

of the ^{13}C NMR signals at 70-25 ppm upon increasing the temperature from -67 to -40°C (slow exchange conditions [8]).

The ΔG^\ddagger values were calculated using the equation $\Delta G^\ddagger = 4.576 \cdot T(10.319 + \log T - \log k)$.

CONCLUSIONS

1. Dissolution of (1,2),(3,4),(5,6)-tripropanobenzene in $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2\text{FCl}$ generated the 1H-(1,2),(3,4),(5,6)-tripropanobenzenonium ion, which is converted by the action of Cl_2 to the 1-chloro-(1,2),(3,4),(5,6)-tripropanobenzenonium cation. NMR spectroscopy indicates that these ions undergo a degenerate rearrangement by 1,2-shift of the H and Cl atoms, respectively, at approximately the same rate to C^2 and C^6 .

2. The experimental value of ΔG^\ddagger of the 1,2-chlorine shift in the chlorosubstituted cation is close to that expected on the basis for the reported dependence of $\Delta G^\ddagger_{\text{Cl}}$ on δC^+ , while the ΔG^\ddagger value for the unsubstituted ion is significantly lower than that expected. This is probably a consequence of a difference in the sensitivity of the σ - and n -type orbitals (H and Cl atoms, respectively) to the effect of orbital orientation.

LITERATURE CITED

1. V. A. Koptug, The Structure and Reactivity of Arenonium Ions [in Russian], Nauka, Novosibirsk (1983), p. 269.
2. V. G. Shubin, in: F. L. Boschke (editor), Topics in Current Chemistry, Vol. 116/117, Springer-Verlag, Berlin (1984), p. 267.
3. V. F. Loktev, M. M. Shakirov, and V. G. Shubin, Izv. Siber. Otdel. Akad. Nauk SSSR, Ser. Khim., No. 12, issue 2, 104 (1985).
4. F. H. Allen, Acta Crystallogr., **37**, 900 (1981).
5. V. F. Loktev, D. V. Korchagina, M. M. Shakirov, and V. G. Shubin, Izv. Siber. Otdel. Akad. Nauk SSSR, Ser. Khim., No. 12, issue 5, 146 (1978).
6. R. Mayer, Chem. Ber., **89**, 1443 (1956).
7. V. F. Loktev, D. V. Korchagina, and V. G. Shubin, Izv. Siber. Otdel. Akad. Nauk SSSR, Ser. Khim., No. 12, issue 5, 135 (1978).
8. L. Piette, NMR and ESR Spectroscopy [Russian translation], Mir, Moscow (1964), p. 112.

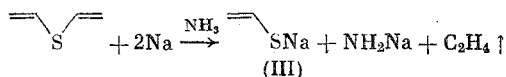
SYNTHESIS OF MONOSUBSTITUTED DIVINYL SULFIDES

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Only a few examples of the synthesis of vinyl (2-organylviny) sulfides have been reported. A mixture of the Z and E isomers of vinyl styryl sulfide (I) was obtained in 50% yield upon treating styrylthiol acetate with acetylene in ethanolic alkali [1, 2]. Sulfide (I) was also synthesized by the addition of the diethyldithiocarbamate anion to acetylene with subsequent splitting of the adduct formed by phenylacetylene [3]. Brandsma et al. [4] have described a multistep synthesis of vinyl 1-propenyl sulfide using vinyl 1-propynyl sulfide.

We have found that sodium ethenethiolate (III) formed in addition to sodium amide upon the reaction of divinyl sulfide with metallic sodium in liquid NH_3 may be used in the synthesis of monosubstituted divinyl sulfides.



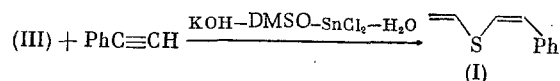
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TABLE 1. Conditions for the Synthesis of (I) from Sodium Ethenethiolate and Phenylacetylene (0.11 mole $\text{CH}_2=\text{CHSNa}$, 0.2 mole $\text{PhC}\equiv\text{CH}$, 200 ml DMSO)

Experiment no.	T., °C	Time, h	H_2O , ml	Yield of (I), %
1*	95-97	5	30	87
2	95-97	5	30	56
3	95-97	5	7	36
4	20-25	5	30	6
5	20-25	96	30	30

*The experiment was carried out in the presence of 0.044 mole $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.176 mole KOH in accord with the equation:
 $\text{SnCl}_2 + 4\text{KOH} \rightarrow \text{K}_2\text{SnO}_2 + 2\text{KCl} + 2\text{H}_2\text{O}$.

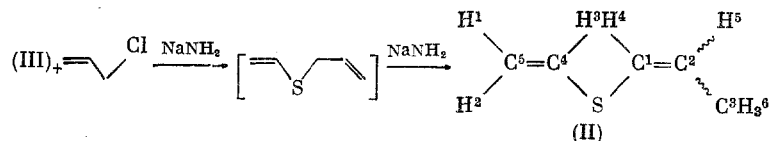
The addition of thiolate (III) to phenylacetylene to form Z-styryl vinyl sulfide (I) proceeds most readily in $\text{KOH-DMSO-SnCl}_2\text{-H}_2\text{O}$ at 95-97°C.



Elimination of SnCl_2 and KOH from the reaction mixture leads to a decrease in the yield of sulfide (I) from 87 to 56% (Table 1, experiments 1 and 2). Facilitation by SnCl_2 was also observed in our previous work on the reaction of sulfur with acetylene in aqueous alkali [5] and in other nucleophilic addition reactions [6-8]. The reasons and usefulness of this effect are now under study.

A decrease in the amount of water from 30 to 7 ml per 0.11 mole thiolate (III) leads to a decrease in the yield of sulfide (I) to 36% (Table 1, experiments 2 and 3). This decrease is probably related to slower protonation of the intermediate $\text{CH}_2\text{CHSCH}=\text{CPh}$ anion. The addition of thiolate (III) to phenylacetylene at 20°C proceeds less efficiently than upon heating (experiments 2, 4, and 5). In this case, stirring the reagents for 5 h gives a 6% yield of sulfide (I), while maintenance for 96 h gives a 30% yield.

The reaction of thiolate (III) with allyl chloride in DMSO proceeds to give a high yield of sulfide (II) in a few minutes at 20°C. The intermediate allyl vinyl sulfide could not be detected in the reaction mixture; this compound is rapidly converted to sulfide (II) by the action of sodium amide.



Thus, an additional promising approach is indicated for the synthetic application of divinyl sulfide which has not become available.

EXPERIMENTAL

The IR spectra were taken neat on a Specord IR-75 spectrometer. The NMR spectra were taken on a Bruker WP-200SY spectrometer. The mass spectra were taken on a Varian MAT-212 mass spectrometer.

Z-Styryl Vinyl Sulfide (I). A solution of 10 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 g KOH in 30 ml water was added to 200 ml DMSO. Then, 15 g of a mixture obtained from 9.5 g divinyl sulfide and 5.1 g sodium in liquid ammonia was added with rapid stirring followed by 20 g phenylacetylene and 0.01 g hydroquinone. The reaction mixture was heated for 5 h at 95-97°C. The mixture was cooled, diluted with water and extracted with ether. The ethereal extracts were washed with water, dried over K_2CO_3 and fractionated in vacuum to give 15.5 g (87%) sulfide

(I), bp 84-85°C (2 mm), d_4^{20} 1.0577, n_D^{20} 1.6309. IR spectrum (ν , cm^{-1}): 3080, 3050, 3020, 2970, 2920, 2875 (νCH), 1590, 1580 ($\nu\text{C}=\text{C}$), 1485 (ν arom), 1435 (νCH_2), 1370, 1350 (δCCH), 1265 (δCH_2), 1065, 1020 (ρCH_2 , νCC), 940 (τCH_2), 900 (νCCH arom), 875 (ωCH_2), 840 (δCCH), 760 (δCCH , arom), 730, 710, 675 (δCCH), 640, 580 (νCS), 515 (δCCH). PMR spectrum (CCl_4 , δ , ppm, J, Hz): 7.28 m (H^6), 6.46 d (H^4), 6.33 q (H^3), 6.20 d (H^5), 5.23 d (H^2), 5.22 d (H^1), $J_{\text{H}^1\text{H}^3} = 9.3$, $J_{\text{H}^2\text{H}^3} = 16.9$, $J_{\text{H}^4\text{H}^5} = 10.6$. Mass spectrum, m/z (rel. intensity, %): 162 (100), 161 (31), 134 (15), 129 (86), 128 (41), 117 (28), 115 (20), 102 (21), 91 (38), 87 (21), 77 (28), 51 (23), 28 (27). Found, %: C 74.34; H 6.38; S 19.60. $\text{C}_{10}\text{H}_{10}\text{S}$. Calculated, %: C 74.03; H 6.21; S 19.76.

Vinyl 1-Propenyl Sulfide (II) (2:3 ratio of Z and E isomers). At 20°C, 10 g of a mixture obtained in liquid ammonia from 6.4 divinyl sulfide and 3.4 g sodium was added to 300 ml DMSO and, 15 min after the addition, 7.8 g allyl chloride was introduced. The mixture was evaporated at 1 mm to give 6.7 g (90%) sulfide (II), bp 107-108°C (720 mm), d_4^{20} 0.9412, n_D^{20} 1.5088. IR spectrum (ν , cm^{-1}): 3090, 3015, 3000, 2965, 2936, 2910, 2870, 2850 (νCH), 1615, 1580 ($\nu\text{C}=\text{C}$), 1435, 1430 (δCH_2), 1370 (δCH_3), 1325 (δCCH), 1265, 1230 (δCH_2), 1055, 1015 (ρCH_2), 945, 930 (τCH_2), 865 (ωCH_2), 760, 715 (δCH), 660, 580 (νCS). ^1H and ^{13}C NMR spectra in acetone- d_6 (δ , ppm, J, Hz): Z-(II): 6.57 d.d (H^3), 6.18 d.q. (H^4), 5.78 d.q. (H^5), 5.19 d (H^1), 5.14 d (H^2), 1.77 d.d (H^6), $J_{\text{H}^1\text{H}^3} = 10.0$, $J_{\text{H}^2\text{H}^3} = 16.8$, $J_{\text{H}^4\text{H}^5} = 9.5$, $J_{\text{H}^4\text{H}^6} = 1.5$, $J_{\text{H}^5\text{H}^6} = 6.9$; 132.32 (C^4), 131.20 (C^2), 121.02 (C^1), 112.02 (C^5), 14.7 (C^3); E-(II): 6.44 d.d (H^3), 6.10 d.q (H^4), 5.83 d.q (H^5), 5.22 d (H^1), 5.18 d (H^2), 1.66 d.d (H^6), $J_{\text{H}^1\text{H}^3} = 10.0$, $J_{\text{H}^2\text{H}^3} = 16.8$, $J_{\text{H}^4\text{H}^5} = 15.0$, $J_{\text{H}^4\text{H}^6} = 1.6$, $J_{\text{H}^5\text{H}^6} = 6.7$; 132.06 (C^4), 127.18 (C^2), 122.68 (C^1), 112.02 (C^5), 18.50 (C^3). Mass spectrum, m/z (rel. intensity, %): 100 (85), 99 (22), 85 (100), 73 (14), 71 (13), 67 (13), 65 (16), 60 (12), 59 (25), 58 (13), 45 (34), 41 (29), 39 (23), 32 (21), 28 (79). Found, %: C 59.89; H 8.06; S 31.51. $\text{C}_5\text{H}_8\text{S}$. Calculated, %: C 59.95; H 8.06; S 32.00.

CONCLUSIONS

Sodium ethenethiolate obtained from readily available divinyl sulfide reacts with allyl chloride and phenylacetylene to form vinyl 1-propenyl sulfide and vinyl styryl sulfide.

LITERATURE CITED

1. N. P. Petukhova and E. N. Prilezhaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2314 (1968).
2. E. N. Prilezhaeva, N. P. Petukhova, and M. F. Shostakovskii, *USSR Inventor's Certificate* No. 198331 (1966); *Byull. Izobr.*, No. 14 (1967).
3. M. G. Voronkov, B. A. Trofimov, S. V. Amosova, N. I. Kazantseva, O. A. Tarasova, and V. V. Kryuchov, *Sixth International Symposium on Organic Sulfur Chemistry*, Bangor (1974), p. C5.
4. F. Vermeer, J. Meijer, C. Eylander, and L. Brandsma, *Rec. Trav. Chim.*, **95**, 25 (1976).
5. B. A. Trofimov, V. A. Potapov, N. K. Gusarova, S. V. Amosova, L. M. Sinegovskaya, and V. Yu. Vitkovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 230 (1983).
6. B. A. Trofimov, S. V. Amosova, N. K. Gusarova, V. A. Potapov, and A. A. Tatarinova, *Sulf. Lett.*, **1**, 151 (1983).
7. N. K. Gusarova, V. A. Potapov, S. V. Amosova, and B. A. Trofimov, *Zh. Org. Khim.*, **19**, 2477 (1983).
8. B. A. Trofimov, N. K. Gusarova, A. A. Tartarinova, S. V. Amosova, and L. M. Sinegovskaya, *Zh. Org. Khim.*, **20**, 1802 (1984).
9. B. A. Trofimov and S. V. Amosova, *Divinyl Sulfide and Its Derivatives* [in Russian], Nauka, Novosibirsk (1983), p. 135.
10. B. A. Trofimov and S. V. Amosova, *Sulfur Rep.*, **3**, 323 (1984).