prepared by the method used by Dreiding, *et al.*,[9] in the ursolate series and was purified by recrystallization from methylene chloride–cyclohexane, m.p. 300–301°, $[\alpha]_D$ −69.5°, infrared absorption as described above.

Anal. Calcd. for $C_{32}H_{46}O_5$: C, 75.25; H, 9.08. Found: C, 75.40; H, 9.12.

The 11,12-enolone (enolic 11,12-diketone) was also isolated when the saturated 12-ketone was employed instead of its Δ^9-unsaturated derivative. It had m.p. 219–220°, gave a dark green coloration with ferric chloride–ethanol, showed infrared absorption at 3430, 1735, 1667 and 1637 cm.$^{-1}$ and corresponds in every way to the compound reported by Barton.[4]

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Diels–Alder Reaction of Anthracene with Nitroölefins. A New Route to 11-Nitro- and 11-Amino-9,10-dihydro-9,10-ethanoanthracenes[1]

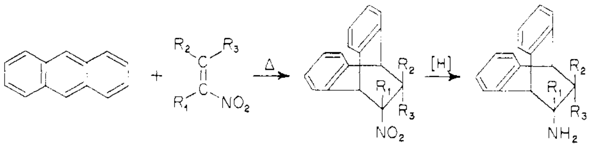
BY WAYLAND E. NOLAND, HOWARD I. FREEMAN AND M. SCOTT BAKER

RECEIVED JULY 27, 1955

The preparation of a series of seven Diels–Alder adducts of anthracene and common nitroölefins unsubstituted, 1- or 2-monosubstituted or 1,2- or 2,2-disubstituted is described; in the latter two cases the practical limits of the reaction appear to have been reached. The four adducts obtained in the best yields (19–62%) have been converted to the corresponding amines and their derivatives. The ultraviolet spectra of all the compounds compare favorably with the spectra of dihydroanthracenes reported in the literature.

Anthracene is known to undergo Diels–Alder reactions with many dienophiles[2] but until recently there were no published reports of a reaction between anthracene and a nitroölefin acting as a dienophile. Hurd and Juel[3] recently reported a reaction with anthracene at 300°, in which 1-nitronaphthalene appears to act as a nitroölefin dienophile with subsequent aromatization of the adduct by loss of nitrous acid. While this paper was being written, Klager[4] reported a 71% yield from the reaction of anthracene and nitroethylene (in excess), a reaction which we have also carried out and about which a preliminary report already has appeared.[5]

We have obtained adducts from reactions between anthracene and nitroölefins 1- or 2-monosubstituted, 1,2-disubstituted or 2,2-disubstituted. In the latter two cases the practical limits of the reaction appear to have been reached, since with β-methyl-β-nitrostyrene (1-phenyl-2-nitropropene) the yield of V was only 2%, with 2-nitro-2-butene the yield of VI was 0.5% and with 2-methyl-1-nitropropene the yield of VII was 0.6%.



I-VII Ia-IVa

Except with the β-nitrostyrenes and 2-methyl-1-nitropropene, polymerization of the nitroölefins appears to be competitive with the Diels–Alder reaction and is an important factor affecting the yield. In general, conditions for obtaining optimum yields were not determined, but with 1-nitropropene the maximum yield of 62% was obtained by adding a solution of 1-nitropropene to a refluxing solution of a fourfold proportion of anthracene in *o*-dichlorobenzene. The tertiary nitro group[6] in IV was formed from 2-nitropropene in reasonable yield, but the additional presence of a substituent on the carbon at the other end of the double bond from the nitro group sharply reduced the yield of V and VI. Refluxing a xylene solution of β-methyl-β-nitrostyrene with a 2.2-fold proportion of anthracene for 3.4 days gave no V and β-methyl-β-nitrostyrene was recovered in 97% yield. Increasing the reaction temperature by using boiling *o*-dichlorobenzene as solvent gave a 2% yield of V. An attempt to substitute an ethyl group for the methyl group in V by using β-ethyl-β-nitrostyrene (1-phenyl-2-nitro-1-butene) gave no reaction with anthracene in either boiling xylene or *o*-dichlorobenzene solutions. That the formation of a quaternary carbon is a difficult process is suggested by the low yield (0.6%) of the fluorescent adduct VII.

Chromatography is effective for separating nitroolefin adducts from their most persistent contaminant, anthracene. Elution with light petroleum (b.p. 60–68°) or solutions of ether in light petroleum removes anthracene from a column of alumina. Where the nitro group is so sterically hindered that it cannot be strongly adsorbed on alumina, as in the tertiary nitro compounds IV–VI, the compounds are eluted just after anthracene with light petroleum or solutions of ether in light petroleum. With the secondary nitro compounds I–III and VII, however, elution with methanol is necessary for complete removal from alumina.

The assignment of the *trans* configuration to II and III is based upon the following facts: (a) Both II and III were regenerated in their original con-

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(1) From the M.S. theses of Howard I. Freeman (on training assignment from the U. S. Air Force Institute of Technology), December, 1953, and M. Scott Baker, June, 1955, and from work by the senior author 1953–1955. Paper presented before the Organic Division at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 16, 1955.

(2) For numerous references see: (a) K. Alder and C. V. Wilson and J. A. Van Allan in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 485–491; (b) M. C. Kloetzel and H. L. Holmes in "Organic Reactions," Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1948, Chapters 1 and 2, (c) J. A. Norton, *Chem. Revs.*, **31**, 319 (1942).

(3) C. D. Hurd and L. H. Juel, THIS JOURNAL, **77**, 601 (1955).

(4) K. Klager, *J. Org. Chem.*, **20**, 650 (1955).

(5) W. E. Noland, *Chem. Revs.*, **55**, 137 (1955).

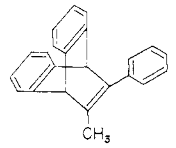
(6) For the first report of the formation of tertiary nitro compounds by the Diels–Alder reaction see W. E. Noland and R. E. Bambury, THIS JOURNAL, **77**, 6386 (1955).

figuration by mild acidification of solutions of their potassium salts, indicating that they were already in the most stable (*trans*) form; (b) both β-nitrostyrene (1-phenyl-2-nitroethene)[7a,b] and 1-nitropropene[7c] appear to exist in the *trans* form, as shown by the fact that a Diels–Alder adduct of each has been proven to have the *trans* configuration.

Catalytic hydrogenation or reduction with iron powder and 1 *N* aqueous ammonium chloride[8] in acetone solution of I–IV yielded the corresponding amines Ia–IVa. Ia was identical with a sample prepared by Wawzonek and Hallum[9] through a series of reactions from anthracene and methyl acrylate or vinyl acetate. Ia, IIIa and IVa were obtained as solids but IIa did not crystallize. IIa was characterized through its acetyl and benzoyl derivatives. Along with the benzoyl derivative there was obtained a small amount of a compound having the correct analysis for the benzoate of the enol form of the benzoyl derivative of IIa. IIIa and IVa were converted to acetyl derivatives and IIIa was also converted to a benzoyl derivative.

The compounds described in this paper have the characteristic benzenoid absorption (see Experimental) of 9,10-dihydroanthracene[10] and its alkyl derivatives,[11] supporting the structural assignments made, whereas longer wave length absorption, such as that characteristic of the greater conjugation of the naphthalene or anthracene nucleus, is absent.

Along with the fluorescent adduct V there was obtained in 1.4% yield a strongly fluorescent hydrocarbon VIII having a composition corresponding to the loss of nitrous acid from V. VIII reacts with one mole of bromine, forming a dibromide IX, but VIII was recovered unchanged from attempted hydrogenation for 6 hours at 2 atm. with platinic oxide catalyst. The ultraviolet absorption maxima of VIII in 95% ethanol at 268 mμ inflection (log ϵ 3.80), 274 (3.86) and 282 (3.89) suggest slightly increased interannular conjugation over that present in the dihydroanthracenes previously described,[10,11] except for dianthracene.[11e] The absorption is similar to that of triptycene, with maxima in 2,2,4-trimethylpentane at 263 mμ inflection (log ϵ 3.25), 271 (3.66) and 278 (3.56),[12] suggesting that the unsaturation may be present between the 11,12-positions of VIII, corresponding to the aromatic unsaturation between the same positions of triptycene. The structure of 9,10-dihydro-9,10-(11-methyl-12-phenyletheno)-anthracene is tentatively assigned to VIII. It was not determined whether VIII was formed directly from the adduct V by loss of nitrous acid or whether, under the reaction conditions used, β-methyl-β-nitrostyrene first loses nitrous acid, forming 1-phenylpropyne, which then forms a Diels–Alder adduct with anthracene.[13] If β-methyl-β-nitrostyrene has the nitro and phenyl groups in the *trans* configuration, as seems most probable, then the loss of nitrous acid would involve *cis*-elimination in either case. *cis*-Elimination of nitrous acid from the adduct V would be consistent with the finding of Cristol and Hause[14] that *cis*-elimination is favored from 9,10-dihydro-9,10-ethanoanthracenes at elevated temperatures.



VIII

In the course of preparing nitroethylene a search was made for the safest and most economical preparation of its precursor, 2-nitroethanol. Three attempts to prepare 2-nitroethanol by bubbling ethylene oxide into aqueous barium nitrite, according to the method of a Tanabe Chemical Industries Co. patent[15] gave no 2-nitroethanol but only a brown, water-soluble polymer. The most satisfactory method for preparing 2-nitroethanol was found to be by the condensation of formaldehyde with a large excess of nitromethane,[16] followed by azeotropic distillation with diphenyl ether.[17] Use of diphenyl ether as a heat dispersing agent also appears desirable in the distillation of 1-nitro-2-propanol, a precursor of 1-nitropropene.

Experimental

Melting points were determined on calibrated thermometers.

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[7] (a) R. T. Arnold and P. N. Richardson, THIS JOURNAL, **76**, 3649 (1954); (b) H. L. Goebel and H. H. Wenzke, *ibid.*, **60**, 697 (1938); (c) E. E. van Tamelen and R. J. Thiede, *ibid.*, **74**, 2615 (1952).

[8] (a) V. O. Lukashevich and M. A. Voroshilova, *Compt. rend. acad. sci. U.R.S.S.*, **2**, 394 (1935); *Org. Chem. Ind.* (*U.S.S.R.*), **4**, 253 (1937), *C. A.*, **32**, 2091 (1938); Russian Patent 51,050, May 31, 1937, *C. A.*, **33**, 4601 (1939); (b) W. E. Noland (with S. M. McElvain), B. A. thesis, University of Wisconsin, 1948; (c) S. M. McElvain, "The Characterization of Organic Compounds," rev. ed., The Macmillan Co., New York, N. Y., 1951, pp. 144–145.

[9] S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

[10] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectrum no. 114 (in cyclohexane). The spectrum in ethanol reported by Badger, Jones and Pearce[11a] is not in agreement and suggests contamination by anthracene in the sample of the latter.

[11] (a) *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracene (in ethanol): G. M. Badger, M. L. Jones and R. S. Pearce, *J. Chem. Soc.*, 1700 (1950); (b) 9,10-dihydro-9,10-(11,12-dicarboxyanhydroethano)-anthracene: C. Dufraisse and I. Gillet, *Compt. rend.*, **225**, 191 (1947); I. Gillet, *Bull. soc. chim.*, 1135 (1950); (c) disodium 9,10-dihydro-9,10-(11,12-dicarboxyethano)-anthracene (in water): E. Clar, *Ber.*, **65**, 512 (1932); (d) butadiene–anthracene copolymer (in cyclohexane): C. S. Marvel and W. S. Anderson, THIS JOURNAL, **75**, 4600 (1953); (e) dianthracene, the photodimer of anthracene: The spectrum obtained by A. Berton, *Compt. rend.*, **208**, 1895 (1939), by reflection from solid dianthracene has five bands between 300–400 mμ and intense absorption below 300 mμ. In contrast, we find that saturated solutions in 95% ethanol or *n*-heptane show gradually decreasing absorption with increasing wave length, except for a maximum at 271–272 mμ and a weaker maximum at 282–283 mμ, *with no absorption at longer wave lengths.* In saturated benzene solution there is likewise no absorption beyond 300 mμ, but absorption rises sharply with decreasing wave length to a maximum at 283 mμ (absorbancy 1.15 in a 2-cm. cell) and rises toward another maximum as the benzene solvent becomes opaque at 278 mμ.

[12] P. D. Bartlett and E. S. Lewis, THIS JOURNAL, **72**, 1005 (1950).

[13] There appears to be no analogy for the reaction of anthracene with an acetylenic hydrocarbon. A recent experiment (with Gordon L. Willette) showed that 1-phenylpropyne does not react with anthracene under the conditions under which VIII was formed.

[14] S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952).

[15] S. Miura (to Tanabe Chemical Industries Co.), Japanese Patent 156,256, April 28, 1943; *C. A.*, **44**, 2008 (1950).

[16] (a) J. Controulis, M. C. Rebstock and H. M. Crooks, Jr., THIS JOURNAL, **71**, 2465 (1949); (b) Harry M. Crooks, Jr., Parke, Davis and Co., Detroit, Mich., private communication, Jan. 8, 1954.

[17] H. T. Roy, Jr. (to the General Tire and Rubber Co.), U. S. Patent 2,710,830, June 14, 1955.

9,10-Dihydro-9,10-(11-nitroethano)-anthracene (I).—Nitroethylene[18] (7.73 g., 0.106 mole), fluorescent grade[19] anthracene (35.7 g., 0.200 mole) and benzene (500 cc.) were heated at 110° in a steel bomb for 8 hours. Cooling and concentration permitted the removal of a crop of anthracene. The remaining solution was evaporated to dryness and triturated with two portions of ether (50 cc. each). Evaporation of the ether gave a residue which, after several recrystallizations from ethanol–water, yielded white crystals of 9,10-dihydro-9,10-(11-nitroethano)-anthracene (8.25 g., 0.0329 mole, 31%), m.p. 106–107°; reported: 71%, m.p. 113–114°[4]; ν_{NO_2} (cm.$^{-1}$) 1549, 1370 in $CHCl_3$, 1546, 1366 in Nujol, ~1543, 1366 in KBr disc, 1365 in CCl_4.

Anal. Calcd. for $C_{16}H_{13}NO_2$ (251.27): C, 76.49; H, 5.18; N, 5.58. Found: C, 76.25; H, 5.48; N, 5.60.

Chromatography was found necessary to remove remaining traces of anthracene, which would otherwise show up in the ultraviolet spectrum. The sample was dissolved in benzene and chromatographed on alumina packed wet with light petroleum (b.p. 60–68°). Elution with benzene removed the traces of anthracene. Elution with chloroform–benzene and finally with ethanol removed the non-fluorescent product. Recrystallization from ethanol yielded a pure sample, m.p. 109–110°, which was shown by its ultraviolet spectrum to be free of anthracene; λ_{max} 95% C_2H_5OH: 250 mμ inflection (log ε 3.05), 257 (3.01), 265 (3.07), 272 (3.09).

9,10-Dihydro-9,10-(11-aminoethano)-anthracene (Ia).—9,10-Dihydro-9,10-(11-nitroethano)-anthracene (3.00 g., 0.0134 mole), platinic oxide (0.30 g.) and ethanol (100 cc.) were shaken with hydrogen at an initial pressure of 2 atm. for 12 hours in a Parr low pressure hydrogenation apparatus. After filtration of the catalyst and evaporation of the ethanol the residue was dissolved in ether and the solution extracted with 5% hydrochloric acid. The acid extract was washed with ether and then basified with sodium carbonate, causing the formation of a white precipitate. The precipitate and alkaline solution were extracted with ether and the ether was evaporated at room temperature, leaving crude product (2.28 g., 0.0115 mole, 86%), m.p. 92–96°. Recrystallization from light petroleum (b.p. 60–68°) yielded fine white needles of 9,10-dihydro-9,10-(11-aminoethano)-anthracene, m.p. 103.5–104.5°; reported: m.p. 104.5–105°[10]; ν_{NH} (cm.$^{-1}$) 3370 in $CHCl_3$ and CCl_4. The infrared spectrum was identical with that of an authentic sample[9,20] and there was no depression in mixed melting point; λ_{max} 95% C_2H_5OH: 252 mμ inflection (log ε 2.81), 259 (2.90), 265 (3.11), 272 (3.19).

9,10-Dihydro-9,10-(*trans*-11-nitro-12-phenylethano)-anthracene (II).—β-Nitrostyrene[21] (2.98 g., 0.0200 mole), technical grade anthracene (7.13 g., < 0.0401 mole) and xylene (50 cc.) were refluxed for 20 hours. The xylene was distilled off under reduced pressure and the residue extracted seven times with boiling absolute ethanol (20 cc. each) (ether may also be used to advantage for this extraction). The last two extracts contained largely anthracene but the first five extracts contained tan to whitish needles (3.52 g., 0.0108 mole, 54%), m.p. 138.5–150°. One or two recrystallizations, with charcoal, from absolute ethanol gave white crystals (2.39 g., 0.00731 mole, 36%), which still contained anthracene—the relative proportion of which increases with each recrystallization. Vacuum-subliming out the remaining anthracene at 100° yielded the analytical sample of non-fluorescent 9,10-dihydro-9,10-(*trans*-11-nitro-12-phenylethano)-anthracene, m.p. 150–151°; ν_{NO_2} (cm.$^{-1}$) 1547 in Nujol, 1365 in CS_2; λ_{max} 95% C_2H_5OH: 252 mμ inflection (log ε 3.19), 258 (3.15), 265 (3.14), 273 (3.06).

Anal. Calcd. for $C_{22}H_{17}NO_2$ (327.36): C, 80.71; H, 5.23; N, 4.28. Found: C, 80.69; H, 5.33; N, 4.47.

Regeneration of 9,10-Dihydro-9,10-(*trans*-11-nitro-12-phenylethano)-anthracene (II) from its Salt.—This reaction was carried out in the presence of potassium nitrite with the intention of preparing the pseudonitrole derivative, but none was obtained. Instead, the nitrite ion served as a buffer and kept the acidity below that which strongly favors the Nef reaction, thus permitting regeneration of the nitro compound.

9,10-Dihydro-9,10-(*trans*-11-nitro-12-phenylethano)-anthracene (5.88 g., 0.0180 mole) was dissolved in ethanolic potassium hydroxide, potassium nitrite (3.0 g.) was added and the mixture was cooled in an ice-bath. An ice-cold solution of sulfuric acid in ethanol (1:3 by volume) was added dropwise, with stirring, until the solution was acid to congo red paper. The blue-green solution containing creamy-white solid in suspension was allowed to warm up to room temperature and stand overnight. There remained a voluminous inorganic precipitate below a pale yellow solution, now neutral to litmus as the result of decomposition of the nitrous acid. The mixture was dissolved in water and ether and the aqueous layer extracted six times with ether. Evaporation of the combined ether extracts left an oil which crystallized upon cooling. Recrystallization, with charcoal, from absolute ethanol gave yellowish-white crystals (3.91 g., 66%), m.p. 146–151°. Another recrystallization yielded crystals (3.15 g., 54%), m.p. 149.5–151°, mixed m.p. with starting material 149.5–151°.

9,10-Dihydro-9,10-(*trans*-11-acetamino-12-phenylethano)-anthracene (Acetyl Derivative of IIa).—9,10-Dihydro-9,10-(*trans*-11-nitro-12-phenylethano)-anthracene (2.94 g.), acetone (75 cc.) and Raney nickel (3.5 g., wet with ethanol) were shaken with hydrogen at an initial pressure of 2 atm. for 16 hours in a Burgess–Parr low pressure hydrogenation apparatus. After filtration of the catalyst and evaporation of the solvent the residue was dissolved in ether and extracted with 2 *N* hydrochloric acid. The amine hydrochloride formed was so slightly soluble that 150 cc. of acid solution were required to dissolve it. Basification with potassium hydroxide solution, extraction with ether and evaporation of the ether gave a pale yellow, viscous oil, which did not crystallize. This oil was warmed with excess acetic anhydride for 6 hours on a steam-bath. The product was recrystallized three times from ethanol and finally from methanol, yielding white platelets of 9,10-dihydro-9,10-(*trans*-11-acetamino-12-phenylethano)-anthracene, m.p. 230.5–231.5°; ν_{NH} (cm.$^{-1}$) 3450, 3340 in CS_2, 3360, 1538 in Nujol; $\nu_{C=O}$ (cm.$^{-1}$) 1690 in CS_2, 1650 in Nujol; λ_{max} 95% C_2H_5OH: 253 mμ inflection (log ε 2.87), 259 (2.98), 265 (3.08), 273 (3.09).

Anal. Calcd. for $C_{24}H_{21}NO$ (339.42): C, 84.92; H, 6.24; N, 4.13. Found: C, 85.01; H, 6.43; N, 4.07.

9,10-Dihydro-9,10-(*trans*-11-benzamino-12-phenylethano)-anthracene (Benzoyl Derivative of IIa).—9,10-Dihydro-9,10-(*trans*-11-nitro-12-phenylethano)-anthracene (10.30 g., 0.0315 mole) was dissolved in acetone (150 cc.) and 1 *N* ammonium chloride solution[8] (50 cc.) and iron powder (10.5 g., 0.188 g. atom) were added. The mixture was refluxed overnight and then the acetone was boiled off, a total of 20 hours of heating. The residue was extracted four times with boiling benzene (50 cc. each), and the small water layer discarded. Workup of the product yielded a sticky yellowish oil, which did not crystallize. This oil was warmed with pyridine (40 cc.) and benzoyl chloride (20 cc.) for one hour on a steam-bath. The product was recrystallized five times, giving from ethanol–water fine white needles of 9,10-dihydro-9,10-(*trans*-11-benzamino-12-phenylethano)-anthracene, m.p. 248–248.5°; ν_{NH} (cm.$^{-1}$) 3440, 3320 in CS_2, 3330, 1535 in Nujol; $\nu_{C=O}$ (cm.$^{-1}$) 1675 in CCl_4, 1671 in CS_2, 1634 in Nujol; λ_{max} 95% C_2H_5OH: 265 mμ inflection (log ε 3.55), 272 (3.41).

Anal. Calcd. for $C_{29}H_{23}NO$ (401.48): C, 86.75; H, 5.78; N, 3.49. Found: C, 86.48; H, 5.90; N, 3.63.

The mother liquor yielded a smaller amount of lumpy white crystals, m.p. 179.5–181°, which were separated by hand from the larger amount of amide present; ν_{NH} none; $\nu_{C=O}$ (cm.$^{-1}$) 1704 in CCl_4; $\nu_{C=N}$ (cm.$^{-1}$) 1660 in CCl_4.

Anal. Calcd. for $C_{36}H_{27}NO_2$ (505.58): C, 85.52; H, 5.38; N, 2.77. Found: C, 85.77; H, 5.71; N, 2.90.

9,10-Dihydro-9,10-(*trans*-11-nitro-12-methylethano)-anthracene (III).—*o*-Dichlorobenzene (50 cc.) was warmed to incipient boiling and anthracene (30.0 g., 0.168 mole) was added. The solution was heated to boiling under a nitrogen atmosphere and a solution of 1-nitropropene[22] (3.7 g., 0.042 mole) in *o*-dichlorobenzene was added dropwise over a pe-

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[18] G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

[19] (a) J. A. C. Yule (to Eastman Kodak Co.), U. S. Patent 2,213,-755, Sept. 3, 1940 [*C. A.*, **35**, 464 (1941)]; (b) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 345, footnote 13.

[20] Kindly provided by Dr. Stanley Wawzonek.

[21] D. E. Worrall in "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 413.

[22] E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928).

riod of 5 minutes. The solution was refluxed until the color changed from yellow to red (80 minutes). The *o*-dichlorobenzene was distilled off under reduced pressure and the residue dissolved in boiling benzene. Cooling and concentration permitted the removal of anthracene (18.9 g.). The filtrate was chromatographed on alumina (300 g.) packed wet with light petroleum (b.p. 60–68°). Any alkali in the alumina had been previously neutralized by boiling with ethyl acetate for 2 hours, followed by activation at 200° for 4 hours. Elution with light petroleum and solutions of anhydrous ether in light petroleum removed anthracene (1.0 g.). Elution with methanol gave crude, yellow adduct (6.98 g., 0.0263 mole, 62%), m.p. 108–117°. Several recrystallizations, with charcoal, from ethanol yielded non-fluorescent white needles of 9,10-dihydro-9,10-(*trans*-11-nitro-12-methylethano)-anthracene, m.p. 122.5–123.5°; ν_{NO_2} (cm.$^{-1}$) 1550, 1374 in $CHCl_3$, 1525, 1376 in Nujol; $\lambda_{max.}$ 95% C_2H_5OH: 250 mμ inflection (log ϵ 3.03), 256 (3.00), 265 (3.04), 272 (3.06).

Anal. Calcd. for $C_{17}H_{15}NO_2$ (265.30): C, 76.96; H, 5.70; N, 5.28. Found: C, 76.64; H, 5.88; N, 5.32.

Regeneration of 9,10-Dihydro-9,10-(*trans*-11-nitro-12-methylethano)-anthracene (III) from its Salt.—By the method of Kornblum and Graham[23] an ice-cold solution of urea (4.00 g.) in 20% acetic acid (30 cc.) was added dropwise, with shaking, to an ice-cold solution of 9,10-dihydro-9,10-(*trans*-11-nitro-12-methylethano)-anthracene (0.10 g.) in Claisen alkali (10 cc.) [a solution of potassium hydroxide (350 g.) in water (250 cc.) diluted to 1.0 l. with methanol], causing the formation of a white precipitate. Extraction with three portions of ether (20 cc. each) caused the precipitate to dissolve. The aqueous layer was further acidified to a *p*H of about 4 with acetic acid, and extracted once more with ether. The combined ether extracts were washed with water and evaporated, yielding starting material (0.07 g., 70%), m.p. 113–117°. Four recrystallizations from ethanol–water gave 0.03 g., m.p. 118.5–119°, mixed m.p. with starting material, 118–119°. The infrared spectrum was identical with that of the starting material.

9,10-Dihydro-9,10-(*trans*-11-amino-12-methylethano)-anthracene (IIIa) (With Patricia A. McVeigh and Dean A. Ostlie).—9,10-Dihydro-9,10-(*trans*-11-nitro-12-methylethano)-anthracene (0.9 g., 0.0034 mole), ethanol (175 cc.) and Raney nickel (4 g.) were shaken with hydrogen at an initial pressure of 2 atm. for 4.5 hours in a Burgess–Parr low pressure hydrogenation apparatus. After filtration of the catalyst and evaporation of the ethanol the residue was dissolved in ether and extracted with dilute hydrochloric acid. Basification with sodium hydroxide solution precipitated a white solid. Recrystallization from ethanol–water yielded *trans*-9,10-dihydro-9,10-(11-amino-12-methylethano)-anthracene (0.38 g., 0.0016 mole, 47%), m.p. 111–113°; ν_{NH} (cm.$^{-1}$) 3390 in $CHCl_3$ and CCl_4, 3380 in Nujol; $\lambda_{max.}$ 95% C_2H_5OH: 252 mμ inflection (log ϵ 2.84), 259 (2.91), 265 (3.09), 272 (3.18).

Anal. Calcd. for $C_{17}H_{17}N$ (235.31): C, 86.77; H, 7.28; N, 5.95. Found: C, 86.69; H, 7.38; N, 6.22.

9,10-Dihydro-9,10-(*trans*-11-acetamino-12-methylethano)-anthracene (Acetyl Derivative of IIIa) (With John H. Peters).—9,10-Dihydro-9,10-(*trans*-11-amino-12-methylethano)-anthracene (0.2 g.) and acetic anhydride (5 cc.) were warmed for 0.5 hours on a steam-bath. The solution was cooled and water (30 cc.) was added, with stirring, causing the formation of a white flocculent precipitate. Recrystallization from 50% acetic acid–water yielded white needles of 9,10-dihydro-9,10-(*trans*-11-acetamino-12-methylethano)-anthracene, m.p. 234.5–235°; ν_{NH} (cm.$^{-1}$) 3290, 1559 in Nujol; $\nu_{C=O}$ (cm.$^{-1}$) 1641 in Nujol; $\lambda_{max.}$ 95% C_2H_5OH: 252 mμ inflection (log ϵ 2.74), 259 (2.88), 265 (3.06), 272 (3.14).

Anal. Calcd. for $C_{19}H_{19}NO$ (277.34): C, 82.28; H, 6.91; N, 5.05. Found: C, 82.31; H, 7.12; N, 5.25.

9,10-Dihydro-9,10-(*trans*-11-benzamino-12-methylethano)-anthracene (Benzoyl Derivative of IIIa) (With Patricia A. McVeigh).—9,10-Dihydro-9,10-(*trans*-11-amino-12-methylethano)-anthracene (0.1 g.), benzoyl chloride (3 cc.) and 20% sodium hydroxide solution (15 cc.) were shaken occasionally for one hour until no odor of benzoyl chloride remained. The heavy white precipitate was recrystallized from ethanol–water, yielding white needles of 9,10-dihydro-9,10-(*trans*-11-benzamino-12-methylethano)-anthracene, m.p. 239.5–240.5°; ν_{NH} (cm.$^{-1}$) 3420 in $CHCl_3$, 3260, 1553 in Nujol; $\nu_{C=O}$ (cm.$^{-1}$) 1652 in $CHCl_3$, 1629 in Nujol; $\lambda_{max.}$ 95% C_2H_5OH: 264 mμ inflection (log ϵ 3.54), 272 (3.44).

Anal. Calcd. for $C_{24}H_{21}NO$ (339.42): C, 84.92; H, 6.24; N, 4.13. Found: C, 84.70; H, 6.49; N, 4.00.

9,10-Dihydro-9,10-(11-nitro-11-methylethano)-anthracene (IV).—2-Nitropropene[18,24] (8.60 g., 0.0988 mole), fluorescent grade[19] anthracene (31 g., 0.174 mole) and benzene (500 cc.) were heated, with shaking, in a steel bomb at 110° for 12 hours. Evaporation of the benzene left a yellowish residue (33.5 g.), which was triturated with ether in small portions, leaving a residue of anthracene (23.5 g.). Evaporation of the ether left a yellowish residue (9.4 g.), which gave, after recrystallization with charcoal from ethanol, white crystals, m.p. 135–150°, still containing anthracene. Sublimation of the anthracene at 60–90° (0.02–0.10 mm.) gave a residue, m.p. 152–153.5°, which, after recrystallization from ethanol, yielded non-fluorescent white chunky crystals of 9,10-dihydro-9,10-(11-nitro-11-methylethano)-anthracene (5.00 g., 0.0189 mole, 19%), m.p. 159–159.5°; ν_{NO_2} (cm.$^{-1}$) 1538, 1384 or 1351 in Nujol, 1385 or 1351 in $CHCl_3$; $\lambda_{max.}$ 95% C_2H_5OH: 250 mμ inflection (log ϵ 3.06), 258 (3.04), 265 (3.09), 272 (3.11).

Anal. Calcd. for $C_{17}H_{15}NO_2$ (265.30): C, 76.96; H, 5.70; N, 5.28. Found: C, 77.14; H, 5.93; N, 5.22.

9,10-Dihydro-9,10-(11-amino-11-methylethano)-anthracene (IVa).—9,10-Dihydro-9,10-(11-nitro-11-methylethano)-anthracene (0.69 g., 0.00260 mole), platinic oxide (0.20 g.) and ethanol (30 cc.) were shaken with hydrogen at an initial pressure of 2 atm. for 30 hours in a Parr low pressure hydrogenation apparatus. After filtration of the catalyst and evaporation of the ethanol the residue was dissolved in ether and extracted with 5% hydrochloric acid. The acid extract was washed with ether and then basified with sodium carbonate, causing the formation of a white precipitate. The precipitate and alkaline solution were extracted with ether and the ether was evaporated at room temperature, leaving crude product (0.50 g., 0.00213 mole, 84%), m.p. 90–91.5°. Several recrystallizations from light petroleum (b.p. 60–68°) yielded white chunky crystals of 9,10-dihydro-9,10-(11-amino-11-methylethano)-anthracene, m.p. 99.5–101.5°; ν_{NH} (cm.$^{-1}$) 3340, 1583 in $CHCl_3$; λ_{max} 95% C_2H_5OH: 252 mμ inflection (log ϵ 2.78), 259 inflection (2.91), 266 (3.11), 273 (3.21).

Anal. Calcd. for $C_{17}H_{17}N$ (235.30): C, 86.77; H, 7.28; N, 5.95. Found: C, 87.03; H, 7.49; N, 5.88.

9,10-Dihydro-9,10-(11-acetamino-11-methylethano)-anthracene (Acetyl Derivative of IVa).—Fine white needles were obtained[25] in 70% yield after two recrystallizations, with charcoal, from light petroleum (b.p. 60–68°), m.p. 148–149°; ν_{NH} (cm.$^{-1}$) 3420, 3320 in CS_2, 3280, 1555 in Nujol; $\nu_{C=O}$ (cm.$^{-1}$) 1681 in CS_2, 1636 in Nujol; $\lambda_{max.}$ 95% C_2H_5OH: 252 mμ inflection (log ϵ 2.75), 259 inflection (2.87), 266 (3.07), 273 (3.17).

Anal. Calcd. for $C_{19}H_{19}NO$ (277.34): C, 82.28; H, 6.91; N, 5.08. Found: C, 82.44; H, 7.01; N, 5.08.

9,10-Dihydro-9,10-(11-nitro-11,12-dimethylethano)-anthracene (VI) (With Raimond Liepins).—Fluorescent grade[19] anthracene (86 g., 0.482 mole) was added in portions to boiling redistilled *o*-dichlorobenzene (167 cc.). While nitrogen was passed into the refluxing solution, 2-nitro-2-butene[26] (50 g., 0.495 mole) in redistilled *o*-dichlorobenzene (58 cc.) was added dropwise during 2.25 hours. After an additional 1.08 hours of refluxing, the *o*-dichlorobenzene was distilled off under reduced pressure and the residue dissolved in boiling benzene (1.0 l.). Cooling and concentration permitted the removal of anthracene. The filtrate was boiled twice with charcoal and chromatographed on alumina (about 200 g.) which had been packed wet with light petroleum (b.p. 60–68°). Any alkali in the alumina had been previously neutralized by boiling with ethyl acetate for 2 hours, followed by activation at 200° for 18 hours. Elution with benzene removed the remaining anthracene,

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[23] N. Kornblum and G. E. Graham, THIS JOURNAL, **73**, 4041 (1951).

[24] B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

[25] Reference 8c, p. 210.

[26] H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

followed closely by a fraction which, after evaporation and treatment with ethanol, gave long needles. Boiling with charcoal and three recrystallizations from ethanol yielded non-fluorescent, long white needles of 9,10-dihydro-9,10-(11-nitro-11,12-dimethylethano)-anthracene (0.6 g., 0.0021 mole, 0.4%), m.p. 130.5–132.5°; ν_{NO_2} (cm.$^{-1}$) 1538, 1388 or 1348 in $CHCl_3$, 1530, 1389 or 1346 in Nujol; $\lambda_{\max}$ 95% C_2H_5OH: 252 mμ inflection (log ε 3.09), 259 (3.08), 266 (3.09), 274 (3.06).

Anal. Calcd. for $C_{18}H_{17}NO_2$ (279.32): C, 77.39; H, 6.13; N, 5.01. Found: C, 77.66; H, 6.40; N, 5.28.

The mother liquor from recrystallization yielded fine white needles of another form (0.2 g., 0.0007 mole, 0.1%), m.p. 109.5–110.5°, which could not be distinguished on the basis of infrared or ultraviolet spectra from the preceding sample; mixed m.p. with preceding sample, 113–132°.

Anal. Found: C, 77.43; H, 6.00; N, 4.93.

9,10-Dihydro-9,10-(11-nitro-11-methyl-12-phenylethano)-anthracene (V) (With Raimond Liepins and William C. Nickles).—Redistilled *o*-dichlorobenzene (100 cc.) was heated to incipient boiling and fluorescent grade[19] anthracene (49.0 g., 0.275 mole) was added in small portions. β-Methyl-β-nitrostyrene[26,27] (48.8 g., 0.299 mole) was similarly added over a period of 8 minutes. The dark orange solution was refluxed for 4 hours, during which time the color changed to dark brown. After the first 0.5 hour and for the remainder of the reflux period the evolution of nitrogen dioxide was noted. The solvent was removed under reduced pressure and the residue dissolved in boiling benzene. Concentration and cooling permitted the removal of four crops of anthracene (38.3 g., 78%). The residual solution (100 cc.) was diluted with an equal volume of light petroleum (b.p. 60–68°) and chromatographed on alumina (about 200 g.) packed wet with light petroleum. Elution with light petroleum removed a strongly fluorescent fraction containing two types of crystals. Further elution with solutions of benzene or ether in light petroleum removed additional material of a single kind, giving white chunky crystals. Rechromatography of the strongly fluorescent first fraction yielded, after several recrystallizations from light petroleum, white crystalline **9,10-dihydro-9,10-(11-methyl-12-phenyletheno)-anthracene (VIII)** (1.12 g., 0.00380 mole, 1.4%), m.p. 171.5–172°; $\nu_{C=C?}$ (cm.$^{-1}$) 1640 in Nujol, ~1637 in KBr disc, 1636 in $CHCl_3$ (a medium weak band in all cases).

Anal. Calcd. for $C_{23}H_{18}$ (294.37): C, 93.84; H, 6.16. Found: C, 94.15, 93.64; H, 6.40, 6.34.

The chunky crystals from the first chromatogram and the second fraction from rechromatography, after two or three recrystallizations from light petroleum, yielded fluorescent, white chunky crystals of 9,10-dihydro-9,10-(11-nitro-11-methyl-12-phenylethano)-anthracene (1.87 g., 0.00549 mole, 2.0%), m.p. 142–143°; ν_{NO_2} (cm.$^{-1}$) 1540, 1385 or 1345 in $CHCl_3$, 1536, 1381 or 1343 in Nujol; $\lambda_{\max}$ 95% C_2H_5OH: 251 mμ inflection (log ε 2.95), 258 (2.94), 265 (3.03), 272 (3.07).

Anal. Calcd. for $C_{23}H_{19}NO_2$ (341.39): C, 80.91; H, 5.61; N, 4.10. Found: C, 81.09, 81.17; H, 5.62, 5.81; N, 4.39, 4.17.

9,10-Dihydro-9,10-(11-methyl-11,12-dibromo-12-phenylethano)-anthracene (IX) (With Raimond Liepins).—A solution of 9,10-dihydro-9,10-(11-methyl-12-phenyletheno)-anthracene (0.3 g., 0.0010 mole) in chloroform (0.5 cc.) was cooled in an ice–salt-bath and a solution of bromine (0.16 g., 0.0010 mole) in chloroform (0.7 cc.) was added dropwise, with shaking. After nearly all of the bromine solution was added, the reaction solution became light orange. Addition was stopped but shaking was continued for 5 minutes more. The chloroform was evaporated at room temperature under reduced pressure, and the residue was recrystallized twice from benzene–ethanol, yielding white crystals of 9,10-dihydro-9,10-(11-methyl-11,12-dibromo-12-phenylethano)-anthracene (>0.2 g., 0.00044 mole, 44%), m.p. 189–190.5°; $\nu_{C=C}$ none in Nujol; $\lambda_{\max.}$ 95% EtOH: 258 mμ (log ε 3.23), 268 (3.20) and 276 (3.14).

Anal. Calcd. for $C_{23}H_{18}Br_2$ (454.20): C, 60.82; H, 3.99. Found: C, 60.91; H, 4.25.

9,10-Dihydro-9,10-(11-nitro-12,12-dimethylethano)-anthracene (VII) (With Ronald E. Bambury and James H. Cooley).—Redistilled *o*-dichlorobenzene (150 cc.) was warmed to incipient boiling and fluorescent grade[19] anthracene (55.0 g., 0.308 mole) was added. The solution was heated to boiling under a nitrogen atmosphere and a solution of 2-methyl-1-nitropropene[28] (8.0 g., 0.079 mole) in *o*-dichlorobenzene (50 cc.) was added dropwise over a period of 10 minutes. The solution was refluxed for 4 hours. The *o*-dichlorobenzene was distilled off under reduced pressure and the residue dissolved in boiling benzene. Cooling and concentration permitted the removal of anthracene (51.6 g.). The filtrate was chromatographed on alumina packed wet with light petroleum (b.p. 60–68°). Elution with light petroleum (2.0 l.) and solutions (2.0 l.) of increasing amounts of anhydrous ether removed a small amount of anthraquinone. Elution with methanol (0.5 l.) removed a strongly fluorescent band containing crude, brownish product (0.32 g.). Recrystallization from ethanol gave white needles (fluorescent in solution only) (0.125 g., 0.000448 mole, 0.6%), m.p. 147.5–151.5°. One more recrystallization, from ethanol–water, yielded the analytical sample (0.063 g.) of 9,10-dihydro-9,10-(11-nitro-12,12-dimethylethano)-anthracene, m.p. 149–150°; ν_{NO_2} (cm.$^{-1}$) 1549, 1377 in $CHCl_3$, 1538, 1376 in KBr disc; $\lambda_{\max}$ 95% C_2H_5OH: 250 mμ (log ε 2.93), 259 (2.95), 266 (3.09), 273 (3.17).

Anal. Calcd. for $C_{18}H_{17}NO_2$ (279.32): C, 77.39; H, 6.13; N, 5.01. Found: C, 77.00, 77.68; H, 6.19, 6.50; N, 5.28.

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