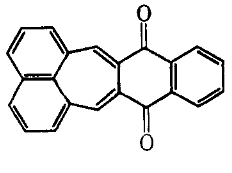
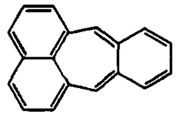
Dehydration of V in refluxing acetic anhydride in the presence of N-phenylmaleimide afforded a single adduct (VI), mp 267–270°, in 55% yield. The nmr spectrum of VI was in agreement with the assigned structure. Thus, in addition to aromatic protons, the spectrum showed only two bridgehead protons at δ 5.12[5] and two protons α to the imide carbonyls at δ 3.78. The latter value supports the assigned *exo* configuration of adduct VI, since model compounds show the δ 3.78 value to be in better accord with a deshielding effect of the naphthalene ring than with the expected greater deshielding effect of a sulfur bridge.[6] It may be noted that the less likely adduct of general structure VII (stereochemistry unspecified) is ruled out by the nmr data, since VII would show aliphatic protons at four different positions.


X


XI

The trapping of 2-thiaphenalene (II) by appropriate dienophiles offers a simple new route to pleiadene derivatives. Using this approach we have succeeded in synthesizing the first example of a pleiadenequinone. Thus, the reaction of sulfoxide V with 1,4-naphthoquinone in a refluxing mixture of pyridine and acetic anhydride afforded, in 51% yield, adduct VIII, mp 289–293°. Peracetic acid oxidation of VIII afforded, in 82% yield, the corresponding sulfone IX, mp 250° dec. Hydrolysis of IX at room temperature in a mixture of tetrahydrofuran and aqueous potassium hydroxide in the presence of air afforded directly, in 32% yield, chocolate brown needles of benzo[*l*]pleiadene-8,13-quinone (X), mp 247–249°. Quinone X appears to be a compound of unusual stability, in contrast to the great instability of pleiadene (XI)[7] and related hydrocarbons.[8,9]

The synthesis and transformations of other adducts of II is under investigation and will form the subject of subsequent reports.

Acknowledgment. We thank the U. S. Army Research Office (Durham) for Grant DA-ARD-D-31-124-G850 in support of this work.

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obtained for all new compounds reported. Nmr spectra were determined in $CDCl_3$. Mass spectra obtained for VIII, IX, and X were in agreement with the assigned structures. The ultraviolet–visible spectrum of X shows the following bands: $\lambda_{max}^{dioxane}$ 239 mμ (log ϵ 4.38), 268 (4.68), 430 sh (4.03), 449 (4.07), 530 sh (3.06), 570 sh (2.75), and 625 sh (2.03).

(5) See ref 2 for nmr values of similar bridgehead protons.

(6) The corresponding pair of protons in the pleiadene–N-phenylmaleimide adduct, which are in an almost identical environment, appear at δ 3.85: M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965). Similar protons appear at fields below δ 3.9 when deshielded by a sulfur bridge: see ref 2.

(7) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965).

(8) M. P. Cava and R. H. Schlessinger, *ibid.*, **21**, 3051 (1965).

(9) M. P. Cava and R. H. Schlessinger, *ibid.*, **21**, 3065 (1965).

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Received April 24, 1967

Reactive Aromatic Heterocycles Containing "Tetravalent Sulfur"[1]

Sir:

We wish to report the generation of naphtho[1,8-*cd*]thiapyran (I, 2-thiaphenalene) and its acenaphthene analog acenaphtho[5,6-*cd*]thiapyran (II, 2-thiaacephenalene), two highly reactive heterocycles derived from the aromatic hydrocarbon *peri*-cycloheptanaphthalene (III)[2] by substitution of a tetracovalent sulfur atom for two sp^2 carbon atoms.[3]

Recently an elegant application of the Pummerer reaction[4] to the synthesis of unusual thiophenes from 2,5-dihydrothiophene sulfoxides has been reported.[5] We have found this transformation also to occur with certain cyclic 2,6-dihydrosulfoxides.[6]

Reaction of 1,8-bis(hydroxymethyl)naphthalene (IV)[2] with phosphorus pentasulfide in carbon disulfide[7] gave in 85% yield sulfide V, mp 102°. Oxidation of V using sodium periodate in aqueous methanol[8] afforded the corresponding sulfoxide VI, mp 230° dec, in 90% yield.[9] Decomposition of VI in refluxing acetic anhydride was found to occur readily, accompanied by the formation of a complicated mixture of products.[10] In contrast, the reaction of N-phenylmaleimide with sulfoxide VI in refluxing acetic anhydride afforded a single highly crystalline adduct VII, mp 278–285°, in 70% yield.

The gross structure of adduct VII was provided by its mass spectrum which, in addition to the parent ion at *m/e* 357, gave rise to a retro-Diels–Alder-type fragmentation pattern with peaks at *m/e* 184 (heterocycle I)[11] and 173 (N-phenylmaleimide) accompanied by a metastable peak at *m/e* 94.84. That the peak at *m/e* 184 represents the parent ion of I is substantiated by the occurrence of a strong peak at *m/e* 152 (parent ion of acenaphthylene; extrusion of sulfur from I) accompanied by a metastable peak at *m/e* 125.57. The *exo* geometry for the adduct VII was indicated by its nmr spectrum which shows the two protons α to the imide carbonyls at δ 3.75, a position similar to that (δ 3.85) of the corresponding protons of the N-phenylmaleimide–

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[1] During this investigation we learned of similar efforts in the laboratory of Professor M. P. Cava. Our results are published simultaneously through mutual agreement.

[2] V. Boekelheide and G. K. Vick, *J. Am. Chem. Soc.*, **78**, 653 (1956).

[3] R. Zahradnik and C. Parkanye, *Collection Czech. Chem. Commun.*, **30**, 3016 (1965).

[4] For recent studies of the Pummerer reaction see (a) L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959); (b) S. Oae, T. Kitaa, S. Kawamura, and Y. Kilaoka, *Tetrahedron*, **19**, 817 (1963).

[5] (a) M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **88**, 4112 (1966); (b) H. Wynberg and D. J. Zwanenburg, *Tetrahedron Letters*, 761 (1967).

[6] All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds reported. Nmr spectra were determined in $CDCl_3$; mass spectra were taken at 70 ev.

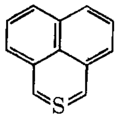
[7] M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965).

[8] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

[9] The structure of VI is confirmed by an infrared band at 1040 cm^{-1}, characteristic of sulfoxides, and by its nmr spectrum which shows six aromatic protons in the δ 7.25–7.92 region and four methylene protons as a singlet at δ 4.4.

[10] Spectral examination (infrared and nmr) of the crude reaction mixture indicates that products containing carbonyl functions do not appear to be present. All attempts to isolate crystalline materials from this mixture have met thus far with no success.

[11] Peaks at 357 and 184 cm^{-1} showed correct ^{34}S isotopic abundance.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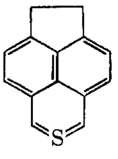
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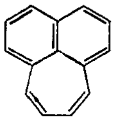
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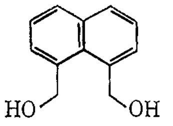
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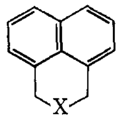
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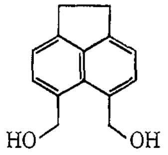
VI, X = SO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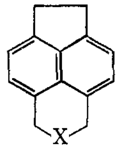
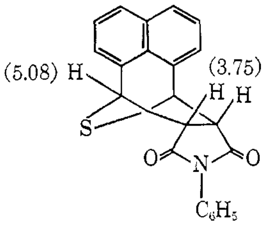

X, X = S
XI, X = SO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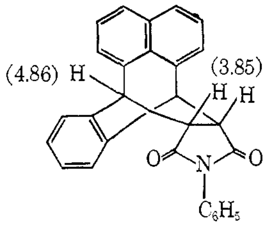
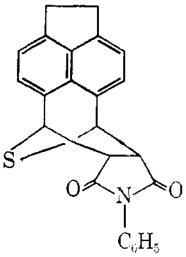

VIII


XII

pleiadene adduct VIII.[7] Molecular models indicate deshielding of these protons in both VII[12] and VIII.

Treatment of 5,6-bis(hydroxymethyl)acenaphthene (IX)[13] with phosphorus pentasulfide in carbon disulfide gave in 80% yield sulfide X, mp 175°. On oxidation with sodium periodate, X afforded the corresponding sulfoxide XI, mp 292° dec, in 70% yield. The reaction of sulfoxide XI with refluxing acetic anhydride again was found to be complicated. However, when XI was allowed to react with N-phenylmaleimide under similar conditions a crystalline adduct XII, mp 342–357°, was isolated in 45% yield. Adduct XII was shown to have the *exo* structure indicated on the basis of its nmr spectrum, which closely resembled that of adducts VII and VIII.

Acknowledgments. This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation and by the Petroleum Research Fund (Grant No. 756-G). We wish to thank Mr. Glenn P. Happ of the Eastman Kodak Company for determination of the mass spectra.

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[12] Other features of the nmr spectrum of VII include the bridgehead protons at δ 5.08 and a broad band of eleven aromatic protons in the δ 7.20–7.81 region.

[13] L. A. Carpino and S. Gowecke, *J. Org. Chem.*, **29**, 2824 (1964).

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Received April 24, 1967

Structure of Phycocyanobilin[1]

Sir:

The structure of the chromophore of the important photosynthetic pigment phycocyanin, present in blue-green algae, has long been of concern. Lemberg[2] described it as a linear tetrapyrrole, but much subsequent work[3] did not establish a structure. A major obstacle was the lack of a suitable preparative procedure for detaching the chromophore, without extensive alteration, from the protein moiety of the pigment. Recently Fujita and Hattori[4] found that refluxing phycocyanin, or even whole blue-green algae, with methanol containing ascorbic acid liberated the chromophore in good yield. Ó Carra and Ó hEocha[5] subsequently showed that the ascorbic acid was not essential to the liberation of the chromophore.[6]

C-Phycocyanin, isolated from *Phormidium luridum* or *Synechococcus lividus*,[7] is purified by standard methods.[8] After dialysis against 0.01 *M* phosphate buffer, pH 6.9, a 2–6% solution of the protein (2–4 g of protein) is diluted with methanol to 90% methanol and refluxed overnight. The blue solution is then centrifuged, evaporated to 200–300 ml, centrifuged, and extracted with petroleum ether (bp 20–40°). Then, 200 ml of freshly destabilized chloroform is added, and the mixture is acidified with glacial acetic acid and quickly washed three times with copious amounts of salt water. The blue chloroform solution is evaporated to dryness (at 30°). The residue is dissolved in 8–10 ml of chloroform containing 2.5% methanol, filtered, and then dried by rotary evaporation at 25°. The residue is taken up in about 4 ml of chloroform–methanol, precipitated by addition of seven volumes of petroleum ether, and washed with petroleum ether. Yields are 40% of the calculated on the assumption that the chromophore constitutes 5% (w/w) of the phycocyanin.

On mass spectrometric examination, phycocyanobilin shows a parent ion at *m/e* 588.293 ± 0.003. $C_{33}H_{40}N_4O_6$ requires 588.2948. This is the only observable ion at low ionizing voltages. The fragmentation pattern of phycocyanobilin[9] was similar to that of bilirubin,[10] showing a relatively weak parent ion and

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] For a review and references to the literature, see R. Lemberg and J. W. Legge, "Hematin Compounds and Bile Pigments," Interscience Publishers, Inc., New York, N. Y., 1949, pp 127, 145–149.

[3] *Cf.* C. Ó hEocha in "Chemistry and Biochemistry of Plant Pigments," T. W. Goodwin, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter 6.

[4] Y. Fujita and A. Hattori, *J. Gen. Appl. Microbiol.* (Tokyo), **9**, 253 (1963).

[5] P. Ó Carra and C. Ó hEocha, *Phytochemistry*, **5**, 993 (1966).

[6] Ó Carra and Ó hEocha[5] concluded that the chromophore liberated by methanolysis of phycocyanin was an "artifact." However, we find the absorption spectra of the methanolysis product to be identical with that of chromophore liberated by the conventional concentrated hydrochloric acid method, taking into account the solvent and acidity dependence of the visible absorption spectra. We have every reason to suppose that the methanolysis and hydrochloric acid products are at least very similar if not identical. Our compound shows very strong absorption maxima at 365–370 mμ in all solvents. In tetrahydrofuran, λ_{max} 590 mμ; in $CHCl_3$, λ_{max} 638 mμ; in CH_3OH–5% concentrated HCl, λ_{max} 680 mμ.

[7] H. F. DaBoll, H. L. Crespi, and J. J. Katz, *Biotechnol. Bioeng.*, **4**, 281 (1962).

[8] A. Hattori, H. L. Crespi, and J. J. Katz, *Biochemistry*, **4**, 1213 (1965).

[9] Measured with A.E.I. MS-9 mass spectrometers. A direct inlet system at ~220°, 70 ev, and 100 μa trap current was used.