# THE INFLUENCE OF STERIC EFFECTS ON THE REGIO- AND STEREOSPECIFICITY OF THE ADDITION OF THIOLATES TO tert-BUTYLACETYLENE IN A PROTON-DONATING MEDIUM*

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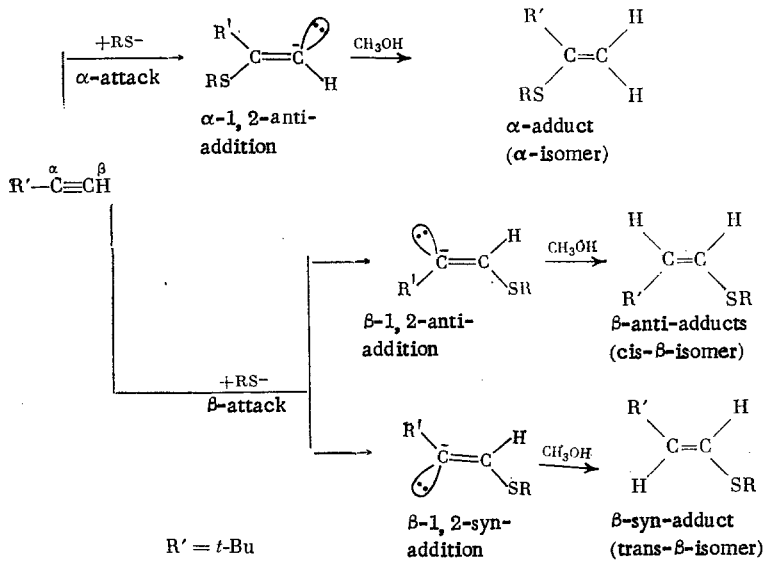
Steric effects substantially affect the direction of the nucleophilic addition of alcohols to 1-alkynes (Me—C≡CH, t-Bu—C≡CH) by changing the $\alpha$ orientation of attack by the alkoxide ion $RO^-$ to $\beta$ orientation with increase in the volumes both of the nucleophile and of the substituent at the C≡C bond [2]. The strongest departures from $\alpha$-regiospecificity are found in t-Bu—C≡CH. Here steric hindrances do not affect the trans-stereospecificity of the process, i. e., the mechanism of 1, 2-anti-addition is not disrupted.

It seemed of interest to compare the results in [2] with the case of stronger nucleophilic reagents (thiols).

In the present work we studied the effect of tert-butyl in t-Bu—C≡CH and of the volume of the attacking nucleophile ($RS^-$) on the regio- and stereospecificity of addition of thiolates of the aliphatic series at the triple bond. Since the nature of the solvent plays an important role in such processes, the reactions were carried out in a proton-donating medium (methanol) in order to approximate the conditions to the reaction of 1-alkynes with $RO^-$ nucleophiles. The expected directions of the reaction by the most probable $Ad_N^2$ mechanism can be represented as follows:




A quantitative measure on the effect of steric factors on the regiospecificity of the reaction is the fraction of the $\beta$-adduct (anti + syn), and a measure of the effect on its stereospecificity is the fraction of the $\beta$-syn-adduct. An essential condition here is the absence of cis—trans isomerization in the $\beta$-adducts.

*For the preliminary Communication, see [1].

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TABLE 1. Properties, Structure, and Ratio of the Products from the Reaction of t-$C_4H_9$—C≡ CH with RSNa($CH_3OH$)

| R | bp, °C (p, mm Hg) | $n_D^{20}$ | PMR spectral data, δ, ppm; J, Hz* | | | | | | Ratio, % | | Charton's steric constant for group R, $\nu_R$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | t-$C_4H_9$, $H_A$, C=C, RS, $H_B$ α-Isomer† | | | t-$C_4H_9$, SR, C=C, $H_D$, $H_C$ cis-β-Isomer† | | | α-isomer | cis-β-isomer | |
| | | | $H_A$, d | $H_B$, s | $J_{H_AH_B}^{gem}$ | $H_C$, d | $H_D$, d | $J_{H_CH_D}^{cis}$ | | | |
| $CH_3$ | 20–22 (3) | 1,4736 | 5,03 | 4,45 | 0,8 | 5,61 | 5,36 | 10,9 | 60 | 40 | 0,35 |
| $C_2H_5$ | 23–25 (2) | 1,4710 | 5,03 | 4,53 | 0,8 | 5,61 | 5,36 | 10,9 | 57 | 43 | 0,38 |
| n-$C_3H_7$ | 21–24 (1) | 1,4612 | 5,02 | 4,53 | 0,8 | 5,62 | 5,36 | 10,9 | 54 | 46 | 0,42 |
| n-$C_4H_9$ | 29–31 (1) | 1,4724 | 5,02 | 4,51 | 0,8 | 5,61 | 5,34 | 10,9 | 52 | 48 | 0,42 |
| i-$C_4H_9$ | 20–22 (1) | 1,4693 | 5,00 | 4,48 | 0,8 | 5,59 | 5,32 | 10,9 | 46 | 54 | 0,55 |
| i-$C_3H_7$ | 20–22 (1) | 1,4664 | 5,12c | 4,62 | 0,0 | 5,69 | 5,38 | 10,9 | 43 | 57 | 0,62 |
| t-$C_4H_9$ | 20–22 (1) | 1,4639 | 5,38c | 5,08 | 0,0 | 5,84 | 5,45 | 10,9 | 11 | 89 | 1,23 |

* The trans isomer is absent ($J_{HCHD}^{trans}$ = 15.3 Hz).

†Other signals (δ, ppm): for the α-isomers 1.15 s (t-Bu-C), 1.37 s (t-Bu-S), 2.14 s (Me-S); for the cis-β-isomers 1.12 s (t-Bu-C), 1.32 s (t-Bu-S), 2.20 s (Me-S).

The use of thiols as nucleophilic reagents requires complete exclusion of the competing free-radicals reaction, especially as t-Bu—C≡ CH adds RSH at an appreciable rate even at a moderate temperature (~ 80°C), giving a mixture of cis- and trans-β-isomers [3]. The free-radical reaction also accompanies the nucleophilic reaction when the experiments are carried out in a nitrogen atmosphere [4]. Atmospheric oxygen dissolved in the reagents clearly acts as initiator.

We developed a special method for realization of the reaction under purely nucleophilic conditions. The ratio of the α and β isomers was established by GLC and PMR spectroscopy with analysis of the reaction products before isolation; both methods gave closely corresponding results. Cis—trans isomerization did not occur during low-temperature distillation of the products. The structure of the products was proved by physicochemical methods and by comparison with substances obtained by an alternative method:

$$(CH_3)_3C—\overset{O}{\overset{\|}{C}}—CH_3 \xrightarrow{RSH} (CH_3)_3C—C(SR)_2CH_3 \xrightarrow[-RSH]{H^+}$$

$$\rightarrow (CH_3)_3C—C(SR)=CH_2 \xrightarrow{CH_3CO_3H} (CH_3)_3C—C(SO_2R)=CH_2$$

$$(CH_3)_3C—C\equiv CH + RSH \xrightarrow[70°]{} (CH_3)_3C—CH=CHSR \xrightarrow{CH_3CO_3H}$$

cis:trans = 30:70

$$\rightarrow \text{cis-}(CH_3)_3C—CH=CHSO_2R + \text{trans-}(CH_3)_3C—CH=CHSO_2R$$

Table 1 gives the properties, PMR spectral data (carbon tetrachloride), and ratios of the reaction products as a function of the structure of the thiol. The overall yield of the product was 25-60%. The trans isomers were absent from the reaction mixtures. The PMR spectra of the trans isomers obtained by an alternative method are given in the experimental section. The spectra of the cis-β- and α-isomers correspond fully to the data in Table 1.

From the obtained results it is seen that in all examples the β-adducts have the cis configuration exclusively. The trans isomers were not found even in traces. Consequently, the steric effects do not affect the stereochemical course of the β-addition of thiols to t-Bu—C≡ CH. The high trans-stereospecificity of the reaction in turn shows that under the developed conditions the β-adducts are only formed by a nucleophilic mechanism of 1, 2-anti-addition.

The absence of RS· radicals in the reaction medium was controlled by several methods. The effect of the addition of the free thiol and of vinyl ethyl sulfide (VES) on the ratio of the regioisomers and on the stereospecificity of the reaction was investigated. The VES was used for the first time as a unique "trap" and at the same time as a test for RS· radicals. It is known that VES does not react with $RS^-$ even when heated but readily adds RSH by a radical mechanism, giving $C_2H_5SCH_2CH_2SR$ (I). The reactivity of VES in this reaction is much greater than that of t-Bu—C≡ CH.

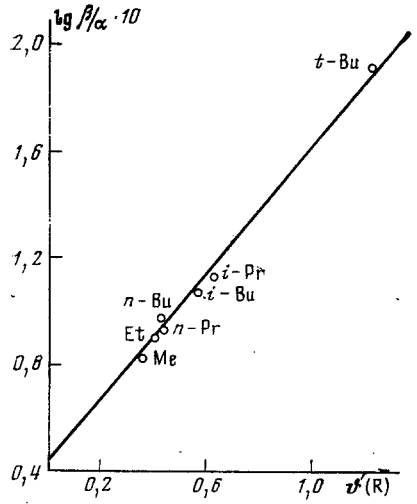
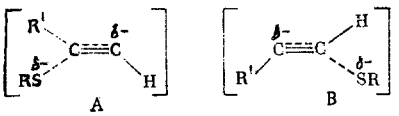



Fig. 1. Correlation of log $(\beta/\alpha \cdot 10)_{t\text{-Bu, RS}}$ with the Charton steric constants v' for substituents R in the reaction of t-Bu—C≡CH with $RSNa(CH_3OH)$.

During the partial formation of the β-adduct by a radical mechanism the addition of VES would reduce its proportion on account of the capture of RS· radicals and would lead to the appearance of the adduct (I). It was found that the introduction of even a twofold excess of VES did not give the adduct (I) and did not give rise to a change in the ratio of α- and β-adducts. The addition of thiol also does not give rise to a change in the ratio of the regioisomers or the stereospecificity of the process. Consequently, the competing free-radical reaction is fully eliminated under the developed conditions.

The structural direction of the nucleophilic addition to a monosubstituted acetylene is usually determined by the nature of the polar effect of the substituent [5]. The results presented in Table 1 show that, contrary to the expected preference for α-attack by the nucleophile, the reaction with t-Bu—C≡CH takes place non-regiospecifically, i. e., at the α and β atoms of the C≡C bond. Here the proportion of β orientation increases with increase in the volume of the added nucleophile. In the case of the most branched reagent $t\text{-}C_4H_9S^-$ 89% of the β-isomer is formed.

The observed behavior can be explained by the effect of steric factors. Since the α- and β-adducts are not converted into each other, their ratio is clearly subject to kinetic control. In our opinion, the ratio of the regioisomers is controlled by steric interaction of the nucleophilic reagent with the α-substituent in the transition state and in accordance with the Curtin—Hammett principle depends only on the difference between the free energy levels of states A and B:




Further evidence for the role of steric effects in the investigated reaction could be the successful correlation of the ratio of β and α adducts with the steric constants. In the literature, however, there are no examples of such correlations for acetylenes. The attempts which we made to correlate log (β/α) with the Taft constants $E_S$ ($E_S^C$, $E_S^0$) did not give the desired results. The reason evidently lay in the too large difference between the structure of the transition state of the investigated reaction and the acid hydrolysis reaction, from which the $E_S$ values were determined. In fact, in the former the substituent is attached to a carbon atom which in the composition of the reaction center changes its valence state from sp to $sp^2$; in the second the substituent is at a carbon atom in the $sp^3$ state.

A thorough acquaintance with the problem of the limits of applicability of the $E_S$ constants shows that in general they apply little to reactions in which the substituent is attached to a carbon atom in the $sp^2$-valence state in the transition state such as, for example, in bimolecular nucleophilic substitution. Great success in this region was achieved by Charton, who calculated new steric constants v and demonstrated their wider applicability in comparison with the $E_S$ constants [6]. Charton also obtained v' steric constants suitable for reactions whose transition state contains a carbon atom attached to a substituent in the $sp^2$ state [7].

TABLE 2. Properties of the Newly Synthesized Compounds

| Compound | Yield, % | bp, °C (p, mm Hg) | $n_D^{20}$ | Molecular formula | Found/calculated, % | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | H | S |
| $(CH_3)_3C-C(SCH_3)=CH_2$ | 80 | 37–37,5(11) | 1,4769 | $C_7H_{14}S$ | 64,86 / 64,55 | 10,88 / 10,83 | 24,62 / 24,62 |
| $(CH_3)_3C-CH=CHSCH_3$ cis/trans =19/81 | 73 | 41–42(8) | 1,4771 | $C_7H_{14}S$ | 64,60 / 64,55 | 10,82 / 10,83 | 24,57 / 24,62 |
| $(CH_3)_3C-CH=CHSC_3H_7-i$ cis/trans =37/63 | 74 | 61–62(8) | 1,4672 | $C_9H_{18}S$ | 68,27 / 68,28 | 11,28 / 11,46 | 20,34 / 20,25 |
| $(CH_3)_3C-CH=CHSC_4H_9-i$ cis/trans =21/79 | 68 | 30–32(1) | 1,4700 | $C_{10}H_{20}S$ | 69,88 / 69,69 | 11,72 / 11,70 | 18,44 / 18,61 |
| $(CH_3)_3C-C(SCH_3)_2CH_3$ | 64 | 40–43(1) | 1,5199 | $C_8H_{18}S_2$ | 53,87 / 53,87 | 10,15 / 10,17 | 35,66 / 35,96 |

We established for the first time that, unlike the Taft $E_S$ constants, Charton's $\nu'$ constants can be used successfully for correlation in acetylenic reaction series. Figure 1 shows the curve for the dependence of $\log(\beta/\alpha)$ on the $\nu'$ steric constants for the R group in the nucleophilic reagent. Mathematical treatment of the results by the method of least squares gave Eq. (1) with correlation coefficient r = 0.998 and mean square deviation from the regression line s = 0.028 (n = seven points)

$$\lg(\beta/\alpha)_{t\text{-Bu, RS}} = -0{,}59 + 1{,}208\cdot\upsilon'_R \quad (1)$$

It is remarkable that analogous treatment of data obtained in the reaction of Me—C≡CH and t-Bu—C≡CH with ROH [2] leads to Eqs. (2) and (3) with the same good correlation coefficients:

$$\lg(\beta/\alpha)_{Me,RO} = -2{,}74 + 1{,}889\cdot\upsilon'_R \quad (2)$$
$$r = 0{,}998,\ s = 0{,}055,\ n = 4$$

$$\lg(\beta/\alpha)_{t\text{-Bu, RO}} = -1{,}23 + 2{,}045\cdot\upsilon'_R \quad (3)$$
$$r = 0{,}996,\ s = 0{,}063,\ n = 7$$

In general form the obtained relationships can be expressed in terms of the equation

$$\lg(\beta/\alpha)_{R',R} = \lg(\beta/\alpha)_{R',H} + \psi_{R'}\upsilon'_R \quad (4)$$

where $(\beta/\alpha)_{R',R}$ is the ratio of the adducts in the reaction of the acetylene R'—C≡CH with the nucleophile $RX^-$ (where X = S, O); $(\beta/\alpha)_{R',H}$ is the same for the standard reagent $RX^-$ (where R = H); $\psi_{R'}$ is a coefficient which reflects the sensitivity of the given reaction series (R' = C≡CH) to the steric effect of the nucleophilic reagent (the R group); $\nu'_R$ is Charton's steric constant for group R in the nucleophile $RX^-$.

Thus, a good correlation is observed between Charton's steric constants and log $(\beta/\alpha)$ both in the series of sulfur and in the series of oxygen nucleophiles. Comparison of data on the RO ($\psi_{R'}$ = 1.9–2.0) and RS ($\psi_{R'}$ = 1.21) series shows that the former is more sensitive to steric effects than the latter. In addition, the discussed data make it possible to see that in the reactions of the two nucleophilic reagents $RO^-$ and $RS^-$, differing only in the electronic nature of the heteroatom (its polarizability) but having identical R groups, the regio orientation of the stronger $RS^-$ meets the requirements of static polarization of the triple bond to a lesser degree. As a result of this the proportion of the β-adduct is higher in the RS series than in the RO series. However, as the steric hindrances increase the dependence of the ratio of the regioisomers on the electronic nature of the heteroatom decreases, and the influence of the steric effect becomes determining.

## EXPERIMENTAL

The PMR spectra of the compounds (0.8–1.0 M) were obtained on a DA-60-IL instrument. The sulfides were used in carbon tetrachloride, the sulfones in $DCCl_3$, HMDS was used as standard, and the spectra were recorded on the δ scale (ppm). The analysis of the AB spectra was realized in accordance with [8]. The ratio of the α and β isomers was determined from the integral curve in the region of the vinyl protons.

The analyses of the sulfides by the GLC method were carried out on a Chrom 3-IKZ chromatograph with a flame-ionization detector on stainless-steel columns. The first was filled with 16% diethylene glycol succinate on Chromosorb C-22 (60–80 mesh, 1.8 m × 3 mm), and the second with 10% polyethyleneglycol adipate on Risorb C (0.2–0.3 mm, 2.4 m × 6 mm). The optimum conditions for analysis of the reaction mixtures [t-Bu—C(SR) = $CH_2$ and cis-t-Bu—CH= CH—SR] on column 1 with helium and hydrogen flow rates of 50 ml/min were

as follows (R, column temperature, evaporator temperature, °C): Me, 48, 110; Et, 58, 120; n-Pr, 80, 120; i-Pr, 70, 120; n-Bu, 82, 140; i-Bu, 80, 120; t-Bu, 64, 120. Under these conditions the $\alpha$-isomers are separated fully from the cis-$\beta$- and trans-$\beta$-isomers. The sulfides are arranged in the following order according to their retention times: $\alpha$-isomer, cis-$\beta$-isomer, trans-$\beta$-isomer.

The mixtures of cis and trans isomers of t-Bu—CH=CH—SR, obtained by free-radical addition, were separated on column 2, and the compounds with the normal chain R were separated better than those with branched radicals. It was not possible to select conditions for the separation of cis- and trans-t-Bu—CH=CH—SBu-t. In this case the ratio of the isomers was established by the PMR method.

tert-Butylacetylene was obtained from 2, 2-dichloro-3, 3-dimethylbutane in DMSO by the method which we developed. Pinacoline dichloride (0.39 mole) and powdered potassium hydroxide (2.3 moles) were placed in a three-necked flask provided with a stirrer, a dropping funnel, and a reflux condenser attached to a descending condenser and a receiver cooled with ice. To the stirred mixture we gradually added 100 ml of DMSO. The mixture heated spontaneously, and t-Bu—C≡CH distilled at 60°C. When the exothermic reaction has ceased, the temperature of the bath was gradually raised to 150°C over 3 h. The obtained t-Bu—C≡CH was dried with sodium sulfate and distilled on a column. The yield was 27 g (85%); bp 36.8-38°C, $n_D^{20}$ 1.3756.

The sodium thiolates were obtained by the reaction of sodium methoxide with a 1.5-fold quantity of RSH in a nitrogen atmosphere. The solution (~1.3 N) contained equimolar amounts of RSNa and $CH_3ONa$.

Reaction of Thiolates with t-Bu—C≡CH in a Methanol Medium. All the operations on the degassing of the reaction tubes and reagents and also the mixing of the reagents and the sealing of the tubes were realized in high-vacuum apparatus with a "manifold" in an argon atmosphere (special purity), which was additionally purified from oxygen by passing through two columns containing activated chromium—nickel catalyst and dehydrated by 4 Å and 5 Å molecular sieves.

When the manifold and the reaction tubes had been heated under a vacuum of $8 \cdot 10^{-3}$ mm Hg and subsequently filled with purified argon (the operation was repeated three to four times) they were connected to the ground glass joints of tubes, in one of which (the measuring tube) we placed t-Bu—C≡CH and in the other a solution of RSNa in methanol. The reagents were thoroughly degassed, periodically cooled to −120°C (in a mixture of ethanol and liquid nitrogen) under a vacuum of $8 \cdot 10^{-3}$ mm Hg, and then thawed. The operation was repeated until the evolution of gas bubbles had completely ceased. After degassing the calculated amount of t-Bu—C≡CH was recondensed in the reaction tube containing the thiolate, cooled in liquid nitrogen. The tube was sealed under vacuum and heated in a thermostat. The reaction conditions were as follows: 150 ± 2°C, 5 h, t-Bu—C≡CH : RSNa : MeONa = 1.5 : 1 : 1 (moles). An equimolar excess of sodium methoxide prevented the formation of the free thiol from the thiolates of the weakly acidic thiols according to the equation RSNa + MeOH ⇌ RSH + MeONa.

Reaction of $CH_3SNa$ with t-Bu—C≡CH. A tube with the degassed reagents [1.8 ml (15 mmole) of t-Bu—C≡CH and 7.5 ml (10 mmole) of 1.3 N $CH_3SNa$ in methanol] was heated in a steel jacket at 150 ± 2°C for 5 h. The reaction products were diluted with 5 ml of ether, washed with sodium hydroxide solution and with water, and dried with sodium sulfate. In the crude product (ether solution) by GLC we found 60.4% of t-Bu—C($SCH_3$)=$CH_2$ and 39.6% of cis-t-Bu—CH=CH—$SCH_3$. By PMR in the undistilled product (ether replaced by carbon tetrachloride) we obtained an $\alpha$/cis-$\beta$ ratio of 60 : 40. The constants of the redistilled compound are given in Table 1.

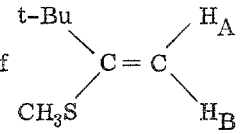
The reactions of t-Bu—C≡CH with the other RSNa compounds, where R = Et, n-Pr, i-Pr, n-Bu, i-Bu, and t-Bu, were realized under identical conditions.

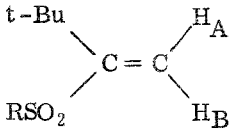
Alternative Syntheses. The $\alpha$-adducts of t-Bu—C(SR)=$CH_2$, where R = Me, Et, n-Pr, n-Bu, were obtained by the catalytic cleavage of the mercaptols of pinacoline t-Bu—C$(SR)_2$—$CH_3$ by the method in [3, 9]. Compounds with R = Me were obtained from them for the first time. The $\beta$-adducts t-Bu—CH=CH—SR, where R = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, and t-Bu, were obtained as mixtures of the cis and trans isomers by free-radical addition of the thiols to t-BuC≡CH by the method in [3]. The compounds with R = Me, i-Pr, and i-Bu were synthesized from them for the first time.

a) 2, 2-Bis(methylthio)-3, 3-dimethylbutane t-Bu—C$(SCH_3)_2CH_3$. A mixture of 6.5 g of anhydrous zinc chloride, 10.0 g (0.10 mole) of $CH_3COC(BH_3)_3$, and 19.2 g (0.40 mole) of $CH_3SH$ was kept in a sealed tube at ~20°C for nine days with periodic shaking. After distillation of the $CH_3SH$ the residue was diluted with ether, washed successively with 2 N hydrochloric acid, sodium bisulfite, saturated sodium bicarbonate solution, and to a neutral reaction with water, and dried with sodium sulfate. After distillation 11.27 g (63.5%) of the

desired compound was obtained. Its properties are given in Table 2.

b) 2-Methylthio-3, 3-dimethyl-1-butene t-Bu—C($SCH_3$) = $CH_2$. The catalytic cleavage of t-Bu—C$(SCH_3)_2$-$CH_3$ was carried out in a distillation flask with a rod-and-disk fractionating column in the presence of p-toluenesulfonic acid at a bath temperature of 40-100°C under a vacuum of 125 mm Hg in a stream of nitrogen. From 7.28 g of the mercaptol after 5 h we obtained 4.23 g (80%) of the desired compound (Table 2).

PMR spectrum of  (carbon tetrachloride, δ, ppm): 5.01 d ($H_A$), 4.43 s ($H_B$), $J^{gem}_{H_AH_B}$ = 0.08 Hz, 2.14 s ($CH_3S$), 1.15 s (t-Bu—C).

For the sulfones*  (DCCl$_3$, δ, ppm): 5.97-5.99 d ($H_A$), 6.21 d ($H_B$), $J^{gem}_{H_AH_B}$ = 1.0 Hz, 1.35 s (t-Bu—C).

c) 1-Methylthio-3, 3-dimethyl-1-butene cis, trans-t-Bu—CH = CHS$CH_3$. A mixture of 2.4 g (50 mmole) of $CH_3SH$, 6.2 g (75 mmole) of t-bu—C≡ CH, 50 mg of DINIIZ, and 9 ml of absolute methanol was heated in a sealed tube in an atmosphere of nitrogen at 70°C for 7 h. The product was washed with water, 20% aqueous potassium hydroxide solution, and with water and dried with sodium sulfate. After distillation 4.47 g (73%) of the desired compound was obtained. PMR spectrum of cis, trans-t-Bu—$CH_D$ = $CH_C$—$SCH_3$ (carbon tetrachloride, δ, ppm): cis isomer 5.56 d ($H_C$), 5.32 d ($H_D$), $J^{cis}_{H_CH_D}$ = 10.9 Hz, 2.19 s ($CH_3$—S), 1.11 s (t-Bu—C); trans isomer 5.78 d ($H_C$), 5.33 d ($H_D$), $J^{trans}_{H_CH_D}$ = 15.3 Hz, 2.14 s ($CH_3$—S), 1.02 s (t-Bu—C), cis : trans = 19 : 81. For the other trans-t-Bu—$CH_D$ = $CH_C$SR (carbon tetrachloride, δ, ppm): 5.72-5.78 d ($H_C$),* 5.33-5.66 d ($H_D$),* $J^{trans}_{H_CH_D}$ = 15.3 Hz, 1.02 s (t-Bu—C), 1.275 s (t-Bu—S), 2.14 s (Me—S). The spectra of the cis-β-isomers coincide fully with the data in Table 1.

The corresponding sulfones have PMR spectra (DCCl$_3$, δ, ppm): cis-t-Bu—$CH_D$ = $CH_C$$SO_2$R 6.02-6.06 d ($H_C$), 6.23-6.34 d ($H_D$), $J^{cis}_{H_CH_D}$ = 13.0 Hz, 1.31 s (t-Bu—C), 1.39 s (t-Bu—$SO_2$); trans-t-Bu—$CH_D$ = $CH_C$—$SO_2$R 6.15-6.16 d ($H_C$), 6.90 d ($H_D$), $J^{trans}_{H_CH_D}$ = 15.5 Hz, 1.11 s (t-Bu—C), 1.35 s (t-Bu—$SO_2$).

## CONCLUSIONS

1. A method which fully eliminates the competing free-radical reaction was developed for the nucleophilic addition of thiols to alkylacetylenes.

2. Under purely nucleophilic conditions steric effects substantially affect the regioorientation of a thiolate ion adding to tert-butylacetylene. The proportion of attack at the β atom of the C≡ C bond increases with increase in the volume of the nucleophilic reagent.

3. The β adducts are formed strictly stereospecifically by a nucleophilic mechanism of 1, 2-anti-addition, and steric effects do not affect the stereochemistry of the process.

4. It was found that the ratio of the regioisomers formed in the reaction of 1-alkynes with thiols and alcohols correlates well with Charton's steric constants for alkyl groups in the nucleophilic reagent.

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* The synthesis of the α-sulfone and also of the cis- and trans-β-sulfones and their chromatographic separation were described in [3, 4, 9].

† When R = t-Bu, $\delta_{H_C} = \delta_{H_D}$ = 5.87 s; in deuteroacetone solution 6.04 d ($H_C$), 5.87 d ($H_D$), $J^{trans}_{H_CH_D}$ = 15.3 Hz.

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## FLUORINATED β-SULTONES

### 46. 2-HYDROHEXAFLUOROPROPANE-2-SULFOFLUORIDE

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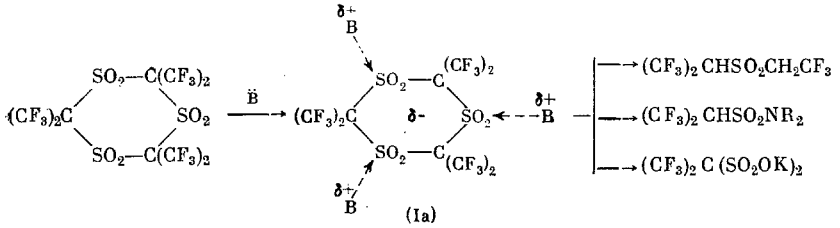
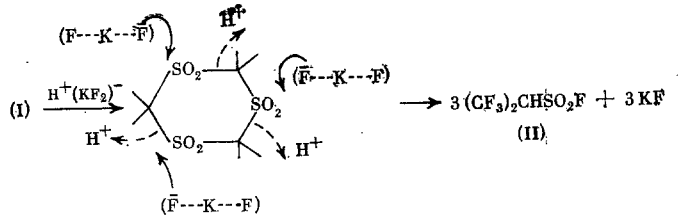
Hexa(trifluoromethyl)cyclotrimethylene-1, 3, 5-trisulfone (I) is exceedingly electrophilic reacting easily with nucleophilic reagents (of the type $\ddot{B}$) and forming rather unstable donor—acceptor complexes (Ia) that decompose to give sulfonyl compounds. In this manner, various sulfones and derivatives of sulfonic acids were obtained [1], for example:



(I) (Ia)

In the present work, the relationship between trisulfone I and potassium fluoride and difluoride was evaluated with the aim of preparing fluoroanhydrides of sulfonic acids. It was shown that trisulfone I does not react with KF even at 100°C. On the other hand, an exothermic reaction is produced on mixing crystalline trisulfone I and potassium difluoride: With as little at 0.01 moles of I the temperature of the reaction mixture reaches 150°C. Controlling such a reaction was possible only by diluting both reagents with inert additives (decalin or $MgSO_4$). In that case, the isolation of 2-hydrohexafluoropropane-2-sulfofluoride (II) was achieved in a yield of 85% (calculated on trisulfone I). The reaction, apparently, starts by an attack of highly nucleophilic potassium difluoride ions on sulfonyl groups and can be illustrated by the following mechanism:



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