**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.

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## 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.

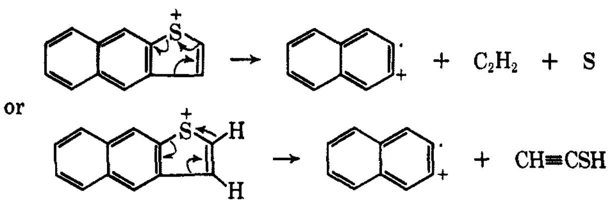
TABLE I

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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(1) I. W. Kinney and G. L. Cook, *Anal. Chem.*, **24**, 1391 (1952).

(2) G. L. Cook and N. G. Foster, *Proc. Am. Petrol. Inst.*, *Sec. III*, **41**, 199 (1961).

(3) N. G. Foster, D. E. Hirsch, R. F. Kendall, and B. H. Eccleston, "The Mass Spectra and Correlations with Structure for 23 Alkylthiophenes," U. S. Department of the Interior, Bureau of Mines, Report of Investigations 6433, 1963.

(4) G. L. Cook and G. U. Dinneen, "Mass Spectra of Organic Sulfur Compounds," U. S. Department of the Interior, Bureau of Mines, Report of Investigations 6698, 1964.

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(6) Compare F. W. McLafferty, "Interpretation of Mass Spectra. An Introduction," W. A. Benjamin, Inc., New York, N. Y., 1966, p 47.

(7) American Petroleum Institute, Research Project 44, "Catalog of Mass Spectral Data," Chemical Thermodynamics Properties Center, Agricultural and Mechanical College of Texas, College Station, Texas, 1947–1967.

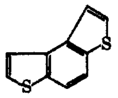
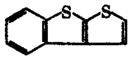
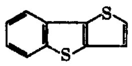
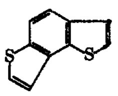
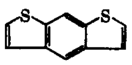
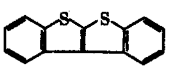
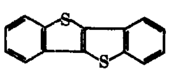
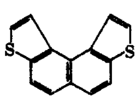
(8) American Petroleum Institute, ResearchProject 48, unpublished spectra.

(9) Unpublished spectra, this laboratory.

(10) E. K. Fields and S. Meyerson, *Chem. Commun.* (London), 708 (1966).

(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.

TABLE II

| Structure | Rel intensity, parent mass less 58 units |
|---|---|
|  | 0.83 |
|  | 0.35 |
|  | 0.32 |
|  | 0.82 |
|  | 0.88 |
|  | 0.26 |
|  | 0.38 |
|  | 0.82 |

peak). In the first set, those isomers containing one original $C_2H_2S$ group have relative intensities of 0.32 and 0.35; those with two such groups, 0.82–0.88. In the second set, the isomers containing no original $C_2H_2S$ group have relative intensities of 0.26 and 0.38; the one with two such groups, 0.82.

To gain some further insight into the loss of CHS from condensed ring thiophenic compounds, we attempted to prepare dibenzothiophene specifically labeled with deuterium at C-4. The synthesis did not go exactly according to plan, but gave a product with the isotopic composition 22.3% $d_2$, 68.5% $d_1$, and 9.2% unlabeled, measured by mass spectrometry at reduced ionizing voltage.[12] The absence of species with more than two deuterium atoms, in light of the equivalence of positions 4 and 6, supports the view that deuterium was introduced at the desired position and that the second atom in the doubly labeled species is at C-6.

Table III shows the parent and parent-less-CHS regions of the spectra of the unlabeled and labeled dibenzothiophenes, corrected for naturally occurring heavy isotopes. Intensity at mass 141, after approximate correction for a small contribution of $C_{11}H_8{}^+\text{-}d$, measures the yield of $C_{11}H_7{}^+\text{-}d_2$ produced by loss of CHS from dibenzothiophene-$d_2$. Comparison[13] with the corresponding data for the unlabeled compound leads to an estimate of 80% for the fraction of $C_{11}H_7{}^+$ ions retaining both deuterium atoms. Even though the hydrogen atoms on C-4 and C-6 are the closest ones to the sulfur in the original dibenzothiophene molecule, they clearly are not preferentially incorporated into the CHS radical lost from the ionized molecule. In fact, the observed retention agrees well, within the limits of a reasonable isotope effect, with the value of 75% calculated for complete loss of identity of all the hydrogens in the parent ion before decomposition.

TABLE III

PARTIAL SPECTRA OF DIBENZOTHIOPHENES[a]

| Mass | Ion[b] | Unlabeled | Labeled[c] |
|---|---|---|---|
| 186 | | . . . | 22.3 |
| 185 | | . . . | 71.1 |
| 184 | $C_{12}H_8S^+$ | 100.0 | 11.7 |
| 183 | | 3.36 | 1.80 |
| 182 | | 2.04 | 0.53 |
| 181 | | 0.11 | 0.06 |
| 180 | | 0.03 | 0.01 |
| 142 | | . . . | 0.25 |
| 141 | | . . . | 2.97 |
| 140 | | 0.76 | 9.49 |
| 139 | $C_{11}H_7{}^+$ | 13.7 | 3.36 |
| 138 | | 1.79 | 0.83 |
| 137 | | 0.79 | 0.28 |
| 136 | | 0.08 | 0.19 |

[a] Corrected for contributions of naturally occurring heavy isotopic species. [b] Formulas listed correspond to unlabeled ions of indicated masses. [c] 22.3% $d_2$, 68.5% $d_1$, and 9.2% unlabeled.

Evidently, the process by which CHS is lost involves some deep-seated reorganization of the molecule.

### Experimental Section

Dibenzothiophene was purchased from Aldrich Chemical Co., Milwaukee, Wis., and recrystallized twice from alcohol; mp 99°. A solution of 9.213 g (0.05 mole) of dibenzothiophene in 150 ml of dry ether was refluxed with 100 ml (0.234 mole) of 15% *n*-butyllithium in hexane for 16 hr.[14] The mixture was cooled to 0°, treated with 15 ml (0.75 mole) of deuterium oxide, and refluxed for 4 hr. The solvent was evaporated and the residue crystallized twice from hexane to give dibenzothiophene-4-*d*, 6.9 g, mp 97–98°.

Naphthothiophene was synthesized in 6% yield by the method of Carruthers and Crowder.[15] It melted at 184–185° (lit. mp 186–189°) after purification by gas chromatography.

Mass spectra were measured with 70-v electrons on a modified[16] Consolidated 21-103 instrument with the inlet system at 250°. For the low-voltage measurements used for isotopic analysis, the repellers were maintained at an average potential of 3 v; exact values were selected for maximum sensitivity.

**Registry No.**—Dibenzothiophene, 80-76-2; naphthothiophene, 268-77-9.

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(12) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950).

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(14) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

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(16) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, 7th Annual Meeting of American Society for Testing Materials Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.

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## The Synthesis and Thermal Decomposition of 3,3-Di-*t*-butyl Diperoxyphthalid[1]

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*Received September 8, 1967*

When the symmetrical phthalyl chloride was allowed to undergo solvolysis[3,4] with *t*-butyl hydroperoxide, a

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(1) Paper XL on Organic Peroxides, originally submitted June 30, 1966.

(2) Postdoctoral Research Associate (1962–1964); presently at Hoechst A.G., Frankfurt-Hochst, Germany.

(3) N. A. Milas, R. J. Klein, and D. G. Orphanos, *Chem. Ind.* (London), 423 (1964).

(4) N. A. Milas, D. G. Orphanos, and R. J. Klein, *J. Org. Chem.*, **29**, 3099 (1964).