258 (4.53), 276 (sh) (4.34), 303 (sh) (3.70), 315 (sh) (3.42), 331 (3.36), 346 (3.32).

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.60; H, 5.28; N, 14.41.

Registry No.—2, 230-10-4; 5, 13100-44-2; 6, 13084-79-2; 11, 13084-80-5; 13, 13084-81-6; benzo[*f*]-guinoline, 85-02-9; 1-hydroxybenzo[*f*][1,7]naphthyridine-2-carboxylic acid, 13095-02-8.

The Halogenation of Acenaphthene Derivatives

BARRY M. TROST AND DAVID R. BRITTELLI

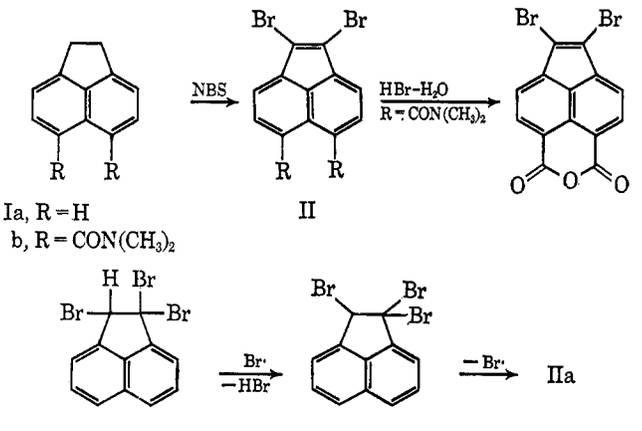
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received February 6, 1967

A common route for the preparation of acenaphthylenes from acenaphthenes involves bromination followed by elimination.[1,2] In conjunction with other synthetic studies, we required 1,2-dihaloacenaphthylenes which we believed would be available by similar methods. When this work began, the only report of such compounds involved a long, tedious procedure.[3] In light of a recent communication,[4] we wish now to report our work toward a simple preparation of 1,2-dibromo- and 1,2-dichloroacenaphthylenes.

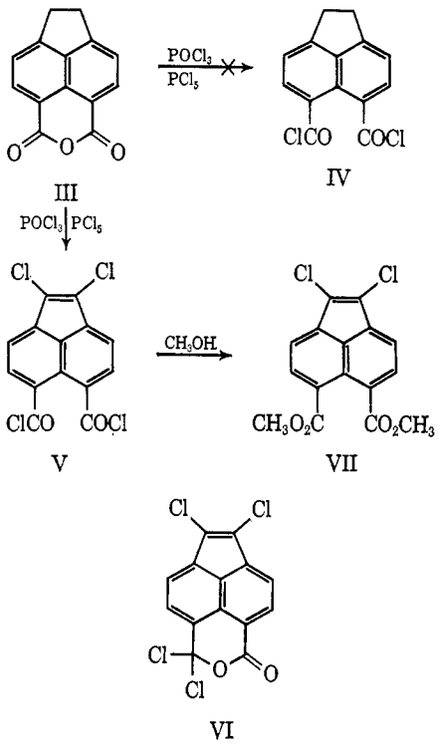
Treatment of acenaphthene with 4 equiv of N-bromosuccinimide yields approximately 80% of a single compound whose spectral properties identify it as 1,2-dibromoacenaphthylene. This procedure was extended to a 5,6-disubstituted acenaphthene with equal success as illustrated in Scheme I. In this latter case, the product was also characterized by hydrolysis to the corresponding acid anhydride. A reasonable rationalization for these reactions involves the tribromide which loses HBr probably by a free-radical pathway as depicted in Scheme I.

SCHEME I



Attempted extension of this free-radical bromination reaction to chlorination has produced equivocal results. Treatment of Ia or b with *t*-butyl hypochlorite has produced only complex mixtures. However, an attempt to convert the acid anhydride III to its acid chloride IV led surprisingly only to the dichloroacenaphthylene diacid chloride V. The nmr spectrum (see the Experimental Section) confirms the acid chloride structure and eliminates the pseudo-acid chloride structure VI. Although we were unable to obtain a good elemental analysis on V owing to sensitivity to hydrolysis, all the spectral data support its structure. It was further characterized by conversion to the dimethyl ester VII (upon treatment with hot methanol) and to the acid anhydride (Scheme II).

SCHEME II



The pathway for formation of V is not clear. This reaction failed with either Ia or Ib. If the reaction proceeded by simple free-radical chlorination by chlorine generated from either PCl_5 or $POCl_3$, both Ia and Ib should react. It is conceivable the formation of V involves a vinylogous Hell–Volhard–Zelinsky reaction.

Experimental Section[5]

1,2-Dibromoacenaphthylene (IIa).—To 1.54 g (10 mmoles) of acenaphthene dissolved in 50 ml of hot carbon tetrachloride was added 7.12 g (40 mmoles) of N-bromosuccinimide and a few crystals of dibenzoyl peroxide. After refluxing for 1 hr, the deep orange mixture was cooled and the succinimide was removed by filtration. The solution was washed with aqueous sodium thiosulfate and then dried over anhydrous magnesium sulfate.

(1) (a) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, **78**, 4939 (1956); (b) A. G. Anderson, Jr., and R. G. Anderson, *ibid.*, **77**, 6610 (1955).

(2) For other studies involving the halogenation of acenaphthenes, see (a) S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **80**, 4327 (1958); (b) F. D. Greene, W. A. Remers, and J. W. Wilson, Jr., *ibid.*, **79**, 1416 (1957).

(3) A. I. Tochilkin, *Zh. Vses. Khim. Obshchestva im. D. I. Mindeleeva*, **6**, 591 (1961); *Chem. Abstr.*, **56**, 7232b (1962).

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

(5) Melting points were taken on a Thomas–Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Models 11 and 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60 spectrometer fitted with a variable-temperature probe. Chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were taken on a CEC 103 C mass spectrometer at an ionizing current of 40 ma and ionizing voltage of 70 v. Analyses were performed by Spang Microanalytical Laboratory and Micro-Tech Laboratories, Inc. Unless otherwise indicated, extractions were performed with chloroform and magnesium sulfate was employed as a drying agent.

Evaporation of solvent produced an orange solid. Recrystallization from ethanol yielded 2.50 g (81% yield) of orange plates, mp 114–115°. The ultraviolet spectrum[6] exhibited maxima at 231 mμ (log ε 4.65), 263 sh (3.65), 270 (3.69), 280 (3.65), 314 (3.99), 322 (4.13), 327 (4.22), 335 (4.07), 345 (3.87), and 351 (3.88). The nmr spectrum[7] exhibited an ABC pattern with H_A 7.85, H_B at 7.65, and H_C at 7.50 ppm, J_{AB} = 2.0 cps and J_{AC} = J_{BC} = 8 cps. The mass spectrum showed a strong molecular ion peak at *m/e* 308, 310, and 312 (characteristic for the presence of 2-Br) and abundant peaks at 231 and 229 (M − Br), 154, 155, and 156 (M^{2+}), 150 (acenaphthyne, base peak), 123, 122, 111, 110, 100, 99, 98, 87, 86, 85, 76, 75, 74, 73, and 63.

Anal. Calcd for $C_{12}H_6Br_2$: C, 46.5; H, 1.9; Br, 51.7. Found: C, 46.4; H, 2.0; Br, 51.6.

1,2-Dibromoacenaphthylene-5,6-dicarboxylic Acid Di-N,N-dimethylamide (IIb).—Treatment of acenaphthene-5,6-dicarboxylic acid di-N,N-dimethylamide[8,9] with N-bromosuccinimide as described above produced the dibromoacenaphthylene derivative, mp 281–282°, as orange crystals after recrystallization from ethanol. It exhibited a carbonyl peak in the infrared spectrum[10] at 1637 cm^{-1}. The ultraviolet spectrum[6] possessed maxima at 234 mμ (log ε 4.58), 268 sh (3.68), 277 (3.68), 288 sh (3.61), 334 (4.18), and 357 (1.08). The nmr spectrum[7] had an AB pattern for 4 H with H_A at 7.53 and H_B at 7.43 ppm and J_{AB} = 7 cps, a singlet for 6 H at 3.11 and a singlet for 6 H at 2.89 ppm. The steric and electronic hindrance to rotation gives rise to the large separation of the absorption bands for the pairs of N-methyl groups. The mass spectrum shows the expected molecular ion peak at 454, 452, and 450 (characteristic of 2-Br) and abundant peaks at 410, 408, and 406 [M − $(CH_3)_2N$], 314 and 312, 235 (base peak), 207, 206, 191, 190, 179, 178, 146, 145, 105, 99, 98, 86, and 67.

Anal. Calcd for $C_{18}H_{16}Br_2N_2O_2$: C, 47.8; H, 3.5; Br, 35.7; N, 6.0. Found: C, 47.9; H, 3.5; Br, 35.6; N, 5.7.

The diamide was hydrolyzed by refluxing a suspension of 15.0 g (0.0331 mole) in 250 ml of 48% aqueous hydrobromic acid for 45 min. The reaction mixture was cooled in an ice bath and the resultant red solid was removed by filtration. After oven drying (~80°) for 15 hr, 1,2-dibromoacenaphthylene-5,6-dicarboxylic anhydride weighed 12.2 g (91% yield). Recrystallization from chloroform produced deep red, microscopic needles, mp >350°. The infrared spectrum[10] showed the characteristic anhydride absorption at 1750 and 1710 cm^{-1}. The ultraviolet spectrum[6] exhibited maxima at 223 mμ (log ε 4.23), 251 (3.99), 343 (3.80), 360 (4.03), 368 sh (3.80), and 376 (3.84).

Anal. Calcd for $C_{14}H_4Br_2O_3$: C, 44.3; H, 1.1; Br, 42.1. Found: C, 44.2; H, 1.1; Br, 42.0.

1,2-Dichloroacenaphthylene Derivatives. A. Diacid Chloride V.—To 3.0 g (12.4 mmoles) of carefully dried acenaphthene-5,6-dicarboxylic acid was added 9.0 g (43.2 mmoles) of phosphorus pentachloride and 9.0 ml (98.9 mmoles) of phosphorus oxychloride. The mixture was refluxed for 20 hr during which time all the solid went into solution. After cooling and removal of solvent *in vacuo*, the residue was treated with carbon disulfide. Filtration removed the insoluble solids and evaporation produced 2.97 g (70% yield) of a deep orange compound, mp 228° dec. The acid chloride infrared[10] carbonyl band appeared at 1750 cm^{-1}. The ultraviolet spectrum[11] exhibited maxima at 220 mμ (log ε 4.49), 257 (3.15), 270 (3.12), 285 (3.10), 291 sh (3.04), 336 sh (3.05), and 346 (3.15). The nmr spectrum[12] confirmed the assignment of the symmetrical acid chloride structure by exhibiting only an AB pattern with H_A at 7.97 and H_B at 7.42 ppm, and J_{AB} = 7 cps.

B. Dimethyl Ester VII.—A suspension of 118 mg (0.341 mmole) of the acid chloride was refluxed in 12.0 ml of methanol on a steam bath. The solid slowly dissolved and as the reaction proceeded, yellow flakes appeared. Upon cooling and filtration of the beautiful yellow flakes, there was obtained 82 mg (72% yield), mp 166–168°. The ester infrared[10] carbonyl band appeared at 1729 cm^{-1}. The ultraviolet spectrum[6] showed maxima at 236 mμ (log ε 4.50), 265 (3.80), 274 (3.84), 281 (3.75), 330 sh (4.12), 338 (4.22), and 352 sh (3.90). The nmr spectrum[7] exhibited a sharp singlet for 6 H at 3.95 and an AB pattern for 4 H with H_A at 7.97, and H_B at 7.65 ppm, and J_{AB} = 7 cps. The mass spectrum showed a molecular ion at *m/e* 336 with the appropriate isotope peaks as well as abundant absorptions at 305 (M − OCH_3, base peak), 262 (M − $CO_2CH_3CH_3$), 220, 219, 218, and 206 (M − $CO_2CH_3 \cdot 2Cl$).

Anal. Calcd for $C_{10}H_{10}Cl_2O_4$: C, 57.0; H, 3.0; Cl, 21.0. Found: C, 57.0; H, 3.1; Cl, 21.1.

C. Acid Anhydride.—A suspension of 1.00 g (2.89 mmoles) of diacid chloride in 500 ml of moist benzene was refluxed for 5 days under nitrogen. A small amount of a black precipitate remained and was removed by filtration. Evaporation of the solution to dryness *in vacuo* produced 790 mg (100% yield) of dark red-brown powder. Recrystallization from chloroform produced deep red needles, mp 350° dec. The infrared spectrum and analytical data indicate that the anhydride crystallized as a hydrate. The characteristic anhydride doublet appeared in the infrared spectrum[10] at 1760 and 1725 cm^{-1}. The ultraviolet spectrum[6] had maxima mμ (log ε 3.20), 344 sh (3.13), 358 (3.19), and 369 sh (3.02). The nmr spectrum[13] exhibited an AB pattern with H_A at 7.85 and H_B at 7.70 ppm, and J_{AB} = 7 cps.

Anal. Calcd for $C_{14}H_4Cl_2O_3 \cdot H_2O$: C, 54.4; H, 1.9; Cl, 23.0. Found: C, 54.8; H, 1.5; Cl, 23.2.

Registry No.—IIa, 13019-33-5; IIb, 13094-92-3; V, 13082-02-5; VII, 13065-24-2; acid anhydride derivative of VII, 13082-03-6; 1,2-dibromoacenaphthylene-5,6-dicarboxylic anhydride, 13019-15-3.

Acknowledgment.—We wish to express our appreciation to the National Institutes of Health (Grant No. GM 13598-01) and the Wisconsin Alumni Research Foundation for support of this work.

(6) Determined as a solution in ethanol.
(7) Determined as a solution in deuteriochloroform.
(8) B. M. Trost, G. Struve, and D. R. Brittelli, to be published.
(9) *Cf.* L. A. Carpino and S. Gowecke, *J. Org. Chem.*, **29**, 2824 (1964).
(10) Determined as a solution in chloroform.
(11) Determined as a solution in cyclohexane.
(12) Determined as a solution in phosphorus oxychloride.
(13) Determined as a solution in DMSO.

The Hydrolysis of 5-Diphenylmethylene-2(5H)-thiophenone[1]

W. R. BIGGERSTAFF, WILLIAM L. HENSON, AND CURTIS E. DIEBERT

Chemistry Department, Fresno State College, Fresno, California 93726

Received November 9, 1967

As an extension of the work in which we prepared 5-diphenylmethylene-2(5H)-thiophenone (I),[2,3] we now wish to report the characterization of three of its hydrolysis products.

Treatment of a methanolic solution of I with 0.1 *N* potassium hydroxide solution at room temperature for 5 days led to the isolation of *cis*-5,5-diphenyl-4-mercapto-2,4-pentadienoic acid disulfide (II) in 71% yield. However, when I was refluxed with aqueous 2 *N* potassium hydroxide solution for 24 hr, the isomeric *trans* acid disulfide III was obtained in 39% yield. A third acid which was subsequently shown to be the *trans* mercapto acid IV was isolated in small amounts from the filtrates of III. When I was refluxed with 0.1 *N* potassium hydroxide for 24 hr, the yield of IV was increased to 36%. Reductive cleavage of the *trans* acid disulfide III produced the *trans* mercapto acid IV. However, as might be expected, cleavage of the *cis* acid disulfide II led invariably to isolation of I.

(1) This investigation was supported by Public Health Service Research Grant CA 06774, from the National Cancer Institute.
(2) W. R. Biggerstaff and K. L. Stevens, *J. Org. Chem.*, **28**, 733 (1963).
(3) *Cf.* A.-B. Hörnfeldt and S. Gronowitz, *Arkiv Kemi*, **21**, 239 (1963), for spectral studies of closely related compounds.