P, 11.63; S, 24.02. Found: C, 54.71; H, 10.30; P, 11.71; S, 22.84.

**2-Carbethoxyethyl Diisobutylphosphinodithioate.**—2-Carbethoxyethyl disulfide (24.0 g, 0.09 mole), diisobutylphosphine (14.6 g, 0.10 mole), and 0.2 g of azobisisobutyronitrile (AIBN) were refluxed for 62 hr in 100 ml of benzene under argon. An additional 0.2 g of AIBN was added and reflux was continued for another 5 hr. Vacuum distillation gave 18.6 g (67%) of product, bp 152–157° (0.20 mm). *Anal.* Calcd for $C_{13}H_{27}PS_2O_2$: C, 50.26; H, 8.76; P, 9.98; S, 20.64. Found: C, 51.59; H, 8.80; P, 10.24; S, 18.35.

**Di-*n*-butyl *n*-Butylphosphonotrithioate.**—*n*-Butyl disulfide (37.1 g, 0.21 mole) and *n*-butylphosphine (9.9 g, 0.11 mole) were refluxed for 67 hr in 75 ml of benzene under argon. AIBN was added at 2, 35, and 65 hr in 0.1-g portions. Vacuum distillation gave 24.3 g (87%) of product, bp 138–144° (0.17 mm). The infrared spectrum was consistent with the proposed structure (PS at 527 and P=S at 638 cm$^{-1}$). *Anal.* Calcd for $C_{12}H_{27}PS_3$: C, 48.30; H, 9.12; P, 10.38; S, 32.20. Found: C, 47.88; H, 8.76; P, 10.36; S, 31.37.

**Phenyl Dicyclohexylphosphinothiolate.**—Phenyl disulfide (22.0 g, 0.10 mole), dicyclohexylphosphine (10.0 g, 0.05 mole), and 0.2 g of hydroquinone were refluxed for 64 hr in 600 ml of 80:20 *t*-butyl alcohol–water. The solvent was removed by vacuum distillation and the residue was crystallized from petroleum ether (bp 30–60°). The yield of white solid was 14.4 g (90%), mp 84–90.5°. A second crystallization gave mp 91–93° (lit.[13] mp 91–93.5°). A mixture melting point with an independently prepared sample[12] gave no depression. *Anal.* Calcd for $C_{18}H_{27}POS$: P, 9.61; S, 9.94. Found: P, 9.56; S, 9.91.

The compound was also prepared in 92% yield by direct reaction of phenyl disulfide and phenyl dicyclohexylphosphinothioite under the same conditions, mp 91.5–93°.

---

[13] M. Grayson, C. E. Farley, and C. A. Streuli, *Tetrahedron*, in press.

---

# 1,4,9,10-Tetrahydroanthracene from the Stepwise Reduction of 9,10-Dihydroanthracene by Lithium in Ammonia[1]

RONALD G. HARVEY

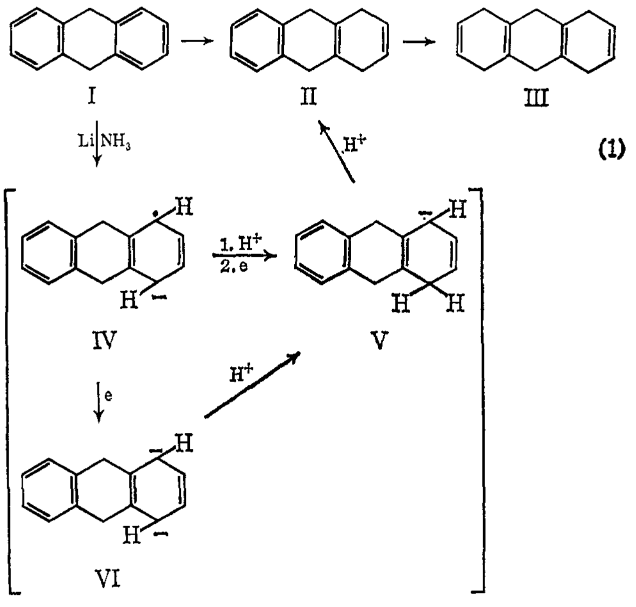
*The Ben May Laboratory for Cancer Research, The University of Chicago, Chicago, Illinois*

*Received July 18, 1966*

Partially reduced polycyclic aromatic hydrocarbons having an internal tetrasubstituted olefinic bond are a relatively unknown class of compounds. With few exceptions, compounds of this type (*e.g.*, 1,2,3,4,9,10-hexahydrophenanthrene[2] and 5,6,11,12-tetrahydrochrysene[3]) have arisen *via* cyclization of precursors with fewer rings.

In the present study we have explored metal–ammonia reduction for the preparation of 1,4,9,10-tetrahydroanthracene (II), the synthesis of which typifies one of the essential problems to achieving controlled step-by-step reduction of higher aromatic systems. Thus, 9,10-dihydroanthracene (I), presumably the initial product from Birch reduction of anthracene, possesses two isolated and equivalent benzenoid rings so that selective, two-stage reduction (*i.e.*, synthesis of II in preference to III) (eq 1 of Chart I) is improbable by conventional techniques. Treatment of anthracene with sodium and alcohol in liquid ammonia is reported to furnish its hexahydro derivative (III),[4,5] while similar reaction in the absence of alcohol provided only the dihydro compound (I).[6] Reduction of I with lithium in methylamine[7] also provides III.

CHART I



An efficient synthesis of II from I has now been achieved. Optimum conditions are as follows. A stirred solution prepared from I (900 mg, 5 mmoles), lithium (2.5 equiv), and 75 ml of dry THF in 150 ml of purified ammonia was maintained at reflux for 2 hr. Reaction was quenched by addition first of alcohol, then of water. The pure substances, I, II, and III (15, 76, and 9%, respectively), were conveniently isolated by *charge-transfer chromatography*[8,9] on a column of silica gel impregnated with 1,3,5-trinitrobenzene. The nmr spectrum of I exhibited aromatic proton resonance at $\tau$ 2.80 and a sharp methylene singlet at 6.10; II showed absorptions at $\tau$ 2.92, 4.27, 6.77, and 7.30 for aromatic, vinylic, and inner and outer ring methylene protons, respectively; for III vinyl protons were unaltered at $\tau$ 4.27, while central and outer methylene protons underwent downfield shift to 7.52 and 7.42, respectively.

The foregoing synthetic procedure, based upon an empirical study of this reduction (Table I), contains several significant features. Firstly, purity of the ammonia is essential,[10] since reduction failed to occur in this solvent taken directly from a commercial cylinder. Iron compounds are apparently responsible, since ferric salts had a similar inhibitory effect. Secondly, maximum yield of II relative to III is favored by the omission of alcohol or other added proton source during the formal reaction period. Thirdly, while a small excess of lithium is necessary to maintain the concentration of

---

[1] This investigation was supported in part by Public Health Service Research Grant 1-R01-CA-08674 from the National Cancer Institute.

[2] B. Belleau, *J. Am. Chem. Soc.*, **75**, 1159 (1953).

[3] E. Cahans, G. Schmidt, and K. Shah, *J. Org. Chem.*, **24**, 556 (1959).

[4] A. J. Birch, P. Fitton, D. C. C. Smith, D. E. Steere, and A. R. Stelfox, *J. Chem. Soc.*, 2209 (1963).

[5] J. Runge, *Z. Chem.*, **2**, 374 (1962).

[6] P. Le Beau, *Compt. Rend.*, **159**, 70 (1914); H. F. Miller and G. B. Bachman, *J. Am. Chem. Soc.*, **57**, 768 (1935).

[7] E. Vogel, *et al.*, *Angew. Chem.*, **78**, 642 (1966).

[8] R. G. Harvey and M. Halonen, *J. Chromatog.*, in press.

[9] This technique has proved invaluable for the efficient separation of closely related hydroaromatic molecules, often virtually impossible to obtain free of one another by recrystallization or conventional chromatography.

[10] Despite reports[6] that in the absence of a proton source anthracene is reduced only as far as I, we have found that reduction beyond this stage proceeds readily, providing that the ammonia is free of metallic impurities. These and related experiments will be published shortly.

TABLE I

REDUCTION OF I BY METAL–AMMONIA SOLUTIONS

| Expt no. | Li/I,[a] equiv/mole | Solvent,[b] ml | Ammonia,[c] ml | Time, min | Product compn, % I | II | III |
|---|---|---|---|---|---|---|---|
| | | A. Reaction Temperature −71° | | | | | |
| 1 | 2 | Ether, 100 | 250[d] | 120 | 100 | 0 | 0 |
| 2 | 2 | Ether, 100 | 250 | 120 | 74 | 25 | 1 |
| 3 | 2 | Ether, 100 | 500 | 120 | 74 | 24 | 2 |
| 4 | 2 (Na) | Ether, 100 | 250 | 120 | 57 | 36 | 7 |
| 5 | 2 (450 mg of I) | Ether, 100 | 250 | 120 | 73 | 26 | 1 |
| 6 | 2 | THF, 100 | 250 | 120 | 54 | 45 | 1 |
| 7 | 2 | THF, 50 | 250 | 120 | 72 | 25 | 3 |
| 8 | 2 | THF, 10 | 250 | 120 | 92 | 7 | 1 |
| 9 | 2 | Alcohol, 25 | 250 | 4 | 81 | 8 | 11 |
| 10 | 2 | Ether, 100 and alcohol, 25 | 250 | 15 | 49 | 43 | 8 |
| 11 | 2 | THF, 100 and alcohol, 2.92 | 250 | 120 | 37 | 53 | 10 |
| 12 | 2 | THF, 100, *t*-BuOH, 0.48 | 250 | 120 | 45 | 48 | 7 |
| 13 | 2 | THF, 100 | 250 | 300 | 40 | 57 | 3 |
| 14 | 4 | THF, 100 | 250 | 300 | 18 | 68 | 14 |
| 15 | 2 (9 g of I) | THF, 1000 | 2500 | 600 | 35 | 62 | 3 |
| | | B. Reaction Temperature −33° | | | | | |
| 1 | 2 | THF, 100 | 250 | 120 | 40 | 53 | 7 |
| 2 | 2 | THF, 100 | 150 | 120[e] | 23 | 68 | 9 |
| 3 | 2 | THF, 100 | 150 | 60[e] | 27 | 65 | 8 |
| 4 | 2 | THF, 75 | 150 | 120[e] | 20 | 70 | 10 |
| 5 | 2.5 | THF, 75 | 150 | 120 | 26 | 65 | 9 |
| 6 | 2.5 | THF, 75 | 150 | 120 | 15 | 76 | 9 |
| 7 | 2.5 | THF, 75 | 150[f] | 120 | 89 | 11 | 0 |

[a] 900 mg of I was employed. [b] Alcohol = ethanol. [c] Commercial ammonia was purified by distillation into the flask through a column of BaO. [d] Ammonia was taken directly from a commercial cylinder. [e] Blue color faded before time stated. [f] $FeCl_3$ (80 mg) was added at start of reaction period.

solvated electrons in the medium, greater excess appears to favor formation of III; the optimum value found was 2.5 equiv. Finally, factors favoring total solution of I in the medium promote greater extent of reaction. Thus, under otherwise standard conditions yields are lower (a) in ether compared with tetrahydrofuran, (b) at −70° compared with −33° (where I was completely dissolved), and (c) with decreasing proportions of tetrahydrofuran at −70° (expt 6–8).

While discussion of the mechanism[11,12] must await more detailed investigation, we tentatively suggest that the importance of low proton concentration is to favor charged intermediates such as IV–VI.[11,12] These species may be expected to resist further addition of solvated electrons to the intact aryl ring to a greater degree than should the neutral II.

We have further observed that reduction of I by lithium in ammonia under Birch conditions (*i.e.*, alcohol present) affords a higher yield of III (80%) than reported to be obtained from anthracene,[4] and in addition provides a modest quantity of II (8%).

### Experimental Section

**Physical Data.**—Melting points were taken on a Leitz Kofler hot-stage microscope and are corrected. Ultraviolet, infrared, and nmr spectra were taken in ethanol, solid KBr, and deuteriochloroform, respectively. Microanalyses were performed by Microtech Laboratories, Skokie, Ill.

**Materials and Methods.**—Ammonia gas (Matheson Co.) was distilled into the reaction vessel through a column of barium oxide (10–20 mesh) except where otherwise indicated. Compound I, supplied by the Aldrich Chemical Co., was dissolved in hot alcohol, filtered to remove a dark, metallic impurity, and recrystallized to furnish pure (by tlc and nmr) I, mp 112–113° (lit.[13] mp 109°). Tetrahydrofuran (THF) was purified either by passage through a column of alumina or by distillation from $LiAlH_4$ and storage over $CaH_2$ under nitrogen. Thin layer plates and columns of silica gel impregnated with trinitrobenzene were prepared by the method previously described.[8]

**Reduction of I with Lithium in Ammonia.**—A solution of I in dry ether or THF was added to a flask containing liquid ammonia at −70° under an atmosphere to helium (preferable to nitrogen owing to the case of lithium nitride formation). At this point either (A) lithium metal was added and the reaction mixture was maintained at the bath temperature for the specified period, or (B) the bath was removed and the solution was brought to reflux before addition of the metal. Reactions were quenched as rapidly as practical by the addition first of alcohol, then water. Products were obtained by filtration after evaporation of ammonia and dilution with water, and product composition was determined by comparison of integrated peak values in the proton nmr spectra. The nonexistence of any significant side products was supported by nmr spectroscopy and by thin layer chromatograms on trinitrobenzene–silica gel.[8]

Recovery of the pure components was most efficiently achieved, not by fractional crystallization, but by charge-transfer chromatography[8] on a column of silica gel impregnated with *s*-trinitrobenzene; the compounds migrated down the column as colored bands and emerged pure and colorless.

The analytical sample of II recrystallized from benzene had mp 105–106.4°; $\lambda_{max}$ 267 m$\mu$ ($\epsilon$ 485) and 273 m$\mu$ ($\epsilon$ 476); $\nu_{max}$ 3030 (vinyl), 1645 (C=C), 741 (CH out-of-plane bending for 1,2-disubstituted benzene), 2825, 1488, 974, 942, and 863 cm.$^{-1}$.

*Anal.* Calcd for $C_{14}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.29; H, 7.67.

**Reduction of I with Lithium in Alcoholic Ammonia.**—Compound I (180 g) in a solution of 450 ml of ethanol, 1 l. of dry THF, and 4 l. of ammonia was treated with 6 equiv of lithium at −70°. Crystallization of the product from chloroform–benzene furnished III: 89.3 g; mp 147.5–148.5° (analytical sample recrystallized from benzene mp 151–152°); $\nu_{max}$ 2825, 986, and 848, and minor bands at 3030, 1645, and 740 cm$^{-1}$.

---

(11) H. Smith, "Organic Reactions in Liquid Ammonia," John Wiley and Sons, Inc., New York, N. Y., 1963.

(12) A. J. Birch, *J. Roy. Inst. Chem.*, 100 (1957).

(13) E. A. Garlock, Jr., and E. Mossetig, *J. Am. Chem. Soc.*, **67**, 2256 (1945).

*Anal.* Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.40; H, 8.70.

Alternate crystallization of the remainder from acetone and from isooctane furnished III and II, respectively, in over-all amounts of 146 (80%) and 14.7 g (8%).

---

# Condensation of 2-Benzoylbenzoic with 2-Naphthylacetic Acid and Synthesis of Benzo[*a*]pentaphene

ANTONIO MARSILI

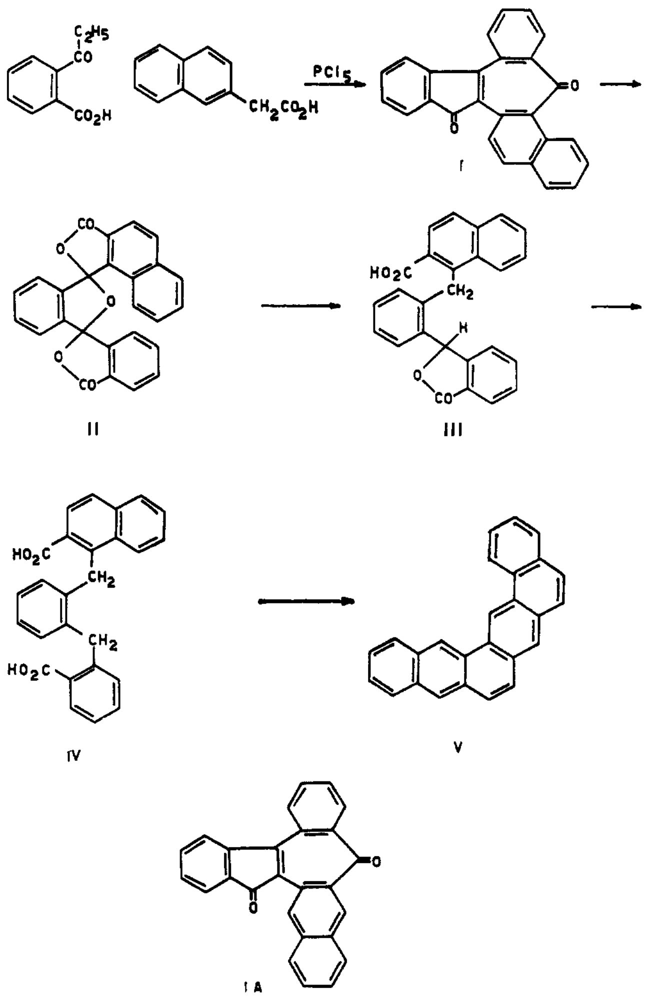
*Istituto di Chimica Farmaceutica e Tossicologicad ell'Universita, Pisa, Italy*

*Received July 13, 1966*

The condensation between 2-benzoylbenzoic and phenylacetic acid to yield a mixture of spiro[3-chloroindene-1,1′-phthalan-3′-one] and 9H,14H-tribenz[*a,e,h*]azulene-9,14-dione, and the easy conversion of the latter compound into pentaphene has previously been reported.[1,2]

When a similar reaction was attempted with 2-naphthylacetic instead of phenylacetic acid as one of the reactants, a single product was isolated for which structure I was assumed on the basis of the infrared absorption spectrum ($\lambda_{CO}$ 5.88 and 6.00 $\mu$) and of consideration of the greater reactivity of the $\alpha$ with respect to the $\beta$ position of the naphthalene nucleus toward electrophilic substitutions. Further work has led to the conversion of I, through the intermediates II, III, and IV, into the still unknown polycyclic aromatic hydrocarbon benzo[*a*]pentaphene (V) (see Scheme I).

SCHEME I



Oxidation of I with potassium permanganate in acetone solution gave the dispiro derivative II (only a single carbonyl absorption band at 5.62 $\mu$). This product, on reduction with zinc dust in aqueous sodium hydroxide, afforded a substance whose infrared spectrum pointed to a five-membered lactone ring ($\lambda_{CO}$ 5.70 $\mu$) and a carboxyl group ($\lambda_{OH}$ 3.11 $\mu$ and $\lambda_{CO}$ 5.82 $\mu$). Structure III was assigned to this compound on the basis of elemental analysis and of the consideration that *o*-(2-naphthoyl)benzoic acid is readily reduced to *o*-(2-naphthylmethyl)benzoic acid by zinc–sodium hydroxide,[3] whereas reduction of 1,1′,3′,1′′-dispirotriphthalane-3,3′′-dione gives only *o*-di(3-phthalidyl)benzene by a similar reaction,[2,4] no reduction taking place beyond this stage. Compound III gave, on protracted reflux with hydriodic acid, the dicarboxylic acid IV and benzo[*a*]pentaphene (V).

The properties of this polycyclic hydrocarbon are different from those of hexaphene,[5] which should be formed if the reaction between 2-benzoylbenzoic and 2-naphthylacetic acid had led to compound IA by condensation at the $\beta$ position of the naphthalene nucleus.

### Experimental Section

Melting points were taken on a Kofler hot stage, and are not corrected. Infrared spectra were recorded, as Nujol mulls, on a Perkin-Elmer Infracord, Model 137, spectrophotometer. Ultraviolet–visible spectra were determined in 95% ethanol using a Beckman Model DU apparatus.

**Condensation between 2-Naphthylacetic and 2-Benzoylbenzoic Acids.**—A mixture of 2-naphthylacetic acid (10 g), 2-benzoylbenzoic acid (12 g), and phosphorus pentachloride (11.3 g) was heated for 1 hr in an oil bath at 140–150°. After addition of benzene (50 ml) the reaction mixture was heated to reflux, then allowed to cool and the solid was filtered to give 5 g of I as red prisms. An analytical sample of the product, after crystallization from xylene, melted at 238–240°.

*Anal.* Calcd for $C_{26}H_{14}O_2$: C, 87.13; H, 3.94. Found: C, 87.45; H, 4.08.

**Oxidation of I with Potassium Permanganate.**—A solution of I (4 g) and potassium permanganate (3.5 g) in acetone (200 ml) was refluxed for 1 hr. After addition of methanol to eliminate excess permanganate and evaporation of the solution, the residue was extracted with 2 *N* sodium carbonate (three 50-ml portions). Acidification of the combined extracts afforded crude II (2.8 g), which was purified by crystallization from benzene. The product so obtained contained benzene, and melted with strong gas evolution at 120–125°.

*Anal.* Calcd for $C_{26}H_{14}O_5 \cdot {}^4/_3\, C_6H_6$: C, 79.99; H, 4.34. Found: C, 80.03; H, 4.26.

Heating *in vacuo* over boiling xylene, caused the substance to lose 21.0% of its weight to yield a vitreous product melting between 140 and 150°.

*Anal.* Calcd for $C_{26}H_{14}O_5$: C, 76.84; H, 3.47. Found: C, 76.95; H, 3.58.

**Reduction of II with Zinc and Alkali.**[6]—A solution of the dispiro derivative II (3 g) in boiling 2 *N* sodium hydroxide (90 ml) was treated portionwise over a 2-hr period with zinc dust (7 g). The mixture was then allowed to boil for a further 2 hr, after addition of 30 ml 2 *N* sodium hydroxide. The hot, alkaline solution

---

(1) A. Marsili and M. Isola, *Tetrahedron Letters*, 3023 (1965).

(2) A. Marsili and M. Isola, *Tetrahedron*, in press.

(3) R. Scholl, C. Seer, and A. Zinke, *Monatsh.*, **41**, 583 (1920).

(4) E. Clar and D. G. Stewart, *J. Chem. Soc.*, 3215 (1951).

(5) E. Clar, *Ber.*, **73**, 81 (1940).

(6) Modification of the procedure is described by Clar; see ref 4.