme 2.

IV will have carbanion and sulfur substituents on the same side of cycle (Scheme 2).

In detailed mechanistic studies of the desulfurization process of hydrocarbon disulfides carried out by Harpp and Gleason [13], it was demonstrated that the reaction proceeds with inversion of configuration, which means that the nucleophile attacks the carbon of the $R_3C–SP^+$ $(R')_3$ intermediate from the backside, leading to a complete inversion of configuration. Assuming that a similar mechanism operates in the case of the reaction of thietanes **1** and phosphines, the attack of the carbanion on the carbon bearing the leaving group in intermediate **I** (Scheme 1) should proceed from the less-hindered side, through the transition where the incoming nucleophile and the leaving group are located on different sides of the plane and free rotation around the C–C bond allows intermediate **I** to rapidly adopt the required geometry. However, due to the geometry of the starting material in the case of thietanes **1l** and **1m,** the reaction with phosphine led to intermediates **III** and **IV**, respectively, with a *cis*- relationship of both substituents. This geometry is not suitable for intramolecular nucleophilic substitution, however, it is sufficient for fluoride ion migration to phosphorous, leading to exclusive formation of dihydrothiophenes **3c** and **d**, rather than the corresponding cyclopropanes.

3. Conclusion

A simple procedure for the conversion of readily available 2,2-bis(trifluoromethyl)thietanes into the corresponding cyclopropanes under the action of tertiary phosphines was developed. This reaction is unprecedented, and to the best of our knowledge has not been reported for hydrocarbon analogs. The corresponding cyclopropanes were isolated, fully characterized, and the structure of the compound bearing a carbazole substituent was confirmed by single crystal X-ray diffraction.

4. Experimental

^1H, $^{13}C\{H\}$, and ^{19}F NMR spectra were recorded on a Bruker DRX-500 (499.87 MHz) instrument using $CFCl_3$ or TMS as an internal standard. $CDCl_3$ was used as a lock solvent. GC and GC/MS analyses were carried out on a HP-6890 instrument, using an HP FFAP capillary column and either TCD (GC) or mass-selective (GS/MS) detectors, respectively. Dry DMF and THF, PPh_3, PBu_3, $[(CH_3)_2N]_3P$ (Aldrich) $[(C_2H_5)_2N]_3P$ (Lancaster) were purchased and used without further purification. Thietanes **1** were prepared according modified procedure using CsF as a catalyst [22]. The synthesis of **1h** and similar materials will be reported separatly. Due to the relatively low boiling points of the majority of cyclopropanes, elemental analysis was not attempted for these new materials. The purity of all isolated compounds established by GC and NMR spectroscopy was at least 97%. Compounds **3c**, **d** were identified by ^1H and ^{19}F NMR [21].

4.1. Crystallography

X-ray data for **2i** were collected at −100 °C using a Bruker 1 K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator. The structure was solved and refined using the Shelxtl [29] software package, refinement by full-matrix least squares on F^2, scattering factors from Int. Tab. Vol. C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC #816328. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e mail: deposit@ccdc cam ac uk.

4.2. Reaction of Thietanes 1a–k with PBu_3 (typical procedure)

The corresponding thietane **1a–i** (10–75 mmol) was added at 5–10 °C to an agitated solution of PBu_3 (10–20 mol.% excess) in 30–100 mL of dry DMF at the rate which allow to maintain internal temperature <10 °C. The reaction mixture was agitated at ambient temperature for 2–6 h, and the product/DMF mixture was transferred at 25–40 °C into −78 °C cold trap under dynamic vacuum (1–3 mm Hg) over 1–3 h. The reaction mixture was washed with water and dried over $MgSO_4$. Cyclopropanes prepared in this way typically had purity 97–98% and were contaminated by 2–3% of DMF (NMR). Cyclopropanes of >99% purity were obtained by distillation.

The reaction of thiolanes **4a** and **b** were carried out similarly, but using a two-fold excess of PBu_3.

Compound **2i** was isolated by diluting the reaction mixture with water (300 mL), extracting with hexane (3 × 100 mL), washing by water (3 × 300 mL), drying over $MgsO_4$ and solvent removal under reduced pressure. The semi-liquid residue was washed by a small amount of cold hexane (~5 mL) and crystallized from hexane.

The reaction of thietanes **1k–m** with PBu_3 were carried out in NMR tube. The thietane was added at 0 °C to a solution of two-fold excess PBu_3 in DMF. Products **2k** and **3a–d** were not isolated, but characterized in mixture by ^{19}F NMR spectroscopy.

Yields, MS, NMR and IR data are given in Tables 1 and 2.

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