Reactions of Sulfides with *t*-Butyl Hypochlorite

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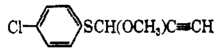
The oxidation with *t*-butyl hypochlorite of a number of sulfides of the general structure $RSCH_2R'$ is described. In methanol or ethanol as solvents and R′ = ethynyl or carbomethoxy groups, no sulfoxide was formed; instead, almost complete conversions to the corresponding α-methoxy- or α-ethoxy-substituted compounds were observed. In the case of R′ = phenyl, mixtures of the α-substituted products with sulfoxides were obtained, whereas with R′ = alkyl, sulfoxides were the sole products. In *t*-butyl alcohol as solvent, however, only the sulfoxide appears to be formed. A plausible reaction sequence is discussed.

The treatment of sulfides with *t*-butyl hypochlorite in methanol has recently been reported[1] as a method for the preparation of sulfoxides. The advantage relative to other methods was the absence of sulfones in the reaction products. We had encountered some difficulties in the per acid oxidation of some propargyl sulfides to the sulfoxides due to the fact that variable amounts of sulfones were formed. Our attention was then focused on the above procedure, and the present paper is a report on this work which in many cases led to other products than sulfoxides.

A methanol solution of phenyl propargyl sulfide (1)[2] was allowed to react with an equimolar amount of *t*-butyl hypochlorite at −78° to give, in 78% yield, a liquid product, homogeneous by gas chromatography. The infrared spectrum shows, besides absorption due to an ethynyl group, a strong band at 1075 cm^{-1} characteristic of the C–O stretching vibration. Only insignificant absorption was observed in the 1000–1050-cm^{-1} region where the sulfoxide group commonly absorbs.[3] Phenyl propargyl sulfoxide was subsequently prepared by per acid oxidation of the corresponding sulfide and its infrared spectrum is different from that of the above reaction product. The nmr spectrum of the compound shows two doublets (J = 2.5 Hz) at τ 7.29 and 4.44, a singlet at 6.56, and a multiplet centered at 2.63 with a peak area ratio of 1:1:3:5, respectively. These data are compatible with the structure 1-methoxy-1-phenylthio-2-propyne (2), which was subsequently confirmed by comparison with an authentic sample, prepared by allowing the sulfide 1 to react, consecutively, with sulfuryl chloride[4] and sodium methoxide. This quite unexpected finding urged us to try the same reaction on a number of sulfides; the results are summarized in Table I.

It can be seen from Table I that the sulfides used in this study have, as a common structural feature, at least one methylene group adjacent to sulfur. They were either known compounds or prepared from the respective thiol and halide according to standard procedures. We found it the most convenient to analyze each reaction mixture on the basis of its nmr spectrum, which in most cases was quite simple; the spectra of sulfoxide-containing mixtures, however, were more complicated because of the strong solvent effect caused by the sulfoxide, resulting in a downfield shift of the acetylenic protons and overlap with other peaks.[5] Gas chromatography was not always satisfactory owing to partial decomposition. The recorded yields are certainly not optimal; indeed, conversions were close to 100% in most cases, but losses occurred during purification. No traces of sulfones were found in any of the experiments.

TABLE I
OXIDATION OF SULFIDES WITH
t-BUTYL HYPOCHLORITE IN METHANOL[a]

Reacn	Sulfide	No.	Product	No.	Yield, %
1	$C_6H_5SCH_2C\equiv CH$	**1**	$C_6H_5SCH(OCH_3)C\equiv CH$	**2**	78
2		**3**		**4**	67
3	$C_6H_5CH_2SCH_2C\equiv CH$	**5**	$C_6H_5CH_2SCH(OCH_3)C\equiv CH$	**6**	60
4	n-$C_4H_9SCH_2C\equiv CH$	**7**	n-$C_4H_9SCH(OCH_3)C\equiv CH$	**8**	63
5	$C_6H_5SCH_2CO_2CH_3$	**9**	$C_6H_5SCH(OCH_3)CO_2CH_3$	**10**	82
6	$C_6H_5CH_2SCH_2CO_2CH_3$	**11**	$C_6H_5CH_2SCH(OCH_3)CO_2CH_3$	**12**	80
7	$(C_6H_5CH_2)_2S$	**13**	$(C_6H_5CH_2)_2SO$	**14**	64[b]
			$C_6H_5CH(OCH_3)SCH_2C_6H_5$	**15**	36
8	$C_6H_5CH_2SCH_3$	**16**	$C_6H_5CH_2SOCH_3$	**17**	88[b]
			$C_6H_5CH(OCH_3)SCH_3$	**18**	12
9	$C_6H_5CH_2SC_6H_5$	**19**	$C_6H_5CH_2SOC_6H_5$	**20**	73[b]
			$C_6H_5CH(OCH_3)SC_6H_5$	**21**	27
10	$C_6H_5SCH_3$	**22**	$C_6H_5SOCH_3$	**23**	90
11	$C_6H_5SCH_2CH_3$	**24**	$C_6H_5SOCH_2CH_3$	**25**	92

[a] Sulfide solutions were 0.38 M. [b] Product ratio determined by nmr.

The oxidation of methyl and ethyl phenyl sulfide (reactions 10 and 11) gave exclusively the corresponding sulfoxides. In all the other reactions a varying degree of substitution at the α carbon occurred, being the exclusive process in reactions 1–6. In most cases the nmr spectra provided conclusive evidence for the assigned structures, but additional evidence was also obtained from the infrared spectra; furthermore, the sulfoxides from reactions 7 through 11 were identified by comparison with authentic samples, and the α-substitution products were hydrolyzed to the corresponding aldehydes or their 2,4-dinitrophenylhydrazones.

The outcome of the reaction is quite dependent on the conditions. In some cases with a high sulfide concentration (>0.5 molar) a saltlike precipitate, difficult to stir, was formed at −78°. The result was lower conversions and poor reproducibility, although the products remained the same. More important is the observation that, in *t*-butyl alcohol as the solvent, sulfide 1 underwent reaction to give the corresponding sulfoxide and none of the α-substituted product; in ethanol, however, 1-ethoxy-1-phenylthio-2-propyne (26) was the sole product. A benzene solution of 1 reacted with *t*-butyl hypochlorite to give an unstable

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[1] P. S. Skell and M. F. Epstein, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 26N. We want to thank Professor Skell for informing us about the experimental details.

[2] G. Pourcelot, P. Cadiot, and A. Willemart, *Compt. Rend.*, **252**, 1630 (1961); G. Pourcelot and P. Cadiot, *Bull. Soc. Chim. France*, 3016 (1966).

[3] L. T. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 357.

[4] F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

[5] E. B. Whipple, J. H. Goldstein, L. Mandell, G. S. Reddy, and G. R. McClure, *ibid.*, **81**, 1321 (1959).

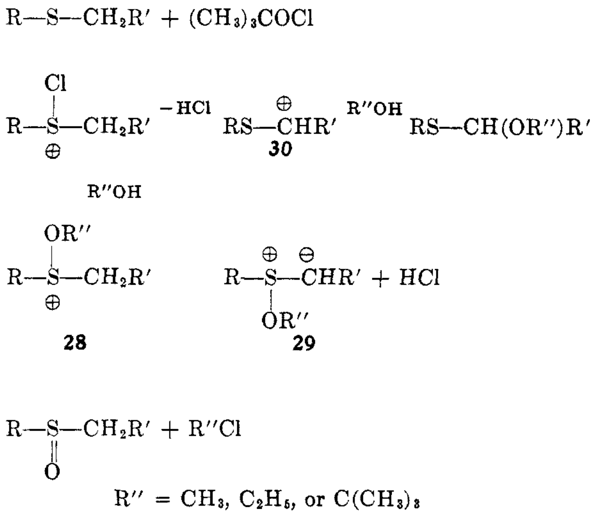
product, in 20% conversion, identified as 1-chloro-1-phenylthio-2-propyne (**27**) on the basis of its nmr spectrum and the fact that it gave compound **2** upon reaction with sodium methoxide.

Discussion

It has long been known that sulfides, having at least one hydrogen at the α carbon, when allowed to react with chlorine[6a] or sulfuryl chloride,[4,6b] give α-chlorinated products. These reactions have been shown to proceed by a polar mechanism involving chlorosulfonium salts as intermediates. Substitution at the α carbon has not previously been observed in reactions of sulfides with *t*-butyl hypochlorite;[1,7–9] however, treatment of carbon tetrachloride solutions of a number of alkyl phenyl sulfides with N-chlorosuccinimide at room temperature afforded the respective α-chloro derivatives in good yields.[10] On the other hand, in hydroxylic solvents N-bromosuccinimide and dibenzyl sulfide gave only the sulfoxide.[11] It is reasonable to assume that the present reaction is polar in nature, but in order to prove this a few reactions of sulfide **1** were carried out. We found that oxygen did not inhibit the formation of compound **2**. No significant change in product conversion was observed in the presence of cyclohexane, and cyclohexyl chloride could not be detected. Finally, methyl methacrylate did not inhibit the formation of **2**. Hence, the reaction probably does not involve free radicals,[12] and, as outlined in Scheme I, a polar mechanism is suggested which resembles the Pummerer reaction.[13]

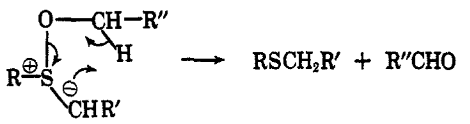
By analogy[6] the initial formation of a chlorosulfonium ion is proposed which reacts with the alcohol (solvent) to give the alkoxysulfonium chloride **28**. This salt[14] can either lose hydrogen chloride, yielding α-substitution products, or form the sulfoxide by elimination of alkyl halide, and/or isobutylene when R″ = *t*-butyl ion. Accordingly, the acidity of the α hydrogens should play an important role in determining the reaction path; electron-attracting substituents (R′), like ethynyl and carbomethoxy, should facilitate hydrogen chloride elimination and hence α substitution, whereas alkyl groups should favor sulfoxide formation. This is in complete agreement with our observations. Particularly the results of reactions 3, 4, 6 and 8 (Table I) clearly demonstrate that substitution occurred exclusively at the carbon bearing the best electron-withdrawing group.

SCHEME I



The drastic difference in product observed when changing the solvent from methanol to *t*-butyl alcohol is readily accommodated by Scheme I. The formation of sulfoxide is so much faster from the *t*-butoxy sulfonium salt than from the methoxy analog as is, in the first approximation, the difference in the ease of formation of *t*-butyl *vs.* the methyl carbonium ion; hence, α substitution should not be important with *t*-butyl alcohol as the solvent.

The loss of hydrogen chloride from **28** is depicted as leading to the carbonium ion **30**[14] either directly by a concerted process or *via* the ylide **29**.[15] No experimental evidence is available from the present work which enables us to choose between these two modes of reaction; it is interesting, however, to note that the fragmentation of such an ylide represents the crucial step in the dimethyl sulfoxide oxidation of alcohols to aldehydes.[16] If such a process were important in the present reaction, low conversion and the formation of formaldehyde (R″ = H) or acetaldehyde (R″ = CH₃) would result; neither was detected in any of our experiments.



Scheme I accounts for the observed 1:1 stoichiometry. Walling and Mintz[9] have shown that in benzene solution the oxidation of diphenyl sulfide or dimethyl sulfide requires approximately 2 moles of *t*-butyl hypochlorite in order to complete the reaction. Consequently, their reaction products were considerably more complex. From reactions of sulfide **1**, we occasionally isolated small amounts of diphenyl disulfide in addition to the products expected according to Scheme I. A plausible explanation comprises an acid hydrolysis of the α-substitution product with subsequent oxidation of the benzenethiol formed.[17] Accordingly, in one experiment we also isolated propargyl aldehyde as its 2,4-dinitrophenylhydrazone derivative.

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[6] (a) H. Böhme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949); (b) W. E. Truce, G. H. Birum, and E. T. McBee, *J. Am. Chem. Soc.*, **74**, 3594 (1952).

[7] R. J. Gritter and D. J. Carey, *J. Org. Chem.*, **29**, 1160 (1964).

[8] C. R. Johnson and D. McCants, *J. Am. Chem. Soc.*, **87**, 1109 (1965).

[9] C. Walling and M. J. Mintz, *J. Org. Chem.*, **32**, 1286 (1967). We want to thank Professor Walling for providing us with a preprint.

[10] D. L. Tuleen and T. B. Stephens, *Chem. Ind.* (London), 1555 (1966); D. L. Tuleen and V. C. Marcum, *J. Org. Chem.*, **32**, 204 (1967).

[11] W. Tagaki, K. Kikukawa, K. Ando, and S. Oae, *Chem. Ind.* (London), 1624 (1964).

[12] It has been reported[7] that the rate of oxidation of diphenyl sulfide with *t*-butyl hypochlorite was enhanced by ultraviolet irradiation, which indicates a radical mechanism, but this could not be confirmed.[9]

[13] (a) R. Pummerer, *Ber.*, **43**, 1401 (1910). (b) W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **28**, 2686 (1963), and references therein.

[14] It is also possible that the α-substitution product derives from the chlorosulfonium ion, which by hydrogen chloride elimination would form the ion **30**.

[15] The carbonium ion **30** may be by-passed since the product can conceivably be formed by a Stevens-type rearrangement of the ylide **29**.

[16] A. H. Fenselau and J. G. Moffat, *J. Am. Chem. Soc.*, **88**, 1762 (1966); K. Torsell, *Tetrahedron Letters*, 4445 (1966).

[17] The alcohols used were not anhydrous. Benzenethiol is readily oxidized to diphenyl disulfide by hypochlorites.

Some recent observations by Johnson and Phillips[18] are relevant to the present discussion. They showed that dibenzylmethoxysulfonium fluoroborate reacted with sodium methoxide in methanol yielding α-methoxybenzyl benzyl sulfide (**15**); similar results were also obtained in the case of benzyl phenyl sulfide.

In view of the good yields and the simplicity of the present reaction, it could be useful for the synthesis of certain hemithio acetals.

Experimental Section[19]

Reagents.—The propargyl sulfides were prepared from their respective thiols and propargyl bromide.

1-Phenylthio-2-propyne (**1**) was prepared in 77% yield.[2]

1-(*p*-Chlorophenylthio)-2-propyne (**3**) was prepared in 76% yield, bp 58° (0.1 mm), n^{24}_{D} 1.5998.

Anal. Calcd: C, 59.18; H, 3.86. Found: C, 58.92; H, 3.99.

1-Benzylthio-2-propyne (**5**) was prepared in 82% yield, 76° (1 mm), n^{24}_{D} 1.5742.

Anal. Calcd: C, 74.03; H, 6.21. Found: C, 73.67; H, 6.35.

1-*n*-Butylthio-2-propyne (**7**) was prepared in 78% yield, bp 78° (30 mm), n^{24}_{D} 1.4769.

Anal. Calcd: C, 65.56; H, 9.43. Found: C, 65.00; H, 9.35.

The other sulfides were either commercial products or prepared by known procedures. *t*-Butyl hypochlorite was obtained from Frinton Laboratories, South Vineland, N. J., and used without further purification.

Reactions of Sulfides with *t*-Butyl Hypochlorite. General Procedures.—To a stirred solution of the sulfide (50 mmoles) in 130 ml of methanol kept at −78°, *t*-butyl hypochlorite (50 mmoles) was added dropwise during a 15-min period. After the addition was completed 3 g of solid sodium bicarbonate was added, and the reaction mixture was allowed to attain room temperature (~2 hr). The solid was filtered, and the filtrate was evaporated on a rotary evaporator, the distillate being collected. The residue and the distillate were then analyzed by gas chromatography and spectroscopy. The pure products were obtained by conventional isolation procedures. No change in the results was observed when the reaction of 1-phenylthio-2-propyne (**1**) was carried out at 0° (ice bath). In this case the hypochlorite was added to a slurry of the sulfide and sodium bicarbonate in methanol. Furthermore, the same results were obtained on both a smaller and a larger scale.

A. 1-Methoxy-1-phenylthio-2-propyne (**2**) was obtained in 78% yield, bp 76° (0.2 mm), n^{25}_{D} 1.5670; $\nu_{\max}$ 3290, 2120 ($C\equiv CH$) and 1075 cm^{-1} (C—O). The nmr spectrum is given in the Discussion section.

Anal. Calcd for $C_{10}H_{10}OS$: C, 67.38; H, 5.65. Found: C, 66.99; H, 5.62.

The compound formed a 2,4-dinitrophenylhydrazone derivative, mp 121° (from carbon tetrachloride), identical with that of propargyl aldehyde (lit.[20] mp 121–122°).

B. A solution of 8.1 g (60 mmoles) of sulfuryl chloride in 30 ml of carbon tetrachloride was added dropwise to a stirred solution of 7.4 g (50 mmoles) of the sulfide **1** in 50 ml of carbon tetrachloride. After the reaction mixture had been heated at 60° for 45 min, the solvent was removed under reduced pressure. A solution of sodium methoxide (50 mmoles) in 50 ml of methanol was added, and the mixture was left at room temperature overnight. After the usual isolation procedure, 4.5 g (50%) of **2** was obtained, bp 70° (0.2 mm), n^{23}_{D} 1.5670, with spectroscopic properties identical with those of the product obtained by method A.

1-(4-Chlorophenylthio)-1-methoxy-2-propyne (**4**) was prepared in 67% yield, bp 71° (0.1 mm), n^{24}_{D} 1.5775; $\nu_{\max}$ 3300, 2110 ($C\equiv CH$) and 1080 cm^{-1} (C—O); the nmr spectrum showed a doublet at 7.31 ($C\equiv CH$), a singlet at 6.58 (OCH_3), a doublet at 4.46 (CH), and a multiplet at 2.67 (ar H), with peak area ratio 1:3:1:4, respectively.

Anal. Calcd for $C_{10}H_9ClOS$: C, 56.47; H, 4.27. Found: C, 56.36; H, 4.47.

1-Benzylthio-1-methoxy-2-propyne (**6**) was prepared in 60% yield, bp 67–68° (0.05 mm), n^{24}_{D} 1.5565; $\nu_{\max}$ 3260, 2120 ($C\equiv CH$) and 1075 cm^{-1} (C—O); the nmr spectrum showed a doublet at 7.40 ($C\equiv CH$), singlets at 6.70 (CH_3) and 6.28 (CH_2), a doublet at 4.83 (CH), and a singlet at 8.80 (ar); the peak area ratio is 1:3:2:1:5, respectively.

Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.30; H, 6.48.

The compound formed the 2,4-dinitrophenylhydrazone derivative of propargyl aldehyde.

1-*n*-Butylthio-1-methoxy-2-propyne (**8**) was prepared in 63% yield, bp 48° (1 mm), n^{24}_{D} 1.4730; $\nu_{\max}$ 3290, 2120 ($C\equiv CH$) and 1075 cm^{-1} (C—O); the nmr spectrum showed multiplets at 9.03, 8.50 and 7.38 (alkyl H), a doublet at 7.30 ($C\equiv CH$), a singlet at 6.69 (CH_3), and a doublet at 4.73 (CH); the area ratio is 9:1:3:1, respectively.

Anal. Calcd for $C_8H_{14}OS$: C, 60.71; H, 8.91. Found: C, 61.16; H, 9.44.

The compound formed the 2,4-dinitrophenylhydrazone derivative of propargyl aldehyde.

Methyl methoxyphenylthioacetate (**10**), was formed in 82% yield, bp 80–86° (0.2 mm), n^{24}_{D} 1.5454; $\nu_{\max}$ 1100 cm^{-1} (C—O); the nmr spectrum showed singlets at 6.55 (OCH_3), 6.43 (CO_2CH_3), and 4.93 (CH) and a multiplet at 2.65 (ar); the peak area ratio is 3:3:1:5, respectively.

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 56.58; H, 5.70. Found: C, 56.56; H, 5.71.

Methyl benzylthiomethoxyacetate (**12**) was obtained in 80% yield by short-path distillation, bath temp 140° (0.025 mm), n^{25}_{D} 1.5404; $\nu_{\max}$ 1090 cm^{-1} (C—O); the nmr spectrum showed singlets at 6.72 (OCH_3), 6.42 ($-CO_2CH_3$), 6.20 (CH_2), 5.20 (CH), and 2.75 (ar H); the peak area ratio is approximately 3:3:2:1:5.

Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24. Found: C, 58.43; H, 6.19.

Dibenzyl sulfoxide (**14**) **and α-Methoxybenzyl benzyl sulfide** (**15**) were obtained admixed with unreacted starting material **13**. Sulfoxide **14** was isolated and recrystallized from methanol, mp 135° (lit.[21] mp 135°). The α-oxidation product **15** was not obtained pure but was easily recognized from the spectra of the mixture, $\nu_{\max}$ 1090, 1070 cm^{-1} (C—O); the nmr spectrum showed singlets at 6.65 (OCH_3), 6.43 (CH_2), and 4.65 (CH) besides aromatic absorption. Benzaldehyde was obtained by acid hydrolysis of the mixture.

Benzyl Methyl Sulfoxide (**17**) **and α-Methoxybenzyl Methyl Sulfide** (**18**).—These were not separated from starting material **16**, but the structures could easily be assigned on the basis of evidence obtained from spectra of the mixture. An authentic sample of sulfoxide **17** was prepared,[22] the nmr spectrum of which could readily be recognized as part of that of the mixture. Compound **18** exhibited $\nu_{\max}$ 1085 cm^{-1} (C—O); the nmr spectrum showed singlets at 8.25 (CH_3), 6.63 (OCH_3), and 4.62 (CH) in addition to aromatic absorption.

Benzyl Phenyl Sulfoxide (**20**) **and α-Methoxybenzyl Phenyl Sulfide** (**21**).—The sulfoxide **20** crystallized from the reaction mixture and was recrystallized from ethanol, mp 125° (lit.[13a] mp 125.5°). From the mother liquor reasonably pure **21** was obtained, bp 113° (0.025 mm), n^{24}_{D} 1.6098; $\nu_{\max}$ 1085 cm^{-1} (C—O); the nmr spectrum showed singlets at 6.51 (OCH_3), 6.00 (CH_3), and 4.32 (CH) besides aromatic absorption.

The mixture afforded the 2,4-dinitrophenylhydrazone derivative of benzaldehyde, mp 239°.

Methyl phenyl sulfoxide (**23**) was obtained pure by distillation, bp 70° (0.025 mm), n^{24}_{D} 1.5734; the compound crystallized in the receiver, mp 25–26° (lit.[23] bp 104–105° (0.7 mm), mp 29.5–30°); $\nu_{\max}$ 1045 cm^{-1}; the nmr spectrum showed a singlet at 7.40 (CH_3) and a multiplet at 2.50 (ar H) with peak area ratio 3:5.

Ethyl phenyl sulfoxide (**25**) was obtained pure by distillation, bp 68–70° (0.05 mm), n^{23}_{D} 1.5668 (lit.[24] bp 146° (13 mm));

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[18] C. R. Johnson and W. G. Phillips, *Tetrahedron Letters*, 2101 (1965).

[19] Boiling points and melting points are uncorrected. Infrared spectra were obtained on Beckman IR-5A and IR-10 spectrometers. The nmr spectra were recorded on a Varian A-60A instrument with carbon tetrachloride or deuteriochloroform as solvents and tetramethylsilane as the internal standard. The chemical shifts are given in τ values.

[20] R. A. Raphael, *J. Chem. Soc.*, S44 (1949).

[21] R. Knoll, *J. Prakt. Chem.*, **113** [2], 45 (1926).

[22] S. Hünig and O. Boes, *Ann.*, **579**, 23 (1953).

[23] C. C. Price and J. J. Hydock, *J. Am. Chem. Soc.*, **74**, 1943 (1952).

[24] H. Hepworth and H. W. Clapham, *J. Chem. Soc.*, **119**, 1188 (1921).

ν_{max} 1040 cm^{-1}; the nmr spectrum showed a triplet at 8.92 (CH_3), a multiplet at 7.25 (CH_2), and a multiplet at 2.48 (ar H) with peak area ratio 3:2:5.

1-Ethoxy-1-phenylthio-2-propyne (**26**) was prepared from **1** according to the general procedure but with ethanol as solvent. During the reaction a small amount of propargyl aldehyde escaped and was trapped as its 2,4-dinitrophenylhydrazone, mp 120–121°. The product was distilled to give 72% of **26**, bp 60–62° (0.05 mm), $n^{24}D$ 1.5585; ν_{max} 1075 cm^{-1} (C—O); the nmr spectrum showed a triplet at 8.81, a quadruplet at 6.25 (OC_2H_5), and doublets of equal intensity at 7.37 ($C\equiv CH$) and 4.44 (CH) besides aromatic absorption.

Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.60; H, 6.20.

Trituration of the distillation residue with methanol gave a small amount of diphenyl disulfide, mp 60°, identical with an authentic sample.

Compound **26** was also prepared from **1** and sulfuryl chloride with subsequent treatment with ethanol. The yield was 51%.

1-Chloro-1-phenylthio-2-propyne (**27**).—A mixture of 1.5 g (10 mmoles) of sulfide **1** and 1 g of sodium bicarbonate in 30 ml of benzene was cooled in an ice bath, and 1.1 g (10 mmoles) of *t*-butyl hypochlorite was added dropwise with stirring. After 1 hr the reaction mixture was filtered and the benzene solution was distilled under reduced pressure. The liquid residue was shown by nmr to consist essentially of starting material and chloride **27** in a ratio of about 4:1; the latter showed doublets of equal intensity at 7.20 ($C\equiv CH$) and 4.29 (CHCl) besides aromatic absorption.

Reaction of 1-Phenylthio-2-propyne (1) with *t*-Butyl Hypochlorite in *t*-Butyl Alcohol.—A mixture of 1.5 g (10 mmoles) of sulfide **1** and 1 g of sodium bicarbonate in 30 ml of *t*-butyl alcohol and 6 ml of pentane was cooled to 0°, and 1.1 g (10 mmoles) of *t*-butyl hypochlorite was added with stirring. The reaction was worked up as usual, and the total product (1.6 g) was analyzed by nmr. The product consisted of phenyl propargyl sulfoxide and starting material **1** in a ratio of about 1:3; furthermore, a small amount of diphenyl disulfide was also present, indicating that some α-substitution product may have been formed.

1-Phenylsulfinyl-2-propyne.—A solution of 29.6 (0.2 mole) of sulfide **1** in 50 ml of methylene chloride was stirred and cooled (ice) while a solution of *m*-chloroperbenzoic acid (0.2 mole) was added dropwise over 2 hr. The product was worked up in the usual way. The crude liquid product was shown by glpc to consist essentially of one compound. Attempted distillation resulted in vigorous decomposition. The spectral properties of the crude product are in agreement with the structure for 1-phenylsulfinyl-2-propyne. Infrared data gave 3160, 2090 ($C\equiv CH$), and 1045 cm^{-1} (SO); the nmr spectrum showed a triplet at 7.52 ($C\equiv CH$), a doublet at 6.40 (CH_2, with J = 2.8 Hz), and complex aromatic absorption centered at 2.4.

Registry No.—**2**, 13864-98-7; **4**, 13864-99-8; **6**, 13865-00-4; **8**, 13865-01-5; **10**, 13865-02-6; **12**, 13865-03-7; **14**, 621-08-9; **15**, 13865-05-9; **17**, 824-86-2; **18**, 13865-06-0; **20**, 833-82-9; **21**, 13865-07-1; **23**, 1193-82-4; **25**, 4170-80-3; **26**, 13865-09-3; **27**, 13865-10-6; 1-phenylsulfinyl-2-propyne, 13865-11-7; *t*-butyl hypochlorite, 507-40-4.

Arylation by Aromatic Nitro Compounds at High Temperatures. III. Reactions of Nitrobenzene with Aromatic Fluorine Derivatives

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Nitrobenzene phenylates fluorobenzene, *p*-difluorobenzene, benzotrifluoride, and hexafluorobenzene in a flow system at 600°. Minor reactions, paralleling the behavior of nitrobenzene under electron impact in the mass spectrometer, lead to the formation of phenol and naphthalene derivatives. Hexafluorobenzene gives product distributions that differ markedly from those of the other three fluoroaromatics as well as those from benzene-d_6. In the reaction with hexafluorobenzene, the phenyl radical from benzoyl peroxide shows greater discrimination than that from nitrobenzene.

The previous paper[1] described formation of the phenyl radical by the thermal decomposition of nitrobenzene and the products from nitrobenzene, alone and in admixture with benzene and benzene-d_6. This article is concerned with the reaction of nitrobenzene with four aromatic fluorine derivatives at 600° to give fluorinated biphenyls and terphenyls, as well as products derived by rearrangement of nitrobenzene to phenyl nitrite and formation of phenoxy radicals.

Experimental Section

Arylations were run in a Vycor tube filled with Vycor beads in an electric furnace maintained at 600 ± 1° under pure dry nitrogen with contact times of 25 ± 3 sec. The vapors were condensed in a bulb at −60°, the condensate was distilled to recover unreacted material, and the residue was analyzed. Analyses were performed with a Consolidated Model 21-103c mass spectrometer with the inlet system at 250 or 325°, with a directly coupled gas chromatograph–mass spectrometer combination[2] also employing a 21–103c instrument with an electron multiplier in place of the Faraday-cup detector, and by gas chromatography on a column of polyethylene glycol sebacate on Chromosorb W. Mass spectra were measured at the conventional 70 ionizing v and at low voltage (7.5 v, uncorrected). For the low-voltage measurements, the repellers were maintained at an average potential of 3 v, the exact values being selected to give maximum sensitivity. The reagents and standards for gas chromatography were purchased from Aldrich Chemicals and used as received. Where purity was critical, the reagent was analyzed and, if necessary, purified by distillation, crystallization, and gas chromatography.

In a typical experiment, a solution of 2.044 ml (0.02 mole) of nitrobenzene in 9.6 g (0.1 mole) of fluorobenzene was passed through a Vycor tube at 600° under nitrogen flowing at 45 cc/min. Contact time was 25 sec. The vapors were condensed in a bulb at −60° and the condensate was distilled to recover 4.9 g of fluorobenzene and give 4.1 g of products, the composition of which is shown in Table I. To compare the products of arylation of hexafluorobenzene by nitrobenzene with those

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[1] E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **89**, 3224 (1967).

[2] R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959); L. P. Lindeman and J. L. Annis, *ibid.*, **32**, 1742 (1960); J. T. Watson and K. Biemann, *ibid.*, **36**, 1135 (1964).