

Diels-Alder Reactions of 5-Substituted Naphthacenes

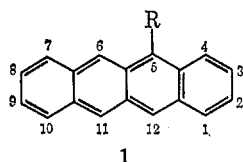
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Diels-Alder reactions of 5-naphthacenealdehyde and 5-bromo-, 5-cyano-, and 5,12-diacetoxynaphthacene occur more readily at the 6,11 than at the 5,12 positions. The maleic anhydride adducts were thermally more stable than those of tetracyanoethylene, and the ethylene adduct of 5,12-diacetoxynaphthacene was quite stable. 5-Naphthacenealdehyde and allyl alcohol condensed at the 5,12 positions owing to acetal formation preceding an intramolecular Diels-Alder reaction. Photooxidation of 5,12-diacetoxynaphthacene occurred at its 6,11 positions to give the corresponding diacetoxyquinone.

Placing a substituent in the 5 position of naphthacene (1) results in a compound possessing two diene sys-



tems capable of reacting competitively with dienophiles. Condensation of such a compound with ethylene or tetracyanoethylene can lead theoretically to two different adducts, with maleic anhydride to four, and with allyl alcohol to eight. However, the Diels-Alder reaction is frequently quite selective and one or two adducts will predominate to the apparent exclusion of the others.

In the condensation of a 5-substituted naphthacene the substituted ring has the site of attack sterically hindered and addition to the unsubstituted ring should be favored. Substituents which increase the electron density of the ring should promote reaction with that ring and perhaps counterbalance the steric hindrance. In a few cases the substituted ring might be the preferred location of addition, but suitable compounds have not yet been tested.

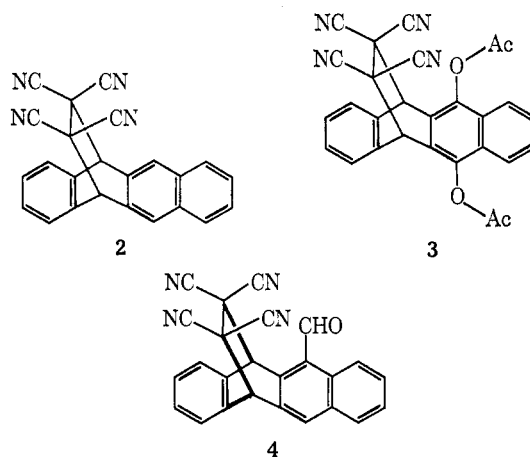
Anthracene has been reported to condense with maleic anhydride five times more rapidly than does 9-bromoanthracene and over one-hundred times more quickly than 9-cyanoanthracene in dioxane at 130°. ²

From these data one would predict that the 6,11 positions should be about five times more reactive than the 5,12 positions in 5-bromonaphthacene and that a Diels-Alder reaction with 5-cyanonaphthacene should go almost exclusively at the 6,11 positions. Although rate data for 9-anthraldehyde and 9,10-diacetoxyanthracene were not available, one would predict that 5,12-diacetoxy- and 5-naphthacenealdehyde would be more reactive at the 6,11 positions.

Tetracyanoethylene (TCNE), being a symmetrical and highly reactive dienophile, was chosen for this investigation in order to avoid the formation of vicinal-nonvicinal and *syn-anti* isomers. Isomers arising from addition of the dienophile across the 5,12 and 6,11 positions of the naphthacene skeleton are the only ones possible. Unfortunately, the TCNE adducts were found to be thermally unstable, and only three of the five adducts which were prepared could be sufficiently characterized to permit an assignment of structure. For instance, TCNE and 5-cyanonaphthacene gave a

product which crystallized from a solution of tetrahydrofuran at -15° as colorless crystals, but these turned orange in less than a day while being dried *in vacuo* at room temperature. The TCNE adducts when heated, either in solution for recrystallization or as a solid in a melting-point tube, quickly produced the color of the starting 5-substituted naphthacene, which indicated that the Diels-Alder reaction was easily reversed. This thermal instability was surprising, since the ethylene, acrylonitrile, allyl alcohol, and methyl acrylate adducts of naphthacene have been found to be quite stable and the nitrile adducts could be separated in glpc at 200°. ³

TCNE was condensed with naphthacene, 5,12-diacetoxynaphthacene, and 5-naphthacenealdehyde at room temperature to give the colorless adducts, 2-4.



The adducts of the latter two dienes were characterized by inspection of their infrared spectra. A single carbonyl absorption at 5.64 μ was observed in the spectrum of 3 indicating the presence of an enolic acetate. ⁴ The spectrum of 4 showed a carbonyl absorption at 5.95 μ , characteristic of an aromatic formyl group. ⁴ The carbonyl absorption of 9,10-dihydro-9,10-ethano-9-anthraldehyde appears at 5.80 μ , ^{5,6a} whereas 1-naphthaldehyde shows an absorption at 5.97 μ . ^{6b} Therefore, adducts 3 and 4 resulted from additions of TCNE in the unsubstituted ring of the naphthacene derivative.

(3) J. S. Meek, F. M. Dewey, and M. W. Hanna, *J. Org. Chem.*, **32**, 69 (1967).

(4) A. K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, pp 43, 44.

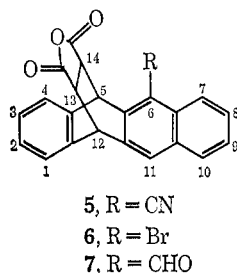
(5) W. R. Benson, Ph.D. Thesis, University of Colorado, 1958.

(6) (a) "Sadtler Standard Spectra," Midget ed, Sadtler Research Laboratories, Philadelphia, Pa., 1959, Spectrum No. 3489; (b) Spectrum No. 8444.

(1) National Science Foundation Predoctoral Fellow, 1963-1965.

(2) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem. Int. Ed. Engl.*, **1**, 268 (1962).

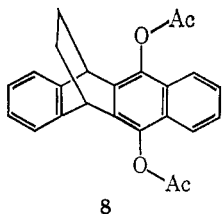
Decomposition resulted when the TCNE adducts of 5-cyano- and 5-bromonaphthacene were recrystallized, and the structure of the adducts was not established. The corresponding maleic anhydride adducts (**5** and **6**) were found to be thermally more stable.



The infrared spectrum of **5** showed a single nitrile absorption at 5.51μ , indicative of an aromatic nitrile,⁷ thereby establishing its structure as that resulting from addition of the dienophile in the unsubstituted ring. The structure of **6** was assigned from its pmr spectrum. Resonances were observed at τ 6.44 (2 H), assigned to the bridge hydrogens on C-13 and C-14, 5.59 (1 H), assigned to the hydrogen on C-12, 5.11 (1 H), assigned to the hydrogen on C-5, and 2.4 (9 H), assigned to aromatic hydrogens. The downfield shift observed for the C-5 hydrogen is that expected for a proton *peri* to a bromine atom. Thus the formation of **6** also resulted from addition of the dienophile in the unsubstituted ring of the naphthacene derivative. It was not determined whether the maleic anhydride adducts of 5-bromo-, 5-cyano-, and 5-naphthacene-aldehyde were the *syn* or the *anti* adducts.

The aldehyde-maleic anhydride adduct was assigned structure **7**, since it showed an aromatic aldehyde carbonyl stretch at 5.96μ in addition to anhydride carbonyl frequencies at 5.40 and 5.63μ . Only in the crudest material was there a hint of absorption at 5.80μ , where the ethylene adduct of 9-anthraldehyde has its aliphatic carbonyl frequency.^{8a}

Ethylene was condensed with 5,12-diacetoxynaphthacene, and a stable adduct (**8**) was obtained. The adduct showed a single carbonyl absorption at 5.69μ characteristic of enolic esters.⁴ As further proof that the ethano bridge was situated on the unsubstituted ring compound, **8** was hydrolyzed and on air oxidation gave a quinone. An attempt to prepare this quinone from 5,12-ethano-5,12-dihydronaphthacene gave a mixture of carbonyl compounds, but reduction and acetylation of this mixture gave rise to some **8**.

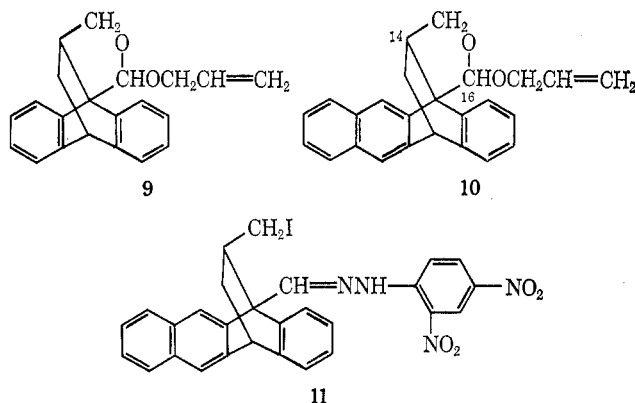


It is noteworthy that adducts **3-8** all resulted from addition of the dienophile in the unsubstituted ring of the naphthacene derivative with virtually the total exclusion of addition in the substituted ring. Since the electronic effects of diene substituents have been

found to be greater with the more electrophilic tetracyanoethylene than with maleic anhydride,⁸ addition in the substituted ring is more likely to occur using maleic anhydride as a dienophile. Also to be considered are the steric repulsions between diene substituents and dienophile substituents, which would undoubtedly be less important with a disubstituted dienophile than with a tetrasubstituted one.

This discovery that a substituent in the 5 position of naphthacene caused adduct formation to occur at the unsubstituted 6,11 positions cast doubt on the structure assigned the maleic anhydride adduct of 5,12-diphenylnaphthacene and that of the 6,13-diphenylpentacene-maleic anhydride adduct. Communication with Allen led to his reexamination of these adducts and established the fact that the Diels-Alder reaction had occurred at the unsubstituted 6,11 positions of the naphthacene and the unsubstituted 5,14 positions of the pentacene and not at the positions bearing the phenyl groups, as was previously suggested.⁹

Allyl alcohol and 9-anthraldehyde react to give compound **9**.¹⁰ Thus it was felt that allyl alcohol and



5-naphthacenealdehyde would give **10**. This product would arise from hemiacetal or acetal formation occurring more rapidly than an intermolecular Diels-Alder reaction at the 6,11 positions. Once hemiacetal or acetal formation occurred, a very rapid intramolecular Diels-Alder reaction would occur at the 5,12 positions and lead to **10**.

The reaction actually gave two white products (**10a** and **10b**) whose analyses corresponded to **10**. Since the products were white, neither could have been the acetal of the starting aldehyde. Cleavage of **10a** and **10b** with hydriodic acid gave in each case the same halogen-containing aldehyde, which was converted into **11** for analysis. The aldehyde carbonyl absorption was at 5.80μ , and a CH aldehyde absorption was found at 3.68μ . The carbonyl frequency is that expected for a bridgehead aldehyde rather than that of an aromatic aldehyde and showed that the Diels-Alder reaction had occurred at the 5,12 positions. Hence **10a** and **10b** were epimeric at either C-16 or C-14. Since both gave the same aldehyde, the difference in stereochemistry had to be at C-16.

An attempt to make a photooxide of 5,12-diacetoxynaphthacene was made to see if radical addition would

(7) J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, p 264.

(8) C. A. Stewart, Jr., *J. Org. Chem.*, **28**, 3320 (1963).

(9) C. F. H. Allen, *Can. J. Chem.*, **45**, 1201 (1967).

(10) J. S. Meek and J. R. Dann, *J. Org. Chem.*, **21**, 968 (1956).

take place at the same site as the Diels-Alder reaction. Oxidation occurred to give 6,11-diacetoxynaphthacene-5,12-quinone.

Experimental Section

13,13,14,14-Tetracyano-5,12-dihydro-5,12-ethanonaphthacene (2).—A mixture of 0.85 g (3.7 mmol) of naphthacene, 0.50 g (3.9 mmol) of tetracyanoethylene, and 30 ml of tetrahydrofuran was stirred at room temperature for 10 min until the solid had dissolved to give a dark orange solution. The solution was allowed to stand for 21 hr and no further change in color was observed. The solvent was evaporated and the solid was collected and washed several times with a few milliliters of benzene to remove the excess tetracyanoethylene. The off-white solid (2) weighed 1.33 g (100%) and melted at 278–286° dec. Two recrystallizations from acetonitrile at –15° raised the melting point to 294–297° dec.

Anal. Calcd for $C_{24}H_{12}N_4$: C, 80.88; H, 3.39; N, 15.72. Found: C, 80.68; H, 3.28; N, 15.56.

The infrared spectrum of 2 showed a nitrile absorption at 4.45 μ . Rapid decomposition of 2 occurred when it was warmed above room temperature in solution or in its crystalline state.

6,11-Diacetoxy-13,13,14,14-tetracyano-5,12-dihydro-5,12-ethanonaphthacene (3).—Naphthacene-5,12-quinone was prepared in 80% yield by oxidizing naphthacene with sodium chlorate and vanadium pentoxide.¹¹ After recrystallization from acetic acid the quinone melted at 277–280°.

5,12-Diacetoxynaphthacene was prepared from naphthacene-5,12-quinone in 53% yield using the method of Fieser.¹² Recrystallization from acetic acid gave orange needles which melted at 279–286°. A mixture of 0.33 g (0.96 mmol) of 5,12-diacetoxynaphthacene, 0.14 g (1.1 mmol) of tetracyanoethylene, and 20 ml of tetrahydrofuran was stirred at room temperature. After 5 min the solid had completely dissolved to give a yellow-orange solution. After the solution stood for 15 hr with no apparent change in color, the solvent was evaporated, leaving a pale yellow solid. Recrystallization of the crude product from acetone-ethanol gave 0.36 g (80%) of almost colorless crystals of 3, mp 267.5–270.0°. Recrystallizations from acetone at room temperature and then at –15° raised the melting point to 270–271° dec.

Anal. Calcd for $C_{28}H_{16}N_4O_4$: C, 71.18; H, 3.41; N, 11.86. Found: C, 71.10; H, 3.45; N, 12.06.

13,13,14,14-Tetracyano-5,12-dihydro-5,12-ethano-6-naphthacenealdehyde (4).—5-Naphthacenealdehyde was prepared in 60% yield from naphthacene and N-methylformanilide in *o*-dichlorobenzene.¹³ After recrystallization from benzene the product melted at 147–150° (dark crimson crystals). A mixture of 0.50 g (2.0 mmol) of 5-formylnaphthacene, 0.26 g (2.0 mmol) of tetracyanoethylene, and 20 ml of tetrahydrofuran was stirred under nitrogen at room temperature for 21 hr. The solvent was evaporated and the resulting dark green solid was washed several times with a few milliliters of benzene to remove tetracyanoethylene. The tan solid weighed 0.63 g (84%) and melted at 190–275° dec. This product decomposed rapidly even when it was warmed gently. It was dissolved in acetonitrile by warming the solution slightly above room temperature and was allowed to crystallize at 0°. A second recrystallization gave the analytical sample. The melting point, determined by inserting a capillary containing the sample into an oil bath already at 260°, was 270–274° dec.

Anal. Calcd for $C_{25}H_{12}N_4O$: C, 78.11; H, 3.15. Found: C, 78.30; H, 3.17.

6,13,13,14,14-Pentacyano-5,12-dihydro-5,12-ethanonaphthacene.—5-Naphthacenealdoxime¹³ was prepared in 100% yield from 5-naphthacenealdehyde and hydroxylamine hydrochloride in pyridine. The rust-red solid melted at 174–181°.

5-Cyanonaphthacene was prepared in 95% yield by dehydrating naphthacene-5-formoxime with acetic anhydride.¹³ Recrystallization from benzene gave crimson crystals melting at 188–194°. A mixture of 0.40 g (1.6 mmol) of 5-cyanonaphthacene, 0.21 g (1.6 mmol) of tetracyanoethylene, and 20 ml of tetrahydrofuran was stirred at room temperature for 18 hr. The solvent was evaporated and the pink solid which resulted was washed with 10 ml of cold benzene. The product weighed 0.60

g (100%) and melted at 259–283° dec. Attempts to recrystallize this product in hot solvents led to colored solutions whose darkening hue indicated a reverse Diels-Alder reaction. When tetrahydrofuran was used as the solvent and allowed to stand for 3 days in a cold room at –15°, colorless crystals were deposited, mp 279–282° dec. (The sample was inserted in an oil bath preheated to 260° and immediately turned red.) An attempt to dry the crystals under vacuum at room temperature resulted in their turning orange in less than 20 hr, and an analysis was not satisfactory.

The infrared spectrum of the crude product showed a nitrile absorption at 4.50 μ with a shoulder at 4.45 μ .

Preparation of 5-Bromonaphthacene.—Reference is made to 5-bromonaphthacene in the literature,¹³ but no method of preparation is given nor are any physical properties included.

The bromination of 2.0 g (8.8 mmol) of naphthacene with 2.0 g (8.9 mmol) of cupric bromide in refluxing carbon tetrachloride was patterned after the preparation of 9-bromoanthracene.¹⁴ The crude product was passed through a short column (2.0 \times 12 cm) of alumina. The resulting bright red solid weighed 1.2 g (92% based on cupric bromide), mp 125–140°. After two recrystallizations from benzene the sample melted at 153–156° (0.52 g, 40%): mol wt (calcd for $C_{13}H_{11}Br$) 307; mass spectrum (70 eV) *m/e* rel intensity 308 (18), 306 (16), 227 (13), 91 (18), 78 (10), 58 (29), and 43 (100).

Addition of Tetracyanoethylene to 5-Bromonaphthacene.—A mixture of 0.35 g (1.1 mmol) of 5-bromonaphthacene, 0.15 g (1.2 mmol) of tetracyanoethylene, and 15 ml of tetrahydrofuran was stirred at room temperature for 1 hr. The bright red color of 5-bromonaphthacene faded gradually to give a bright yellow solution. The solvent was removed using a rotary evaporator and left a yellow oil. The product was precipitated by dissolving the oil in a few milliliters of tetrahydrofuran and adding 25 ml of petroleum ether. The resulting pale yellow solid was collected, yield 0.50 g (100%), mp 238–241° dec. Recrystallization from tetrahydrofuran at –15° raised the melting point to 270–272° dec. Further attempts at recrystallization resulted in rapid decomposition.

6-Cyano-5,12-dihydro-5,12-ethanonaphthacene-13,14-dicarboxylic Acid Anhydride (5).—A mixture of 0.45 g (1.8 mmol) of 5-cyanonaphthacene, 0.40 g (4.1 mmol) of maleic anhydride, and 10 ml of *p*-xylene was refluxed for 11.5 hr. The reaction mixture was cooled and the resulting tan solid was collected by filtration. Concentration of the filtrate and treatment with 20 ml of petroleum ether yielded additional solid material. The combined solid (5) weighed 0.45 g and melted at 263–269° dec. Recrystallizations from acetonitrile and ethyl acetate raised the melting point to 308–311° dec. (The capillary tube was inserted in the oil bath at 290°.)

Anal. Calcd for $C_{22}H_{13}NO_3$: C, 78.62; H, 3.73. Found: C, 78.45; H, 3.70.

The infrared spectra of the analytical sample and the crude product showed a single nitrile absorption at 4.51 μ , characteristic of aromatic nitriles.⁴ 9-Cyano-9,10-dihydro-9,10-ethanoanthracene shows a nitrile absorption at 4.44 μ .⁵

6-Bromo-5,12-dihydro-5,12-ethanonaphthacene-13,14-dicarboxylic Acid Anhydride (6).—A mixture of 0.40 g (1.3 mmol) of 5-bromonaphthacene, 0.50 g (5.1 mmol) of maleic anhydride, and 10 ml of *p*-xylene was refluxed (135°) for 0.5 hr. The xylene was evaporated under a jet of air and the resulting tan crystals were collected on a filter and washed with 10 ml of ethanol, yield 0.50 g (95%), mp 242–282°. Two recrystallizations from benzene-petroleum ether mixtures gave 0.15 g (28%) of colorless crystals of 6, mp 301–304° dec. One additional recrystallization raised the melting point to 306–309° dec.

Anal. Calcd for $C_{22}H_{13}BrO_3$: C, 65.20; H, 3.23. Found: C, 65.47; H, 3.43.

The nmr spectrum of 6 was run in *sym*-tetrachloroethane at 100° on a Varian A-60 spectrophotometer.

6-Formyl-5,12-dihydro-5,12-ethanonaphthacene-13,14-dicarboxylic Acid Anhydride (7).—A mixture of 0.34 g (1.3 mmol) of 5-naphthacenealdehyde, 0.40 g (4.1 mmol) of maleic anhydride, and 12 ml of benzene was refluxed for 22 hr. Upon cooling a tan solid separated from the red-brown solution. After the solid was collected, the filtrate was concentrated and the additional solid which separated was combined with the first crop, yield 0.39 g (83%), mp 263–268°. This product was recrystallized from acetonitrile-tetrahydrofuran at –15°, and a mixture of

(11) H. W. Underwood, Jr. and W. L. Walsh, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 553.

(12) L. F. Fieser, *J. Amer. Chem. Soc.*, **53**, 2329 (1931).

(13) M. Martynoff, *Compt. Rend.*, **238**, 249 (1954).

(14) D. C. Nonhebel, *Org. Syn.*, **43**, 15 (1963).

tetrahydrofuran and petroleum ether (bp 60–70°) (Skellysolve B) at –15° to give the analytical sample of **7**, mp 317–320° dec. (The sample was inserted in the oil bath at 290°.)

Anal. Calcd for $C_{23}H_{14}O_4$: C, 77.96; H, 3.98. Found: C, 77.78; H, 4.07.

This adduct appeared to be thermally more stable than **4**.

6,11-Diacetoxy-5,12-dihydro-5,12-ethanonaphthacene (8).—A mixture of 2.0 g (5.8 mmol) of 5,12-diacetoxynaphthacene, 0.1 g of hydroquinone, and 100 ml of benzene was placed in a glass liner which was in turn placed in a 0.5-l. stainless steel bomb. The bomb was charged with 200 psi of ethylene and the apparatus was heated at 188–194° with shaking for 22 hr, during which time the pressure rose to 800 psi. The solution was removed from the liner and the solvent was evaporated. The resulting oil gradually solidified to a tan solid. The yield of crude **8** was 2.23 g, mp 189–213°. The product was recrystallized twice from benzene–petroleum ether, once from methanol, and four times from ethyl acetate–petroleum ether to give the analytical sample, mp 219.5–222.0°.

Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.17; H, 5.33.

Alkaline Hydrolysis of 8.—A mixture of 0.36 g (1.0 mmol) of **8**, 10 ml of 20% sodium hydroxide solution, and 30 ml of ethanol was warmed on a steam bath for 30 min. The color of the solution became blood red immediately. The solution was cooled and carefully neutralized with 30% sulfuric acid. The ethanol was evaporated on a rotary evaporator, and the resulting solid was washed into a separatory funnel and extracted with ether–benzene. As the extract was shaken, it gradually turned bright yellow owing to air oxidation of the hydroquinone to 5,12-dihydro-5,12-ethano-6,11-naphthacenequinone. After the ether was evaporated on a steam bath, the remaining solution was filtered, and to it was added an equal volume of petroleum ether. Crystallization was initiated by partial evaporation of the solvent with a slow stream of air. Bright yellow crystals formed, yield 0.20 g (67%), mp 200–210°. The product was recrystallized twice from ethyl acetate–petroleum ether and three times from ethanol to give the analytical sample, mp 206–209°.

Anal. Calcd for $C_{26}H_{14}O_2$: C, 83.90, H, 4.93. Found: C, 84.15; H, 5.20.

The infrared spectrum had a carbonyl absorption at 6.05 μ and strong absorptions at 8.30, 11.35, 13.02, and 13.35 μ .

A solution of 0.65 g of 5,12-dihydro-5,12-ethanonaphthacene⁹ in 10 ml of acetic acid was heated to 50°, and 1.5 ml of 30% hydrogen peroxide was added. As the temperature was raised to 80°, the color of the solution gradually became bright yellow. After 1 hr an additional 0.5 ml of hydrogen peroxide was added, and heating was continued at 80–84° for a total of 10 hr. The solvent was evaporated to give 0.76 g of a bright yellow solid which melted at 146–169°. Three recrystallizations from ethyl acetate raised the melting point to 172–174°. The elemental analysis was unsatisfactory for the anticipated quinone.

A solution of 0.26 g of this oxidation product in 15 ml of benzene was hydrogenated over palladium on charcoal (10%) for 1 hr in a modified Brown hydrogenation apparatus. The hydrogen atmosphere was replaced with nitrogen and the mixture was heated with 0.4 g of anhydrous sodium acetate and 13 ml of acetic anhydride for 15 hr. After standing for 2 days the catalyst was removed by filtration, and the solution was concentrated and allowed to crystallize. The resulting yellow crystals weighed 0.10 g and were shown to be starting material by an undepressed mixture melting point. Concentration of the mother liquor resulted in the crystallization of a small amount of **8**, mp 205–215°. It was identified from its infrared spectrum.

Further work-up of the mother liquors gave a small amount of another acetate melting at 253–259°. Its infrared spectrum was markedly different from the spectrum of **8**. Too little sample was isolated to permit its structure to be determined.

Condensation of Allyl Alcohol and 5-Naphthacenealdehyde.—A mixture of 1.20 g (4.7 mmol) of 5-naphthacenealdehyde, 12 ml of allyl alcohol, and 0.1 g of hydroquinone was heated in a sealed tube at 154° for 12 hr. The resulting brown oil was chromatographed on alumina. The majority of the product (1.16 g), which was eluted with benzene, was an almost colorless oil. Crystallization occurred from cold petroleum ether to give a white solid, which was then recrystallized from the same solvent to give 0.20 g of colorless crystals, mp 168–176°. Several recrystallizations from petroleum ether and then from tetrahydrofuran–petroleum ether gave pure **10a**, mp 176–178°.

Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.71; H, 6.25. Found: C, 84.42; H, 6.46.

The mother liquor from **10a** was rechromatographed on alumina. Comparison of the infrared spectra of the fractions indicated the presence of ca. 0.3 g of **10b** in the first few fractions. Repeated recrystallizations from petroleum ether gave the analytical sample, mp 112.7–115.7°.

Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.71, H, 6.25. Found: C, 84.50; H, 6.09.

The infrared spectra of these two compounds showed an absence of a carbonyl group, but did show bands indicative of a vinyl group. The spectrum of **10a** showed major bands at 9.30, 9.90, 10.75, 11.00, 11.46, 13.30, and 13.40 μ ; **10b** showed absorptions at 9.25, 9.96, 10.90, 11.20, 13.30, and 13.40 μ .

Cleavage of 10a and 10b with Hydrogen Iodide.—To a hot solution of 52 mg of **10b** in 6 ml of acetic acid was added 2 ml of hydrogen iodide (47–50%). The reaction mixture was heated under nitrogen for 1.5 hr at 120°. After cooling it was poured into 100 ml of cold water. The resulting white precipitate weighed 0.050 g (83%) and melted at 84–100°. It gave a positive Beilstein test. Attempts to recrystallize this product from benzene resulted in decomposition. The cleavage product was dissolved in a few milliliters of alcohol, and a solution of 2,4-dinitrophenylhydrazine in ethanolic sulfuric acid was added. After a few minutes a yellow solid precipitated yield 0.05 g (70%), mp 155–170°. Recrystallizations from ethyl acetate–petroleum ether and ethyl acetate–pentane at 0° gave the analytical sample of **11**, mp 178–179° dec. The violet color of iodine vapor was evolved on melting.

Anal. Calcd for $C_{25}H_{21}IN_4O_4$: C, 55.64; H, 3.50. Found: C, 55.37; H, 3.29.

Using the same procedure, 0.10 g of **10a** was cleaved, giving 0.11 g (92%) of the aldehyde, mp 90–100°. The crude 2,4-dinitrophenylhydrazine derivative melted at 161–169° dec and gave a positive Beilstein test. The aldehydes and the derivative had the same infrared spectra as the samples obtained from **10a**.

Photooxidation of 5,12-Diacetoxynaphthacene.—A solution of 0.46 g (1.3 mmol) of 5,12-diacetoxynaphthacene in 125 ml of acetone was allowed to stand in the sunlight in a stoppered flask for 1 month. Evaporation of the solvent left a gummy, yellow solid. This was dissolved in ethanol, treated with charcoal, and filtered. Crystallization yielded 0.14 g (28%) of fine, yellow needles, mp 220–225°. The infrared spectrum showed carbonyl absorptions at 5.70 and 5.99 μ . The product was 5,12-diacetoxy-6,11-naphthacenequinone, which is reported to begin to soften at 215° and melt at 220–235°.¹⁵

Registry No.—**2**, 23790-72-9; **3**, 23790-71-8; **4**, 23790-73-0; **5**, 23843-58-5; **6**, 23790-76-3; **7**, 23843-59-6; **8**, 23843-60-9; **10**, 23790-77-4; **11**, 23843-62-1; 6,13,13,14,14-pentacyano-5,12-dihydro-5,12-ethanonaphthalene, 23790-74-1; 5-bromonaphthacene, 23790-75-2; 5,12-dihydro-5,12-ethano-6,11-naphthacenequinone, 23843-61-0.

(15) S. Gabriel and E. Leupold, *Chem. Ber.*, **31**, 1281 (1898).