slowly to 350° by a Woods metal-bath, while a stream of dry nitrogen was swept through the flask. The temperature of the bath was kept at 350–370° for 5 hours. At the end of 5 hours, the anthracene was removed by sublimation. The residue was extracted in a Soxhlet apparatus with hot benzene for 40 hours. The benzene solution was freeze-dried for 48 hours at 0.1 to 0.05 mm. pressure. A 110 mg. yield of a fluffy, tan powder was obtained, which was very soluble in benzene, chloroform and carbon disulfide and partially soluble in carbon tetrachloride. It was insoluble in methanol and acetone. The material appeared to melt at 240–250°. The infrared spectrum of the tan powder was almost identical to the spectra obtained from the product of the chloranil dehydrogenation reaction. All absorption maxima characteristic of *p*-polyphenyls were present, with the maximum at 811 cm.$^{-1}$ corresponding to 1–4 aromatic substitution being the most intense absorption. The spectrum also showed maxima corresponding to saturated carbon–hydrogen bond vibrations at 2930 and 2850 cm.$^{-1}$, indicating incomplete aromatization. Analysis of the product gave the empirical formula $(C_6H_{5.7})_x$.

Anal. Calcd. for $(C_6H_4)_x$: C, 94.74; H, 5.26. Found: C, 91.59; H, 7.21.

Some autoxidation apparently occurred after the attempted dehydrogenation.

Attempted dehydrogenation of poly-1,3-cyclohexadiene using N-bromosuccinimide in the presence of benzoyl peroxide and also using sulfur in boiling dimethylformamide gave products which were indicated by their infrared spectra to possess some aromatic character.

URBANA, ILL.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

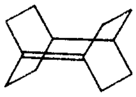
Anthracene Photodimers. I. Elimination and Substitution Reactions of the Photodimer of 9-Bromoanthracene[1]

BY DOUGLAS E. APPLEQUIST, ROBERT L. LITLE, EDWIN C. FRIEDRICH AND ROBERT E. WALL

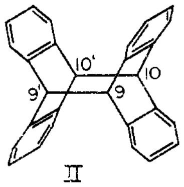
RECEIVED JULY 31, 1958

Chemical evidence for the head-to-tail structure of the photodimer of 9-bromoanthracene has been obtained. The dimer has been found to undergo transannular elimination of bromine with zinc, lithium aluminum hydride or organolithiums to give a new tetracyclododecane ring system. Products from halogen–metal exchange and from possible elimination–addition reactions have also been characterized. *t*-Butoxide ion has been found to dehydrobrominate the dimer with simultaneous ring opening to a 9,9′-dianthryl. Some examples of photoadducts of anthracene with substituted anthracenes have been discovered.

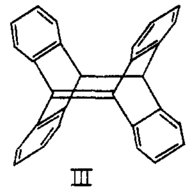
An olefin possessing a unique variety of strain is tricyclo[4.2.2.2^{2,5}]dodecene-1 (I), since the σ-bonds around the double bond must be distorted out of the nodal plane of the π-bond, and yet as a result of the symmetry of the molecule, the coplanarity of the *p*-orbitals of the π-bond is undisturbed. Thus although I formally violates Bredt's rule,[2] it may be expected to have appreciable stability, and might be isolable in pure form. Compound I would be of interest as a tool for observing the chemical consequences of the σ–π-interference strain mentioned above and for a study of the stereochemistry of addition and elimination reactions in the same sense that bridgehead substituted compounds have been used to expose stereochemical requirements of substitutions reactions.[3] The only known examples of the tricyclododecane skeleton of I are anthracene photodimer II and the dimers of substitutued anthracenes.[4]



I



II



III

9-Anthraldehyde, methyl 9-anthroate and 9-hydroxymethylanthracene have been shown to give the head-to-head dimers (9,9′-disubstituted dianthracenes),[4] and it was anticipated that 9-bromoanthracene would dimerize in the same manner to give a compound which could be debrominated to 9,9′-dehydrodianthracene (III), a simple derivative of I.

9-Bromoanthracene did in fact dimerize readily in benzene solution in sunlight, but the only dimer isolated was 9,10′-dibromodianthracene (IV), the head-to-tail product, as shown by its zero dipole moment[5] and by the debromination to 9,10′-dehydrodianthracene (V) with zinc, lithium aluminum hydride or organolithiums, as discussed below. The simple free radical mechanism suggested by Greene[4] for the dimerization does not appear to account for the structure of the 9-bromoanthracene dimer. It is hoped that further work in progress will clarify the nature of the product-determining transition state.

The reaction of IV with zinc in acetone or with lithium aluminum hydride in tetrahydrofuran gave mainly dianthracene (II), but also small amounts of V, a thermostable, colorless, crystalline solid, subliming at about 320° and melting at 369–370°. It showed absorption maxima at 212 mμ (pseudomax., log ϵ 4.82) and 290 mμ (log ϵ 3.35), in satisfactory agreement with a structure containing four *o*-xylene chromophores.[6] The saturated character of V was demonstrated by its failure to react with

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(1) Presented at the 131st Meeting of the American Chemical Society at Miami, Fla., in April, 1957.

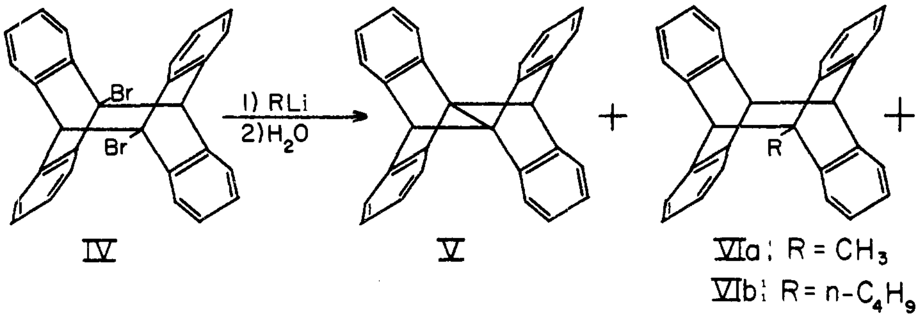
(2) F. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

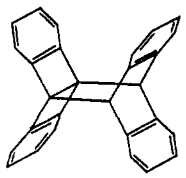
(3) D. E. Applequist and J. D. Roberts, *ibid.*, **54**, 1065 (1954).

(4) F. D. Greene, S. L. Misrock and J. R. Wolfe, Jr., THIS JOURNAL, **77**, 3852 (1955).

(5) D. E. Applequist, E. C. Friedrich and M. T. Rogers, *ibid.*, **81**, 457 (1959).

(6) Compare with the spectra of 9,10-dihydroanthracene (R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectrum 114), triptycene (P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950)) and dianthracene (C. A. Coulson, L. E. Orgel, W. Taylor and J. Weiss, *J. Chem. Soc.*, 2961 (1955)).

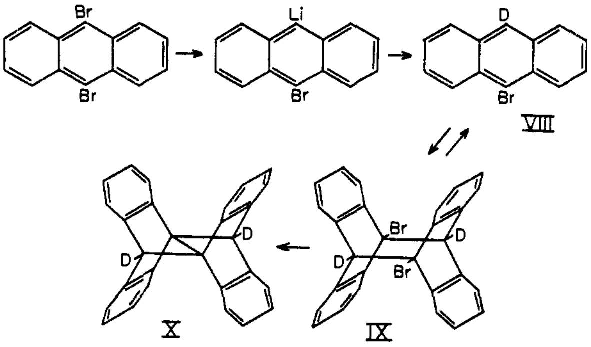



VII

bromine, alkyllithiums, osmium tetroxide, perbenzoic acid, hydrogen (platinum catalyst) or lithium aluminum hydride.

Further to distinguish V from the possible isomeric compounds III and VII, a sample of IV bearing two deuterium atoms per molecule (Chart I) on the bridgeheads was converted to V by the reaction with phenyllithium (see below). The resulting V still contained two deuterium atoms per molecule, excluding the possibility that the bridgehead hydrogens were removed in the elimination and hence making III and VII most unlikely structures.

CHART I



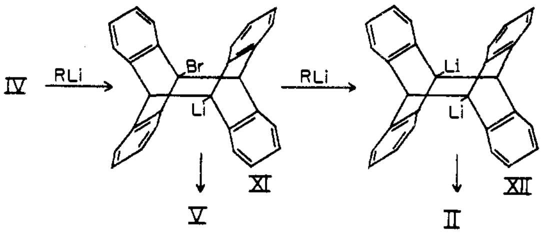
The possibility that the deuterium atoms in the dimer IX had rearranged in the photochemical step to positions other than the bridgeheads was ruled out by thermal conversion of IX to the monomer, whose infrared spectrum was identical to that of VIII before dimerization.

Particularly interesting were the reactions of dimer IV with organolithium reagents. Compound IV reacted with methyllithium in ether–benzene to give mainly II with small amounts of V and a new hydrocarbon, 9-methyldianthracene (VIa). The structure of VIa was suggested by its conversion to an equimolar mixture of anthracene and 9-methylanthracene on melting, and finally was established by independent synthesis of VIa by irradiation of a solution containing both anthracene and 9-methylanthracene. Photoadducts formed by reaction of two different anthracenes were not previously known.

Compound IV reacted with *n*-butyllithium in hexane–benzene to give some II and V, but mainly VIb, which was similar to VIa in properties. Phenyllithium in benzene–ether reacted with IV to give an 80% yield of V, together with some II, and this reaction is therefore the method of choice for the preparation of V.

The probable mechanisms for the formation of II and V from IV and lithium reagents are shown in Chart II. The relative yields of II and V would be determined by the competition between the second halogen–metal exchange to give XII and the loss of lithium bromide from XI to give the dehydrodianthracene (V), accounting for the dependence of the relative yields upon the nature of the organolithium. It is of interest that XII has no long existence in the solvents studied (benzene–ether or benzene–hexane), but abstracts protons from the solvent to form II, as shown by failure to trap XII with formaldehyde or deuterium oxide.

CHART II



The loss of lithium bromide from XI appears to be a unique reaction, in that displacements at the bridgehead bearing bromine (nucleophilic displacement) and at the bridgehead bearing lithium (electrophilic displacement) both occur with inversion of configuration. Electrophilic displacements most probably proceed preferentially with retention of configuration, unless there is a free carbanion intermediate.[7] Although it is possible to regard the reaction XI→V as a stepwise process, one step being the inversion of a free carbanion, such a hypothesis appears unlikely since the inverted carbanionic center would already be so close to the bromine-bearing carbon (as seen from qualitative inspection of models) that the carbon–bromine bond would already be substantially broken in the inverted carbanion to avoid enormous repulsion energy. Another possibility is that lithium bromide is lost by a free-radical chain process. This unlikely hypothesis, if correct, would not detract from the novelty of the reaction, since free-radical displacements at tetrahedral carbons rarely, if ever, occur.[8] The occurrence of the reaction suggests that electrophilic displacements may in general have a lower order of stereospecificity than nucleophilic displacements, in the sense that the latter occur *only* with inversion of configuration (except stepwise reactions) whereas

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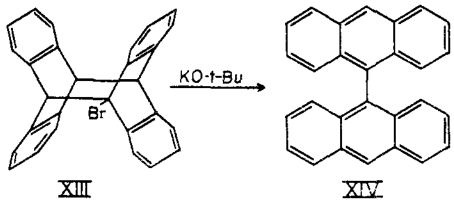
(7) S. Winstein and T. G. Traylor, THIS JOURNAL, **78**, 2597 (1956).

(8) R. A. Herrmann and R. M. Noyes, *ibid.*, **78**, 5764 (1956).

the former *prefer* retention, but may occur with inversion if no other path is available.

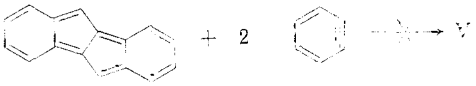
The possible mechanisms of formation of the 9-alkyldianthracenes (VI) are also of great interest. A most attractive possibility is that a 9,9′-dehydro compound of type III is formed by dehydrohalogenation and that the excess alkyllithium then adds to the double bond, followed by replacement of lithium by hydrogen in the usual manner. Loss of the second halogen by halogen–metal exchange would lead to the observed products VIa and VIb. It might be expected that there would be some double dehydrohalogenation of IV, leading to dialkyldianthracenes. These were not found, although the experimental difficulties were such that small amounts might have escaped detection. An alternative possibility is that bridgehead lithium derivatives, such as XII, displace halide from the alkyl halides formed in the exchange reactions, but this hypothesis requires that XII be much more nucleophilic than the alkyllithium which was present in excess in most experiments. Such an order of nucleophilicity would seem unlikely on steric grounds, but would be consistent with the unusual instability of the lithium reagents in hydrocarbon solvents. Experiments designed to distinguish the possible mechanisms for formation of VI are in progress.

Since the evidence already present was at least encouraging as to the possibility of preparing bridgehead olefin III by dehydrohalogenation, attempts were made using potassium *t*-butoxide, a reagent which would be expected to remove HBr but which would be unlikely to add to the resulting olefin. The reaction of (XIII) 9-bromodianthracene with *t*-butoxide in refluxing *t*-butyl alcohol gave 9,9′-dianthryl (XIV) in 40% yield and anthracene in 60% yield. (XIII was prepared by irradiation of a solution of anthracene and 9-bromoanthracene in benzene). Compound XIV was formed also by the reaction of dibromodianthracene (IV) with *t*-butoxide, although less cleanly than in the former case. The ring opening which accompanies these eliminations may be a thermal reaction of III, or it may be simultaneous with loss of hydrogen bromide and hence be a further illustration of the relative reluctance of alkoxides, as compared with organolithiums, to promote *cis*-dehydrohalogenations.[9] Driving force for removal of bromide might be provided by ring opening and by electrophilic participation of organolithium in these respective cases.



XIII XIV

An attempted independent synthesis of 9,10′-dehydrodianthracene (V) failed, but is perhaps of some interest. The reaction of excess magnesium and *o*-fluorobromobenzene in the presence of dibenzopentalene (XV) would lead to V if XV were capable of reacting as a diene with benzyne (XVI) in the same manner that anthracene has been found to react.[10] The reaction was run in tetrahydrofuran at room temperature and led to a mixture of products in which the benzyne trimer, triphenylene, was definitely present, and in which no V or XV was detectable by infrared analysis. The specific fate of XV was not learned. Localization energy calculations,[11] using the molecular-orbital (LCAO) data of Pullman,[12] predict that XV should be substantially less reactive than anthracene in the Diels–Alder reaction, the predicted localization energy for the former being about 19 kcal./mole (0.562 γ)[12a] less favorable than for the latter. There nevertheless appeared some hope of success in the present experiment, since the high calculated resonance energy of XV (2.98 γ)[12b] seems inconsistent with the lack of aromatic properties of the substance.[13] Since the XV was destroyed by a competitive side reaction in the attempted Diels–Alder reaction, conclusions as to the validity of the molecular-orbital calculations cannot be drawn.



XV XVI

Acknowledgment.—The authors are indebted to the Alfred P. Sloan Foundation for a grant in support of this research.

Experimental[14]

9,10′-Dibromodianthracene (IV).[15]—A solution of 62 g. (0.241 mole) of 9-bromoanthracene,[16] m.p. 97–102°, in 500 ml. of benzene was divided into three portions and exposed to September sunlight in Pyrex flasks for 16 days. Compound IV separated as 27.1 g. of massive greenish crystals, which were recrystallized from benzene to give 26.8 g. of slightly colored IV, m.p. 205° (dec. to give 9-bromoanthracene, m.p. 102.8–104.2°). Further recrystallization gave a colorless analytical sample, m.p. 201–202.4° dec.; the reported[15b] m.p. is 274°.

Anal. Calcd. for $C_{28}H_{18}Br_2$: C, 65.39; H, 3.53. Found: C, 65.76; H, 3.91.

9-Methyldianthracene (VIa).—A solution of 0.25 g. (0.0013 mole) of 9-methylanthracene,[17] m.p. 80–81°, and 0.25 g. (0.0014 mole) of sublimed anthracene in 20 ml. of benzene was irradiated through Pyrex with a 275-watt sunlamp for three days. Evaporation of the solvent gave crude VIa, which was recrystallized several times from benzene until the infrared spectrum remained constant. Compound VIa is much more soluble in benzene than the dimers of an-

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[9] (a) R. L. Letsinger and E. Bobko, This Journal, **75**, 2649 (1953); (b) S. J. Cristol, R. F. Helmreich and R. E. Bly, Jr., Fourteenth National Organic Chemistry Symposium of the American Chemical Society, Lafayette, Ind., June 13–16, 1955.

[10] G. Wittig and R. Ludwig, *Angew. Chem.*, **68**, 40 (1956).

[11] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 516.

[12] (a) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson editeurs, Paris, 1952; (b) B. Pullman, A. Pullman, E. D. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg and J. Pontis, *J. chim. phys.*, **49**, 24 (1952).

[13] C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).

[14] Melting points are uncorrected. Microanalyses were performed under the direction of Mr. Josef Nemeth at the University of Illinois. Infrared spectra were recorded by Mr. Paul McMahon, Mr. James Brader, and their staff, also at the University of Illinois.

[15] (a) H. Meyer and A. Eckert, *Monatsh. Chem.*, **39**, 241 (1918); (b) O. Fischer and H. Ziegler, *J. prakt. Chem.*, [2] **86**, 289 (1912).

[16] P. D. Bartlett, S. G. Cohen, J. D. Cotman, Jr., N. Kornblum, J. R. Landry and E. S. Lewis, This Journal, **72**, 1003 (1950).

[17] A. Sieglitz and R. Marx, *Ber.*, **56**, 1619 (1923).

thracene or 9-methylanthracene, which precipitate from solution as they are formed under the above conditions; VIa melted at 218–220° dec., remelt 155–180°. An equimolar mixture of anthracene and 9-methylanthracene melted at 155–182°, and a mixture of this mixture with melted VIa showed no significant depression in m.p.

Anal. Calcd. for $C_{29}H_{22}$: C, 94.01; H, 5.99. Found: C, 93.65; H, 6.00.

9-Bromodianthracene (XIII).—A solution of 0.50 g. (0.0019 mole) of 9-bromoanthracene and 0.34 g. (0.0019 mole) of anthracene in 20 ml. of benzene was irradiated as in the preceding experiment for two days. A precipitate of 0.22 g. of dianthracene (II) was filtered off and the remaining crude XIII was purified by recrystallization from benzene and finally from cyclohexene; colorless plates, m.p. 203–205° dec., remelt 147–160°. An equimolar mixture of 9-bromoanthracene and anthracene melted at 155–165°, and a mixture of the latter mixture with melted XIII melted at 148–160°. It was shown that the dimers of anthracene and 9-bromoanthracene are separated readily by recrystallization from benzene, ruling out the possibility that XIII is a 1:1 complex of these two.

Anal. Calcd. for $C_{28}H_{19}Br$: C, 77.25; H, 4.36. Found: C, 76.89; H, 4.42.

Reaction of IV with Phenyllithium. 9,10′-Dehydrodianthracene (V).—To a warm solution of 1 g. (0.00194 mole) of IV in 100 ml. of anhydrous benzene was added 10 ml. of 1.08 *M* phenyllithium (from bromobenzene and lithium) in ether. A white solid precipitated immediately. The mixture was allowed to stand for 30 min. and was then mixed with water, which left undissolved 0.56 g. of crude V, subl. 320°, m.p. > 350°. Another 0.08 g. of crude V was recovered from the organic phase. Contamination by dianthracene (II) was shown by comparison of the infrared spectrum with that of an authentic sample of II prepared by two days irradiation (sunlight) of a benzene solution of anthracene. Pure V was obtained by fusion of 0.54 g. of crude V (to decompose II) at 325° followed by recrystallization from 100 ml. of benzene to give 0.501 g. of white crystals, m.p. 369–370° (sealed tube), containing no II visible in the infrared spectrum. The ultraviolet spectrum of pure V in isoöctane solution showed a pseudomax. at 212 mμ (log ε 4.82) and a maximum at 290 mμ (log ε 3.35).

Anal. Calcd. for $C_{28}H_{18}$: C, 94.88; H, 5.12; mol. wt., 354.4. Found: C, 94.64; H, 5.32; mol. wt., 387 (ebullioscopic in butanone).[18]

Reaction of IV with Methyllithium.—To a warm solution of 1 g. (0.00194 mole) of IV in anhydrous benzene was added 10 ml. of 0.94 *M* methyllithium (from methyl iodide and lithium) in ether. The mixture was heated under reflux overnight (nitrogen atmosphere) and then treated with excess water, which left two liquid phases and 0.42 g. of crude II (61% yield, m.p. 260–280° dec.). The organic phase was boiled down to about 25 ml. and allowed to cool, which yielded 0.07 g. of crude V, m.p. 265–310°, shown by infrared analysis to be mainly V with small amounts of II present. Evaporation of the mother liquor gave 0.12 g. of a sticky, bromine-free (Beilstein test) solid, which was recrystallized twice from acetic acid and once from alcohol to give VIa as a white powder, 15 mg., m.p. 213–230° dec., to give a material which remelted over a broad range up to 179°. The infrared spectrum of VIa produced in this way was identical with that described above, and the infrared spectrum of the once-melted material was identical with that of an authentic 1:1 mixture of anthracene and 9-methylanthracene.

A similar reaction was run in which formaldehyde (from 10 g. of dry paraformaldehyde heated to 200°) was passed into the reaction mixture in a nitrogen stream before water was added. The products were essentially the same, no trace of hydroxyl compounds being detected.

Reaction of IV with *n*-Butyllithium.—To a warm solution of 1 g. (0.00194 mole) of IV in 100 ml. of anhydrous benzene was added 10 ml. of 0.44 *M* *n*-butyllithium (from *n*-butyl bromide and lithium) in hexane. The solution turned yellow immediately and a precipitate formed within one min. The mixture was heated under reflux for one hour. Addition of water dissolved the precipitate and gave two clear liquid phases. The organic phase was boiled down to 75 ml. and cooled to give 149 mg. of crude II, m.p. 254–263° (dec. with sublimation of purple-fluorescent crystals of anthracene). A second crop, 51 mg., m.p. 265–315°, was shown by its infrared spectrum to be a mixture of II and V. Evaporation of the mother liquor gave 0.60 g. of crude VIb as a gummy yellow solid, readily soluble in benzene, cyclohexane, acetone and ethanol, m.p. 72–157°. A sample of this material was chromatographed on alumina with pentane to give as the major eluent a white solid, m.p. 160–165° dec., which was recrystallized from methanol to give pure VIb, m.p. 168–171° (dec. to give sublimate of purple-fluorescent crystals). The infrared spectrum of this material was nearly the same as that of the crude yellow gum, and was also closely similar to that of VIa.

Anal. Calcd. for $C_{32}H_{28}$: C, 93.16; H, 6.84. Found: C, 92.73; H, 7.03.

In a very similar reaction, with pentane replacing hexane in the solvent mixture, the lithium reagents present at the end of the reaction (30 min. at room temperature) were destroyed with 1 ml. of 99.5% deuterium oxide. Dianthracene (II) (0.20 g., m.p. 264–266°, remelt 214–215°) was isolated as above and found by infrared examination and falling-drop deuterium analysis to contain no deuterium, within experimental error.

Anal. Calcd. for $C_{28}H_{18}D_2$: D, 10 atom %. Found: D, 0.2 atom %.

Reaction of IV with Zinc.—Refluxing acetone was allowed to wash 1.70 g. of IV from a Soxhlet thimble into a stirred, heated suspension of 2 g. of zinc dust in acetone. After 40 hr., the acetone was evaporated off, and the remaining gray solid was extracted for a total of three days in a Soxhlet apparatus with benzene. Dianthracene (II) amounting to 0.84 g. (m.p. 255–263.5°, remelt 214–217.6°) separated from the benzene extract. The liquid phase was evaporated to dryness, and the orange, solid residue (0.21 g.) was recrystallized from benzene to yield 0.04 g. of crude V which turned dark when heated to 250°. This was recrystallized once again from benzene to give crude V, which decomposed moderately at 268–330°, but without melting. An infrared spectrum showed it to be V contaminated with about 30% of II.

Reaction of IV with Lithium Aluminum Hydride.—A mixture of 2 g. (0.00389 mole) of IV, 100 ml. of anhydrous tetrahydrofuran and 2 g. (0.053 mole) of lithium aluminum hydride was stirred and heated at reflux temperature for two hours. The excess hydride was destroyed carefully with a solution of 5.6 ml. of concd. sulfuric acid in 50 ml. of water. The resulting mixture was diluted with 200 ml. of water and 200 ml. of benzene, and then filtered to obtain 1.10 g. of II as a colorless solid. The organic phase was washed with water and then concentrated to 40 ml. The cooled solution deposited 172 mg. of crude V, no melting up to 345° but shrinking at 270° and yielding some purple-fluorescent anthracene crystals by sublimation. Pure samples of V were obtained by the technique of heating the crude V to 345° and then recrystallizing, as described under the reaction of phenyllithium with IV. From 30 mg. of crude V was obtained 12 mg. of pure V, which showed no melting below 357° and from which no anthracene could be sublimed.

Chemical Properties of 9,10′-Dehydrodianthracene (V).—Samples of V were irradiated (tungsten lamp) in solution in benzene or carbon tetrachloride in the presence of small excesses of bromine until the bromine color had disappeared (1.5 hr. in carbon tetrachloride). The solvents were removed and the residues examined by infrared spectroscopy. In each case, some V was recovered and no trace of IV was found.

Unchanged samples of V also were recovered from 43 hr. with 0.08 *M* methyllithium in benzene–ether under reflux, 12 hr. with 0.05 *M* *n*-butyllithium in benzene–hexane under reflux, 34 days in solution with 0.04 *M* osmium tetroxide in benzene containing 1% pyridine, 7 days with lithium aluminum hydride in tetrahydrofuran under reflux, 8 days in solution with 0.3 *M* perbenzoic acid in benzene, and one day in a Parr shaker in acetic acid solution with active platinum catalyst and 4 atmospheres of hydrogen.

Ozone in ethyl acetate or chlorine in benzene reacted with V to give mixtures of soluble products which were not identified.

9-Bromoanthracene-10-^{2}H (VIII).—To a suspension of 20.0 g. (0.0595 mole) of 9,10-dibromoanthracene in 500 ml. of anhydrous ether was added, under nitrogen, 100 ml. of 0.60 *M* phenyllithium in ether.[19] The flask was tightly

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(18) Clark Microanalytical Laboratory, Urbana, Ill.

(19) B. M. Mikhailov and V. P. Bronovitskaya, *Zhur. Obshchei Khim.*, **22**, 157 (1952).

stoppered and shaken vigorously for 5 min., then allowed to stand with intermittent shaking for an additional 15 min. at 21°. The resulting yellow-orange solution contained traces of undissolved solid. The flask was then fitted with a reflux condenser through which was added 2.5 ml. (2.75 g., 0.14 mole) of deuterium oxide. The flask was shaken until boiling had subsided and then allowed to stand overnight. The mixture was filtered and the solid washed with ether until the washings were colorless. The combined filtrates were evaporated to dryness and the residue recrystallized from 95% ethanol to give 10.9 g. (73%) of VIII as pale yellow needles, m.p. 98–100°. A second recrystallization from the same solvent gave a sample of m.p. 100–101°. The infrared spectrum of VIII (in carbon disulfide) showed considerably less detail in the 650–1000 cm.$^{-1}$ region than in that of 9-bromoanthracene, and was characterized by strong absorptions at 760, 782 and 917 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_8DBr$: D, 11.11 atom %. Found: D, 11.22 atom %.

9,10'-Dibromodianthracene-9',10-$^2H_2$ (IX).—In a 200-ml., round-bottom, Pyrex flask connected by way of a reflux condenser to a constant pressure nitrogen reservoir and placed 8 cm. in front of a General Electric type RS sunlamp, a solution of 8.0 g. of VIII in benzene was irradiated for 167 hours. The separated solid (6.5 g.) was filtered off. The filtrate was treated with charcoal and concentrated to give a second crop, 0.6 g., total 7.1 g. (89%). After two recrystallizations from benzene, IX was obtained as white prisms, m.p. 202–203.5°, remelt 100–101°. The infrared spectrum (KBr pellet) differed from that of IV in the absence of a strong peak at 777 cm.$^{-1}$ and the presence of a medium-intensity peak at 976 cm.$^{-1}$. The infrared spectrum of the monomer obtained by melting a sample of IX was identical with that of VIII.

Anal. Calcd. for $C_{28}H_{16}D_2Br_2$; D, 11.1 atom %. Found: D, 10.5 atom %.

9,10'-Dehydrodianthracene-9',10-$^2H_2$ (X).—One gram of IX was treated with phenyllithium as in the preparation of V described above. The product was isolated and purified in the usual manner; m.p. 368–369° (sealed tube). The infrared spectrum of X (potassium bromide pellet) was similar to that of V but showed a distinctive strong peak at 1627 cm.$^{-1}$ and lacked a medium-intensity peak at 916 cm.$^{-1}$.

Anal. Calcd. for $C_{28}H_{16}D_2$: C, 94.35; H ("total H"), 5.65; D, 11.11 atom %. Found: C, 94.55; H, 5.50; D, 11.00, 11.12.

The anthracene obtained by fusion of the crude X showed absorption in the infrared at 841 and 792 cm.$^{-1}$, characteristic of anthracene-9-^{2}H.[20] The spectrum was identical with that of an authentic sample of anthracene-9-^{2}H prepared by a method to be described in a future report. This result is consistent with the mechanism shown in Chart II.

Reaction of Potassium *t*-Butoxide with 9-Bromodianthracene (XIII).—To a solution of potassium *t*-butoxide prepared by dissolving 2 g. (0.051 g. atom) of potassium in dry *t*-butyl alcohol was added a solution of 0.350 g. (0.0008 mole) of 9-bromodianthracene (XIII) in 50 ml. of dry *t*-butyl alcohol. The mixture was heated under reflux in a nitrogen atmosphere for three days. To the cooled reaction mixture were added 50 ml. of benzene and 100 ml. of water. The benzene phase was separated and boiled down stepwise to obtain first 0.114 g. (40%) of 9,9'-dianthryl (XIV) (m.p. 305–308°), and then 0.171 g. (60%) of anthracene (m.p. 210–212°). Both were identified by mixed melting points and comparison of the infrared spectra with those of authentic samples; XIV (m.p. 312–314°) was prepared for comparison by reduction of anthrone with tin.[21]

A similar reaction was run between IV and potassium *t*-butoxide to give a 40% yield of crude XIV, m.p. 275–300°, identified by its infrared spectrum and by mixed melting point of a recrystallized sample (m.p. 309–312°) with an authentic sample. The remainder of the product was a mixture which included bromine-containing compounds, and was not further investigated.

***meso*-Diphenylsuccinic acid** was prepared by a procedure of Curtin and Thamm.[22] In a typical run, 225 g. of phenylacetic acid and 275 g. of di-*t*-butyl peroxide were heated under reflux for 97 hours. The cooled mixture deposited 36 g. (16%) of product, m.p. 245–246°.

Indeno[2,1-*a*]indene (XV) was prepared from *meso*-diphenylsuccinic acid by the method of Blood and Linstead,[13] using literature procedures appropriate for the various steps.[23] The final product was purified by recrystallization from benzene. It softened at 280° and charred at higher temperatures. Its ultraviolet spectrum agreed with that in the literature,[13] and the extinction coefficients indicated that it was about 90% pure.

***o*-Fluorobromobenzene.**—A mixture of 25 ml. of water and 30 ml. of concentrated hydrochloric acid was cooled in an ice–salt-bath to a temperature below 5°. *o*-Bromoaniline hydrochloride made from 50 g. of *o*-bromoaniline and 50 ml. of concentrated hydrochloric acid was added, followed by aqueous sodium nitrite solution until starch–iodide test paper indicated that an excess of nitrous acid was present. Then 55 g. of 50% fluoroboric acid was added, and the mixture was stirred for 30 min. while the temperature was kept below 10°. The solid which separated was filtered and washed with successive portions of ice-water, methanol and ether. It was allowed to dry in a current of air overnight and was then heated in a distilling flask connected to a long condenser, several receivers in series cooled in Dry Ice and acetone, and finally a gas bubbler containing saturated sodium bicarbonate solution. After the reaction had begun, it was allowed to proceed with only occasional gentle heating until gas evolution ceased. The liquid which collected in the receivers was washed four times with 10% sodium hydroxide solution and once with water, and was then dried over calcium chloride and distilled to give 6.9 g. of *o*-fluorobromobenzene, b.p. 156–157° (750 mm.).[24]

Reaction of XV with *o*-Fluorobromobenzene and Magnesium.—A mixture of 0.230 g. of XV, 2.0 g. of *o*-fluorobromobenzene, 50 ml. of dry tetrahydrofuran and 1.5 g. of magnesium turnings was stirred at room temperature under nitrogen for 77 hours. The reaction mixture was filtered from some unreacted magnesium and some insoluble product, and the filtrate was evaporated to dryness under vacuum. The residue was dissolved in ether, washed with several portions of dilute hydrochloric acid, and again evaporated to dryness. The solid residue (0.35 g.) showed none of the characteristic absorption bands of 9,10'-dehydrodianthracene (V) or of unreacted dibenzopentalene (XV). All of the peaks of triphenylene were present. The precipitated product collected with the unreacted magnesium had nearly the same infrared spectrum as the product which remained in solution.

A similar reaction was run at the reflux temperature for several hours, and gave the same product mixture.

Urbana, Ill.

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[20] V. Gold and F. A. Long, This Journal, **75**, 4543 (1953).

[21] F. Bell and D. H. Waring, *J. Chem. Soc.*, 267 (1949).

[22] R. C. Thamm, Doctoral Thesis, University of Illinois, 1957; "Univ. Microfilms" (Ann Arbor, Mich.), Publ. No. 23395, 156 pp.

[23] (a) W. Roser, *Ann.*, **247**, 152 (1888); (b) C. L. Reimer, *Ber.*, **14**, 1802 (1881); (c) K. Brand and K. O. Müller, *ibid.*, **55**, 601 (1922); (d) S. Wawzonek, This Journal, **62**, 745 (1940).

[24] Since this experiment was done, we were informed by Prof. H. J. Dauben, Jr., that the purity of the diazonium fluoroborate is critical, and that greatly improved yields may be obtained if careful precautions are taken to wash the fluoroborate free of impurities.