A Variable Mechanism for the Nucleophilic Vinylic Substitutions in a Series of *gem*-Dihalogenated Alkenes by a Bidentate Sulfur Nucleophile: An Experimental and AM1 Theoretical Study

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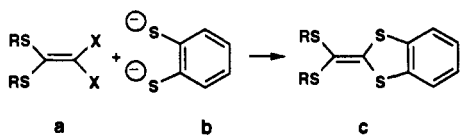
The nucleophilic substitutions of a series of *gem*-dihalogenated alkenes **3**, **5**, **7**, **8**, and **9** $(RS)_2C{=}CX_2$ (X = Cl, F) with 1,2-benzenedithiolate **b** have been studied. Depending on the structures of the R groups (alkyl, saturated and unsaturated cycloalkyls, aromatic ring), the course of the reactions and the structures of the yielded products are modified. In the frame of the addition–elimination-type mechanism for these nucleophilic substitutions, the energy contents of the anionic intermediates, resulting from the additions of the nucleophile **b** to the unsaturated centers, is calculated at the AM1 method level. For the compounds **5**, **7**, **8**, and **9**, the calculated energies nicely corroborate the experimental results. For **3**, anionic intermediates are no longer found by calculation, and a synchronous single-step substitution is strongly suggested.

The nucleophilic vinylic substitutions of *gem*-dihalogenated substrates, such as **a**, by a bidentate sulfur nucleophile, such as 1,2-benzenedithiolate **b**, can be considered as a general synthetic route to unsymmetrical tetrathia-substituted ethenes **c** (eq 1); if the R substituents

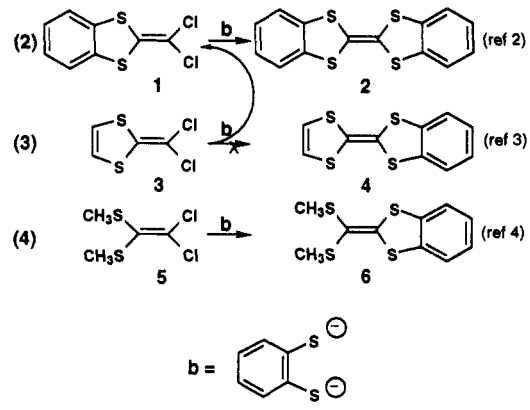


(1)

are, in addition, parts of a 1,3-dithiole ring, this process could then be a new entry to the preparation of unsymmetrical tetrathiafulvalenes (TTF), for which very few syntheses are available.[1] Several studies have been published along this line,[2-4] but the course of all the reported reactions have not followed this simple picture (eq 1). In fact, depending on the nature of R, dramatic differences in the structures of the products have been found (Scheme I).

The first example of this process (i.e., the substitution of tetrachloroethene by **b**) is the old Hurtley–Smiles synthesis of dibenzo-TTF (**2**);[2] the last step of this synthesis is depicted in reaction 2 (Scheme I). This process has been more recently reinvestigated,[3] with the study being aimed at its modification for the synthesis of the monobenzo-TTF (**4**) (reaction 3, Scheme I). However, the authors had not detected the expected compound **4**. The substitution of **3** by **b** leads surprisingly again to **2** through the intermediate formation of the *gem*-dichloroalkene **1**.[3] On the other hand, starting from the alkyl-substituted substrate **5**, we have found[4] the expected substitutions leading, this time, to **6** and similar compounds.

Scheme I



As part of our interest in the synthesis of new donors,[5] we needed a new access to unsymmetrical TTF's. We decided to reexamine these nucleophilic vinylic substitutions, in order to investigate the scope of the process and to rationalize the results summarized above which were, at first sight, inconsistent. Using a broader series of *gem*-dihalogenated alkenes, we have investigated such substitutions both experimentally and theoretically using the semiempirical[6] AM1 method.[7]

Few theoretical studies have been devoted to the nucleophilic substitutions at vinylic centers;[8] a very complete analysis of such reactions has been carried out with model systems, on the ab initio computational level.[9] Semiempirical (MNDO) calculations have been conducted to investigate the mechanism of the parent nucleophilic aromatic substitution,[10] but not such studies are found for the nucleophilic vinylic substitutions.

We would like to report here the unexpected results of our experimental and theoretical AM1 approach. They involve a new insight into the course of this series of

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nucleophilic substitutions and suggest a modification of the nature of the mechanism as a function of the substituents on the sulfurs from a multistep addition–elimination to a single-step synchronous process.

Experimental Section

General. Details of instrumentation have been reported recently.[11]

Preparation of Trichloroacetaldehyde Dimethyl Thioacetal (5A).[4] Trichloroacetaldehyde hydrate (42 g, 0.25 mol) was introduced in 98% H_2SO_4 (90 mL) at 0 °C, and an excess of CH_3SH (45 mL), condensed at ca. −20 °C, was added. The reaction mixture was stirred at 0 °C for 2 h, and stirring was then maintained overnight at room temperature. The solution was slowly added to ice (500 g) and the mixture extracted with ether. The extracts were washed with water and dried over $MgSO_4$. The ether was evaporated, and the compound 6 isolated after distillation under vacuum, 21 g (37.5%); bp = 135–140 °C/25 mmHg. The very unpleasant smelling liquid solidified when stored in a refrigerator: NMR (δ_H, $CDCl_3$) 2.4 (s, 6H), 4.3 (s, 1H); MS (EI) m/e 225 ± 1 (M^+).

Preparation of Compounds 7A, 8A, and 9A: General Procedure. Into a solution of the appropriate trihaloacetaldehyde (40 mmol) in dry chloroform (60 mL) was added the required dithiol (40 mmol) dissolved in boron trifluoride ethyl etherate (12 mL, 96 mmol) at room temperature. The mixture was stirred for 48 h, poured into water (50 mL), and extracted with dichloromethane (2 × 60 mL). The combined extracts were washed successively with sodium hydroxide solution (10%) and with water and dried over $MgSO_4$ and the solvent evaporated; the products were isolated by vacuum distillation or purified by recrystallization to yield the following compounds.

2-(Trichloromethyl)-1,3-dithiane (7A): from trichloroacetaldehyde and 1,3-propanedithiol; colorless needles; 6.1 g (65%); mp = 123–124 °C (from absolute ethanol); NMR (δ_H, $CDCl_3$) 2.05 (m, 2H), 2.75 (m, 2H), 3.2 (m, 2H), 4.5 (s, 1H). Anal. Calcd for $C_5H_7Cl_3S_2$: C, 25.25; Cl, 44.84; S, 26.94. Found: C, 25.38; Cl, 44.92; S, 27.16.

2-(Trichloromethyl)-1,3-dithiolane (8A): from trichloroacetaldehyde and 1,2-ethanedithiol; colorless liquid; 7.6 g (85%); bp = 146 °C/18 mmHg; NMR (δ_H, $CDCl_3$) 3.30 (m, 2H), 3.45 (m, 2H), 5.35 (s, 1H); MS(EI) m/e 223 ± 1 (M^+). Anal. Calcd for $C_4H_5Cl_3S_2$: C, 21.48; H, 2.24; Cl, 47.65; S, 28.63. Found: C, 21.49; H, 2.29; Cl, 47.46; S, 28.63.

2-(Trifluoromethyl)-1,3-dithiolane (9A): from trifluoroacetaldehyde (40 mmol) and 1,2-ethanedithiol (14 mmol); colorless liquid; 3.5 g (50%); bp = 76–78 °C/50 mmHg; NMR (δ_H, $CDCl_3$) 3.28 (s, 4H), 4.72 (q, 1H, $^3J_{HF}$ = 7 Hz); MS(EI) m/e 174 (M^+). Anal. Calcd for $C_4H_5F_3S_2$: C, 27.57; H, 2.87; F, 32.76; S, 36.78. Found: C, 27.42; H, 2.84; F, 32.61; S, 35.58.

Preparation of 1,1′-Dichloro-2,2′-bis(methylthio)ethene (5).[4] The compound 5A (14.5 g, 64 mmol) was dissolved in anhydrous DMSO (100 mL), and potassium *tert*-butoxide (10 g, 89 mmol) was added in small portions. After the mixture had been stirred overnight at room temperature, water (200 mL) was added and the reaction mixture extracted with ether. The organic phase was dried over $MgSO_4$, the ether evaporated, and the residue vacuum distilled. 5: light yellow liquid; 8.9 g (80%); bp = 112–116 °C; NMR (δ_H, $CDCl_3$) 2.5 (s); MS (EI) m/e = 189 ± 1 (M^+).

Preparation of *gem*-Dihalogenoalkenes 7 and 8: General Procedure. Into a solution of the appropriate trihalogeno dithioacetal (13 mmol) in anhydrous DMSO (15 mL) was added ethyldiisopropylamine (2.6 g, 20 mmol) and the mixture stirred overnight at 80 °C. Water (100 mL) was added and the mixture extracted with ether (3 × 20 mL), the combined extracts were successively washed with diluted HCl (10%) and with water and dried over $MgSO_4$, and the solvent was evaporated. Chromatography of the residue on a silica gel column eluting with toluene/cyclohexane (20:80 v/v) afforded the product alkenes. There were obtained the following compounds.

2-(Dichloromethylene)-1,3-dithiane (7): from 7A; colorless liquid; 2.2 g (85%); NMR (δ_H, $CDCl_3$) 2.07 (t, 2H, J = 6 Hz), 2.94 (t, 4H, J = 6 Hz); MS(CI) m/e = 201 ± (M^+). Anal. Calcd for $C_5H_6Cl_2S_4$: C, 29.85; H, 2.98; Cl, 35.32; S, 31.84. Found: C, 29.8; H, 3.12; Cl, 35.3; S, 32.01.

2-(Dichloromethylene)-1,3-dithiolane (8): from 8A; a colorless solid; mp 36–38 °C (lit.[12] mp 24–25 °C); 2.25 g (90%); NMR (δ_H, $CDCl_3$) 3.5 (s); MS(EI) m/e 187 ± 1 (M^+). Anal. Calcd for $C_4H_4Cl_2S_2$: C, 25.67; H, 2.14; Cl, 37.97; S, 34.22. Found: C, 25.84; H, 2.2, Cl, 37.71; S, 34.31.

2-(Difluoromethylene)-1,3-dithiolane (9): from 9A; to a solution of 9A (0.6 g, 3.45 mmol) in anhydrous ether (10 mL), at −78 °C was added MeLi (1.6 M in ether; 2.2 mL, 3.5 mmol) dropwise. The mixture was stirred for 15 min at this temperature and slowly warmed to room temperature overnight. Water (50 mL) was added and the compound extracted with ether (2 × 30 mL). The combined extracts were washed with water and dried over $MgSO_4$. The ether was evaporated, and the compound 9 (light yellow liquid; 0.4 g (75%); NMR (δ_H, C_6D_6) 2.46 (s); MS (EI) m/e 154 (M^+)) was used rapidly in the next step without further purification.

Nucleophilic Substitutions of 5, 7, 8, and 9 by 1,2-Benzenedithiol Dilithium Salt *b*: General Procedure. Into a solution of 1,2-benzenedithiol (0.46 g, 3 mmol) in anhydrous ether at 0 °C was added a solution of butyllithium (2 M in pentane, 2 mL, 6 mmol)) by syringe under an argon atmosphere. The salt b precipitated, and the mixture was stirred for an additional hour. The solvent was evaporated by argon bubbling, and the remaining solid was dissolved in oxygen-free DMF (10 mL). A stoichiometric amount of the dihalogenoalkene was added, and the reaction mixture was stirred for 12 h at 80 °C, unless otherwise noted. The cooled mixture was poured into water (30 mL) and the precipitated compound (9) filtered or extracted with toluene (4 × 20 mL). The extracts were dried over $MgSO_4$, the solvent was evaporated, and the residue was filtered and purified by recrystallization or by flash chromatography (eluting with toluene/cyclohexane (40:60 v/v)). The following compounds were obtained.

2-[Bis(methylthio)methylene]-1,3-benzodithiole (6): from 5; a colorless solid; 0.49 g (63%); mp 58 °C (from pentane); NMR (δ_H, $CDCl_3$) 2.3 (s, 6H), 7.05–7.15 (m, 4H). Anal. Calcd for $C_{10}H_{10}S_4$: C, 46.51; H, 3.88; S, 49.61. Found: C, 46.65; H, 3.86; S, 49.87.

2-(1,3-Benzodithiole-2-ylidene)-1,3-dithiane (10): from 7; a light yellow solid, 0.6 g (75%); mp 147–148 °C (from cyclohexane); NMR (δ_H, $CDCl_3$) 2.2 (m, 2H), 2.9 (m, 2H), 7.05–7.25 (m, 4H). Anal. Calcd for $C_{11}H_{10}S_4$: C, 48.8; H, 3.7; S, 47.4. Found: C, 48.6; H, 3.78; S, 47.46.

2-(1,3-Benzodithiole-2-ylidene)-1,3-benzodithiole (2) and 2-(1,3-Benzodithiole-2-ylidene)-1,3-dithiolane (11) (from 8). The following compounds were isolated after flash chromatography: unreacted 8 (0.135 g, 0.7 mmol); 11, a yellow solid (0.06 g, 10% based on consumed 8). Experimental data: NMR (δ_H, $CDCl_3$) 3.5 (s, 4H), 7.1–7.4 (m, 4H); MS (CI) m/e 257 (MH^+); 2 was identical (MS(CI), m/e 305 (MH^+)) with an authentic sample,[3] 0.09 g (13%, based on consumed starting material).

2-(1,3-Benzodithiole-2-ylidene)-1,3-dithiolane (11): from 9; a yellow solid; 0.53 g (70%); mp 183–185 °C (from cyclohexane) (lit.[12] mp 184–185 °C). Anal. Calcd for $C_{10}H_8S_4$: C, 46.87; H, 3.12; S, 50.0. Found: C, 46.8; H, 3.12; S, 50.1.

Computational Procedure. The calculations reported here were done by the AM1 method,[7] using the MNDO parameters for sulfur. The calculations have been performed on a FP264 processor linked to VAX4200 computer using the Gaussian 86–88 set of programs.[13] The energy-minimum geometries have been optimized by the gradient method.

In order to assess the accuracy of these AM1 semiempirical[6] calculations, the stabilities of the two conformers of the anion

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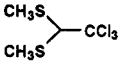
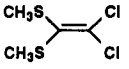
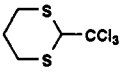
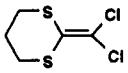
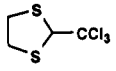
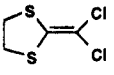
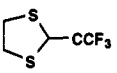
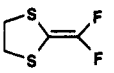
Table I. Syntheses of *gem*-Dihalogenated Alkene Series

RSH	dithioacetal (yield, %)	*gem*-dihalogenoalkene (yield, %)
CH_3SH	 **5A** (37.5)	 **5** (80)
	 **7A** (65)	 **7** (85)
 X = Cl	 **8A** (85)	 **8** (90)
 X = F	 **9A** (50)	 **9** (75)

[a] Sulfuric acid, concd. [b] Borontrifluoride etherate. [c] tBuOK. [d] Ethyldiisopropylamine.

CH_2SH^-[14] as well as the anion CH_3S^- were also calculated at the ab initio level[15] using minimal MINI 1+ and double ζ 6–31 G++ basis sets, and Mulliken population analysis was carried out as well. Both AM1 and ab initio levels gave satisfactory and consistent results (see supplementary material).

Results

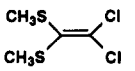
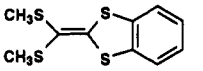
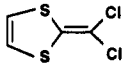
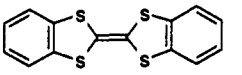
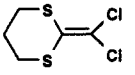
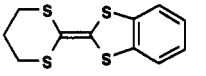
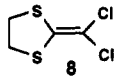
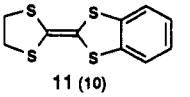
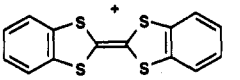
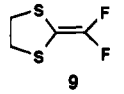
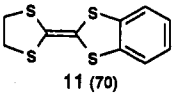
The Nucleophilic Vinylic Substitutions. The *gem*-dihalogenoalkenes **5**, **7**, **8**, and **9** were obtained in acceptable yields from the corresponding trihaloacetaldehydes (Table I) by acid-catalyzed thioacetalizations followed by base induced double-bond formations.

The substitutions by the 1,2-benzenedithiolate **b** were studied in DMF, and the results of the present reactions as well as the previous literature data are summarized in the Table II.

For the dichloroalkenes **3**, **5**, **7**, and **8**, a rather high temperature (80 °C) was needed, and two different behaviors are found: (i) expected "normal" chlorine substitutions **5** → **6** (entry 1) and **7** → **10** (entry 3), and (ii) "abnormal" substitutions **3** → **2** (entry 2), in which the all four substituents of the starting alkene were removed by the entering nucleophile. An interesting experiment involves the dithiolane-containing substrate **8** (entry 4). In this case a mixture of the "normal" and "abnormal" processes lead to **10** and **2**, respectively, although they are observed in poor yields. Starting with difluoroalkene **9**, the reactions are much faster, take place at room temperature, and yield the "normal" behavior; the compound **11**, resulting from the substitutions of fluorines, is isolated from **9**, in good yield (entry 5).

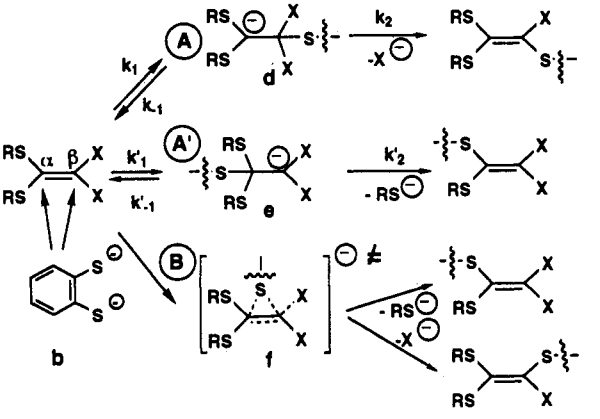
AM1 Calculations. A multitude of mechanisms are available for the nucleophilic vinylic substitutions.[16] The most common is the addition–elimination mechanism,

Table II. Nucleophilic Substitution of the *gem*-Dihalogenated Alkenes by 1,2-Benzenedithiol Dilithium Salt b

entry	alkene	resulting substitn compds (yield, %)
1[a]	 **5**	 **6** (63)
2[b]	 **3**	 **2** (30)
3[a]	 **7**	 **10** (75)
4[a]	 **8**	 **11** (10)  **2** (13)
5[c]	 **9**	 **11** (70)

[a] 80 °C in DMF. [b] Boiling acetonitrile (ref 3). [c] rt DMF.

Scheme II



which can proceed either in two-step sequences via negatively charged intermediates **d** or **e** (Scheme II, routes A or A') or via the concerted mechanism (route B) when **f** is a transition state. The multistep process has been advocated in many examples, while unequivoqual evidence for the latter single step (or synchronous) mechanism appears only in a few instances.[17] Assuming that the multistep addition–elimination process is operative in the presently studied series, we have calculated the relative energies of the optimized anionic intermediates **e** and **d** by the AM1 method. Starting with the dichloroalkene series of compounds **3**, **5**, **7**, and **8**, we find two dramatically different behaviors (Table III): (i) For the substrates **5**, **7**, and **8**, the calculated intermediates **d** are generally lower in energy than the intermediates **e**. That is, the route A

(14) Downard, K. M.; Sheldon, J. C.; Bowie, J. H.; Lewis, D. E.; Hayes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 8112.
(15) See, for example: Dehareng, D.; Dive, G.; Ghuysen, J. M. *Theor. Chim. Acta* **1991**, *79*, 141.
(16) For general reviews see: (a) Rappoport, Z. *Recl. Trav. Chim. Pays Bas* **1985**, *104*, 309. (b) Rappoport, Z. *Acc. Chem. Res.* **1992**, *25*, 474.
(17) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7.

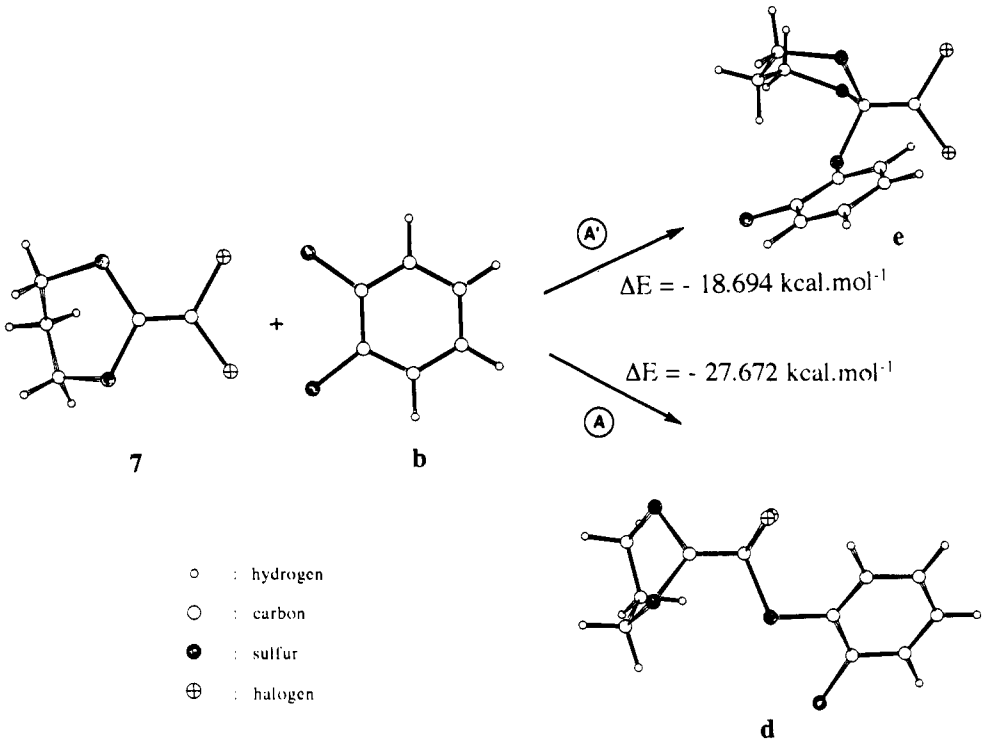


Figure 1. Stereoviews of the optimized conformations of the anionic intermediates **e** and **d** (Scheme II) for the substitution **7** → **10** (Table I, entry 3), obtained by the AM1 calculations.

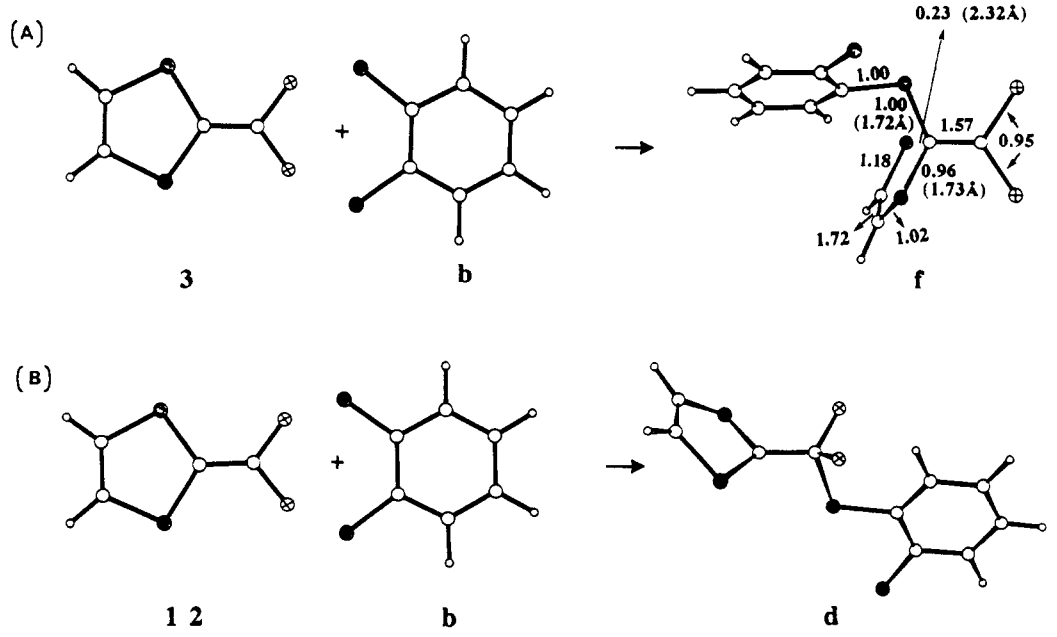


Figure 2. (A) Calculated nucleophilic reaction of **b** with the dichloroalkene **3**; no anionic intermediates **e** or **d** are found, but synchronously with the addition of the nucleophile, bond elongations (and ruptures) of the substrate occur: the 1,3-dithiole ring-opening is shown here; several selected bond orders at such a transition state **f** are included (significant distances in parentheses). (B) Calculated nucleophilic reaction of **b** with the difluoroalkene **12**; only the stable anionic intermediate **d** is found this time.

is favored over route A′ (Scheme II); such calculated intermediates **e** and **d** are depicted for the alkene **7** in Figure 1. (ii) For compound **3**, which has been found to behave "abnormally" (Table II, entry 2), stable anionic intermediates **e** and **d** are no longer favored. Instead, when additions of the nucleophile to either of the unsaturated carbons are stimulated, *synchronous bond-elongations (and ruptures) occur for the other groups of this same center* (i.e, sulfurs of the dithiole ring or chlorine, see Figure 2A).

The different values of the calculated energies of the anionic intermediates **d** and **e** for the investigated series of dichloroalkenes, **5**, **7**, and **8**, are summarized in Table III.

Finally, the calculations were effected on the difluoroalkenes series **9** and **12** (Chart I), and the results are shown in Table IV. For **9**, as might be expected due to the fluorines, only the energy of the intermediate **d** is obtained, and no energy minimum corresponding to **e** is found.

Table III. AM1-Calculated Energy Contents[a] of Anionic Intermediates e and d for the Dichloroalkenes 3, 5, 7, and 8

compd	e	d
5[b]	17.725	33.033
7[c]	18.694	19.353
8[b]	19.353	24.166
3[d]		

[a] The energies are expressed in kcal·mol^{-1} by reference to the energy-minimized starting reagents. [b] See supplementary material for the corresponding figures. [c] See Figure 1. [d] No anionic intermediates are calculated, but synchronous bond ruptures are evidenced as the nucleophile comes close to the unsaturated centers (see Figure 2).

Chart I

9 12

Table IV. AM1-Calculated Energy Contents[a] of the Anionic Intermediate d[b] for the Difluorinated Compounds 9 and 12

compd	d
9[c]	19.442
12[d]	17.288

[a] The energies are expressed in kcal·mol^{-1} from the energy-minimized starting reagents. [b] No stable e intermediates are found. [c] See supplementary material for the corresponding figure. [d] See Figure 2.

For the last compound 12, a difluorinated (although not yet synthetized) analogue of 3, a behavior similar to 9 but completely different from 3 is calculated (Figure 2B). The synchronous single-step mechanism is not observed, as it was for 3. Instead, a single energy minimum corresponding to **d** is found. For these two compounds, the calculated energies for the intermediates **d** (Table IV) decrease on going from 9 to 12.

Discussion

Let us first consider the series of substrates, 3, 5, 7, and 8 and discuss the results within the mechanistic frame defined in the Scheme II. The compounds 5 and 7 lead to the products which result from the expected substitutions of the halogens (Table II, entries 1 and 3), and a nice correlation is found with the results of AM1 calculations. The involved anionic intermediate (route A, **d**) is found to be more stable than the alternate intermediate **e** (route A′), by 15.308 (for 5) and 8.978 (for 7) kcal/mol^{-1}, respectively (Table III). For compound 8, which gives a mixture of the substitution products 2 and 11 (Table III, entry 4), stable anionic intermediates **e** and **d** are also found by the calculations and are considered as signature of a multistep addition–elimination process. However, the energy difference between **e** and **d** (4.813 kcal/mol^{-1}) is now significantly lower. This fact probably reflects a competition in the case of 8 between the routes A vs A′ (i.e., attack on C_α or C_β, Scheme II) and leads to the products 2 and 11, respectively. It is worth noting that the remarkable difference we observe in the reactivity of 7 vs 8 is mediated by the lower energy content of the anionic intermediate **d**, derived from 7 as compared to 8 (Table III). This effect reflects the well-known stabilization of the anions derived from 1,3-dithianes.[18]

On the other hand, the results of the AM1 calculations for the dichloroalkene 3, which leads to the unexpected product 2[3] (Table II, entry 2), point to the occurence of a completely different reaction mechanism. No stable anionic charge develops on either of the carbons when the nucleophile is brought to the proximity of the corresponding unsaturated centers (Figure 2), but a single-step synchronous substitution is found (route B, Scheme II).[19]

This behavior reminds us of the very interesting hypothesis put forward by Rappoport that "*the transition state in nucleophilic vinylic substitution is variable*".[17] Our results suggest that in addition to the modifications of the regiochemistry (C_α or C_β) of the entering nucleophile (see 7 vs 8) the *positions of the transition states* also depend strongly on the sulfur group structural features in the series of substrates considered. A shift from the multistep routes A′ and/or A for 5, 7, and 8 to a single-step synchronous substitution for 3 takes place. The occurence of this shift depends on the stability of the carbanions **d** or, in other words, their "*ability to accomodate negative charge*";[17] the lowering of the energy content of **d** parallels a collapse from a two-step into a single-step mechanism. Compare the stabilization energies of **d** for 5, 7, and 8 (Table III) to the available value for 12 (Table IV) as a model compound containing the same 1,3-dithiole ring as 3.

Finally, if we consider the experimental conditions needed for the substitution of the *gem*-difluoroalkene 9, as compared to the dichloro congener 8 (Table II, footnotes a and c), a pronounced substituent effect is observed. Substitutions of fluorines in 9 are faster than chlorines in 8. This effect is, qualitatively, additional support to the multistep addition–elimination process, in this case. The simultaneous modification of the selectivity in the reaction of difluoroalkene 9 in which a single product is formed (Table II, entry 5) is a consequence of the exclusive formation of the intermediate **d** (Table IV).

For 12, a *gem*-difluoro analogue of 3, a single step mechanism is no longer found (Figure 2b) but an anionic intermediate **d**, with a stabilization energy comparable to 9, is found (Table IV). This result suggests the substrate 12 as one interesting possibility to be investigated, among others,[20] as a new access to the preparation of unsymmetrical TTFs (eq 1).

In summary, this study clarifies the mechanistic aspects of the vinylic nucleophilic substitutions of our *gem*-dichloroalkenes series, with particular emphasis on the high sensitivity of these substitutions to the nature of the group on the sulfurs. The results of the AM1 calculations nicely correlate the experimental results and allow, for the compound 3, a new insight into the mechanism of the process. Clearly, this method might be used with a reasonable accuracy, in the case of large molecular systems involved in such substitutions reactions, as an alternative to more elaborate and more time-consuming ab initio methods. Finally, for a purely synthetic purpose, the study of the *gem*-difluoroalkene 12, suggested by the results of

(18) See, for example: Bartness, J. E.; Hays, R. L.; Khatri, H. N.; Misra, R. N.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 4746 and references cited therein.

(19) The calculations do not discriminate between the two possible nucleophilic synchronous substitutions on C_α or C_β (1,3-dithiole ring opening by sulfur expulsion or chlorine substitution); this result rules out, however, the mechanistic discussion[3] based on the consideration of the relative stabilities of the type **e** and **d** intermediates.

(20) Schaunmann, E.; Winter-Extra, S.; Kummerck, K.; Scheiblich, S. *Synthesis* **1990**, 271.

our AM1 calculations, is a tempting possibility; work is in progress toward this direction.

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Supplementary Material Available: *Z*-Matrix at the equilibrium geometries, including the connectivity and the optimized variables, total energy (expressed in hartrees), and maximum gradient component g_{max} (in Hartree/bohr or rad) as well as the labeling of the atoms used for the calculations on the compounds **b**, **3**, **5** (**e**, **d**), **7** (**e**, **d**), **8** (**e**, **d**), **9** (**d**), and **12** (**d**) and the results of the calculations on the AM1 and ab initio levels (using minimal basis sets MINI 1, MINI4, STO-3G augmented with sp diffuse functions, and double ζ 6-31G++ basis set) on the anions derived from methanethiol (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.