which may be chosen as models for the ground state. If these heats of hydrogenation are compared with those for models of the transition state, such as propylene and *trans*-2-butene,[13] a rate difference of 1.5 kcal can be accounted for. That is to say, the heats of hydrogenation allow one to estimate that 1-phenylpropyne is about 4 kcal more stable than ethynylbenzene in the ground state while the transition state models indicate that the methyl compound is only 2.5 kcal more stable at that point. This leads to the prediction that the energy of activation for 1-phenylpropyne hydration should be 1–2 kcal larger than that for phenylacetylene hydration.

1-Phenylpropyne differs from phenylacetylene in another way. Hyperconjugation has been shown[1,6] to make an important contribution to the factors governing the stability of the transition state leading to the vinyl cation intermediate. In any substituted phenylacetylene this stabilizing interaction is removed. If one plots the data for the relative rates of hydration of 1-phenylpropyne, phenylpropiolic acid,[4] and phenylbenzoylacetylene[5] against σ^* values, phenylacetylene is hydrated 70 times more rapidly than predicted by the correlation line. It thus appears that phenylacetylene is anomalously reactive, partly due to hyperconjugation in the transition state and partly due to bond energy differences in the initial state.

Experimental Section

1-Phenylpropyne was purified by distillation and checked by vpc. The kinetic methods used have been described previously.[6] The progress of a kinetic run was followed by observing the increase in absorbance at 256 mμ.

Registry No.—**1,** 673-32-5.

[13] G. B. Kistiakowsky, J. R. Ruhoff, H. H. Smith, and W. E. Vaughn, *J. Am. Chem. Soc.*, **57**, 976 (1935).

The Preparation of Symmetrical Diaryl Sulfoxides from N,N′-Thionyldiimidazole

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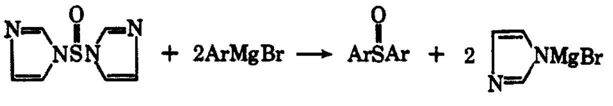
In attempting to prepare symmetrical diaryl sulfoxides we have found the existing methods to be not wholly satisfactory. We wish to report a new synthesis using N,N′-thionyldiimidazole, an intermediate described by Staab,[2] which affords reasonable yields of sulfoxide when treated with arylmagnesium halides (eq 1). In most cases the method offers a greater ease of work-up of the reaction mixtures and purification of the resultant sulfoxides. Although only *para*-substituted diaryl sulfoxides have been made in this laboratory, the method appears to be generally applicable to preparation of symmetrical diaryl sulfoxides. The only requirement is that the desired aryl halide by capable of forming a Grignard reagent. The sulfoxides prepared are listed in Table I.



(1)

Table I

Diaryl sulfoxide	% yield	Mp, °C[a]	Recrystn solvent
Phenyl	35	69.5–70.5 (70.5)[b]	Ether
p-Tolyl	40	94–95 (96)[c]	Ligroin
p-Anisyl	60	97–98.5 (93–94)[d]	Acetone
Mesityl	84	153.5–154[e] (153.5–154)	Ether
p-N,N-Dimethylaminophenyl	50	155, 151.5[f]	Acetone

[a] Literature melting points are given in parentheses. [b] C. E. Colby and C. S. McLoughlin, *Ber.*, **20**, 195 (1887). [c] F. Loth and A. Michaelis, *ibid.*, **27**, 2540 (1894). [d] S. Oae and C. Zalut, *J. Am. Chem. Soc.*, **82**, 5359 (1960). [e] S. Oae, T. Kitao, Y. Kitaoka, and S. Kawamura, *Bull. Chem. Soc. Jap.*, **38**, 546 (1965). [f] A. Michaelis and P. Schindler, *Ann.*, **310**, 137 (1900).

General Preparation of Sulfoxides.—All the sulfoxides in Table I were prepared by addition of a solution of N,N′-thionyldiimidazole to a previously prepared solution of the desired Grignard reagent according to the following general directions.

Thionyl chloride (12 g, 0.10 mole) was added dropwise with stirring and cooling in an ice bath to a solution of imidazole (28 g, 0.41 mole) in 250 ml of anhydrous tetrahydrofuran. A white precipitate formed immediately. After cooling for several minutes, the reaction mixture was rapidly filtered by suction under a nitrogen atmosphere. The clear filtrate was added dropwise over a 15-min period to a Grignard solution at room temperature made from magnesium (9 g, 0.38 g-atom) in 50 ml of anhydrous tetrahydrofuran and 0.33 mole of the desired aromatic halide in 100 ml of anhydrous tetrahydrofuran. The reaction mixture was stirred at room temperature for 1 hr and then hydrolyzed by pouring into 400 ml of an ice-dilute hydrochloric acid mixture. The organic and aqueous layers were separated and the aqueous layer was extracted with three 100-ml portions of diethyl ether or chloroform. The combined extracts were washed with 100 ml of saturated sodium bicarbonate solution, separated, and again washed with 100 ml of water. The organic solution was dried over anhydrous magnesium sulfate, the drying agent filtered off, and the solvent removed using a rotary evaporator. The residue crystallized on cooling and, in most cases, merely washing with cold ether yielded pure product. Crystallization solvents are included in Table I.

Nmr and ir spectra and melting points were consistent for all the compounds listed. The sulfoxides were oxidized to the known sulfones using hydrogen peroxide in acetic acid[3] and reduced to the known sulfides using sodium iodide in hydrochloric acid solution.[4]

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[1] National Institutes of Health Predoctoral Fellow.

[2] (a) H. A. Staab and K. Wendel, *Angew. Chem.*, **73**, 26 (1961); (b) H. A. Staab, *ibid.*, **74**, 407 (1962); (c) H. A. Staab, K. Wendel, and A. Datta, *Ann.*, **694**, 78 (1966); (d) H. A. Staab and K. Wendel, *ibid.*, **694**, 86, 91 (1966).

[3] W. E. Parham and J. D. Jones, *J. Am. Chem. Soc.*, **76**, 1068 (1954).

[4] E. N. Karaulova and G. D. Gal'peru, *Zh. Obshch. Khim.*, **29**, 3033 (1959); *Chem. Abstr.*, **54**, 12096*d* (1960).

Registry No.—N,N′-Thionyldiimidazole, 3005-50-3; diphenyl sulfoxide, 945-51-7; di-*p*-tolyl sulfoxide, 1774-35-2; di-*p*-anisyl sulfoxide, 1774-36-3; dimesityl sulfoxide, 3972-22-3; di-*p*-N,N-dimethylaminophenyl sulfoxide, 15156-67-9.

Some Aspects of the Decomposition of Dibenzothiophene and Naphthothiophene under Electron Impact

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In the hope that the mass spectra of dibenzothiophene and naphthothiophene might differ enough to distinguish between the isomers and to permit analysis of mixtures of them, we measured the spectra of the two compounds. In particular, the reported correlations of CHS^+ and $C_2H_3S^+$ intensities in the spectra of alkylthiophenes with the respective numbers of unsubstituted and methyl-substituted carbons adjacent to the sulfur atom[1-5] suggested that relative intensity at mass 139, corresponding to loss of CHS, might be appreciably greater in the spectrum of naphthothiophene than in that of dibenzothiophene. In the spectra of such relatively large molecules, the peak corresponding to as small as fragment as CHS^+ is likely to include contributions from processes other than primary ones,[6] therefore the odds are against a clear correlation between intensity of this peak and structural details of the original molecule. The parent-less-CHS ion, on the other hand, is more likely to arise largely by a primary process and thus its intensity may reasonably be expected to reflect the original structure provided no interfering rearrangement intervenes before decomposition. This condition is crucial and is met only in part in the processes by which alkylthiophenes break down to CHS^+ and $C_2H_3S^+$.[2-5]

The spectra of dibenzothiophene and naphthothiophene, shown in part in Table I, are remarkably similar. Relative intensity at mass 139 is greater in the spectrum of naphthothiophene than in that of dibenzothiophene, but the difference is slight. Similarly, the spectra show only small intensity differences at the masses corresponding to primary loss of C_2H_2, S, HS, and C_3H_3; the difference at the parent mass less H_2S is somewhat greater, but no explanation is readily apparent. These findings prompted us to examine the available spectra[7-9] of other compounds (16 in all) consisting of unsubstituted, single condensed-ring nuclei containing thiophene and benzene rings in various numbers and configurations. Again, we were unable to find any correlation between molecular structures and relative intensities at the masses corresponding to primary loss of C_2H_2, S, HS, H_2S, C_3H_3, or CHS.

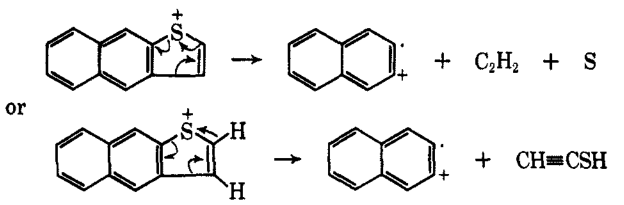
TABLE I

PARTIAL SPECTRA OF $C_{12}H_8S$ ISOMERS[a]

Mass	Ion	Neutral particle(s) lost from parent ion	Dibenzothiophene	Naphthothiophene
184	$C_{12}H_8S^+$	None	100.0	100.0
158	$C_{10}H_6S^+$	C_2H_2	1.87	1.70
152	$C_{12}H_8^+$	S	5.95[b]	5.19[b]
151	$C_{12}H_7^+$	HS	1.40[b]	1.49[b]
150	$C_{12}H_6^+$	H_2S	1.05	1.60
145	$C_9H_5S^+$	C_3H_3	0.81	0.70
139	$C_{11}H_7^+$	CHS	14.6	17.6
126	$C_{10}H_6^+$	C_2H_2S	0.76	1.40

[a] Intensity at parent mass ≡ 100.0. [b] Corrected for naturally occurring heavy isotopic contributions associated with peaks lower by one and two mass units.

In contrast, the spectra of the two isomers show markedly different, though small, intensities at mass 126, corresponding to loss of C_2H_2S from the parent ions. In view of the nearly equal relative intensities in the two spectra of the peaks corresponding to primary loss of either C_2H_2 or S, one might expect about equal probabilities for formation of the mass 126 ion from the isomers by successive loss of the two fragments, in either order. The observed difference suggests a proportionately larger contribution in the case of naphthothiophene from loss of the elements of C_2H_2S in a concerted process, possibly as a single moiety, from the unrearranged parent ion, *i.e.*, unzipping of the thiophene ring to yield a naphthalyne ion. Such a process would parallel the postulated,[10,11] pyrolytic formation of benzyne from the 1,4-addition product of thiophyne to thiophene, and of thiophyne by a reverse Diels–Alder reaction of benzothiophyne, and a seemingly similar process in the decomposition of naphthalene-1,8- and -2,3-dicarboxylic anhydrides under electron impact.



Loss of C_2H_2S in a one-step primary process can similarly account for, and thus gains support from, a correlation between relative intensity[7] at the resultant mass number and molecular structure of the two sets of isomers shown in Table II (the intensity scale in all spectra is defined by assigning a value of 100.0 to the parent

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(11) E. K. Fields and S. Meyerson, in "Organosulfur Chemistry," M. J. Janssen, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 8.