studies), and (3) the observed trends in product distribution.

Product distribution was essentially independent of pH and (bi) sulfite concentration over the range studied (pH 6.0–8.2; S_T = (0.5–2.0) × 10^{-3} M; Table I) as determined by HPLC after incubation of PhNHOH at 28 °C with (bi)sulfite in deoxygenated phosphate buffer (0.0025 M) for at least 7 half-lives. The low relative yield of *o*-aminophenol may arise from steric restriction of attack by water at the ortho position of IIa to form an intermediate, IIIa, of apparent greater steric strain than its precursor. Similarly, the relatively high yield of *p*-aminophenol may reflect relief of steric strain in IIb following attack by water to form IIIb. In all cases *p*-aminobenzenesulfonate was formed in greater yield than *o*-aminobenzenesulfonate, again reflecting steric resistance to attack at the ortho sites.

This reactivity of PhNHOH toward the strong nucleophile (bi)sulfite suggests that, in some cases, arylhydroxylamine-mediated carcinogenesis may involve direct nucleophilic aromatic attack by a strong endogenous nucleophile with concerted expulsion of hydroxide, to form an intermediate that can either rearrange to form a stable product or undergo a further nucleophilic addition reaction (even with relatively weak nucleophilic species; i.e., H_2O in the study described above) followed by elimination involving formation of potentially mutagenic species. Such a scheme offers a possible alternative mechanism for arylation of endogenous materials by arylhydroxylamines not requiring the intermediacy of short-lived free radicals or nitrenium ions and now requires further investigation in more biochemically relevant systems.

Experimental Section

Phenylhydroxylamine was synthesized by reduction of nitrobenzene with zinc and ammonium chloride.[23] All buffers were demetalated by extraction with dithizone as previously described.[24]

Kinetic studies were carried out at 28 ± 0.5 °C by incubating PhNHOH in deoxygenated 0.0025 M phosphate buffer maintained at a constant ionic strength (μ = 0.5) with sodium perchlorate in the presence of sodium (bi)sulfite ((0.5–2.0) × 10^{-3} M).

Samples were taken at timed intervals for a minimum of 5 half-lives and analyzed by HPLC. Components were separated on a Waters μBondapak C_{18} column (30 cm × 4.6 mm i.d.) by using a mobile phase of methanol:water (15:85) containing 0.26 M NH_4(OAc) and 0.015 M nickel acetate. A flow rate of 2 mL min^{-1} was maintained and effluent monitored spectrophotometrically at 254 nm. Retention volumes for *p*-aminobenzenesulfonate, o-aminobenzenesulfonate, *p*-aminophenol, *o*-aminophenol, phenylhydroxylamine, and aniline were 3, 4.4, 5, 9.0, 9.9, and 13.1 mL, respectively.

Product distribution was determined by HPLC after incubation for ≥7 half lives.

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Registry No. PhNHOH, 100-65-2; aniline, 62-53-3; *o*-aminophenol, 95-55-6; *p*-aminophenol, 123-30-8; *o*-aminobenzenesulfonate, 88-21-1; *p*-aminobenzenesulfonate, 121-57-3.

Ramberg–Bäcklund Reaction of 1,3-Dibromo-1*H*,3*H*-naphtho[1,8-*cd*]thiopyran 2,2-Dioxide. Formation of Acenaphthyne Intermediate

Juzo Nakayama,* Etsuo Ohshima, Akihiko Ishii, and Masamatsu Hoshino

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

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Radical bromination of 1*H*,3*H*-naphtho[1,8-*cd*]thiopyran 2,2-dioxide (**15**) gave the corresponding monobromo sulfone **16** (48%), dibromo sulfone **12** (43%; cis/trans = 64/36), and tribromo sulfone **17** (5%). Ramberg–Bäcklund reaction of **12** was investigated under a variety of conditions with expectation of the formation of thiirene dioxide **11** from which generation of acenaphthyne (**5**) would be expected both thermally and photochemically. Observed characteristic features of the reaction are as follows: (i) the use of triethylamine as base yielded 1-bromoacenaphthylene (**20**; 39%) and debrominated products **15** (5%) and **16** (9%); (ii) the use of sodium methoxide as base afforded decacyclene (**3**) surprisingly, though in a trace amount, in addition to **20** (75%) and acenaphthylene (**18**; 9%); (iii) the use of potassium *tert*-butoxide as base gave an improved yield of **3** (5%) along with **20** (36%) and **18** (27%). The formation of **3** may best be rationalized by assuming the generation of acenaphthyne intermediate **5** from **11** by loss of sulfur dioxide.

We have previously shown that thermolysis of the potassium salt of acenaphthenequinone bis(tosylhydrazone) (**1**, Scheme I) in solution yields 1,8-dicyanonaphthalene (**2**) and decacyclene (**3**).[1] The result may best be explained by the initial formation of a bis(diazo) compound or its ring-closed isomer **4**, which either gives **2** with loss of one molecule of nitrogen or yields acenaphthyne (1,2-dehydroacenaphthylene, **5**) with loss of two molecules of nitrogen, and then **5** results in the formation of **3**. The purpose of the present study is to generate **5** by another method in order to establish the true existence of this highly strained molecule as an intermediate.

The most strained cycloalkyne, whose existence was convincingly established, is norbornyne (bicyclo[2.2.1]-hept-2-yne, **6**).[2,3] 2-Lithio-1-chlorobicyclo[2.2.1]hept-2-ene

(1) Nakayama, J.; Segiri, T.; Ohya, R.; Hoshino, M. *J. Chem. Soc., Chem. Commun.* **1980**, 791–792.

(2) (a) Gassman, P. G.; Valcho, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4768–4770. (b) Gassman, P. G.; Gennick, I. *Ibid.* **1980**, *102*, 6863–6864.

0022-3263/83/1948-0060$01.50/0

(7), when warmed to 45 °C in a solution, generates **6** with elimination of lithium chloride, while 2-lithio-1-bromoacenaphthylene (**8**) is surprisingly thermally stable and has no tendency to produce **5** with loss of lithium bromide.[4] This indicates that **5**, whose five-membered ring is a part of a rigid aromatic system, is more strained than **6**.[5]

Thiirene dioxide **9**, prepared by treatment of **10** with triethylamine (modified Ramberg–Bäcklund reaction), is fairly thermally stable because of its special conjugative effect, but when heated in boiling benzene, it loses sulfur dioxide to produce diphenylacetylene.[6,7] We therefore undertook preparation of thiirene dioxide **11**, from which generation of **5** would be expected photochemically or thermally. The Ramberg–Bäcklund reaction of 1,3-dibromo-1*H*,3*H*-naphtho[1,8-*cd*]thiopyran 2,2-dioxide (**12**) was chosen as a synthetic method for **11**.

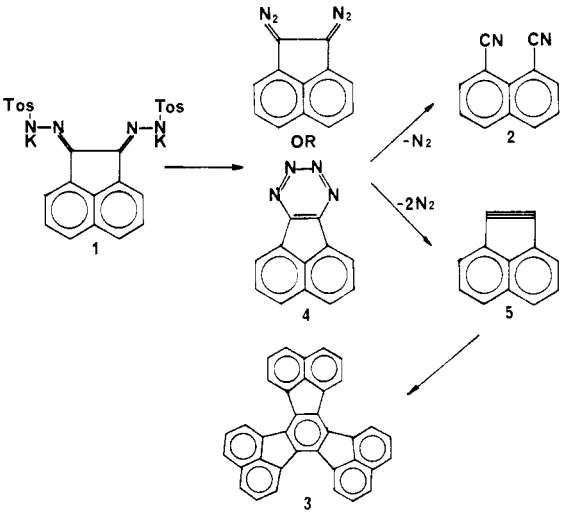
During the preparation of this paper, generation of **5** by photolysis of diazoketone **13** (Scheme I) was reported by Chapman et al.[8,9] These authors have succeeded in the determination of infrared and ultraviolet spectra of **5** in an argon matrix at 15 K.

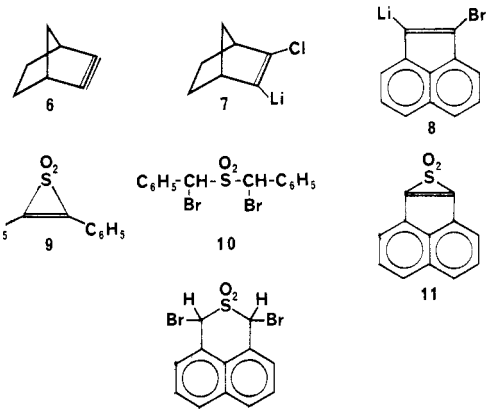
Results and Discussion

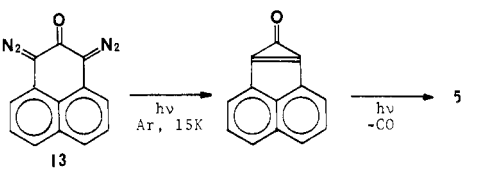
Preparation of 12. Preparation of **12** by bromination of 1*H*,3*H*-naphtho[1,8-*cd*]thiopyran (**14**)[10] followed by oxidation with peracid was first attempted. However, neither bromination of **14** with bromine[6b] nor *N*-bromosuccinimide (NBS)[11] gave any isolable pure dibrominated product.

Although early work indicated that simple benzyl and alkyl sulfones do not undergo free-radical bromination,[12] a recent study by Bordwell and Doomes has shown that benzylic sulfones undergo moderately efficient α-bromination when heated with NBS in refluxing carbon tetrachloride containing benzoyl peroxide (BPO).[13] We then

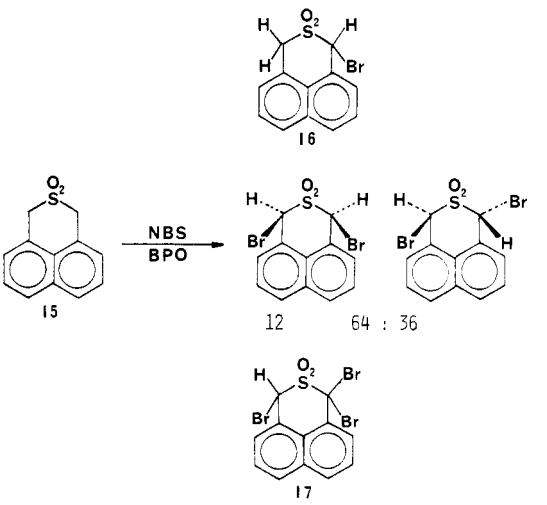
Scheme I







Scheme II



(3) For cyclopentynes, see: (a) Wittig, G.; Krebs, A.; Pohlke, R. *Angew. Chem.* **1960**, *72*, 324. (b) Wittig, G.; Krebs, A. *Chem. Ber.* **1961**, *94*, 3260–3275. (c) Wittig, G.; Pohlke, R. *Ibid.* **1961**, *94*, 3276–3286. (d) Wittig, G.; Weinlich, J.; Wilson, E. R. *Ibid.* **1965**, *98*, 458–470. (e) Montogomery, L. K.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 4750–4751. (f) Montogomery, L. K.; Scardiglia, F.; Roberts, J. D. *Ibid.* **1965**, *87*, 1917–1925. (g) Wittig, G.; Heyn, J. *Liebigs Ann. Chem.* **1972**, *756*, 1–13. (h) Chapman, O. L. *Pure Appl. Chem.* **1979**, *51*, 331–339. (i) Bolster, J. M.; Kellog, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 2868–2869. For other derivatives: (j) Wittig, G.; Heyn, H. *Chem. Ber.* **1964**, *97*, 1609–1618. (k) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1142–1143. (l) Reinecke, M. G.; Newman, J. G. *Ibid.* **1976**, *98*, 3021–3022. (m) Del Mazza, D.; Reinecke, M. G. *Heterocycles* **1980**, *14*, 647–649. (n) Reinecke, M. G.; Newman, J. C.; Chen, L.-J. *J. Am. Chem. Soc.* **1981**, *103*, 2760–2769.

(4) Rasheed, K. *Tetrahedron* **1966**, *22*, 2957–2966.

(5) The ethylene bridge in acenaphthene pulls the peri-carbon atoms together, thus reducing the C(2a)–C(9)–C(8a) angle to 112°, and causes a widening of the C(5)–C(5a)–C(6) angle to 128° (Erlich, H. W. E. *Acta Crystallogr.* **1957**, *10*, 699–705). Therefore, the increase of unsaturation of the C_1–C_2 bond of this ring system requires more deformation of the naphthalene ring, and this would in turn make the five-membered ring of **5** most strained.

(6) (a) Carpino, L. A.; McAdams, L. V., III *J. Am. Chem. Soc.* **1965**, *87*, 5804–5805. (b) Carpino, L. A.; McAdams, L. V., III; Rynbrandt, R. H.; Spiewak, J. W. *Ibid.* **1971**, *93*, 476–484.

(7) For general reviews of the Ramberg–Bωddacklund reaction, see: (a) Paquette, L. A. "Mechanism of Molecular Migrations"; Thyagarajam, B. S., Ed.; Interscience: New York, 1968; Vol. 1, pp 121–156. (b) Paquette, L. A. *Acc. Chem. Res.* **1968**, *1*, 209–216. (c) Paquette, L. A. "Organic Reactions"; Wiley: New York, 1977; Vol. 25, pp 1–71. (d) Bordwell, F. G. "Organosulfur Chemistry"; Jansen, M. J., Ed.; Interscience: New York, 1968; Chapter 16.

(8) Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G.; *J. Am. Chem. Soc.* **1981**, *103*, 7033–7036.

(9) Our work was presented at the 32nd Symposium on Reaction Mechanisms, Chemical Society of Japan, Tsukuba, Japan, Oct 22, 1981.

(10) (a) Cava, M. P.; Pollack, N. M.; Repella, D. *J. Am. Chem. Soc.* **1967**, *89*, 3640–3641. (b) Schlessinger, R. H.; Ponticello, I. S. *Ibid.* **1967**, *89*, 3641–3642.

(11) Tuleen, D. L. *J. Org. Chem.* **1967**, *32*, 4006–4008.

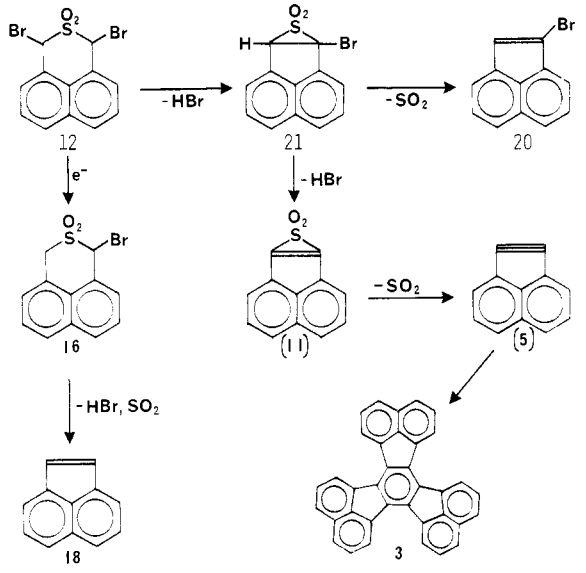
(12) (a) Bolck, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; p 185. (b) Backer, H. J.; Stevens, W.; Dost, N. *Recl. Trav. Chim. Pays-Bas* **1948**, *67*, 451–458.

Table I. Ramberg-Bäcklund Reaction of 12[a]

run	conditions: base	solvent	temp, °C	time, h	products (yield, %)
1	Et_3N	CH_2Cl_2	reflux	7	**20** (39), **16** (9), **15** (5)
2	MeONa	MeOH	rt[b]	18	**20** (75), **18** (9), **3** (trace)
3	*t*-BuOK	*t*-BuOH	27	18	**20** (33), **18** (23), **3** (5)
4	*t*-BuOK	*t*-BuOH	reflux	1.5	**20** (36), **18** (27), **3** (5)
5	*t*-BuOK	THF	rt	18	**20** (26), **18** (5), **12**[b]
6	*t*-BuOK	Me_2SO	rt	18	complex mixture
7	BuLi	THF	rt	18	complex mixture

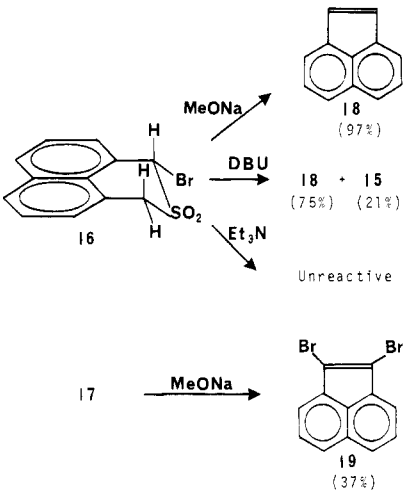
[a] The reaction was conducted in 20 mL of the solvent with 0.5 mmol of **12** and 5 mmol of the base. [b] Room temperature. [c] Yield was not determined.

Scheme III



examined bromination of the known sulfone **15**,[14] obtained from **14** by oxidation with *m*-chloroperbenzoic acid in 92% yield. Prolonged heating of **15** with excess NBS in the presence of BPO in refluxing carbon tetrachloride afforded monobromo sulfone **16** (48%), dibromo sulfone **12** (43%), a tribromo sulfone **17** (5%). Sulfone **12** consists of a mixture of cis and trans isomers in a ratio of 64:36. Both isomers were obtained in a pure form by column chromatography. The cis isomer has mp 204–205 °C and the trans isomer, mp 217–218 °C. The ^1H NMR spectrum of the monobromo sulfone **16** shows a large downfield shift of one of the methylene protons (δ 5.47) relative to the other (δ 4.44) in deuteriochloroform, indicating that the system is mobile, allowing considerable 1,3-diaxial interaction between one of the methylene protons and the bromine.[14b] The methine protons signal of *trans*-**12** appears at δ 6.73 as singlet, which is far lower than that of *cis*-**12**, which occurs at δ 5.27 as a singlet in deuteriochloroform. This result is attributed to the inevitable 1,3-diaxial interaction in the trans isomer between the methine protons and the bromines, thus drawing a sharp distinction between the two isomers.

Scheme IV



Bromination of the monobromo sulfone **16** in a similar way gave **12** (45%) and **17** (7%) with recovery of 33% of **16**. Attempted ionic bromination of **15** did not give **12** satisfactorily (Scheme II).

Ramberg–Bäcklund Reaction of 12.[15] The Ramberg–Bäcklund reaction of **12** was examined under a variety of conditions. A mixture of cis and trans isomers in a ratio of about 64:36 was employed in all of the cases. The results are summarized in Table I.

α,α'-Bis(bromobenzyl) sulfone (**10**), when heated with triethylamine in refluxing dichloromethane, gives thiirene dioxide **9** in a good yield.[6] We therefore first treated **12** with triethylamine in refluxing dichloromethane with expectation of obtaining thiirene dioxide **11**. Although the monobromo sulfone **16** was inert under the conditions,[15] **12** smoothly reacted with triethylamine (Scheme III) and gave 1-bromoacenaphthylene (**20**, 39%) and debrominated products **16** (9%) and **15** (5%). Disappointingly, there was no sign of the formation of **11**. Compound **20** is apparently produced by loss of sulfur dioxide from halo episulfone **21**, which is a common intermediate of Ramberg–Bäcklund reactions of α,α- and α,α'-dihalo sulfones.[7] The formation of **15** and **16** deserves mention. The fact that **16** is further reduced to **15** leads to the conclusion that sulfur dioxide produced from **21** is responsible for the debromination of **12** and **16** since **16** was inert toward triethylamine in boiling dichloromethane as described.[15] This agrees with the explanation that the debromination of α,α-dibromo sulfones to the corresponding monobromo derivatives observed

(13) (a) Bordwell, F. G.; Doomes, E.; Corfield, P. W. R. *J. Am. Chem. Soc.* **1970**, *92*, 2581–2583. (b) Bordwell, F. G.; Doomes, E. *J. Org. Chem.* **1974**, *39*, 2526–2531.

(14) (a) Meyers, C. Y.; Malte, A. M.; Matthews, W. S. *J. Am. Chem. Soc.* **1969**, *91*, 7510–7512. (b) Bordwell, F. G.; Doomes, E. *J. Org. Chem.* **1974**, *39*, 2531–2534.

(15) Prior to the examination of Ramberg–Bäcklund reaction of **12**, the behavior of **16** and **17** toward bases was tested. The Ramberg–Bäcklund reaction of **16** with sodium methoxide as base had been investigated from a mechanistic point of view, and the evidence pointed to a two-stage (carbanion) mechanism, despite the presence of a geometry that would appear to favor a one-stage (concerted) mechanism.[14b] Treatment of **16** with sodium methoxide in methanol gave acenaphthylene (**18**, 97%) as the exclusive product as previously reported.[14b] However, **16** is inert toward triethylamine in refluxing dichloromethane, while treatment of **16** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dichloromethane at ambient temperature yielded the debrominated sulfone **15** (21%) unexpectedly in addition to **18** (75%). This seems to be the first example of reductive debromination of α-monobromo sulfone observed during Ramberg–Bäcklund reaction, while it is known that the Ramberg–Bäcklund reaction of α,α-dibromo sulfones is sometimes accompanied by debromination of the starting materials.[16] Treatment of tribromide **17** with sodium methoxide in methanol at room temperature afforded 1,2-dibromoacenaphthylene (**19**; 37%; Scheme IV) and a considerable amount of a sulfonic acid.

during Ramberg–Bäcklund reaction is due to sulfite ion formed.[16,17]

Compound **12** was next treated with sodium methoxide in boiling methanol. In this case, surprisingly enough, decacyclene (**3**) was formed, though in a trace amount, along with **20** (75%) and **18** (9%). The above result may be explained by assuming two pairs of competing processes. One is the competition between process of dehydrobromination from **12** yielding the episulfone **21** and that of debromination yielding **16**, which subsequently gives rise to **18**. The other competition occurs in **21**, which competitively loses sulfur dioxide or hydrogen bromide to produce **20** or thiirene dioxide **11**, respectively. **11** must be thermally unstable because of the large strain imposed upon the three-membered ring and thus expels sulfur dioxide to give acenaphthyne **5**, which results in the formation of **3**.

Encouraged by the above result, next we treated compound **12** with potassium *tert*-butoxide, since we thought that the use of strong base could promote the base-induced dehydrobromination from **21**. In fact, treatment of **12** with potassium *tert*-butoxide in *tert*-butyl alcohol at 27 °C afforded an improved yield of **3** (5%) in addition to **20** (33%) and **18** (23%). Refluxing a mixture of **12** and potassium *tert*-butoxide in *tert*-butyl alcohol also gave a 5% yield of **3** along with **20** (36%) and **18** (27%). Control experiments showed that neither **20** nor **18** gave **3** under the conditions, and the starting material was recovered quantitatively.

The use of tetrahydrofuran as solvent and potassium *tert*-butoxide as base did not give **3** but afforded **20** (26%), **18** (5%), and **12**. The use of dimethyl sulfoxide as solvent and the same base resulted in a complex mixture. Similarly, the use of butyllithium as base in tetrahydrofuran afforded a complex mixture.

Next we tried to trap **5** with diene. We failed to obtain an adduct of **5** with furan, however. When the reaction was carried out in the presence of excess furan with potassium *tert*-butoxide as base in *tert*-butyl alcohol, only **3** (7%), **20** (19%), and **18** (10%) were obtained.

Acenaphthyne **5** is apparently a short-lived species, and if it were generated in the present system, it would be in a low concentration. It is unlikely that such a short-lived species in a low concentration trimerizes to give **3**. However, it also seems that at least one molecule of free acenaphthyne **5** must intervene in the formation of **3**, even though formation of **3** by trimerization of three molecules of **5** is unlikely. Control experiments rule out the formation of **3** from **18** or **20**. The formation of **3** was also observed by us in the thermolysis of **1**, where generation of **5** was strongly suspected.[1] In addition, **5** generated by photolysis of **13** gives rise to **3** (in this case the precursor compound to **5** is a cyclopropenone that is isoelectronic with **11**).[8] The formation of trimers, in yields ranging from 2% to 44%, has been used as evidence for the formation cyclooctyne,[18] cycloheptyne,[19] cyclohexyne,[19a] and cyclopentyne.[2b,3d] In the light of these results, it is likely that Ramberg–Bäcklund reaction of **12** produces acenaphthyne **5** as an intermediate in low efficiency, although trapping of **5** with diene cannot be attained.

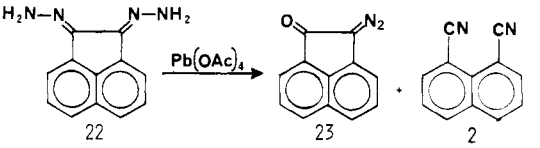
(16) Scholnic, F. Dissertation, University of Pennsylvania, 1955.
(17) (a) Bordwell, F. G.; Hoyt, E. B., Jr.; Jarbis, B. B.; Williams, J. M., Jr. *J. Org. Chem.* **1968**, *33*, 2030–2035. See also: (b) Bordwell, F. G.; Wolfinger, M. D.; O'Dwyer, J. B. *Ibid.* **1974**, *39*, 2516–2519.
(18) Wittig, G.; Fisher, S. *Chem. Ber.* **1972**, *105*, 3542–3552.
(19) (a) Breslow, R.; Altman, L.; Krebs, A.; Mohasci, E.; Murata, I.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1326–1331. (b) Wittig, G.; Meske-Schüller, J. *Justus Liebigs Ann. Chem.* **1968**, *711*, 65–75.

Table II. IR and ^{1}H NMR Data for Bromo Derivatives of 1*H*,3*H*-Naphtho[1,8-*cd*]thiopyran 2,2-Dioxide

compd	IR (ν_{SO_2}), cm^{-1}	^{1}H NMR, δ [a]
16	1320, 1120	4.44 (1 H, dd, J = 17, 3 Hz),[b] 5.47 (1 H, d, J = 17 Hz), 6.06 (1 H, d, J = 3 Hz), 7.3–8.2 (6 H, m)
cis-**12**	1343, 1330, 1160, 1134	5.27 (2 H, s), 7.4–8.2 (6 H, m)
trans-**12**	1335, 1170, 1160, 1140, 1130	6.73 (2 H, s), 7.4–8.2 (6 H, m)
17	1345, 1165	7.3–8.6 (7 H, m)[c]

[a] $CDCl_3$ as solvent. [b] Lit.[14b] 4.43 (1 H, dd, J = 16, 3 Hz), 5.42 (1 H, d, J = 16 Hz), 6.03 (1 H, d, J = 3 Hz), ~7.7 (6 H, m). [c] Signal of methine proton overlaps that of aromatic protons.

Attempted Generation of 5 by Oxidation of Acenaphthenequinone Dihydrazone. During the course of this study, successful generation of 2,2,5,5-tetramethyl-1-thiacyclopentyne by oxidation of 2,2,5,5-tetramethyl-1-thiacyclopentane-3,4-dione dihydrazone has been reported.[3i] Therefore generation of **5** by oxidation of the dihydrazone **22** was also examined. Treatment of **22** with lead tetraacetate in dichloromethane afforded a



22 23 2

complex mixture from which diazo ketone **23** (20%) and dicyanonaphthalene **2** (1.6%) were obtained. Bis(diazo) compound **4** should be a precursor of **2** as in the case of the pyrolysis of **1**, but expected **3** was not isolated in this case. The formation of **23** is of interest, but mechanism of its formation is uncertain.

Experimental Section

Proton magnetic resonance spectra were obtained on a Varian A-60D spectrometer; chemical shifts relative to internal Me_4Si are expressed in the δ scale. Infrared spectra of solids were taken with KBr disks, and those of liquids with films, with a JASCO IRA-2 instrument. Melting points were determined with a Mel-Temp apparatus by using open capillaries.

1*H*,3*H*-Naphtho[1,8-*cd*]thiopyran (14). Reportedly treatment of 1,8-bis(hydroxymethyl)naphthalene with phosphorus pentasulfide in carbon disulfide yields **14** in 85% yield.[10b] However, in our experiments a mixture of **14** and 1*H*,3*H*-naphtho[1,8-*cd*]pyran in a ratio of about 1:1 was always formed. A mixture of 1,8-bis(hydroxymethyl)naphthalene[20] (24.5 g, 0.13 mol) and phosphorus pentasulfide (44.4 g, 0.2 mol) in carbon disulfide (780 mL) was refluxed for 7.5 h. The solvent was removed, and 400 mL of dichloromethane was added to the residue. Insoluble materials were filtered off. The filtrate was evaporated and the residue chromatographed on an alumina column (400 g, Merck, Art 1078). Elution with carbon tetrachloride gave 9.0 g (37%) of **14** (mp 95–97 °C (lit. mp 96–97 °C,[10a] mp 102 °C[10b])), 7.8 g (32%) of 1*H*,3*H*-naphtho[1,8-*cd*]pyran (mp 81–82 °C (lit.[21] mp 82–83.5 °C)), and 11.6 g of a mixture of them.

1*H*,3*H*-Naphtho[1,8-*cd*]thiopyran 2,2-Dioxide (15). A mixture of 7.4 g (40 mmol) of **14** and 17.0 g (99 mmol) of *m*-chloroperoxybenzoic acid in 400 mL of dichloromethane was stirred for 2 h at room temperature and then refluxed for 3 h. The mixture was cooled, and the resulting precipitate was filtered off. The filtrate was washed with 2 N NaOH and then with water, dried, and evaporated to leave 7.9 g (92%) of **15**. Material recrystallized from benzene melted at 240–242 °C (lit.[14b] mp 244–245 °C).

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Table III. Melting Points and Elemental Analyses for Bromo Derivatives of 1*H*,3*H*-Naphtho[1,8-*cd*]thiopyran 2,2-Dioxide

			calcd, %				found, %			
compd	mp, °C	mol formula	C	H	S	Br	C	H	S	Br
16	195-197.5[a,b]	$C_{12}H_9BrO_2S$	48.50	3.05	10.79	25.89	48.53	3.05	10.74	27.00
cis-**12**	204-205 dec[b]	$C_{12}H_8Br_2O_2S$	38.33	2.14	8.53	42.49	38.35	2.13	8.53	42.48
trans-**12**	217-218 dec[b]	$C_{12}H_8Br_2O_2S$	38.33	2.14	8.53	42.49	38.37	2.09	8.58	42.75
17	203 dec[c]	$C_{12}H_7Br_3O_2S$	31.68	1.55	7.05	52.59	31.68	1.52	7.01	52.67

[a] Lit.[14b] mp 197-198 °C. [b] Recrystallized from chloroform. [c] Recrystallized from benzene.

Bromination of 15 with *N*-Bromosuccinimide. A mixture of 3.79 g (17.4 mmol) of **15**, 9.28 g (52.2 mmol) of NBS, and 20 mg of BPO in 500 mL of carbon tetrachloride was refluxed. Periodically reflux was stopped and BPO and NBS were added. The mixture was refluxed for a total of 50 h, and 150 mg of BPO and 6.45 g of NBS were further added. The resulting mixture was partitioned between 500 mL of dichloromethane and 200 mL of water. The organic layer was separated, washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column (300 g, Merck, Art 7734) with benzene as eluent and with 100-mL fractions. From fractions 16 and 17 was isolated 408 mg (5.2%) of 1,1,3-tribromo-1*H*,3*H*-naphtho[1,8-*cd*]thiopyran 2,2-dioxide (**17**). From fractions 25–27 was obtained *trans*-1,3-dibromo-1*H*,3*H*-naphtho[1,8-*cd*]thiopyran 2,2-dioxide (**12**) in a pure form. Fractions 39 and 40 gave pure *cis*-**12**. Fractions 28–38 consisted of a mixture of cis and trans isomers of **12**. A total of 2.78 g (42.6%) of **12** was thus obtained. Fractions 41–60 contained 2.50 g (48.4%) of 1-bromo-1*H*,3*H*-naphtho[1,8-*cd*]thiopyran 2,2-dioxide (**16**).

The reaction was repeated several times. Analysis of the crude reaction mixture by ^{1}H NMR showed that *cis*- and *trans*-**12** were formed in a ratio of about 64:36.

Physical properties and elemental analysis results of the bromo derivatives of 1*H*,3*H*-naphto[1,8-*cd*]thiopyran 2,2-dioxide are summarized in Tables II and III.

Radical Bromination of 16. The sulfone **16** (1.05 g, 3.5 mmol) was brominated by use of 2.52 g (14.1 mmol) of NBS and 30 mg of BPO in 200 mL of carbon tetrachloride in a similar manner as described above. The mixture was refluxed for 48 h. Purification by column chromatography afforded 600 mg (45%) of **12** and 114 mg (7%) of **17** with recovery of 347 mg (33%) of **16**.

Ramberg–Bäcklund Reaction of 16. (a) Sodium Methoxide as Base. A solution of sodium methoxide (3.7 mmol) was prepared by dissolving 85.1 mg of sodium in 15 mL of anhydrous methanol. After 148.5 mg (0.5 mmol) of **16** was added, the mixture was stirred for 16.5 h at room temperature. The resulting yellow mixture was evaporated. Dichloromethane (50 mL) and water (10 mL) was added to the residue. The dichloromethane layer was separated, washed with water, dried, and evaporated. The remaining solid was chromatographed on silica gel (20 g, Merck, Art 7734) to give 74 mg (97%) of acenaphthylene (**18**), mp 91–93 °C.

(b) Triethylamine as Base. A mixture of 141 mg (0.475 mmol) of **16** and 197 mg of triethylamine in 20 mL of dichloromethane was refluxed for 5.5 h. Analysis by TLC showed that no reaction occurred.

(c) DBU as Base. A mixture of 238 mg (0.8 mmol) of **16** and 365 mg (2.4 mmol) of DBU in 15 mL of dichloromethane was stirred for 1 h at room temperature. The resulting red solution was washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column. Elution with hexane gave 91 mg (75%) of **18**, mp 91–93 °C. Further elution with chloroform gave 38 mg (21%) of **15**, mp 240–242 °C.

Ramberg–Bäcklund Reaction of 17. A solution of sodium methoxide (3.3 mmol) was prepared by dissolving 75 mg of sodium in 15 mL of anhydrous methanol. After the addition of 178 mg (0.39 mmol) of **17**, the mixture was stirred for 17 h at room temperature under nitrogen. The mixture was evaporated, and the residue was partitioned between dichloromethane (50 mL) and water (5 mL). The organic layer was washed with water, dried, and evaporated. The remaining orange solid was purified by column chromatography on silica gel (20 g; hexane as eluent) to give 45 mg (37%) of **19**, mp 114–114.5 °C (lit.[4] mp 114–115 °C). The aqueous layer was acidified with 12 N HCl and then evaporated to dryness. Methanol (5 mL) was added to the residue and the insoluble material was filtered. The filtrate was evaporated to leave an oragne solid whose IR spectrum showed the characteristic absorptions of a sulfonic acid.

Ramberg–Bäcklund Reaction of 12. In all of the cases, **12** used is a mixture of cis and trans isomers in a ratio of about 64:36.

(a) Triethylamine as Base. A mixture of 188 mg (0.5 mmol) of **12** and 506 mg (5 mmol) of triethylamine in 20 mL of dichloromethane was refluxed for 7 h under an atmosphere of nitrogen. The reaction mixture was washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column. Elution with benzene gave 45 mg (39%) of 1-bromoacenaphthylene (**20**)[22] as a yellow oil whose spectral data are fully consistent with those of authentic specimen. Further elution with the same solvent gave 13 mg (9%) of **16** and 5 mg (5%) of **15**.

An authentic sample of **20** was conveniently prepared as follows. To a stirred solution of acenaphthylene (**18**) (4.57 g, 30 mmol) in 100 mL of carbon tetrachloride was added bromine (4.79 g, 30 mmol) in carbon tetrachloride (15 mL) during 1.5 h, and the mixture was stirred overnight at room temperature. After 100 mL of chloroform was added, the mixture was washed with water, dried, and evaporated. The residual brown solid was recrystallized from hexane (active charcoal) to give 5.46 g (58%) of 1,2-dibromoacenaphthene, mp 116.5–117.5 °C.

A mixture of 7.6 g (24.3 mmol) of 1,2-dibromoacenaphthene and 7.4 g (48.6 mmol) of DBU was stirred at room temperature overnight. The mixture was washed with water, dried, and evaporated. The residual oil was distilled to give 4.81 g (86%) of **20** as yellow oil, bp 138–140 °C (2 mmHg) (lit.[22b] bp 120–122 °C (0.4 mmHg)).

(b) Sodium Methoxide as Base. A solution of sodium methoxide (5.57 mmol) was prepared by dissolving 128 mg of sodium in 20 mL of methanol. After the addition of 188 mg (0.5 mmol) of **12**, the mixture was stirred for 18 h at room temperature under nitrogen. The resulting yellow mixture was evaporated, and dichloromethane (50 mL) and water (10 mL) were added to the residue. The dichloromethane layer was separated, washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column. Elution with carbon tetrachloride gave first **20**, then a mixture of **20** and **18**, and **18** finally (the yields of **20** and **18** were estimated to be 75% and 9%, respectively, by ^{1}H NMR analysis). Further elution with the same solvent gave decacyclene (**3**) in a trace amount. The identity of **3** was confirmed by its characteristic fluorescent nature and by comparison of the R_f value from TLC (R_f 0.50, CCl_4, silica gel $40F_{254}$, Merck) with that of authentic specimen.[22a]

(c) Potassium *tert*-Butoxide as Base. (i) In *tert*-Butyl Alcohol. A mixture of 188 mg (0.5 mmol) of **12** and 561 mg (5 mmol) of potassium *tert*-butoxide in 20 mL of anhydrous *tert*-butyl alcohol was stirred for 18 h at 27 °C under nitrogen. The solvent was removed under reduced pressure, and dichloromethane (50 mL) and water (10 mL) were added to the residue. The dichloromethane layer was separated, washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column. Elution with carbon tetrachloride gave 53 mg of a yellow oil that consisted of **20** (33%) and **18** (23%) in a ratio of about 59:41 (analysis by ^{1}H NMR). Further elution with the same solvent gave 4 mg (5%) of **3** as yellow crystals, mp 373 °C (lit.[23b]

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(23) (a) Decacyclene, mp >325 °C, is commercially available from Aldrich. (b) Dziewoński, K. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 962. (c) Pouchert, C. J. "Aldrich Library of Infrared Spectra"; Aldrich: 1970; p 441.

mp 387 °C), whose IR spectrum is fully consistent with that of authentic specimen.[23c]

A mixture of 188 mg (0.5 mmol) of **12** and 561 mg (5 mmol) of potassium *tert*-butoxide in 20 mL of *tert*-butyl alcohol was refluxed for 1.5 h under nitrogen. The resulting mixture was treated as described above to give **3** (5%), **18** (27%), and **20** (36%).

(ii) In Tetrahydrofuran. To a stirred solution of potassium *tert*-butoxide (65 mg, 0.58 mmol) in anhydrous THF (18 mL) was added a solution of **12** (109 mg, 0.29 mmol) in 5 mL of THF at −15 °C. The mixture was gradually warmed to room temperature and stirred for additional 18 h. The solvent was removed under reduced pressure, and the residue was partitioned between dichloromethane and water. The dichloromethane layer was separated, washed with water, dried, and evaporated. Column chromatography of the residue gave **18** (5%), **20** (26%), and the starting material (yield was not determined).

(iii) In Dimethyl Sulfoxide. A mixture of 188 mg (0.5 mmol) of **12** and 561 mg (5 mmol) of potassium *tert*-butoxide in 20 mL of anhydrous Me_2SO was stirred for 18 h at room temperature under nitrogen. The resulting dark brown mixture was partitioned between dichloromethane (150 mL) and water (100 mL). The dichloromethane layer was separated, washed with water, dried, and evaporated to leave 28 mg of a brown oil, from which no pure product could be obtained by column chromatography.

(d) Butyllithium as Base. A solution of butyllithium in hexane (5 mmol) was added to a stirred solution of **12** (0.5 mmol) in 20 mL of anhydrous THF under nitrogen. The mildly exothermic reaction occurred. After being allowed to stand overnight, the mixture was quenched with water and evaporated to dryness. The residue was taken up in dichloromethane, washed with water, dried, and evaporated. Analysis of the residue TLC showed the presence of at least five products. Chromatographic purification did not given any pure identified product.

Reaction of 18 and 20 with Potassium *tert*-Butoxide. A mixture of 152 mg (1 mmol) of acenaphthylene (**18**) and 1.12 g (10 mmol) of potassium *tert*-butoxide in 40 mL of anhydrous *tert*-butyl alcohol was refluxed for 1.5 h. Treatment of the mixture gave **18** quantitatively. The formation of **3** was not observed at all.

A mixture of 231 mg (1 mmol) of 1-bromoacenaphthylene (**20**) and 1.12 g (10 mmol) of potassium *tert*-butoxide in 40 mL of *tert*-butyl alcohol was refluxed for 1.5 h. Compound **20** was recovered quantitatively, and formation of **3** was not observed.

Ramberg–Bäcklund Reaction of 12 in the Presence of Furan. A mixture of **12** (188 mg, 0.5 mmol), potassium *tert*-butoxide (561 mg, 5 mmol), and furan (2 mL) in anhydrous *tert*-butyl alcohol (20 mL) was stirred for 23.5 h at room temperature under nitrogen. The resulting yellow mixture was partitioned between dichloromethane (150 mL) and water (100 mL). The dichloromethane layer was separated, washed with water, dried, and evaporated. Purification of the residue by column chromatography afforded **3** (7%), **18** (10%), and **20** (19%). Adduct of furan with acenaphthyne was not obtained.

Oxidation of Acenaphthenequinone Dihydrazone (22) with Lead Tetraacetate. To a stirred suspension of **22**[4,24] in 100 mL of dichloromethane was added a solution of 4.88 g (11 mmol) of lead tetraacetate in 20 mL of dichloromethane over a period of 50 min. After the completion of addition, the mixture was stirred for an additional 20 h. The inorganic precipitate was removed by filtration, and the filtrate was washed with water, dried, and evaporated. The residue was subjected to a silica gel column chromatography. Elution with carbon tetrachloride gave a few yellow crystalline compounds in a small amount, structures of which could not be determined. The column was next eluted with dichloromethane, and eluates were evaporated and rechromatographed on a silica gel column. Elution with hexane/ethyl acetate (2:1) gave diazo ketone **23** (196 mg, 20%), mp 97 °C (lit.[25] mp 94 °C), and then dicyanonaphthalene **2** (16 mg, 1.6%), mp 233.5–234.5 °C (lit.[26] mp 232 °C).

Registry No. **2**, 5690-48-2; **3**, 191-48-0; *cis*-**12**, 83831-93-0; *trans*-**12**, 83831-94-1; **14**, 203-85-0; **15**, 29376-61-2; **16**, 51392-61-1; **17**, 83831-95-2; **18**, 208-96-8; **19**, 13019-33-5; **20**, 54736-49-1; **22**, 1932-07-6; **23**, 2008-77-7; 1*H*,3*H*-naphtho[1,8-*cd*]pyran, 203-84-9; 1,8-bis(hydroxymethyl)naphthalene, 2026-08-6; 1,2-dibromoacenaphthene, 14209-08-6.

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Oxidation of Sulfides by Acyclic α-Azohydroperoxides

Alfons L. Baumstark*[1] and Pedro C. Vasquez

Laboratory for MBS, Department of Chemistry, Georgia State University, Atlanta, Georgia 30303

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The oxidation of sulfides with a series of substituted benzylazobenzene α-hydroperoxides (**2a–f**) produced the corresponding sulfoxides in good yield (~90%) in C_6D_6 at 34 °C. The reaction was found to be of the first order with respect to α-azohydroperoxide and to sulfide in aprotic medium. The reaction of BzSPh with acyclic α-azohydroperoxide **2a** [MeOArCH(OOH)N=NPh] in C_6D_6 was found to be slower than the corresponding oxidation with 3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole in $CDCl_3$. The relative reactivity series of sulfides with α-azohydroperoxide **2a** was found to be Me_2S (25) > BzSMe (14) > PhSMe (2.5) > BzSPh (1.0). This is similar to that observed for the reaction of the sulfides with hydrogen peroxide in protic solvent and reflects the relative nucleophilicities of the sulfides. The second-order rate constants for the reaction of a series of substituted benzylazobenzene α-hydroperoxides with PhSMe and BzSMe exhibited an excellent correlation with σ values. Both LFERs had ρ values of approximately 1.0. The results were interpreted to be consistent with nucleophilic attack of the sulfide on oxygen. Concomitant transfer of the hydroperoxy proton to the azo nitrogen would account for the lack of the requirement of general acid catalysis in aprotic medium.

The oxidation of sulfides to sulfoxides is readily accomplished[2] with peracids, hydrogen peroxide, and organic hydroperoxides. Sulfide oxidations are extremely rapid with peracids and show no dependence on acid catalysis. For hydroperoxides, S-oxidation reactions are generally characterized by the requirement of general acid catalysis. A general acid is apparently necessary in the transition state to facilitate the loss of ROH. In aprotic media, the hydroperoxide must serve as the general acid as well as the oxidant (the reaction rates become second order in hydroperoxide).

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