mixture of 40 g. of zinc dust, 1 g. of zinc bromide, and 150 ml. of anhydrous alcohol was heated to the boiling point and 58 ml. of 1,1,2-tribromo-1,2-difluoroethane was added dropwise. The work-up gave 68 g. (94%) of the mixture of geometric isomers, which was resolved in two (in series) vacuum-jacketed Todd columns (metal spiral) with a vacuum-jacketed distilling head; the latter was connected to a reflux condenser cooled with a mixture of Dry Ice and acetone. The descending condenser was cooled also in this manner.

Fractionation of the above product gave after repeated distillations one isomer, boiling at 13.0° , and a second, boiling at 16.0° . The fractionation was repeated until either of the two compounds boiled within a 0.1° range and further distillation did not cause any change in the infrared spectrum.

The infrared spectra were determined using a Perkin-Elmer infrared spectrophotometer, Model 137, with sodium chloride prisms. The samples (solutions in carbon tetrachloride for the range 850-4500 cm.⁻¹, in carbon disulfide for the range 675-850 cm.⁻¹) were prepared as follows²³: the compound was dis-

 $(23)\;$ This method proved most useful for all substances boiling below room temperature.

tilled directly into a small glass ampoule of known weight; the ampoule was sealed; the two glass parts were cleaned and weighed, so that the weight of the substance measured was known. For the measurements, the ampoules were broken under the solvent in a suitable vessel.

The vapor phase chromatography of 1,2-dibromo-1,2-difluoroethylene was attempted in a column of 1.5 m., packed with tricresyl phosphate (10%) on Chromosorb W, which was effective in the separation of the two isomers of 1,2-dibromo-2-fluoroethylene,¹ and also in columns of 3.5 m., packed with either Dow Corning 550 fluid (10%) or Cambridge Industries Co. LAC-2-R446 polyester (10%) on Chromosorb W; temperatures were $25-100^{\circ}$.

The n.m.r. studies were carried out with the Varian high resolution n.m.r. spectrometer, Model HR-60, at a frequency of 56.4 Mc./sec. using the side-band technique. For the proton resonance spectra, a 0.5% solution of tetramethylsilane in carbon tetrachloride, for the F¹⁹ resonance spectra, a solution of Freon 11 (trichlorofluoromethane) in the same solvent served as internal reference standard.²⁴

(24) G. Filipovich and G. V. D. Tiers, J. Phys. Chem., 63, 761 (1959).

Bridgehead Dehydrohalogenation in the Photodimer of 9-Chloroanthracene

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The previously reported reaction of the photodimer of 9-bromoanthracene with alkyllithiums to give alkylated dianthracenes is shown by deuterium labeling not to be an elimination-addition mechanism as previously supposed. The photodimer of 9-chloroanthracene, however, does react with aryllithiums through an elimination-addition-elimination sequence to give aryldehydrodianthracenes. The intermediate olefin formally violates the Bredt rule. Efforts to isolate it have been thus far unrewarded.

It was reported a few years ago^1 that the photodimer (1) of 9-bromoanthracene reacted with alkyllithiums to produce, among other products, 9-alkyldianthracenes (2). It was felt that the most probable mechanism for



such a conversion was an elimination-addition through an intermediate 9,9'-dehydrodianthracene (type **3**), followed by protolysis of the bridgehead lithium. One of the halogens was removed by some reductive process, and in fact a common product was the parent dianthracene.



It has now been found that the dimer of 9-bromoanthracene-10-d reacts with n-butyllithium in pentane-

(1) D. E. Applequist, R. L. Litle, E. C. Friedrich, and R. E. Wall, J. Am. Chem. Soc., **81**, 452 (1959). benzene to give 2 ($R = n-C_{\rm f}H_{\rm 9}$) with no loss of deuterium. The elimination-addition mechanism is thus unequivocally ruled out.

The question of mechanism of formation of 2 is not settled, although a free-radical coupling of the sort proposed to explain random coupling products in simple alkyl cases² seems most attractive. The bridgehead free radical in the present case is almost certainly not seriously destabilized by strain.³ The radical could also serve conveniently to account for reduction, since it could abstract hydrogen atoms from solvent or butyl radicals.

Perhaps a more difficult mechanistic question is raised by the reduction of 1 with lithium aluminum hydride. It has been found that reduction with lithium aluminum deuteride in THF gives dianthracene-9,10'- d_2 (4), identified by its conversion to anthracene-9-d upon melting. On the other hand, reduction with lithium aluminum hydride with a D₂O isolation procedure gave unlabeled dianthracene.⁴ If we exclude frontside SN2 reaction as a reasonable mechanism, then we are left with reagent-promoted ionization of the bridgehead bromide and hydride transfer to the carbonium ion, or some free-radical path like that proposed above for alkyl coupling. The present data do not distinguish these possibilities.

For the reasons earlier given,¹ substances of structure type 3 still seemed attractive research objectives,

 ^{(2) (}a) D. E. Applequist and D. F. O'Brien, *ibid.*, 85, 743 (1963); (b)
 D. Bryce-Smith, J. Chem. Soc., 1603 (1956).

⁽³⁾ D. E. Applequist and L. Kaplan, J. Am. Chem. Soc., 87, 2194 (1965).
(4) Professor P. D. Bartlett has informed us that the opposite labeling pattern emerges in reductions of 9-bromotriptycene; *i.e.*, the bridgehead proton comes from the water added after the reduction.

and a study of the reactions of the dimer of 9-chloroanthracene⁵ with bases was therefore undertaken with the expectation that the competing halogen-metal interchanges, homolytic halogen removal, and ionization reactions would all be less favorable and thus allow

interchanges, homolytic halogen removal, and ionization reactions would all be less favorable and thus allow dehydrohalogenation to appear. This expectation has been realized, and the remainder of this discussion presents the results of these studies.

When the dichlorodianthracene 5 was treated with phenyllithium in refluxing ether-benzene, besides the reduction products dianthracene (15%) and 9-chloro-



dianthracene (24%) (6, also prepared by photoaddition of anthracene to 9-chloroanthracene), a 21% yield was obtained of an aryldehydrodianthracene (7a or b, Ar



= phenyl). A closely similar set of products (in 27, 34, and 20% yields, respectively) was obtained with ptolyllithium, only with Ar = p-tolyl in 7. The interesting new compounds of type 7a or 7b were characterized by their high melting points without decomposition (323-324° when Ar = phenyl, 348° when Ar =p-tolyl), by their n.m.r. spectra in molten naphthalene, which showed the bridgehead hydrogens and methyl hydrogens (Table I), and by their ultraviolet spectra

TABLE I

N.M.R. SPECTRA IN MOLTEN NAPHTHALENE WITH FERROCENE AS INTERNAL STANDARD FOR SHIFT AND INTENSITY

Compd.	τ, p.p.m.	Relative area (atoms/molecule)
7a or b, $Ar = phenyl$	5.0	0.8
7a or b, $Ar = p$ -tolyl	4.99	0.9
	7.61	3.0
8	5.0	2.0

(shown in Figure 1). The comparison of the latter spectra with those of the two known dehydrodianthracenes $\mathbf{8}^1$ and $\mathbf{9}^6$ is particularly interesting. Both



- (5) D. E. Applequist, E. C. Friedrich, and M. T. Rogers, J. Am. Chem. Soc., 81, 457 (1959).
- (6) D. E. Applequist and R. Searle, ibid., 86, 1389 (1964).



Figure 1.—Ultraviolet spectra of the dehydro dimers in methylene chloride.

compounds 7 have nearly identical chromophores, and they are in turn nearly identical with that of the 9,10dehydrodianthracene 9, about whose structure there is very little room for doubt. It is tempting therefore to assign structures 7a to the two substances reported here, and we do so tentatively.

Whether structure 7a or 7b is the correct one is of little moment as far as the conclusion to be drawn from these results is concerned. It seems nearly inescapable that in the reaction described there is first an elimination to form 10, followed by a one- or two-step addition-elimination sequence to form 7.



Three lines of confirmation of this proposed mechanism have been found. First, when 9,10-dichlorodianthracene (11)⁶ was subjected to the phenyllithium treatment, the same substance 7 (Ar = phenyl) was obtained, though the isolated yield was only 3.5% in this case. The mechanism requires that 5 and 11 give a common intermediate (10) in forming 7, but the relative amounts of this and other reactions could well be different for the two dichlorides.

Second, when the bridgehead hydrogens of 5 were replaced with deuterium, the isolable yield of 7 (Ar = phenyl) dropped to 1.3% and the yield of dianthracene went up to 36%. The two products contained 1.10and 1.96 deuterium atoms/molecule, respectively, as expected. The yield shift suggests a large primary isotope effect (expected for a simple dehydrohalogenation) in the formation of 7 but not in the reduction process.

Third, the reaction of 9-chlorodianthracene (6) was of interest because it provided an opportunity for the elimination and addition steps, but not for the final elimination. It reacted with phenyllithium in refluxing ether-benzene to give 31% of dianthracene and, by vapor chromatography of the remaining mixture, 10% 9-chloroanthracene, 9% anthracene, and 3.5%9-phenylanthracene (anthracene dimers would revert to monomers in the injection port; so it was not clear at what point the phenyldianthracene derivative dissociated). Thus, the elimination-addition sequence apparently works to some extent even when the final step is precluded. A control showed that 6 did not dissociate thermally to monomers under the conditions of the phenyllithium reaction, and that 9-phenylanthracene therefore did not result from reaction of 9-chloroanthracene. The possibility that phenyl replaced chlorine at a bridgehead by a free-radical coupling like that proposed above for alkyllithiums and bridgehead bromines cannot be excluded certainly, but, since aryllithiums showed no tendency to perform in such a manner with the favorable bromine compound, the chance seems small that they would do so in the present case.

Dehydrohalogenations of 5 were attempted with triphenylmethylsodium in ether-benzene and t-butyllithium in pentane-benzene with the hope that these reagents would be capable of the elimination step but would not then add to the intermediate 10. The former, however, gave 8 as the only high-melting isolable product (18% yield), indicating a strong preference of tritylsodium for halogen-metal interchange in preference to other reactions, even when the halogen is chlorine.⁶ The t-butyllithium gave a 61% yield of reduction product, dianthracene, and a trace of 8, with no sign of dehydrohalogenation. n-Butyllithium in pentane-benzene gave similar behavior, yielding 85% of dianthracene, 7% of 2, and 1.4% of 8. The last observation is in striking contrast with the result of reaction of 1 with the same reagent, which gave mainly 2. If formation of 2 and reduced product both proceed by way of bridgehead free radicals as postulated above then it is surprising to find the particular halogen affecting the ratio of these two kinds of products, but, since the reaction temperatures were not the same, a real halogen effect cannot be claimed with certainty.

Efforts to isolate substances of type **3** by other types of reactions are proceeding.

Experimental⁷

Reaction of 9.10'-Dibromodianthracene-9', $10-d_2$ with *n*-Butyllithium.—The starting 9,10'-dibromodianthracene- $9',10-d_2$ was found by combustion analysis to contain 94.6% of the calculated amount of deuterium. To a solution of 0.9314 g. (0.00184 mole) of this compound in 100 ml. of warm anhydrous benzene was added by pipet 15 ml. of a 0.75 M solution of *n*-butyl-lithium in pentane.¹ The cloudy yellow mixture was allowed to stand for 10.5 hr. To the pale yellow mixture, now containing considerable white precipitate, was added 100 ml. of deionized water. The organic layer was separated and filtered to remove 87.1 mg. of gray solid whose melting point, 278°, and infrared spectrum showed it to be dianthracene- $9,10'-d_2$ (described below). A second crop of the same compound, 76.2 mg., separated upon concentration of the organic layer to half of its original volume. The filtrate of this material was evaporated to dryness in an air stream and the resulting sticky yellow solid (0.72 g.) was rinsed onto a filter with a little pentane. The undissolved solid (0.22 g.)was nearly white and no longer sticky. It was extracted with 50 ml. of acetone-methanol (2:1 by volume) and filtered. The filtrate was boiled down to a volume of 7 ml. and cooled. There separated 100.0 mg. of very pale yellow solid, m.p. 184-187°, whose infrared spectrum indicated it to be a mixture of dianthracene-9,10'- d_2 and 9-n-butyldianthracene-9',10- d_2 . From the filtrate of this material was obtained a second crop of nearly white solid, m.p. 176-180°. The infrared spectrum of this material was free from dianthracene-9,10'- d_2 bands, and was very similar to that of known 9-*n*-butyldianthracene except for a sharp band at 721 cm.⁻¹. This compound was submitted for analysis.

Anal. Calcd. for $C_{32}H_{28}D_2$: C, 92.71; H, 6.75; D, 7.14 atom %. Found: C, 91.82; H, 6.82; D, 6.47 atom %.

Although only 90.6% of the theoretical deuterium content was found, the starting material contained only 94.6% of the theoretical amount, so the product is only 4.0 relative % deficient.

The residue from the acetone-methanol extraction was 20.3 mg. more of dianthracene-9,10'- d_2 . The total yield of this substance isolated pure was 29.4%.

Reaction of 9,10'-Dibromodianthracene with Lithium Aluminum Deuteride.-To a solution of 0.5745 g. (0.00112 mole) of 9,10'dibromodianthracene (1) in 100 ml. of anhydrous tetrahydrofuran was added 0.30 g. (0.00715 mole) of 95.0% lithium aluminum deuteride. The reaction mixture was stirred and heated at reflux for 2 hr., then stirred at room temperature overnight. To the lemon yellow suspension, 10 ml. of deionized water was added cautiously from a dropping funnel. The resulting yellow slurry was filtered by suction, air dried, and transferred to a Soxhlet thimble from which it was extracted with benzene for 24 hr. The benzene deposited 170.9 mg. of dianthracene-9,10'- d_2 , which was identified by comparison of its infrared spectrum with that of the known compound. This sample was dried and submitted for deuterium analysis by the falling-drop method. Further extraction of the residue in the Soxhlet thimble for 3 days afforded another 84.3 mg. of crystals whose infrared spectrum was identical with that of the first crop. The melting point of this material was 176-179°, with a small residue melting at 322°. The total yield of dianthracene-9, $10'-d_2$ isolated was thus 64%.

Anal. Calcd. for $C_{28}H_{18}D_2$: D, 10.00 atom %. Found: D, 9.00 atom %.

Since the deuterium analysis was low, it seemed possible that the sample might be contaminated with 9,10'-dehydrodianthracene (although no indiction of the presence of that substance was seen in the infrared spectrum). The sample was therefore pyrolyzed in a small sublimator, and the monomer was allowed to sublime at atmospheric pressure. The anthracene-9-d thus obtained was found to have an infrared spectrum identical with that of a known sample.

A similar reduction using lithium aluminum hydride followed by D_2O led to an anthracene sample with only 0.4 atom % deuterium.

Reaction of 9,10'-Dichlorodianthracene with *p***-Tolyllithium**.— A 25-ml. portion of 1.39 N *p*-tolyllithium in ether was added to a solution of 3 g. (0.0071 mole) of 5 in warm anhydrous benzene under a nitrogen atmosphere, and the resulting milky white mixture was heated under reflux for 23 hr. Water (100 ml.) was added cautiously and reflux was continued for another hour. The cooled mixture was filtered to remove 0.68 g. (27%) of crude dianthracene, which after recrystallization from benzene melted at 249-255° and remelted at 210-212°. The organic phase was evaporated to dryness to leave a yellow, oily material which was recrystallized from cyclohexene to give 0.625 g. of crude 7 (Ar = p-tolyl), m.p. >330°. After sublimation at 225-240° (0.04 mm.), a sample melted at 348°.

Anal. Caled. for $C_{35}H_{24}$: C, 94.56; H, 5.44. Found: C, 94.59; H, 5.42.

When the same procedure was repeated using 5 g. of 5 and the lower melting products were exhaustively crystallized from cyclohexene, 1.57 g. of a crude, thermally unstable, colorless solid was obtained, m.p. 215°, remelting at 160°. Recrystallization from 1:1 benzene-cyclohexane gave a substance which melted at 220° and remelted at 160-200° to give a 1:1 molar mixture of anthracene and 9-chloroanthracene (identified by the infrared spectrum). The substance was therefore assigned structure 6.

Reaction of 9,10'-Dichlorodianthracene with Phenyllithium.— In reactions carried out essentially like the above reaction of *p*tolyllithium but using phenyllithium, yields of as high as 15%of dianthracene, 24% of 6, and 21% of the new phenyldehydrodianthracene (7, Ar = phenyl) were obtained. Crude 7 melted at 316-320°, and an analytical sample, prepared by heat treatment to destroy dianthracenes, recrystallization from xylene, and sublimation at 180° (0.2 mm.), melted at 320-322°. At other times (and with other thermometers), melting points as high as 324° were observed.

Anal. Calcd. for $C_{34}H_{22}$: C, 94.85; H, 5.15. Found: C, 94.79; H, 5.26.

⁽⁷⁾ Melting points are uncorrected. Infrared spectra were determined in part by Mr. Dick Johnson and associates, n.m.r. spectra by Mr. Oliver Norton, and microanalyses by Mr. Josef Nemeth and associates.

Reaction of 9,10'-Dichlorodianthracene with n-Butyllithium.---To a solution of 1.00 g. (0.0024 mole) of 9,10'-dichlorodianthracene in 100 ml. of warm anhydrous benzene was added 15 ml. of a 0.702 M solution of *n*-butyllithium in pentane. The mixture was heated at reflux under a nitrogen atmosphere for 15 hr. Excess lithium reagent was destroyed by addition of 100 ml. of water and the mixture was allowed to cool. The organic laver with suspended solid was separated and washed twice with 100ml. portions of deionized water. The organic mixture was then filtered to remove 669.5 mg. of white solid, m.p. 275-280°, whose infrared spectrum confirmed its identity as dianthracene. Evaporation in vacuo of the clear benzene filtrate left 0.42 g. of a yellow oil in which some solid was suspended. The oil was diluted with 50 ml. of absolute methanol and 20 ml. of reagent grade acetone, heated on a steam bath, and filtered to remove 38.9 mg. of white solid whose infrared spectrum and melting point (268-270°) identified it as dianthracene. Thus dianthracene was obtained in 84.8% yield. All attempts to crystallize the methanol-acetone-soluble oil failed. In another experiment, however, from the oily residue isolated as above in a reaction run on the same scale in a similar fashion, 70.8 mg. of white solid was obtained whose infrared spectrum indicated it to be crude 9-n-butyldianthracene in approximately 7% yield. In still another experiment, a pyrolytic treatment of the soluble fraction followed by recrystallization from benzene gave a 1.4%yield of 8, m.p. 370°, identified by its ultraviolet spectrum.

Reaction of 9,10'-Dichlorodianthracene with t-Butyllithium.---To a solution of 2.00 g. (0.00471 mole) of 9,10'-dichlorodianthracene in 100 ml. of refluxing benzene was added 22.4 ml. (0.0094 mole) of t-butyllithium (0.42 M in pentane). The heating bath was removed, the reaction mixture was stirred overnight and filtered, and the residue was washed with water to leave 1.09 g. of solid. Comparison of the infrared spectrum of the solid with spectra of authentic samples showed that the solid was chiefly dianthracene (65%). The spectrum had, however, eight maxima in addition to the dianthracene spectrum-these maxima were attributable to 9,10'-dehydrodianthracene (8). Of the solid, 0.379 g. was melted at 260-290° to decompose dianthracene and the product was recrystallized from benzene. Insoluble in benzene was 0.0016 g. (0.3%) of 9,10'-dehydrodianthracene, identified only by comparison of its infrared spectrum (weak) with that of an authentic sample. From the filtrate of the reaction mixture, 0.95 g. of material was obtained by evaporation of the solvent, but no identifiable products were isolated from this material.

Reaction of Triphenylmethylsodium with 9,10'-Dichlorodianthracene.—To a slurry of 4.00 g. (0.00940 mole) of 9,10'-dichlorodianthracene in 500 ml. of benzene was added 36.8 ml. (0.019 mole) of triphenylmethylsodium in ether. After 24 hr. at room temperature, a precipitate, 1.61 g., was filtered, washed with water, and recrystallized from xylene to yield 0.52 g. (16%) of 9,10'-dehydrodianthracene (8), identified by comparison of its infrared spectrum with that of an authentic sample. Evaporation of the filtrate left 6.02 g. of gum. Although the gum was chromatographed, no identifiable products were obtained.

From a similar reaction involving 1.00 g. (0.00235 mole) of 9,10'-dichlorodianthracene and 17.4 ml. (0.00574 mole) of triphenylmethylsodium in ether there was obtained 0.22 g. (26%) of crude 8, identified by comparison of its infrared spectrum with that of an authentic sample. Recrystallization of 0.10 g. of the crude from xylene gave 0.07 g. of a product, m.p. >340°.

9-Phenyl-9',10'-dehydrodianthracene (7a, Ar = Phenyl) from the Reaction of Phenyllithium and 9,10-Dichlorodianthracene (11).—The 9,10-dichlorodianthracene used in the reaction was free of the impurity, 9,10'-dichlorodianthracene (5). The vapor phase chromatogram on silicone rubber of the starting material showed peaks corresponding only to anthracene and 9,10dichloroanthracene from the thermal decomposition of 11.⁸ Vapor phase chromatography of a mixture showed that a 7% contamination of 11 by 5 was easily detectable by the appearance in the chromatogram of a peak corresponding to 9-chloroanthracene from the thermal decomposition of 9,10'-dichlorodianthracene.

9,10-Dichlorodianthracene (7.00 g., 0.0165 mole) was dissolved in 400 ml. of benzene and 180 ml. (0.245 mole) of phenyllithium in ether was added. At an oil-bath temperature of 90–95°, 225 ml. of solvent was distilled from the mixture—the final vapor temperature was 74°. After 12 hr. at reflux, the reaction was cooled and quenched with 100 ml. of distilled water. The mixture was filtered to remove 2.31 g. (39%) of dianthracene, identified by its infrared spectrum. Water was separated from the filtrate and the organic layer was dried over sodium sulfate. Successive concentrations followed by washing of the gummy material obtained with acetone gave the following solids: 0.0353 g., m.p. 260-275°; 0.208 g., m.p. 269-305°; 0.194 g., m.p. 266-303°; and 0.0638 g., m.p. 263-282°. The second and third solid fractions were melted and recrystallized from xylene to obtain 0.231 g. (3.3%) of 9-phenyl-9',10'-dehydrodianthracene (7a, Ar = phenyl), identified by comparison of the infrared above. Sublimation at 210° and 0.2-mm. pressure with 80% recovery produced an analytical sample, m.p. 314-321°.

Anal. Calcd. for C₁₄H₂₂: C, 94.85; H, 5.15. Found: C, 95.12; H, 5.04.

The ultraviolet spectrum between 240 and 390 m μ was identical with that of the authentic sample. Vapor phase chromatography showed that the analytical sample contained 2% of 8 or 9.

Photochemical Synthesis of 9-Chlorodianthracene (6).—A solution of 6.00 g. (0.0337 mole) of anthracene and 7.20 g. (0.0337 mole) of 9-chloroanthracene in 475 ml. of benzene was exposed to the September–October sunlight for 47 days. A solid, 4.07 g., which, according to its infrared spectrum, was chiefly composed of unwanted dimers, was filtered and discarded. The solvent was evaporated from the filtrate and the remaining solid was recrystallized from benzene to give 5.62 g. (43%) of 9-chlorodianthracene, m.p. 192–195° dec. with a remelt temperature of 150–163°. The melting point of a 1:1 molar mixture of the melted 9-chlorodianthracene and the 1:1 molar mixture melted at 152–165°. Anal. Calcd. for C₂₈H₁₉Cl: C, 86.07; H, 4.86. Found:

C, 85.85; H, 5.02.

Reaction of 9-Chlorodianthracene with Phenyllithium .---Phenyllithium in ether (100 ml., 0.13 mole) was added to a slurry of 4.306 g. (0.0110 mole) of 9-chlorodianthracene in 200 ml. of benzene. Solvent was distilled from the mixture until the vapor temperature reached 74°-44 ml. was distilled in all. The reaction mixture was heated at reflux for 8.3 hr., then cooled in ice, and 50 ml. of water was added. The resulting solid, 1.416 g., was filtered and slurried in boiling benzene. Insoluble in benzene was 1.157 g. (30%) of dianthracene, and 0.0678 g. (2%) of dianthracene crystallized from the benzene on cooling. Dianthracene was identified by comparison of its infrared spectrum with that of an authentic sample. The filtrate from the reaction mixture was dried and evaporated to give 3.12 g. of crude product. Vapor phase chromatography on silicone rubber at 225° of the crude product gave the following results. (1) From 10.9 mg. of crude product was collected 1.2 mg. (9% yield) of anthracene identified by its retention time and by comparison of its infrared spectrum with that of an authentic sample. (2) From 22.2 mg. of crude product was collected 1.6 mg. (10% yield) of 9-chloroanthracene, identified by comparison of its infrared spectrum with that of an authentic sample. (3) From 29.9 mg. of crude product was collected 0.9 mg. (3% yield) of 9-phenylanthracene, identified by its retention time and by comparison of its infrared spectrum with that of an authentic sample. (4) From 29.9 mg. of crude product was obtained in two fractions 0.6 mg. of unidentified substances with retention times longer than that of 9-phenvlanthracene.

In a control experiment, it was shown that 9-chlorodianthracene treated as above but without the phenyllithium, including 10.3 hr. at reflux, did not dissociate to an extent detectable by ultraviolet spectroscopy. It was shown that 4.5% of 9chloroanthracene in 6 made a conspicuous difference in the spectrum.

9-Chloro-10-bromoanthracene.—To a stirred suspension of 34 g. (0.16 mole) of 9-chloroanthracene in 500 ml. of glacial acetic acid was added dropwise a solution of 8 ml. (24.8 g., 0.155 mole) of bromine in 50 ml. of acetic acid. After addition was complete (30 min.), 15 g. (0.18 mole) of anhydrous sodium acetate was added, and the suspension was stirred for another 30 min., then poured into 1 l. of cold water. The mixture was filtered, and the resulting tan solid was washed with water and recrystallized from benzene to give 30 g. (65%) of yellow needles, m.p. 215-216° (lit.⁴ m.p. 210.5-211°).

⁽⁸⁾ The Ph.D. Thesis of R. Searle, University of Illinois, 1963, may be consulted for details.

⁽⁹⁾ B. M. Mikhailov and M. Sh. Promyslov, Zh. Obshch. Khim., 20, 338 (1950).

9-Chloroanthracene-10-d.-To a suspension of 45 g. (0.155 mole) of 9-chloro-10-bromoanthracene in 500 ml. of anhydrous ether was added 0.153 mole (250 ml. of 0.63 M solution) of phenyllithium in ether. The mixture was swirled vigorously for 2 min. and intermittently for 20 min. To the resulting orange-yellow suspension was added 4 ml. (4.4 g., 0.22 mole) of deuterium oxide, and the mixture was shaken until the exothermic reaction had subsided. After a few hours, the mixture was filtered, and the solid residue was washed with ether until the washings were colorless. The ether was removed from the combined filtrates and the residue was recrystallized from cyclohexane to give, first, 2 g. of starting material, m.p. 215-216°, and second, 18 g. of the crude desired product, m.p. 98-101° (with an unmelted residue). The solid residue from the reaction mixture was extracted with boiling benzene to give another 8 g. of starting material, which made the yield of product 70%. A sample of product was recrystallized again from cyclohexane to give yellow needles, m.p. 101-102°. The infrared spectrum showed a number of differences from that of 9-chloroanthracene, including the absence of two strong bands normally present at 882 and 944 cm. -1

9,10'-Dichlorodianthracene-9',10- d_2 .—The photodimerization in sunlight of 9-chloranthracene-10-d in 68% yield was done as described before⁵ for 9-chloroanthracene.

Anal. Caled. for $C_{28}H_{16}D_2Cl_2$: D, 11.11 atom %. Found: D, 11.20 atom %.

Reaction of 9,10'-Dichlorodianthracene-9',10- d_2 with Phenyllithium.—To a solution of 8.9 g. (0.0208 mole) of the dimer in 600 ml. of warm benzene was added 320 ml. of 0.24 *M* phenyllithium in ether. The mixture was heated under reflux (nitrogen atmosphere) for 20 hr., quenched with 150 ml. of water, and refluxed for another 30 min. The cooled reaction mixture deposited 1.7 g. of crude dianthracene-9,10'- d_2 , m.p. 250-260° dec. The benzene layer was evaporated to dryness and the residue was digested with cyclohexane to leave 3.2 g. of very crude 7, m.p. 200–280° dec., as a yellowish powder. This material was melted, recrystallized twice from cyclohexene, melted again, and recrystallized four more times from cyclohexene to give 0.116 g., m.p. 305–310°. The infrared spectrum was similar to that of undeuterated 7, but with an extra peak at 644 cm.⁻¹. A 95-mg. sample of this was sublimed at 100–110° (0.6–1.0 mm.) to give a small sublimate, m.p. 290°. The temperature was raised to 240–267° (0.3 mm.), and 80 mg. of sublimate was collected in two fractions, m.p. 310–317° and 308–310°. The former was analyzed for deuterium, the latter for carbon and hydrogen.

Anal. Calcd. for $C_{34}H_{21}D$: C, 94.63; H, 5.37; D, 4.55 atom %. Found: C, 94.12; H, 5.22; D, 5.01 atom %.

In another run, using 3 g. of dimer, more care was taken to isolate dianthracene-9,10'- d_2 by successive concentration of the reaction mixture filtrate, and 0.9 g., m.p. 240-270° dec., was obtained. This was decomposed at the melting point to anthracene-9-d, which was recrystallized from cyclohexene to give fluorescent platelets, m.p. 212-216°. The infrared spectrum showed strong absorption at 841 and 792 cm.⁻¹ as reported by others.¹⁰

Anal. Calcd. for $C_{14}H_9D$: D, 10.0 atom %. Found: D, 9.8 atom %.

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Ion Radicals. V. Phenothiazine, Phenothiazine 5-Oxide, and Phenothiazone-3 in Acid Solutions^{1,2}

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The reactions of phenothiazine (I), phenothiazine 5-oxide (II), and phenothiazone-3 (III) in acidic solutions have been studied by ultraviolet, visible, and e.s.r. spectroscopy. Solutions of II in 96% sulfuric acid are stable; it is proposed that they contain the protonated phenazothionium ion (VI). Similarly, solutions of III in 96% sulfuric acid are stable, and it is proposed that they contain the protonated hydroxyphenazothionium ion (XIII). Solutions of I in 96% sulfuric acid contain the phenothiazine cation radical (IV) which, in time, is further oxidized to VI. It is shown that III in 59% sulfuric acid is converted to the hydroxyphenothiazine cation radical (XI). It is also shown that in aqueous sulfuric acid II is converted not only to the cation radical IV but also to XI. Mechanisms are proposed for these reactions. It is proposed that in aqueous sulfuric acid II is in equilibrium with protonated II (VII) and with the phenazothionium ion (V) arising from dehydration of VII. The cation radical IV is formed from VII by loss of the hydroxyl radical to solvent. The cation radical XI is formed in solutions of II by a sequence of reactions involving nucleophilic attack of water on V and oxidation of the hydroxylated intermediate. It is proposed that the formation of XI from solutions of III in aqueous sulfuric acid occurs by hydroxyl loss from protonated 3-hydroxyphenothiazine 5-oxide, the last being formed by the hydration of the 3-hydroxyphenazothionium ion (IX). II, IV-VI, IX, XI, and XIII are characterized by ultraviolet, visible, and, where applicable, e.s.r. spectroscopy.

The chemistry of phenothiazine (I) has enjoyed continued interest during the past 50 years, formerly because of the connection between I and numerous dyestuffs, such as Lauth's violet (3,7-diaminophenothiazine) and methylene blue, and latterly because of the pharmacological properties of substituted phenothiazines. In particular, the behavior of I toward oxidizing agents and the relationship that this behavior bears to the chemistry of phenothiazine 5-oxide (II) and phenothiazone-3 (III) have received a great deal of attention. It is now known, from the pioneering work of Michaelis,³ that I undergoes a one-electron oxidation to form a cation radical, which was proposed to have, in sufficiently acidic solution, the structure IV.

The radical IV, prepared by the oxidation of I with bromine or lead tetracetate in acetic acid solution, was characterized spectroscopically by a series of bands between 400 and 550 m μ . Subsequently, Lewis and

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