

55% sodium hydride dispersed in mineral oil, and then with 6.56 g. (0.0543 mole) of dimethylaminopropyl chloride. After the same type of work-up, there was obtained 6.5 g. of an oil which was converted to a hydrochloride and recrystallized from alcohol (3.2 g., m.p. 138–142°). After drying, the melting point rose to 157–158.5°.

*Anal.* Calcd. for  $C_{13}H_{21}ClN_2O_2S$ : C, 51.22; H, 6.94; N, 9.19. Found: C, 51.31; H, 7.02; N, 8.87.

**6-Bromo-3,4-dihydrosulfostyryl (Probable Structure) (18).**—A solution of 0.27 g. (0.0015 mole) of N-bromosuccinimide in a small amount of DMF was added to a suspension of dihydrosulfostyryl in DMF. Heat was evolved, and the solution turned yellow. After 5 min., the solution was diluted with water, and the product precipitated (m.p. 175–180°, 0.3 g.). A sample recrystallized from ethyl acetate–pentane melted at 183–186°.

*Anal.* Calcd. for  $C_8H_8BrNO_2S$ : C, 36.8; H, 3.06; N, 5.34. Found: C, 36.9; H, 3.02; N, 5.25.

**6,8-Dibromo-3,4-dihydrosulfostyryl (Probable Structure) (19).**—A solution of 3.56 g. (0.02 mole) of N-bromosuccinimide in DMF was treated with 1.85 g. (0.01 mole) of dihydrosulfostyryl in a manner similar to that described above. Dilution of the reaction mixture with water gave the dibromide; after recrystallization from ethyl acetate–pentane, there was obtained 1.7 g. of product (m.p. 191–193°; mixture melting point with monobromide, 140–160°).

*Anal.* Calcd. for  $C_8H_6Br_2NO_2S$ : C, 28.18; H, 2.06; N, 4.11. Found: C, 28.51; H, 2.18; N, 4.03.

In some instances when the bromination was carried out, a mixture of mono- and dibromo products was obtained, m.p. 150–170°. These could be separated by chromatography over

alumina, using 1:1 benzene–ethyl acetate. The monobromo compound was eluted first.

**6-Bromo-N-methyl-3,4-dihydrosulfostyryl (Probable Structure) (20).**—A mixture of 3.9 g. (0.02 mole) of N-methyldihydrosulfostyryl and 3.6 g. (0.02 mole) of N-bromosuccinimide was stirred with 15 ml. of DMF. The solids slowly dissolved, and heat was evolved. The reddish brown solution was heated for 5 min. on the steam bath, then was diluted with water and the resulting precipitate was recrystallized from ethyl acetate–pentane (3.6 g., m.p. 109–111°). When a 100% excess of N-bromosuccinimide was used, again only the monobromide was obtained, in high yield.

*Anal.* Calcd. for  $C_9H_{10}BrNO_2S$ : C, 39.15; H, 3.63; N, 5.08. Found: C, 39.28; H, 3.63; N, 5.48.

**6-Bromo-3,4-dihydrocarbostyryl.**—Solutions of 7.35 g. (0.05 mole) of 3,4-dihydrocarbostyryl in warm DMF and 8.9 g. (0.05 mole) of N-bromosuccinimide in DMF were mixed and heated on a steam bath for 5 min. The solution was cooled and diluted with water, and the solid that separated was filtered and recrystallized from alcohol (5.2 g., m.p. 170–172°, lit.<sup>10</sup> m.p. 170–171°).

**6,8-Dibromo-3,4-dihydrocarbostyryl.**—Dihydrocarbostyryl (0.75 g., 0.005 mole) was brominated with 1.8 g. (0.01 mole) of N-bromosuccinimide in the same manner as described above. From this reaction there was obtained, after one recrystallization from ethanol, 0.65 g. of product (m.p. 144–146°, lit.<sup>10</sup> m.p. 147–148°).

**Acknowledgment.**—We wish to thank Dr. James W. Wilson for many helpful discussions, and Mr. Irving Fried for technical assistance.

## Substituted Perinaphthenyl Anion Radicals<sup>1</sup>

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2,3-Dihydroperinaphthen- $\Delta^{1\alpha}$ -malononitrile, 2,3-dihydroperinaphthen- $\Delta^{1\alpha}$ -ethyl cyanoacetate, and 2,3-dihydroperinaphthen- $\Delta^{1\alpha}$ -cyanoacetamide have been synthesized. Organic bases catalyze the dehydrogenation of these compounds to the corresponding cyanomethylene perinaphthenes. The anion radical of perinaphthen- $\Delta^{1\alpha}$ -malononitrile was obtained by reaction with metallic sodium in tetrahydrofuran (THF). Its e.s.r. spectrum closely resembles that of radicals generated during the dehydrogenation reaction, for which a mechanism involving electron-transfer steps is proposed.

Abstraction of a hydrogen atom, a hydride ion, or a proton from the methylene group of perinaphthene generates the corresponding free radical, carbonium ion, or carbanion, respectively. The symmetry and extensive conjugation of these species imply considerable stability,<sup>2</sup> which is borne out by the successful generation of all three systems.<sup>3–5</sup> Structural consideration indicates that a substituted perinaphthenyl radical anion should be accessible from a perinaphthene derivative in which the methylenic hydrogens are replaced by an exocyclic double bond. If the substituents of this double bond are highly electronegative, the negative charge can be stabilized external to the ring system, while the electron is delocalized within the ring system. Cyanomethyleneperinaphthenes constitute appropriate precursors of this type. In this paper we describe the synthesis of perinaphthen- $\Delta^{1\alpha}$ -malononitrile and perinaphthen- $\Delta^{1\alpha}$ -ethyl cyanoacetate, and the generation of corresponding radical anions.

## Results and Discussions

The dihydrocyanomethylene derivatives were prepared from perinaphthanone (1) by the Cope modification of the Knoevenagel condensation. Malononitrile gave 2,3-dihydroperinaphthen- $\Delta^{1\alpha}$ -malononitrile (2a) in approximately 50% yield. It was necessary to establish that the product indeed had the structure of 2a, and not that of the tautomer 3a. The compound 3a, by analogy with perinaphthene, would be expected to provide the corresponding free radical by reaction with oxygen. E.s.r. measurements in oxygen-saturated ethanolic solutions at room temperature showed no evidence of radical formation. Further proof of structure 2a comes from the n.m.r. spectrum. This shows absorption at 3.23–3.37 p.p.m. (3.8 protons), which can be assigned to the methylenic groups, and a complex multiplet (5.83 protons) centered at 7.98 p.p.m., which is due to the aromatic hydrogen atoms.

Compounds 2b and 2c were prepared in a similar manner, but in somewhat lower yields.

The dehydrogenation of compound 2a was attempted by several methods. Refluxing its solution in several solvents with chloranil or dichlorodicyanoquinone (DDQ) was unsuccessful. Bromination with N-bromosuccinimide gave a product which could not be

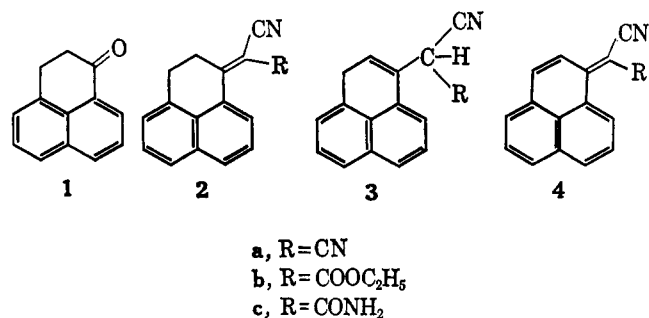
(1) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964; Abstract, p. 84S.

(2) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2184 (1952).

(3) D. H. Reid, *Tetrahedron*, **8**, 339 (1958).

(4) R. Petit, *J. Am. Chem. Soc.*, **82**, 1972 (1960).

(5) (a) F. C. Stehling and K. W. Bartz, *J. Chem. Phys.*, **34**, 1976 (1961); (b) J. E. Bennett, *Proc. Chem. Soc.*, 144 (1961).



completely dehalogenated. Perinaphthen- $\Delta^{1\alpha}$ -malononitrile (**4a**) was obtained in poor yield by heating compound **2a** with palladized charcoal. The compound **4a** was found to be extremely resistant to hydrolytic cleavage under alkaline conditions, but under acidic conditions a small amount of perinaphthenone could be detected. Its structure was further established by conventional methods and by n.m.r. spectroscopy. The compound is quite insoluble and its spectrum in deuteriochloroform at elevated temperature was unsatisfactory. The spectrum in trifluoroacetic acid shows a complex signal centered at 7.88 p.p.m. corresponding to 7.14 protons. A doublet appears at 9.35 p.p.m. ( $J = -8$  c.p.s.), and accounts for 0.94 protons. This doublet is tentatively assigned to the proton at position 2.

The standard, piperidine-catalyzed Knoevenagel condensation of ketone **1** with malononitrile furnishes compound **2a** and a small quantity of a by-product which was identified as perinaphthen- $\Delta^{1\alpha}$ -malononitrile (**4a**). This finding led to the development of the novel base-catalyzed dehydrogenation of compounds **2a** and **2b**. The addition of an equimolar amount of triethylamine to a solution of compound **2a** in acetonitrile or THF yielded **4a** in approximately 45% yield. It was established that air was necessary for the completion of the reaction. Whereas, in general, the aliphatic and alicyclic secondary and tertiary amines are effective in this reaction, aromatic amines and stronger bases such as sodium hydroxide and sodium methoxide are ineffective. In fact, prolonged contact with the latter in THF leads to extensive polymerization. The attempted conversion, **2c**  $\rightarrow$  **4c**, gave at least six products from which a deep red material was isolated ( $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$  460  $\mu$ ). The elemental analysis was unsatisfactory for compound **4c**.

Perinaphthenone is quite unreactive to malononitrile. Using an excess of malononitrile with either the ketone or its aniline bisulfite addition compound,<sup>6</sup> in the presence of piperidine, compound **4a** was obtained after extensive chromatography (1% yield).

The anion radical of perinaphthen- $\Delta^{1\alpha}$ -malononitrile was generated by reacting a degassed solution of compound **4a** in THF with metallic sodium, and its e.s.r. spectrum is shown in Figure 1. By analogy to the seven-quartet spectrum of the perinaphthenyl radical,<sup>7</sup> and, particularly, to the six-quartet spectrum of the hydroxyperinaphthenyl radical,<sup>8</sup> it is evident that the

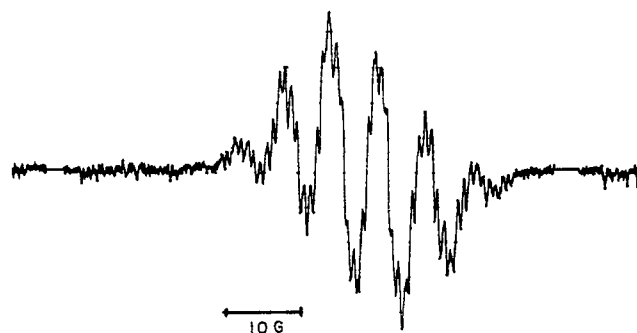


Figure 1.—E.s.r. absorption spectrum of the anion radical **6** derived from perinaphthen- $\Delta^{1\alpha}$ -malononitrile **4a** and sodium.

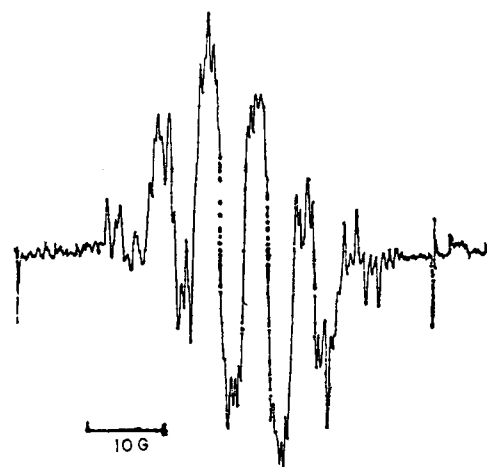


Figure 2.—E.s.r. spectrum of the anion radical derived from perinaphthen-1-one and sodium.

sextet in Figure 1 arises from the interaction of the unpaired electron with the protons located at positions 3, 4, 6, 7, and 9. The protons at positions 2, 5, and 8, and possibly nitrogen are responsible for further splittings. No decay in the intensity and the fine structure of the spectrum was observed. The close resemblance of Figure 1, with the e.s.r. spectrum of sodium ketyl of perinaphthen-1-one (Figure 2) suggested the possibility of cleavage of compound **4a**<sup>9</sup> to perinaphthen-1-one. An examination by thin layer chromatography of the hydrolyzed product of the sodium anion radical of **4a** showed that the ketone is not formed under the present condition.

In order to characterize the intermediates in the triethylamine-catalyzed dehydrogenation of compound **2a**, the addition of the components was carried out with rigorous exclusion of air, and the progress of the reaction was followed by e.s.r. spectrum. The spectrum obtained after 12 hr. (Figure 3) is very similar to that of the anion radical of **4a**. On standing, however, the spectrum became increasingly complex owing to superimposition of other interactions. The final spectrum (96 hr.) containing many lines has not been interpretable and is assumed to be due to the formation of complex radical mixtures. When the solution was exposed to air, the signal slowly decayed with the

(6) L. F. Fieser and L. W. Newton, *J. Am. Chem. Soc.*, **64**, 917 (1942).

(7) P. B. Sogo, M. Nakazaki, and M. Calvin, *J. Chem. Phys.*, **26**, 1343 (1957).

(8) We have observed that photolysis of perinaphthen-1-one in isopropyl alcohol generates a relatively stable free radical whose e.s.r. spectrum can be described in terms of six primary lines (1:5:10:10:1) of split 7.1 gauss.

Each line is further divided into quadruplets (1:2:2:1) of 1.8-gauss line width. H. Koller, G. P. Rabold, K. Weiss, and T. K. Mukherjee, *Proc. Chem. Soc.*, 332 (1964).

(9) R. Dehl and G. K. Franekel [*J. Chem. Phys.*, **39**, 1793 (1963)] reported that, under unpurified nitrogen ambient, the electrolytic generation of the anion radicals from 9-substituted fluorenes produced 9-fluorenone.

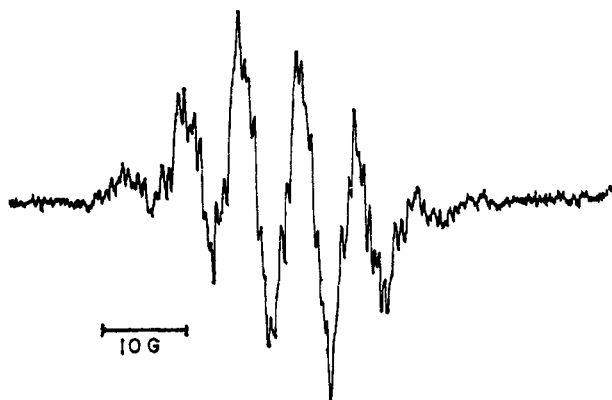


Figure 3.—E.s.r. absorption spectrum of the anion radicals derived from 2,3-dihydroperinaphthen- $\Delta^{1a}$ -malononitrile **2a** and triethylamine.

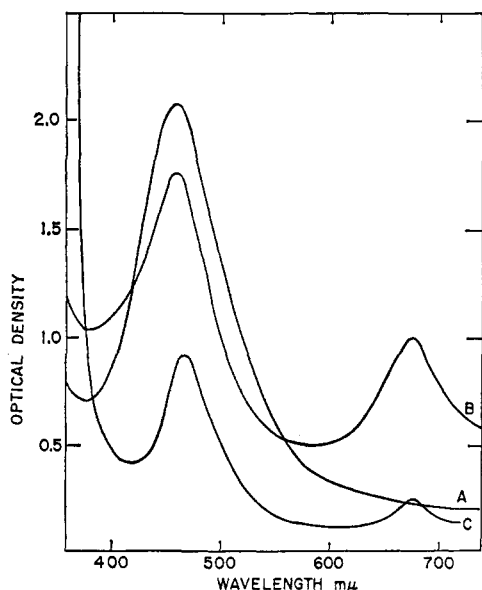
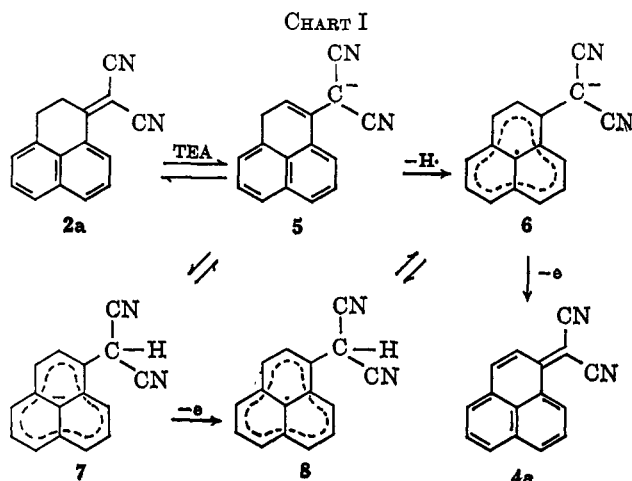


Figure 4.—(A) Spectrum of compound **4a** in THF; (B) spectrum of the sodium anion radical of **4a** in THF; (C) reaction of compound **2a** and triethylamine in THF. (The spectra of B and C are in degassed solutions.)

separation of compound **4a**. Several runs were made using different concentrations of the compound **2a**. In all cases, spectrum similar to Figure 3 was first formed, followed by extensive swamping due to other paramagnetic species. The compounds **2b** and **2c** behaved similarly to triethylamine and gave radicals which initially showed basic sextet structure in the e.s.r. However, the final spectra, after long intervals, were again extremely complex.

The formation of the anion radical of **4a** as an intermediate in the dehydrogenation reaction is further corroborated from the absorption spectra taken in absence of air. Addition of triethylamine to the solution of **2a** in THF caused the appearance of two new bands (Figure 4C.) The long wave-length band at  $675\text{ m}\mu$  is characteristic of the anion radical of **4a**. The second weak band at  $465\text{ m}\mu$  is indicative of partial dehydrogenation of **2a** to **4a**, even in absence of air. On exposure to air, however, absorptions at  $675$  and  $375\text{ m}\mu$  (due to compound **2a**) rapidly disappeared, and the absorption at  $465\text{ m}\mu$  intensified, followed by the precipitation of **4a**.

On the basis of the above observations, a mechanism involving electron-transfer steps from resonance sta-



bilized carbanions<sup>10,11</sup> is suggested (Chart I). The first step is considered to be a proton abstraction from **2a** by triethylamine; the resulting anion (**5**), being a perinaphthene derivative, will react with air to give the anion radical **6**. The latter, by loss of one electron may be converted to the product **4a**. Alternatively, the perinaphthene anion radical (**6**) may be formed *via* its protonated form (**8**), which in turn is derived from **7** by an electron-transfer step. In absence of air, this electron is transferred to the electronegative dicyanomethylene group of **2a**. However, no evidence regarding the structure of the radical ion of **2a** could be obtained from e.s.r. spectra. It can only be surmized that its lifetime is much shorter than the anion radical **6**, and that it is rapidly converted either to the starting material or to unidentified products. In this connection it should be pointed out that under no conditions could the yield of compound **4a** be raised above 50%. This fact was further confirmed by spectroscopic analysis of the reaction mixture prepared at several concentration ranges of the reactants. The effectiveness of organic bases relative to strong bases such as sodium methoxide may be due to the former leaving a substantial portion of compound **2a** to function as the electron acceptor. In conclusion, it should be noted that a number of tautomeric species in equilibrium are present in this reaction. Presumably, the driving force of the formation of **4a** is derived from the fast rate of electron or hydrogen atom transfer from the species **6** or **8**.

### Experimental

All melting points were obtained in a Mel-Temp block and are uncorrected. The infrared spectra were measured on a Perkin-Elmer Model 221 spectrophotometer, and the ultraviolet spectra on a Cary Model 14 recording spectrophotometer. The n.m.r. spectrum was determined with a Varian A-60 instrument using tetramethylsilane as an internal standard. The microanalyses were performed by Dr. S. M. Nagy at Massachusetts Institute of Technology, Cambridge, Mass., and by the Galbraith Laboratories, Inc., Knoxville, Tenn.

**E.s.r. Measurements.**—The e.s.r. spectra were obtained with a Varian Model V4500 spectrometer operating with 100-kc. modulation. A  $TE_{102}$  cavity was employed, and care was taken to avoid saturation of the signal. The solvents used were purified by distillation from sodium. All measurements were made at room temperature with thoroughly degassed solutions, which

(10) G. A. Russell, E. G. Janzen and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

(11) O. W. Webster, *ibid.*, **86**, 2898 (1964).

were prepared on a high vacuum line. A 4-mm.-o.d. Pyrex sample tube was fitted with two side arms, one for the solvent and the other consisting of a series of interconnected bulbs for the sodium. A mirror of the metal was deposited in the bulb nearest to the sample tube by fractional vacuum distillation. Next, THF, which was previously degassed, was transferred onto the solute in the sample tube. At this point the apparatus was sealed, and the anion radical was generated by allowing the solution to contact the metal for several minutes. Dilution studies were made by transferring solvent by distillation to and from one of the side arms.

**2,3-Dihydroperinaphthen- $\Delta^{1\alpha}$ -malononitrile (2a). Method A.**—A mixture of 18.2 g. (0.1 mole) of perinaphthanone (1),<sup>12</sup> 7.2 g. (0.109 mole) of malononitrile, and 6 ml. (0.104 mole) of glacial acetic acid in 200 ml. of benzene was refluxed, while ammonium acetate (2 g.) was added in three batches. The water formed in this reaction was continually removed by a Dean-Stark separator until 3 ml. was collected (3.5 hr.). The crude product (12 g., 52%) was washed with cold water and crystallized from absolute alcohol to yield 10 g. (43%) of 2,3-dihydroperinaphthen- $\Delta^{1\alpha}$ -malononitrile, m.p. 175–178°. The analytical sample, m.p. 176.5–178.5°, was prepared by three crystallizations from ethyl alcohol. The infrared spectrum taken in chloroform showed maxima at 3050 (CH) and 2249  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ),  $\lambda_{\text{max}}^{\text{CHCl}_3}$  380  $\mu$  ( $\epsilon$  13,761) and 274  $\mu$  ( $\epsilon$  24,521).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{10}\text{N}_2$ : C, 83.45; H, 4.37; N, 12.16. Found: C, 83.64; H, 4.62; N, 11.91.

**Method B.**—The ketone 1 (9.1 g., 0.05 mole) and malononitrile (3.6 g., 0.06 mole) were mixed and melted on a water bath. After 10 min., an aqueous solution of  $\beta$ -alanine<sup>13</sup> (10 ml. containing 50 mg.) was added to the melt. The color changed from yellow to brown. After a few minutes, the cooled reaction mixture was washed thoroughly with water, dried, and crystallized from ethyl alcohol. The yield was 48%, m.p. 174–178°.

**Method C.**—A mixture of 1.82 g. (0.01 mole) of perinaphthanone (1) and 1 g. (0.015 mole) of malononitrile were melted on a water bath. When 2 drops of piperidine were added, the melt became deep red in color. The flask was cooled at room temperature and the product was worked up as before to furnish 1.35 g. of material. Chromatography over silica gel using benzene as eluent gave 1.0 g. of compound 2a and 50 mg. of deep red crystals, m.p. 232–234°, which were identical in all respects with the product obtained by palladium-charcoal dehydrogenation of 2a.

**Perinaphthen- $\Delta^{1\alpha}$ -malononitrile (4a). Method A.**—Compound 2a (0.23 g., 1 mmole) was dissolved in 25 ml. of boiling acetonitrile. On addition of 0.13 ml. (1 mmole) of triethylamine, the color changed to a deep red. After standing overnight, the deposited crystals were filtered and washed with cold methyl alcohol. The yield of the product was 95 mg. (41%), m.p. 234–236°. The analytical sample was prepared by chromatography over silica gel using chloroform as eluent followed by recrystallization from acetonitrile. The infrared spectrum in chloroform showed a band at 2225  $\text{cm}^{-1}$  (conjugated  $\text{C}\equiv\text{N}$ );  $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$  473  $\mu$  ( $\epsilon$  22,100), 392 (5720), 374 (4000), 331 (3650), 275 (27,500), and 268 (26,100).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_8\text{N}_2$ : C, 84.19; H, 3.53; N, 12.27, mol. wt., 228.27. Found: C, 84.41; H, 3.63; N, 11.97. mol. wt.,<sup>14</sup> 228.

**Method B.**—Compound 2a (0.23 g.) was thoroughly mixed with 0.1 g. of palladium on charcoal (10%), and was heated

under reduced pressure ( $\sim 8$  mm.) at 220° for 2 hr. The sublimate was chromatographed through a short silica gel column and was recrystallized from acetonitrile, m.p. 234–236°. This material was identified with product from method A.

**2,3-Dihydroperinaphthen- $\Delta^{1\alpha}$ -ethyl Cyanoacetate (2b).**—To a solution of 9.1 g. (0.05 mole) of perinaphthanone and 6.7 g. (0.06 mole) of ethyl cyanoacetate in 100 ml. of benzene was added 3 ml. (0.05 mole) of glacial acetic acid and 1 g. of ammonium acetate. The mixture was refluxed with a water separator, until no further water was collected in the trap (5 hr.). The reaction mixture was cooled and washed successively with water, 2% sodium bicarbonate solution, and water. The benzene layer was dried. Evaporation of the solvent under reduced pressure left a gummy residue. Recrystallization from methyl alcohol gave 3.4 g. (25%) of the product, m.p. 100–105°. The analytical sample was prepared by chromatography and subsequent recrystallization from methyl alcohol: m.p. 106–107°; infrared (in chloroform) bands at 2240 ( $\text{C}\equiv\text{N}$ ) and 1725  $\text{cm}^{-1}$  (ester);  $\lambda_{\text{max}}^{\text{CHCl}_3}$  365  $\mu$  ( $\epsilon$  10,200) and 267  $\mu$  ( $\epsilon$  18,100).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{16}\text{NO}_2$ : C, 77.96; H, 5.45; N, 5.05. Found: C, 78.22; H, 5.45; N, 4.90.

**2,3-Dihydroperinaphthen- $\Delta^{1\alpha}$ -cyanoacetamide (2c).**—A mixture of 18.2 g. (0.1 mole) of perinaphthanone, 9.24 g. (0.11 mole) of cyanoacetamide, 6 ml. (0.1 mole) of glacial acetic acid, and 2 g. of ammonium acetate dissolved in 200 ml. of benzene was refluxed for 12 hr. with a water separator. Work-up in the usual manner provided 2.5 g. (10%) of white needles: m.p. 177° dec. (ethyl alcohol);  $\nu_{\text{max}}^{\text{Nujol}}$  2250 ( $\text{C}\equiv\text{N}$ ) and 1675  $\text{cm}^{-1}$  (amide);  $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$  360  $\mu$  ( $\epsilon$  9680) and 266  $\mu$  ( $\epsilon$  18,000).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}$ : C, 77.40; H, 4.87; N, 11.29. Found: C, 77.56; H, 4.84; N, 11.16.

**Perinaphthen- $\Delta^{1\alpha}$ -ethyl Cyanoacetate.**—Compound 2b (1.0 g., 3.4 mmoles) was dissolved in 30 ml. of acetonitrile and 0.2 ml. of triethylamine was added. After standing for 24 hr. the dark colored solution was evaporated to dryness and the gummy residue was chromatographed on a silica gel column. Only the fractions showing ultraviolet absorption maxima at 462  $\mu$  were collected. Evaporation of the combined benzene eluates left a red residue from which 200 mg. (21%) of compound 4b, m.p. 86°, was obtained after another chromatography and two crystallizations:  $\lambda_{\text{max}}^{\text{CH}_2\text{CN}}$  462  $\mu$  ( $\epsilon$  15,800), 390 (4970), 330 (2310), and 270 (20,400).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{14}\text{NO}_2$ : C, 78.53; H, 4.76; N, 5.09. Found: C, 78.39; H, 4.76; N, 4.93.

**Attempted Hydrolysis of 4a. Alkaline Conditions.**—A mixture of 140 mg. (0.6 mmole) compound 4a and 150 mg. (3.37 mmoles) of sodium hydroxide was dissolved in 30 ml. of dioxane, 1 ml. of water was added, and the mixture was refluxed for 4 hr. The color of the solution first became green and then brown. An amorphous solid was isolated from the neutralized reaction mixture. This showed no carbonyl absorption in its infrared spectrum. Thin layer chromatography revealed no perinaphthenone.

**Acid Conditions.**—Hydrogen chloride was bubbled for 7 hr. through a refluxing suspension of 290 mg. (1.2 mmoles) of compound 4a in 50 ml. of methyl alcohol. After removal of hydrogen chloride the mixture was filtered, when 245 mg. of the starting material was recovered. Evaporation of the filtrate left a small residue in which presence of perinaphthenone was detected by infrared and ultraviolet spectra and by thin layer chromatography.

**Acknowledgment.**—We wish to thank Mr. Gary P. Rabold for assistance during some of the optical measurements, and Dr. Karl Weiss for helpful discussions.

(12) L. F. Fieser and M. D. Gates, Jr., *J. Am. Chem. Soc.*, **62**, 2335 (1940).

(13) D. S. Acker and W. R. Hertler, *ibid.*, **84**, 3372 (1962).

(14) We are indebted to Professor K. Biemann of the Massachusetts Institute of Technology, Cambridge, Mass., for mass-spectrometric determination of this molecular weight.