Table I

R_f	Amount, mg	Identified as[a]
0.60	110	Acetophenone
0.52	350	γ-Benzoylbutyronitrile (**13**)
0.29	80	ω-Methylsulfonylacetophenone (**12**)
0.22	80	**2**
0.08	115	*b*

[a] Identification is based on ir and nmr spectra and on R_f values. [b] Not identified.

compound was irradiated for 60 min under the same conditions as described above. A multitude of products was obtained on tlc, but acetophenone was not detected.

Registry No.—**3** (X = Br), 34502-55-1; **3** (X = Cl), 34502-56-2; **4** (X = Cl), 34502-57-3; **4** (X = Br), 34502-58-4; **4** (X = I), 34502-59-5; **4** (X = H), 34502-60-8; **7**, 34502-61-9; **8**, 34502-62-0; **9**, 34502-63-1; **10**, 34502-64-2; **11**, 34502-16-4.

Acknowledgment.—The authors wish to thank Mrs. M. Goldstein, Microanalytical Laboratory of the Hebrew University, for some of the elementary analyses. This research was supported in part by a grant from the California Biochemical Foundation to Mr. D. Diller. The authors are indebted to Mr. R. Knafo for the drawings.

The Pyrolysis of 2*H*-Naphth[1,8-*cd*]isothiazole 1,1-Dioxide and Its 2-Phenyl Analog

D. C. De Jongh*[1] and G. N. Evenson

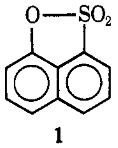
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received December 20, 1971

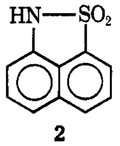
The pyrolytic reactions of 2*H*-naphth[1,8-*cd*]isothiazole 1,1-dioxide (**2**) and 2-phenylnaphth[1,8-*cd*]isothiazole 1,1-dioxide (**3**) are described. The major products from the pyrolysis of **2** were 2-cyanoindene (**5**) and 3-cyanoindene (**6**) (1.2/1, 68%). The major product from the pyrolysis of **3** was 7*H*-benz[*k,l*]acridine, in 43% yield. The mass spectra of **2** and **3** are discussed. Synthetic routes to **5** and **6** were developed in order to aid in their identification in the mixture obtained from the pyrolysis of **2**.

We have reported the mass spectra and pyrolyses of *o*-phenylene sulfite,[2,3] *o*-phenylene carbonate,[4,5] 2-pyrone, and 2-pyridone.[6] This procedure has recently been used by Chapman to obtain cyclopentadienone on a low-temperature ir cell from *o*-benzoquinone, *o*-phenylene sulfite, and *o*-phenylene carbonate.[7]

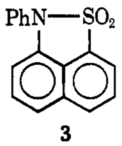
As part of this project, we have pyrolyzed naphth[1,8-*cd*]-1,2-oxathiole 2,2-dioxide (**1**).[8] The formation of the products which are isolated can be rationalized in terms of loss of SO_2 from **1**, followed by the trapping of the intermediate which results. We have also studied 2*H*-naphth[1,8-*cd*]isothiazole 1,1-dioxide (**2**) and 2-phenylnaphth[1,8-*cd*]isothiazole 1,1-dioxide (**3**) and describe our procedures and results in this article.



1



2



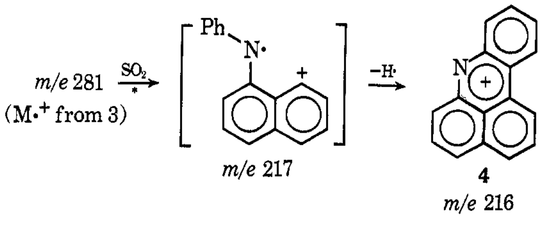
3

Results and Discussion

The major peaks in the mass spectrum of **2** arise from loss of SO_2 from the molecular ions, followed by H· or HCN (eq 1). The most intense fragment ion is *m/e* 141, and a metastable peak is present for the loss of SO_2 from *m/e* 205. Similar behavior is observed from **3** (eq 2). However, in this case the most intense fragment ion results from the elimination of SO_2 followed by H·. It is possible to postulate a stable structure (**4**) for *m/e* 216, which may explain its high relative intensity (eq 3). However, no evidence is available to support these postulations.

$$\begin{tikzcd} \begin{matrix} m/e\ 205\ (100\%) \\ (\mathrm{M}\cdot^{+}\ \text{from}\ \mathbf{2}) \end{matrix} \arrow[r, "-SO_2", "*"'] & m/e\ 141\ (52\%) \arrow[r, "-\mathrm{H}\cdot"] \arrow[dr, "-\mathrm{HCN}"'] & m/e\ 140\ (27\%) \\ & & m/e\ 114\ (27.5\%) \end{tikzcd} \tag{1}$$

$$\begin{tikzcd} \begin{matrix} m/e\ 281\ (100\%) \\ (\mathrm{M}\cdot^{+}\ \text{from}\ \mathbf{3}) \end{matrix} \arrow[r, "-SO_2", "*"'] & m/e\ 217\ (55\%) \arrow[r, "-\mathrm{H}\cdot"] \arrow[d, "-\mathrm{HCN}"] & m/e\ 216\ (82\%) \arrow[d, "-\mathrm{HCN}"] \\ & m/e\ 190\ (8\%) & m/e\ 189\ (11\%) \end{tikzcd} \tag{2}$$



(3)

On the basis of these facile losses of SO_2 from **2** and **3** in the mass spectrometer, we were encouraged to try to find products from similar losses of SO_2 pyrolytically.

Compound **2** was pyrolyzed in a stream of N_2 by sublimation into a pyrolysis zone containing a heated coil constructed from chromel wire. A series of cold traps condensed the products as they emerged from the pyrolysis zone. The highest yields were obtained when the temperature was 720–740° and when the pressure of N_2 was 3.0–3.5 mm. The ir spectrum of

---

[1] Departement de Chimie, Université de Montréal.

[2] (a) D. C. De Jongh and R. Y. Van Fossen, *J. Org. Chem.*, **37**, 1129 (1972); (b) D. C. De Jongh, R. Y. Van Fossen, and A. Dekovich, *Tetrahedron Lett.*, 5045 (1970).

[3] D. C. De Jongh, R. Y. Van Fossen, and C. F. Bourgeois, *ibid.*, 271 (1967).

[4] D. C. De Jongh and D. A. Brent, *J. Org. Chem.*, **35**, 4204 (1970).

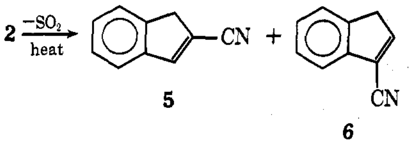
[5] D. C. De Jongh, D. A. Brent, and R. Y. Van Fossen, *ibid.*, **36**, 1469 (1971).

[6] D. A. Brent, J. D. Hribar, and D. C. De Jongh, *ibid.*, **35**, 135 (1970).

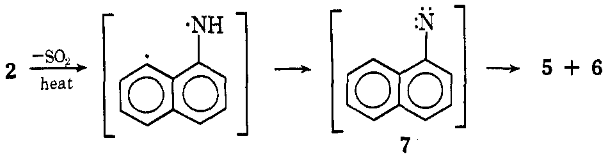
[7] O. L. Chapman and C. L. McIntosh, *Chem. Commun.*, 770 (1971).

[8] D. C. De Jongh and G. N. Evenson, *Tetrahedron Lett.*, 4093 (1971).

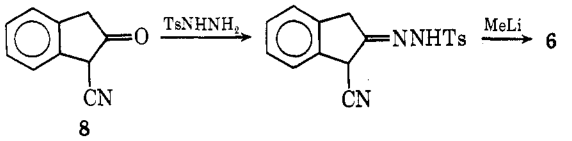
the products showed the presence of a cyano group, and the mass spectrum gave a molecular ion at *m/e* 147, corresponding to a formula of $C_{10}H_7N$. These data can be explained by a loss of SO_2 from **2** upon pyrolysis, and rearrangement to a nitrile. The nmr spectrum could be interpreted in terms of a 1.2:1 mixture of 2-cyanoindene (**5**) and 3-cyanoindene (**6**). A yield



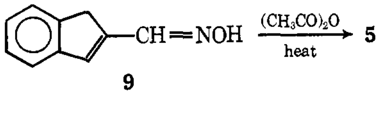
of 68% was determined. The isomers could not be separated by vacuum distillation, although there was separation by gas chromatography. It is possible that the cyanoindenes **5** and **6** form *via* a nitrene intermediate (**7**). Nitrenes similar to **7** undergo ring contraction to form nitriles, which at higher temperatures experience CN migrations.[9-11] For example, 3-cyanoindene (**6**) was the product from pyrolysis of 1,2-naphthotriazole, and 2-cyanoindene (**5**) was obtained from 2,3-naphthotriazole, at 500°.[11] At 1000° (0.25 mm), a ratio of 1.3:1 was obtained for **5**:**6**, when either pure **5** or **6** was pyrolyzed; at 800° (0.02 mm), the ratio of **5**:**6** was 1:1.5.[11] Thus, the two cyanoindenes are equilibrated at temperatures around 800°.



Our identification of the mixture of cyanoindenes **5** and **6** was verified by their syntheses and comparison of physical data obtained from the mixture with those from the authentic samples. 3-Cyanoindene (**6**) was synthesized from the known compound,[12] 1-cyano-2-indanone (**8**), as shown in eq 4. 2-Cyanoindene (**5**) was synthesized by dehydration of the oxime **9**[13] of 2-indenal as shown in eq 5.

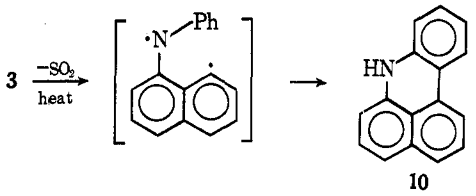


(4)



(5)

Pyrolysis of 2-phenylnaphth[1,8-*cd*]isothiazole 1,1-dioxide (**3**) also leads to a product resulting from initial loss of SO_2. Compound **3** was pyrolyzed at a temperature of 680° and a nitrogen pressure of 3.0–3.5 mm. The pyrolysis product was identified as 7*H*-benz[*k*,*l*]acridine (**10**) and was isolated in 43% yield. Compound **10** can form by loss of SO_2 and intramolecular trapping of the intermediate which forms. The formation of **10** resembles the process postulated in eq 3, leading to ion **4**.



Thus, **2** and **3** lose SO_2 upon pyrolysis, and the products which are isolated result from rearrangement to stable molecules. The fragmentation of their molecular ions proceeds *via* loss of SO_2 also, and this fact was used to predict their pyrolysis products. In attempts to trap intermediates which might form prior to formation of **5**, **6**, and **10**, we used methanol in the nitrogen stream in one experiment and substituted carbon dioxide for nitrogen in another experiment.[8] The results did not change in either case.

Experimental Section

Melting points were determined by the open-capillary method and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrometer; ultraviolet spectra were recorded on a Perkin-Elmer 202 spectrometer, in ethanol. Nuclear magnetic resonance spectra were determined on either a Varian A-60A spectrometer or a Varian T-60, using carbon tetrachloride or deuterioacetone as solvents and tetramethylsilane as the internal standard. Mass spectra were obtained from an Atlas CH4 or an AEI MS902 mass spectrometer; the ionizing energy was 70 eV. The MS902 was used for exact-mass measurements at high resolution.

Gas chromatographic studies were performed on a Hewlett-Packard 5750 research chromatograph with a thermal conductivity detector. The column used was 3.5 ft × 0.25 in., 5% Silicon Oil DC 550 on 60–80 Chromosorb W.

Elemental analyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind.

The Pyrolysis Unit.—The pyrolysis unit utilizes an internal heating probe and thermocouple. The pyrolysis zone was made from 24-mm Vicor tubing, with Pyrex tubing used in the remainder of the unit. The heating and thermocouple probe was made from two 5-mm double-bore ceramic rods sealed with epoxy cement into a $\mathbb{T}$ 24/40 inner joint. One rod houses the 16-gauge copper electrical leads, and the other, the 20-gauge Chromel–Alumel thermocouple. The heating element is a Chromel-wire coil, stretched between the two copper leads. The coil was made from 120 cm of 20 gauge wire and is 11 mm in diameter and 80 mm in length. The thermocouple head is centered within the heating coil. The pyrolysis zone is insulated from the surrounding environment with glass wool packing. The remainder of the unit is wrapped in a heating tape consisting of asbestos tape interwoven with Chromel wire and controlled with variacs. The tape consists of two sections, one controlling the sublimation chamber and the other the area leading to the pyrolysis zone. This latter tape is necessary in order to eliminate condensation of products along the walls. The unit is provided with a side arm which is used to introduce trapping agents.

The nitrogen-gas flow is controlled by a flow meter, and the nitrogen is dried ($CaCl_2$) before entering the sublimation chamber. The hot gases from the pyrolysis zone are condensed by an air trap followed by a series of liquid nitrogen traps. The vacuum line is connected to these traps and the pressure is measured with a mercury manometer and McLeod gauge.

Pyrolysis Procedure.—The starting material is placed into the sublimation chamber and the entire system is flushed with nitrogen. The vacuum is applied and the pressure is regulated with the nitrogen flow meter. The heating tapes are connected and the variacs are set at their specific voltages. The temperature within the pyrolysis zone is observed with a pyrometer, and the pyrolysis is started as soon as a constant temperature is achieved, by turning on the variac controlling the sublimation chamber. This tape is heated slowly, and pyrolysis, on the average, takes 1–1.5 hr for a 0.5-g sample.

---

(9) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 5569 (1968).

(10) C. Wentrup and W. D. Crow, *Tetrahedron*, **27**, 361 (1971).

(11) C. Wentrup and W. D. Crow, *ibid.*, **26**, 3965 (1970).

(12) C. W. Moore and J. F. Thorpe, *J. Chem. Soc.*, 165 (1908).

(13) Z. Arnold, *Collect. Czech. Chem. Commun.*, **30**, 2783 (1965).

2*H*-Naphth[1,8-*cd*]isothiazole 1,1-Dioxide (2).—In the synthesis of **2**, 15.0 g (0.067 mol) of 1-amino-8-naphthalenesulfonic acid (J. T. Baker) was added to 58.4 g (0.38 mol) of $POCl_3$, and the solution was refluxed for 3 hr. The excess $POCl_3$ was vacuum distilled, and the residue was added to 350 g of ice. After this was allowed to stand at room temperature for 3 hr, the solid was filtered and dissolved in benzene. Recrystallization gave 4.3 g (31.3%) of pale yellow needles. Vacuum sublimation provided further purification and gave a white solid: mp 176–177° (lit.[14] mp 177–178°); ir (CH_2Cl_2) 3300, 1600, 1495, 1460, 1325, 1290, 1162, 1143, 818 cm^{-1}; mass spectrum, molecular ion at *m/e* 205 (base peak).

Anal. Calcd for $C_{10}H_7NO_2S$: C, 58.5; H, 3.44; N, 6.83. Found: C, 58.3; H, 3.52; N, 6.85.

2-Phenylnaphth[1,8-*cd*]isothiazole 1,1-Dioxide (3).—The sodium salt of 1-anilino-8-naphthalenesulfonic acid (J. T. Baker) (118 g, 0.37 mol) was added to 269 g (1.75 mol) of $POCl_3$ and refluxed for 20 hr. The excess $POCl_3$ was distilled and the solid was added to ice water; the solid was then filtered. Purification by means of column chromatography (silica gel with benzene) gave 46 g (44.2%) of a pale yellow solid: mp 163–165° (lit.[15] mp 165°); ir (CH_2Cl_2) 1590, 1490, 1375, 1320, 1179, 1160, 1145, 816 cm^{-1}.

Anal. Calcd for $C_{16}H_{11}NO_2S$: C, 68.1; H, 3.93; N, 4.96. Found: C, 68.3; H, 3.97; N, 4.97.

2-Cyanoindene (5).—The oxime **9** of 2-indenal was prepared by a known procedure, mp 127–129° (lit.[13] mp 128–130°). The oxime was dehydrated by a procedure analogous to the procedure developed by Mowry and Morner for formation of α,β-unsaturated nitriles from aldoximes.[16] Oxime **9** was added to an excess of acetic anhydride. The mixture was heated and the acetic anhydride was distilled under vacuum. Sublimation of the product gave a 58% yield of a white, crystalline solid, mp 40–42° (lit.[11] mp 39–40°). Nmr, ir, uv, and mass spectral data agree with those published for **5**.[11]

Anal. Calcd for $C_{10}H_7N$: C, 85.1; H, 5.00; N, 9.92. Found: C, 85.2; H, 5.10; N, 9.90.

3-Cyanoindene (6).—3-Cyanoindene (**6**) was prepared from 1-cyano-2-indanone (**8**). Compound **8** was synthesized by the method described by Moore and Thorpe,[12] mp 173–175° dec (lit.[12] mp 172° dec).

The tosylhydrazone of 1-cyano-2-indanone was prepared by adding an equimolar amount of **8** (6.75 g) to 8.0 g of tosylhydrazine in 100 ml of 1% EtOH–HCl. The solution was refluxed for 0.5 hr, the solution was cooled, and water was added. The tosylhydrazone of **8** was filtered and recrystallized from EtOH–H_2O, yield 7.78 g (55.7%), mp 202–203° dec.

The tosylhydrazone was reduced by a procedure reported by Shapiro and Heath.[17] The hydrazone (7.78 g) was dissolved in 100 ml of anhydrous ether and 25 ml of a 2.0 *M* solution of CH_3Li in ether was added slowly with stirring under an inert atmosphere. The slurry was stirred at room temperature for 1 hr, and then 20 ml of water was added. The ether layer was separated, washed with aqueous $NaHCO_3$, and then dried over Na_2SO_4. A dark oil was obtained upon evaporation of the ether. A small amount of 3-cyanoindene was obtained upon vacuum distillation of the oil; it was sufficient for identification, bp 36–37° (0.2 mm); ir, uv, nmr, and mass spectral data agreed with those published for **6**.[11] High-resolution mass spectrometry showed a molecular ion at *m/e* 141.0578 (calcd for $C_{10}H_7N$: 141.0594).

Pyrolysis of 2*H*-Naphth[1,8-*cd*]isothiazole 1,1-Dioxide (2).—A temperature of 720–740° was used along with a system pressure of 3.0–3.5 mm of nitrogen. Compound **2** was sublimed into the nitrogen stream and led through the pyrolysis zone, and products were condensed in the traps. A brown oil was isolated after the traps were washed with methylene chloride. Mass spectral, uv, ir, and nmr data indicated that the product was a mixture of 2- and 3-cyanoindene. The oil was purified by vacuum distillation and compared with the authentic samples of **5** and **6**, the syntheses of which are described above. In a typical experiment, a 1.2:1 ratio of **5**:**6** was obtained in a yield of 68% for the two products. No starting material was recovered.

Pyrolysis of 2-Phenylnaphth[1,8-*cd*]isothiazole 1,1-Dioxide (3).—Compound **3** was pyrolyzed by subliming it into a zone maintained at 680° in a nitrogen stream with a system pressure of 3.0–3.5 mm. The cold traps were washed with acetone, and the wash was concentrated to 10 ml. Water was added (400 ml), and the mixture was cooled and filtered. The product was 7*H*-benz[*k,l*]acridine (**10**), mp 123–125° dec (lit.[18] mp 125° dec). The yields for two experiments were 38.6 and 39.1% (42.9 and 43.5% if the unreacted starting material is accounted for in the calculations).

The 2,4,7-trinitro-9-fluorenone derivative had mp 183–185° dec. The spectrum of **10** (70 eV) showed *m/e* (rel intensity) 217 (100), 216 (37), 190 (4), 189 (6).

Registry No.—**2**, 603-72-5; **3**, 20027-18-3; **5**, 29005-25-2; **6**, 29872-81-9; **8** tosylhydrazone, 34414-22-7; **10** 2,4,7-trinitro-9-fluorenone derivative, 34414-23-8.

Acknowledgments.—Partial support of this work by means of a grant from the National Institutes of Health is acknowledged. Facilities of l'Université de Montréal were generously provided for preparation of this manuscript.

---

[14] F. Dannerth, *J. Amer. Chem. Soc.*, **29**, 1319 (1907).

[15] W. M. Cumming and G. D. Muir, *J. Roy. Tech. Coll.*, **3**, 562 (1936); *Chem. Abstr.*, **30**, 4491 (1936).

[16] D. T. Mowry and R. R. Morner, *J. Amer. Chem. Soc.*, **69**, 1831 (1947).

[17] R. H. Shapiro and M. J. Heath, *ibid.*, **89**, 5734 (1967).

[18] H. Sieper, *Chem. Ber.*, **100**, 1646 (1967).