Analysis of this sample for deuterium by nmr spectroscopy indicated that *no* deuterium exchange had occurred.

Benzylmagnesium Chloride and Ethyl Chlorocarbonate.—To ethyl chlorocarbonate (65.1 g, 0.6 mol) in 100 ml of anhydrous ether was added slowly 750 ml of a 0.4 *M* solution of benzylmagnesium chloride in ether. The temperature of the reaction mixture was kept at 0 to −5° by a Dry Ice–acetone bath. After this addition was completed, the mixture was stirred for 1 hr and then hydrolyzed with 100 ml of 15% hydrochloric acid followed by 100 ml of water. Following the usual work-up, the solvent was removed and the residue analyzed by vpc (4 ft × 0.25 in. stainless steel column packed with Apiezon L on 60–80 mesh Chromosorb W). The following products[20] were identified: ethyl phenylacetate (31%), tribenzylcarbinol (21%), ethyl *o*-toluate (12%), β,β-bis(benzyl)styrene (13%), and diethyl homophthalate (1%). Neither ethyl *p*-toluate nor diethyl homoterephthate could be detected by vpc.

To 3 g of the crude reaction product in 250 ml of boiling water containing 25 g of KOH was slowly added 13 g of finely powdered potassium permanganate. The mixture was refluxed 4 hr, and then the excess permanganate was destroyed by adding a small amount of ethanol. The heavy manganese dioxide precipitate was washed with a small amount of dilute alkali, and the filtrate and washings were combined and acidified with hydrochloric acid. The organic acids were extracted with ether and then esterified with diazomethane. Analysis by vpc (4 ft × 0.25 in. Apiezon L on Chromosorb W) showed the products to be methyl benzoate and dimethyl phthalate in that their nmr and infrared spectra matched those of an authentic sample. No dimethyl terephthalate could be detected.

Benzylmagnesium Chloride and Ethyl Formate.—The procedure was the same as that described for ethyl chlorocarbonate except that 44.4 g (0.6 mol) of ethyl formate was used. Analysis of the product was by vpc (5 ft × 0.25 in. column packed with 5% FFAP on 60–80 mesh Chromosorb W). Only phenylacetaldehyde was formed in any quantity (14%) in addition to considerable amounts of tar (25 g). The following materials were also identified: benzaldehyde (3%), benzyl formate (5%), β-phenylethyl formate (3%), benzyl alcohol (4%), and β-phenylethanol (1%).[21]

The crude mixture obtained from this reaction was oxidized by permanganate in essentially the same way as for ethyl chlorocarbonate. After work-up and esterification with diazomethane, the methyl esters were again analyzed by gc. Only methyl benzoate and dimethyl phthalate were found; no dimethyl terephthalate could be detected.

Registry No.—Benzylmagnesium chloride, 6921-34-2; benzyllithium, 766-04-1; *o*-(*n*-propyl)ethylbenzene, 16021-20-8.

Acknowledgment.—This research was supported by the U. S. Army Research Office (Durham) to whom the authors are deeply indebted.

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[20] Each of these materials was isolated by gc and were identical in retention time, nmr, and infrared spectra with authentic samples. The percentages listed are yields based on benzylmagnesium chloride and were determined by vpc using ethyl benzoate as an internal standard.

[21] The yields given are based on benzylmagnesium chloride and were obtained by gc using *o*-bromotoluene as an internal standard.

Metal–Ammonia Reduction. III. Stepwise Transformation of Polycyclic Aromatic Hydrocarbons[1,2]

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Reduction of benz[*a*]anthracene to dodecahydrobenz[*a*]anthracene in controlled stages *via* di-, tetra-, hexa-, octa-, and decahydrobenz[*a*]anthracene is achieved by means of lithium dissolved in liquid ammonia or liquid amine solvents. Utilization of nuclear magnetic resonance spectra and mass spectra to distinguish isomeric hydroaromatic structures is described.

Although the reduction of aromatic ring systems by alkali metals dissolved in liquid ammonia was observed by LeBeau and Picon[3] in 1914, it was not until the elegant investigations of Birch[4] and his collaborators that the method achieved acceptance as a major synthetic tool. The state of current knowledge, summarized in an excellent comprehensive monograph by Smith,[5] is surprisingly deficient regarding substances other than monobenzenoid molecules. Naphthalene,[3,6,7] anthracene,[8-10] phenanthrene,[7,11] pyrene,[12] fluorene,[13] and acenaphthene[8] are apparently the only polycyclic aromatic hydrocarbons to be investigated. Precautions for the exclusion of impurities known to affect the course of such reactions (trace metals,[2,14] peroxides, oxygen[15]) are seldom mentioned in the earlier literature, and characterization of the hydroaromatic products is often unsatisfactory by modern standards. Extensive reduction, often accompanied by disproportionation of products, is common. Also, the stepwise reduction of compounds possessing three or more fused aromatic rings had not been described prior to our studies in this field.[2,16]

Since controlled transformation of polycyclic aromatic hydrocarbons would provide hydroaromatic substances of considerable interest as synthetic intermediates,[17] we undertook to reinvestigate the

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[1] This investigation was supported in part by U. S. Public Health Service Research Grant CA-08674 from the National Cancer Institute. Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] Part II: R. G. Harvey and K. Urberg, *J. Org. Chem.*, **33**, 2571 (1968).

[3] P. LeBeau and M. Picon, *Compt. Rend.*, **158**, 1514 (1914).

[4] A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

[5] H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, part 2, John Wiley and Sons, Inc., New York, N. Y., 1963.

[6] C. B. Wooster and F. B. Smith, *J. Amer. Chem. Soc.*, **53**, 179 (1931); A. J. Birch, A. R. Murray and H. Smith, *J. Chem. Soc.*, 1945 (1951); W. Hückel and H. Schlee, *Ber.*, **88**, 346 (1955).

[7] W. Hückel and H. Bretschneider, *Ann.*, **540**, 157 (1939).

[8] P. LeBeau and M. Picon, *Compt. Rend.*, **159**, 70 (1914).

[9] H. F. Miller and G. B. Bachman, *J. Amer. Chem. Soc.*, **57**, 768 (1935).

[10] A. J. Birch, *et al.*, *J. Chem. Soc.*, 2209 (1963); J. Runge, *Z. Chem.*, **2**, 374 (1962); *J. Prakt. Chem.*, [4] **31**, 280 (1966).

[11] S. Mejer, *Bull. Acad. Polon. Sci., Chim.*, **9**, 773 (1961).

[12] O. Neunhoeffer and H. Woggon, *Ann.*, **600**, 34 (1956); O. Neunhoeffer, H. Woggon, and S. Dähne, *ibid.*, **612**, 98 (1958).

[13] W. Hückel and R. Schwen, *Ber.*, **89**, 481 (1956).

[14] H. L. Dryden, Jr., G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

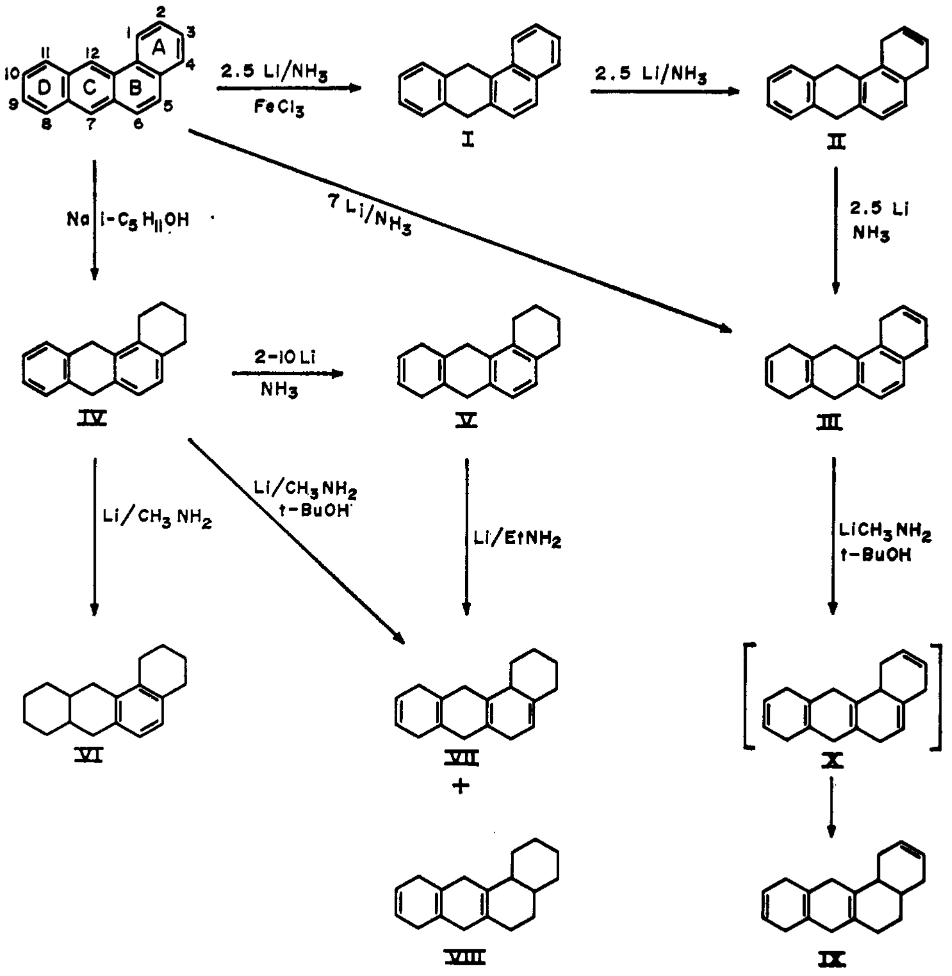
[15] J. F. Eastham and D. R. Larkin, *J. Amer. Chem. Soc.*, **81**, 3652 (1959).

[16] R. G. Harvey, *J. Org. Chem.*, **32**, 238 (1967).

[17] For example, compounds with an internal double bond, such as V and VI, may serve as precursors to polycyclic hydrocarbons having a cyclopropyl ring fused along the ring juncture. Synthesis of several such unusual molecules will be reported shortly.

SCHEME I

STEPWISE REDUCTION OF BENZ[a]ANTHRACENE



addition of alkali metals to higher ring systems in ammonia and amine solvents. A preliminary paper described[16] reduction of 9,10-dihydroanthracene to the tetra and hexahydro stages by lithium in liquid ammonia and verified that conditions play a dominant role in the reduction of this polycyclic aromatic hydrocarbon.[18] Limitation of reduction to a single stage was favored, predictably, by low lithium-hydrocarbon ratios (optimum $\sim$2.5) and by total solution of the aromatic compound. Also, it proved advantageous to withhold addition of the proton source (*i.e.*, alcohol) until late in the reaction period, then to add it rapidly.

The present paper reports stepwise conversion of the more complex polycyclic aromatic hydrocarbon, benz[a]anthracene, through the dodecahydro level. For the assignment of structural formulas to the derivatives, the techniques of nmr and mass spectroscopy were utilized extensively. Also, qualitative assessment of product distribution was achieved by charge-transfer chromatography[19] on thin layers of silica gel impregnated with *s*-trinitrobenzene.

Results

Treatment of benz[a]anthracene with lithium[20] in liquid ammonia under standard conditions led to 1,4,7,8,11,12-hexahydrobenz[a]anthracene (III) in separate consecutive reactions *via* 7,12-dihydrobenz[a]anthracene (I) and 1,4,7,12-tetrahydrobenz[a]anthracene (II) (Scheme I). Each reaction proceeded in good yield (Table I). Owing to the enhanced resistance of III to further transformation, direct synthesis of III from benz[a]anthracene proved to be practicable, with 7–10 equiv of lithium being optimum.

The positions of the incoming hydrogens were accurately predicted through consideration of the relative stabilities of the intermediate radical anions and/or dianions. Qualitatively, these were assumed to be secondary > tertiary and benzyl > allyl > aliphatic. Quantitative predictions are theoretically possible; according to HMO theory, the protons may be expected to attach to the positions of highest electron density in the hydrocarbon dianion.[21] However, the coefficients of the lowest vacant molecular orbitals have not been calculated, except for benz[a]anthracene.[22]

Benz[a]anthracene is known to form a 7,12-dilithio adduct.[23] The nmr spectrum of I displayed a pair of doublets at τ 5.67 and 5.87 (J = 3 Hz) assigned to the

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[18] However, the effect of variation of conditions may be different from that for monobenzenoid substances, owing to the probable importance of dianionic intermediates in more highly conjugated molecules.

[19] R. G. Harvey and M. Halonen, *J. Chromatog.*, **25**, 294 (1966).

[20] Preliminary tests indicated reactions of anthracene and benz[a]anthracene to proceed more cleanly with lithium than with sodium.

[21] E. Hückel, International Conference on Physics, London, 1934, Vol. II, p 9.

[22] A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 425.

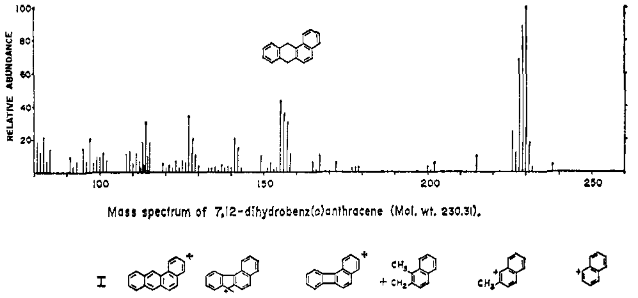
[23] W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936).

Table I

Hydrobenz[*a*]anthracene Compounds

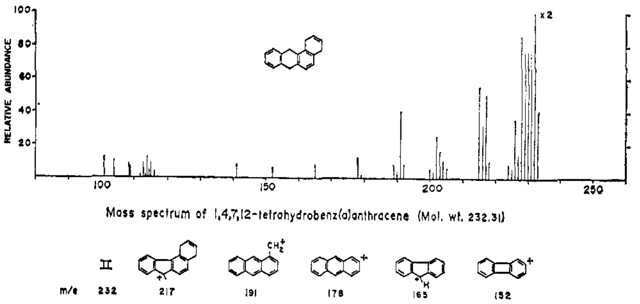
Compound	Formula	Mp, °C	Yield, %	R_f × 100[a]	Calcd, % C	Calcd, % H	Found, % C	Found, % H
I	$C_{18}H_{14}$	111–112[b]	94	19				
II	$C_{18}H_{16}$	100.5–102	66	26	93.06	6.94	93.35	6.91
III	$C_{18}H_{18}$	141–42	82	32	92.26	7.74	92.44	7.77
IV	$C_{18}H_{18}$	69.5–70.3[c]	65	35				
V	$C_{18}H_{20}$	111–111.5	94	35	91.47	8.53	91.58	8.42
VI	$C_{18}H_{24}$	113.5–114.4	54	60	89.94	10.06	89.83	9.94
VII	$C_{18}H_{22}$	133.5–134	70	59	90.70	9.30	90.50	9.35

[a] R_f values are for chromatography on thin layers of silica gel impregnated with *s*-trinitrobenzene prepared as previously described[14] employing benzene–heptane 3:7 as the eluting solvent. [b] Lit.[21] mp 112–112.5°. [c] Lit.[25] mp 69.3–69.9°.



Mass spectrum of 7,12-dihydrobenz(a)anthracene (Mol. wt. 230.31).

Figure 1.



Mass spectrum of 1,4,7,12-tetrahydrobenz(a)anthracene (Mol. wt. 232.31)

Figure 2.

C-12 and C-7 benzylic protons, respectively, on the basis of the greater downfield shift of the methyl protons of 1-methylnaphthalene (τ 7.33) relative to those of the 2 isomer (τ 7.52).

At the second stage, the least substituted ring (A in Scheme I) of the more reactive naphthalene portion of I may be expected to be most susceptible to attack. Compare the resulting 1,4 dianion (benzylic–allylic) with the alternative intermediates formed by attack at ring B (5,12a dianion having a negative charge at a ring juncture) or at ring D (diallylic 8,11 dianion). In agreement with the predicted structure, II, there occurred in the nmr region a broad singlet at τ 3.97 (two vinylic protons), a doublet at τ 2.87 (J = 3.5 Hz), an apparent singlet at τ 2.78 (aromatic protons at C-5,6, and C-8–11, respectively), and singlets at τ 7.10 and 7.57 (benzylic protons at C-7,12 and C-1,4, respectively). Assignment of the τ 7.10 peak to the C-7,12 protons is based on the identity of this value with that observed for the benzylic protons of 9,10-dihydroanthracene.[16] The least substituted of the two aromatic rings of II should provide greatest stabilization for a 1,4 radical anion. Assignment of structure III to the third stage product was supported in the nmr spectrum by apparent singlets at τ 4.10 and 4.20 (vinylic protons at C-2,3 and C-9,10, respectively; the latter is consistent with τ 4.20 and 4.27 for the related protons of 9,10-dihydroanthracene[16] and V, respectively) and by additional peaks for the appropriate numbers of protons at τ 7.33 (allylic), 2.90 (aromatic), and 6.73, 6.72, and 6.85 (benzylic at C-1,4, C-7, and C-12, respectively; the latter appeared as doublets, J = 7 Hz).

The resistance of III to further reduction necessitated employment of the more powerful lithium–amine system of Benkeser.[24] However, the strong tendency of this reagent toward extensive isomerization and reduction of double bonds indicated the desirability of short reaction time and careful control of other conditions. In order to devise satisfactory conditions, a series of test reactions were carried out with 1,2,3,4,7,12-hexahydrobenz[*a*]anthracene (IV), obtained from treatment of the parent aromatic hydrocarbon with sodium in refluxing isoamyl alcohol.[25] Delayed or slow addition (>5 min) of alcohol to a solution of IV and lithium in methylamine favored formation of 1,2,3,4,7,7a,8,9,10,11,11a,12-dodecahydrobenz[*a*]anthracene (VI) or further reduction products. Conversely, reduction in the presence of *t*-butyl alcohol furnished 1,2,3,4,6,7,8,11,12,12b-decahydrobenz[*a*]anthracene (VII) plus a lesser proportion of a further reduction product, VIII. It is likely that VI arises from the intermediate octahydro derivative, V, *via* base-catalyzed isomerization of the double bonds into conjugation followed by further reduction, rather than *via* direct reduction of the unsaturated bonds,[24] a kinetically unfavorable process. V was most efficiently synthesized directly from IV with lithium in ammonia. The structure of V was supported by peaks at τ 4.20 (two vinylic protons), 3.08 (two aromatic protons), 7.33 (four allylic protons), 8.20 (four aliphatic protons as a quintet, J = 3 Hz), and a broad absorption at τ 6.84 (benzylic protons) in the nmr spectrum.

Lithium–methylamine (or ethylamine) reduction of V furnished VII and VIII accompanied by traces of minor products. Finally, treatment of III with lithium and *t*-butyl alcohol in methylamine provided 1,4,4a,5,6,7,8,11,12,12b-decahydrobenz[*a*]anthracene (IX) rather than the expected octahydro derivative, X.

The tendency toward isomerization and polyreduction in amine solvents necessitated caution in assigning structures VI–IX. The extent of reduction was determined with high accuracy from the mass spectra. The parent peak of VII and IX appeared at *m/e* 238 cor-

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[24] R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *J. Org. Chem.*, **28**, 1094 (1963).

[25] L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, **59**, 2502 (1937).

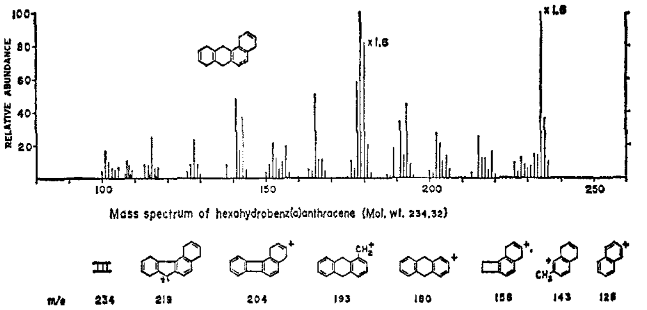


Figure 3.

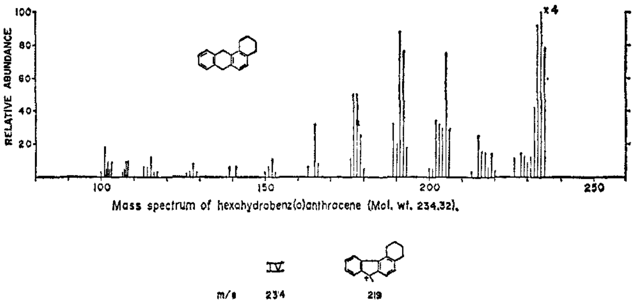


Figure 4.

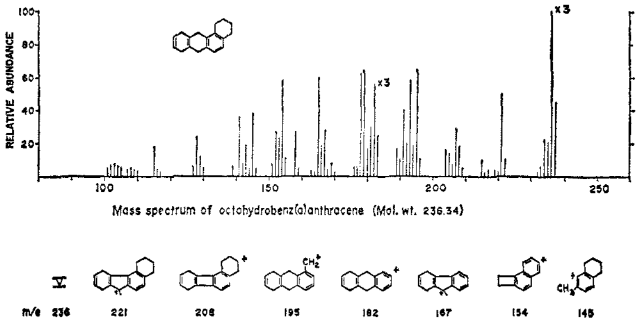


Figure 5.

responding to $C_{18}H_{22}$ (decahydro), while those of VI and VIII were found at *m/e* 240 corresponding to $C_{18}H_{24}$ (dodecahydro). Positions of the double bonds were deduced by analysis of nmr and mass spectral data.

Observed cleavage patterns, generally consistent with current knowledge of the behavior of cyclic olefins under electron beam bombardment,[26] were distinguished by a high proportion of peaks of relatively large mass (Figures 1–8). Also evident is a strong tendency toward aromatization. Associated with each major fragment are a series of peaks identified as arising *via* successive loss of allylic hydrogen until the fully aromatic ion is attained. Loss of methylene accounts for a series of commonly observed minor peaks (*e.g.*, *m/e* 165, 215, and 217 in Figure 2). Double loss of methylene with formation of biphenylene derivatives also appears to take place (*e.g.*, *m/e* 202 in Figure 1). The position, or positions, from which such loss occurs may be ascertained with decreasing certainty as the number of possibilities increases (*i.e.*, with increasing extent of reduction). The suggested probable structures indicated below the figures[27] should be viewed in this light. Finally, cyclic olefins may be expected to decompose *via* the well-known retro Diels–Alder pathway.[26,28,29] Indeed, the spectrum of IX, the only compound in the series I–IX to contain a suitable cyclohexene ring, exhibits a major peak (*m/e* 184) indicative of loss of a butadiene fragment. Analogous decomposition of the nonconjugated cyclohexadiene structures of III, V, and VII–IX with release of an acetylenic component was not detected. This process appears, therefore, to be relatively unfavorable. On the other hand, the presence of fused aromatic rings on one or both of the double bonds of 1,4-cyclohexadiene generally leads to fragments which may be rationalized as arising from reversal of the Diels–Alder reaction. Formation of benzyne may be involved (eq 1).

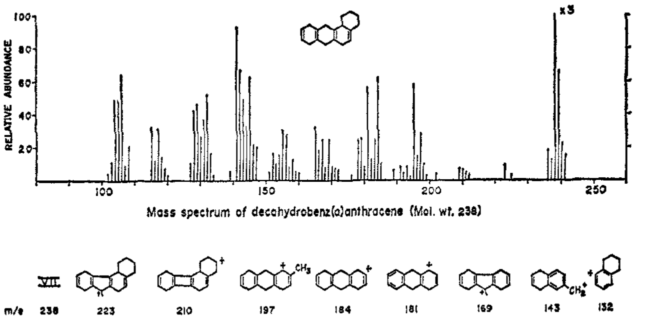


Figure 6.

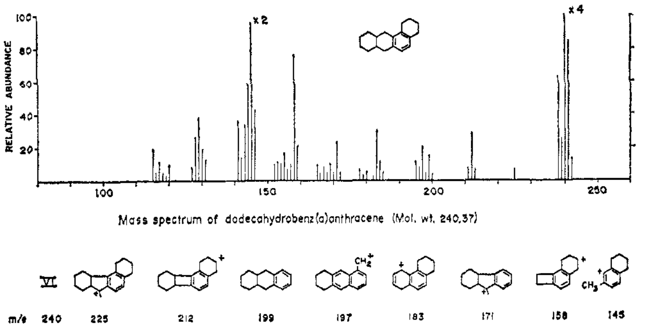


Figure 7.

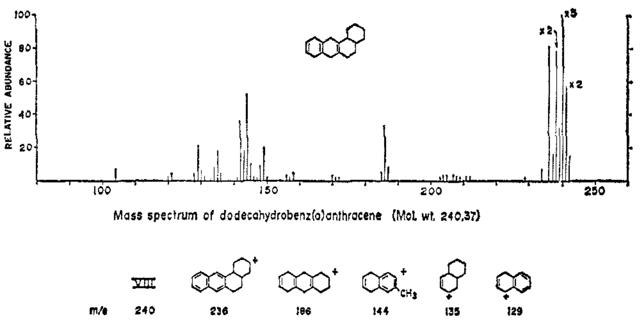
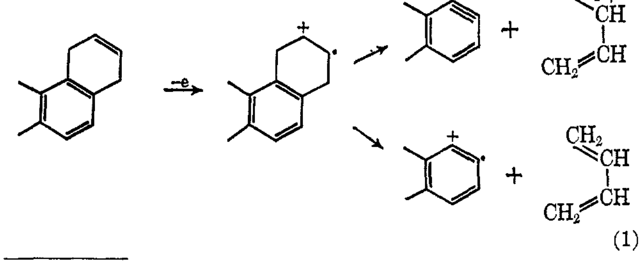


Figure 8.



(1)

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[26] K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[27] The benzylic cations in these figures may exist partially or even exclusively as the corresponding tropylium ions; see S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

[28] K. Biemann, *Angew. Chem.*, **74**, 102 (1962).

[29] H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

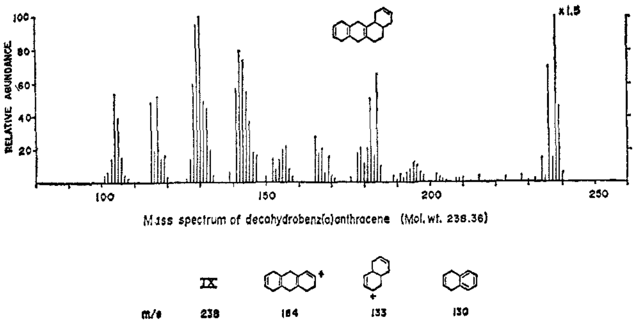
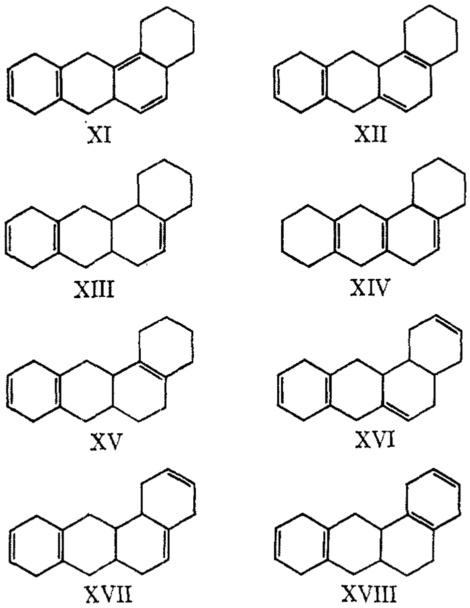


Figure 9.

The mass spectral data proved to be a valuable supplement to the nmr data in ruling out certain possible isomeric structures. Thus, the alternative structure XI for the decahydrobenz[*a*]anthracene (VII) obtained from treatment of IV or V with lithium in methylamine is inconsistent with the presence of three vinylic protons in the nmr region, appearing as a singlet at τ 4.25 (2 H at C-9,10) and a broad band at τ 4.62 (1 H at C-5) (Chart I). A second alternative formula, XII, may not be rejected on the basis of proton resonance data alone, owing to the broad overlapping nature of the singly allylic and aliphatic bands. However, the absence of a fragment in the *m/e* 210 region of the mass spectrum (corresponding to reverse Diels–Alder reaction in the cyclohexene ring) argues strongly against XII.

CHART I



Similarly, VIII was established as the formula of the triolefin obtained from the same reaction. Alternative structures XIII and XIV failed to satisfy the nmr absorption pattern which displayed bands at τ 4.30 (2 H), 7.45 (4 H), and 7.55 (4 H) due to vinylic, outer ring allylic and adjacent ring allylic protons, respectively. The final reasonably probable structure, XV, was most convincingly excluded by the absence of any significant peaks in the *m/e* 212 region of the mass spectrum, corresponding to loss of ethylene from ring A.

The second dodecahydro compound was identified as VI on the basis of chemical probability, nmr spectrum (two aromatic protons at τ 3.17), and mass spectral cracking pattern.

For the remaining decahydro compound, three structures (XVI–XVIII) must be considered in addition to the assigned structure, IX. XVI and XVII may be rejected as incompatible with the nmr data (four vinylic hydrogens, τ 4.30). The major peak at *m/e* 184 in the mass spectrum, while not readily explicable in terms of XVIII, is simply interpreted as resulting from the retro Diels–Alder reaction in IX (as discussed earlier).

The structures of the hydroaromatic products I–V conform closely to prediction based on consideration of the relative stabilities of the intermediate charged precursors. It is less obvious why reduction of the B ring of V should furnish VII rather than XII. Both structures place a charge on a tertiary position in the intermediate, and should be favored in preference to XI which would necessitate charge at two tertiary carbon atoms. Models indicate VII to be free to adopt a relatively unstrained conformation bent in the C ring, whereas XII is considerably more rigid and strained. The origin of VIII and IX is presumably *via* isomerization of the appropriate double bond of VII and X into conjugation, followed by subsequent rapid reduction.

Finally, it should be pointed out that the hydrobenz[*a*]anthracene compounds reported herein represent only a small fraction of many conceivable isomeric structures. Other isomers may be made available by combination of the metal–ammonia technique with other methods of hydrogenation.[30]

Experimental Section

Physical Data.—Melting points were taken on a Leitz Kofler hot-stage microscope and are corrected. Proton nmr spectra were obtained on a Varian Model A-60 spectrophotometer with chemical shifts reported relative to tetramethylsilane in deuteriochloroform. For mass spectral analysis an A.E.I MS9 double-focusing mass spectrometer was employed with the source set at 200° and the electron beam energy at 70 eV.

Material and Methods.—Ammonia, monomethylamine, and monoethylamine (Matheson Co.) were distilled into the reaction vessel through a column of barium oxide (10–12 mesh) except where otherwise indicated. Benz[*a*]anthracene (Terra Chemicals, Inc.) was dissolved in hot ethanol, filtered, and recrystallized (mp 160–162°). 1,2,3,4,7,12-Hexahydrobenz[*a*]anthracene (IV) was prepared by reduction of benz[*a*]anthracene with sodium and isoamyl alcohol, according to the method of Fieser and Hershberg.[25] Tetrahydrofuran (THF) was purified by distillation from $LiAlH_4$ and stored over CaH_2 under nitrogen. Lithium wire (Lithium Corp. of America) was wiped free of oil and washed with hexane before use. Thin layer plates of silica gel impregnated with *s*-trinitrobenzene were prepared by the method previously described.[15] Silica gel for column chromatography (Davison, Grade 950, mesh 60–200) was activated by heating overnight at 100°.

All reductions in ammonia were carried out employing the conditions reported earlier[2,16] unless specific variations are cited. Precautions for the exclusion of atmospheric oxygen and moisture were scrupulously followed; all reductions were carried out under helium (preferable to nitrogen owing to the ease of lithium nitride formation).

7,12-Dihydrobenz[*a*]anthracene (I).—A solution of benz[*a*]anthracene (1.14 g, 5 mmol) in 75 ml of dry THF was added to a flask containing 150 ml of liquid ammonia and 40 mg of ferric chloride. To the resulting solution at reflux temperature was added lithium wire (85 mg, 12 mg-atoms). The blue color of the

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[30] For example, catalytic hydrogenation of benz[*a*]anthracene[25] yields 8,9,10,11-tetrahydrobenz[*a*]anthracene, the lithium–ammonia reduction of which should lead to a different series of hydrobenz[*a*]anthracene derivatives than reported herein.

solution was discharged after 2 hr by rapid addition of alcohol. After evaporation of the ammonia and dilution with water, the product was obtained by filtration. It was taken up in acetone and filtered to remove a residue; the solvent was removed *in vacuo* to provide I (1.08 g, mp 111–112°).

1,2,7,12-Tetrahydrobenz[*a*]anthracene (II).—A similar procedure was followed for the reduction of I, except that ferric chloride was omitted. The oily yellow solid obtained was purified by chromatography on silica gel to give II as white flakes, mp 96–98°.

1,4,7,8,11,12-Hexahydrobenz[*a*]anthracene (III) was obtained both directly from II and from benz[*a*]anthracene, in both cases employing a method analogous to that employed for preparation of II. With benz[*a*]anthracene as the starting material, 7–10 equiv of lithium/mol of benz[*a*]anthracene provided optimum yield (Table I); greater excess led to increasing quantity of minor side products (detected on thin layers of trinitrobenzene on silica gel). These substances are suspected to arise from isomerization of double bonds into conjugation, followed by their reduction, rather than from hydrogenation of the B ring.

1,2,3,4,7,8,11,12-Octahydrobenz[*a*]anthracene (V).—To a solution of IV (1.17 g, 5 mmol) in 75 ml of THF and 150 ml of liquid ammonia was added lithium (694 mg, 100 g-atoms). The stirred solution was maintained at gentle reflux for 3 hr; then 20 ml of ethanol in 30 ml ether was added from a dropping funnel over a 45-min period. After evaporation of the ammonia, the solution was partitioned between ether and water. The ether phase was dried over magnesium sulfate and evaporated to dryness. Recrystallization of the resulting white solid from ethanol gave pure V (Table I).

Reduction of IV with Lithium in Methylamine.—IV (1.17 g, 5 mmol) was added to a solution of lithium (347 mg, 50 g-atoms) in 250 ml of liquid methylamine at reflux; 30 sec later 5 ml of *t*-butyl alcohol was added as rapidly as practicable. When the intense blue color of the solution disappeared (8 min), ethanol (5 ml) and water (10 ml) were added. Removal of the amine by evaporation, followed by partition of the product between ether and water, gave the crude product, recrystallization of which from ethanol furnished pure VII (Table I).

The mother liquors were evaporated to dryness and chromatographed on a column of silica gel prepared in petroleum ether (bp 30–60°). Elution with hexane gave the dodecahydro compound VI (42 mg) followed by an oily solid (445 mg), identified as the isomer VIII. Recrystallization from ethanol–methanol at 4° furnished pure VIII (Table I), a compound which appeared to be especially sensitive to autooxidation.

An analogous reaction in which the *t*-butyl alcohol was added 15 min after the lithium (243 mg, 7 g-atoms) over a 5-min period furnished VI as the major product. Recrystallization from ethanol gave the analytical sample of VI (mp 113.5–114.5°, white needles). Thin layer chromatography of the mother liquor showed a major spot of higher R_f value (probably, therefore, a tetradecahydro derivative) which was not investigated further.

Reduction of III with Lithium in Methylamine.—Lithium (208 mg, 6 g-atoms) was added to a solution of 3 ml of *t*-butyl alcohol in 250 ml of methylamine at reflux. Then 2 min later III (1.17 g, 5 mmol) was added, followed by 15 ml THF in order to bring into solution the incompletely dissolved hydrocarbon. The blue color disappeared within 10 min. Work-up in the usual manner gave an oil (1.12 g), revealed by thin layer chromatography to contain two principal components. Chromatography on silica gel with elution by hexane furnished IX (716 mg) as a viscous oil.

Registry No.—I, 16434-59-6; II, 16434-60-9; III, 16434-61-0; IV, 16434-62-1; V, 16434-55-2; VI, 16452-37-2; VII, 16434-56-3; VIII, 16434-57-4; IX, 16434-58-5.

A Method for the Addition of the Elements of Ketene to Some Selected Dienes in Diels–Alder Fashion

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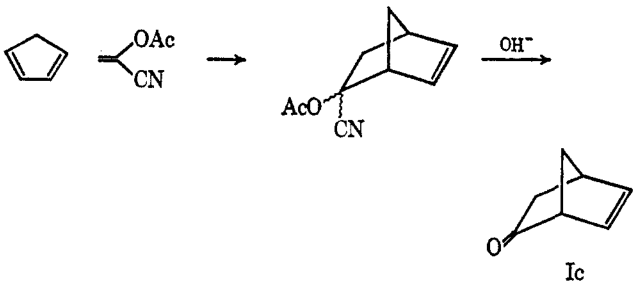
New and improved syntheses for dehydronorcamphor, bicyclo[2.2.2]oct-2-en-5-one, and tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonan-8-one and the syntheses of tricyclo[4.2.2.0^{2,5}]deca-3,7-dien-9-one and tricyclo[3.2.2.0^{2,4}]non-6-en-8-one are described. These syntheses consist of Diels–Alder or homo Diels–Alder addition of acrylonitrile, chlorination of the nitrile adduct with phosphorus pentachloride, followed by hydrolysis of the resulting α-chloronitrile with potassium hydroxide in aqueous dimethyl sulfoxide.

The addition of ketenes to dienes yields products in which a cyclobutanone moiety is produced by cycloaddition of the ketene to a single double bond.[1] This mode of reaction is distinguished from normal Diels–Alder addition in which a double bond adds 1,4 across a conjugated system. The alternative routes available for achieving the syntheses of addition products, which conceptually are the result of Diels–Alder addition of ketene, have been complicated by two factors. Dienophiles capable of forming adducts which are easily convertible to ketones, such as vinyl acetate, will not add easily to the less reactive dienes. On the other hand, dienophiles that do add easily to most dienes such as acrylonitrile or acrylate esters are not easily convertible to the corresponding ketone. Bartlett and Tate[2] suggested an elegant solution to this problem in their synthesis of dehydronorcamphor (Ic) from α-acetoxyacrylonitrile and cyclopentadiene (Scheme I). This method suffers principally from the commercial unavailability of α-acetoxyacrylonitrile.[3]

SCHEME I



In more recent studies Paasivirta and Krieger[4] prepared dehydronorcamphor (Ic) and bicyclo[2.2.2]oct-2-en-5-one (IIc) from chloronitriles, which were obtained by adding α-chloroacrylonitrile to cyclo-

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(1) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 2 (1962).

(2) P. D. Bartlett and B. E. Tate, *J. Amer. Chem. Soc.*, **78**, 2473 (1956).

(3) R. M. Nowak, *J. Org. Chem.*, **28**, 1182 (1963).

(4) J. Paasivirta and H. Krieger, *Suomen Kemistilehti, B*, **38**, 182 (1965); J. Paasivirta, *Suomen Kemistilehti, A*, **39**, 120 (1966); see also H. Krieger and S. E. Masar, *ibid.*, **39**, 119 (1966).