AN EVALUATION OF 9,10-DISODIO-9,10-DIHYDROANTHRACENE AS A SYNTHETIC INTERMEDIATE

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We were interested in developing a practical general synthesis for 9,10-disubstituted anthracenes capable of undergoing condensation polymerization. Representative methods found in the literature (1–5) were not sufficiently general. Recently, Miller, Amidon, and Tawney (6) showed that the readily available 9,10-dichloromethylanthracene could be converted by familiar displacement reactions into a variety of functional 9,10-disubstituted anthracenes. The chief disadvantage of their synthesis, and a serious one, is that dichloromethylanthracene is a potent allergen; a worker, once sensitized, may be unable ever to handle it again.

The addition of alkali metals to arylated unsaturated systems such as phenylated ethylenes, naphthalene, anthracene, phenanthrene, and larger polynuclear hydrocarbons has been known for some time as a result of the work of Schlenk, Bergmann, Ziegler, Wooster, and others (7). They observed, in brief, that the addition products could be converted into dihydro acids by carbonation, and that the adducts were prone to disproportionate. Mikhailov has demonstrated more recently that the reaction of sodio and lithio adducts of anthracene, benzanthracene, phenanthrene, and the like with alkyl halides and with ethylene oxide is a useful route to potentially carcinogenic hydrocarbons (8). Wright (9) has studied the corresponding reactions of stilbene-metal adducts.

It seemed odd that other reactions of dimetallodihydroanthracenes had not been explored. *A priori*, they would be expected to react much like simple organoalkali compounds. We turned first to a way of accelerating the formation of the addition compounds. Schlenk reported that 100 hours was required to induce sodium chips to add to anthracene in ether-benzene solution; lithium required 150 hours. Mikhailov was able to reduce the time to about 9 hours by operating in ethylene glycol dimethyl ether solvent (8c) and using sodium "shot." In our hands, however, the rate of addition of sodium was not much faster than the abstraction of hydrogen from this solvent by the intermediate disodiodihydroanthracene (II). When the solution prepared by Mikhailov's technique was carbonated with an anhydrous Dry Ice slurry, either substantial amounts of anthracene were recovered (incomplete addition) or a great deal of 9,10-dihydroanthracene (III) was formed at the expense of the diacid (IV). Further, the acidic fraction always contained a considerable amount (as high as 30%) of 9,10-dihydroanthracene-9-carboxylic acid (V) resulting from stepwise hydrogen abstraction.

G. F Wright (private communication) has pointed out that traces of hydroxylic contaminants in glycol ethers greatly accelerate ether cleavage. This may explain the difference between our experience and Mikhailov's.

Preliminary experiments in tetrahydrofuran using conventional sodium "shot" were qualitatively similar, though addition appeared to be relatively more rapid than hydrogen abstraction. A sodium dispersion[1] with particle size 10–30 μ was added very rapidly in tetrahydrofuran at room temperature, and in two hours the yield of II (measured as IV) was 70% based on I. A small amount of III was present, together with unreacted I. Longer times or higher reaction temperatures increased the quantity of III at the expense of II. Excess sodium, which could not be removed after addition was complete, would certainly cause unpleasant side reactions when reagents other than carbon dioxide were added. The experiments described below were conducted with the inky blue solution of II in tetrahydrofuran; a 70% yield of II was assumed, and the quantities of other reagents were based upon this value.
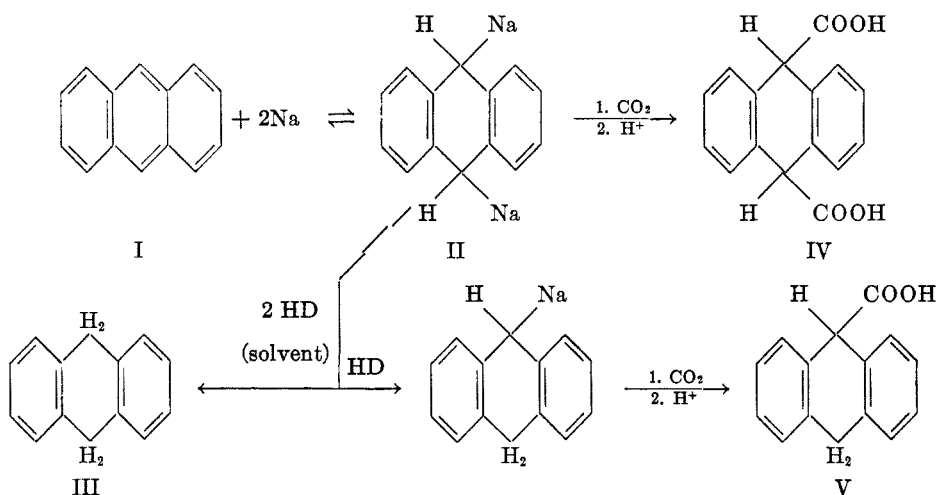
It was expected that II would (a) displace halogens from reactive halides such as allyl chloride, chloroacetone, and ethyl haloacetate [simple alkyl halides, especially methyl, do so react (8)], (b) add to the carbonyl group in benzoyl chloride or β-propiolactone, (c) open the ring in ethylene and propylene oxides and epichlorohydrin, and (d) add in the conjugate manner to benzalacetophenone and acrylonitrile. Since II could become aromatic by loss of its two sodium atoms to another unsaturated system more reactive toward addition of sodium, such a transmetalation might occur upon addition of a reagent, and would result in a serious lowering of the yield. Further, since organosodium compounds are in general strong bases, hydrogen-metal interconversion might well occur with compounds displaying acidic hydrogens where a lower-energy anion than that of II could form.

In the reactions studied, we observed that striking color changes occurred as the reagent was added slowly to the deep blue solution of II. Often an "end

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[1] Sodium dispersed in an inert solvent in the presence of dispersing and stabilizing agents. *Cf.* Hansley, *Ind. Eng. Chem.*, **43**, 1759 (1951).

point" appeared as the blue color changed abruptly to orange or yellow when about 70% of the calculated quantity of second component had been added; this corresponds roughly to the assumed yield of II determined by carbonation. Regrettably, in almost all cases, the bulk of the II was converted either to I or III. The anthracene formed was usually far in excess of the amount unreacted in carbonation experiments, so it appears that transmetalation is very easy. The III is not formed simply by hydrolysis of unreacted II during workup, since the color of II is so intense that even traces can be visually detected.

Allyl chloride reacted with II to form a small amount of 9-allyl-9,10-dihydro-anthracene; the latter reduced permanganate solution and its infrared spectrum exhibited a double-bond peak. Ethylene oxide reacted with II to form a variety of products, one of which, m.p. 113–116.5°, exhibited a hydroxyl peak in the infrared; it could not be purified for analysis, however. The product is different from that previously obtained by Mikhailov (10). Propylene oxide yielded a small amount of product after molecular distillation which appeared to be 9,10-dihydro-9,10-bis(2-hydroxypropyl)anthracene on the basis of analysis and infrared spectrum.

Benzalacetophenone appeared to be transmetalated, since substantial amounts of anthracene were recovered. Two other products, m.p. 268° and 206–207.5°, were isolated in small amounts, but these probably arose from further reaction of metalated benzalacetophenone.[2] Acrylonitrile was not rapidly polymerized by II, although most organometallic reagents polymerize it readily. Since much anthracene was recovered, it seems that acrylonitrile also was transmetalated.

It may be concluded from these results and those of Mikhailov that II is a useful reagent for the preparation of III or IV and for certain alklyated anthracenes. Transmetalation and hydrogen abstraction are the preferred modes of reaction of II with most reagents which otherwise react well with Grignard reagents and simpler organoalkali compounds.[3]

<center>EXPERIMENTAL[4]</center>

Preparation of solutions of 9,10-disodio-9,10-dihydroanthracene (II). Anthracene (Matheson, m.p. 213–214°) was recrystallized from benzene; m.p. 216–218° (corr.). Tetrahydrofuran (Dupont or Matheson) was refluxed with sodium and was freshly distilled to remove peroxides; the fraction boiling at 65° was employed. The sodium dispersion was supplied as a 45% dispersion in toluene, average particle size 20μ; we are indebted to National Dis-

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[2] Conant and Cutter (15) obtained two compounds, m.p. 194° and 266°, by reduction of benzalacetophenone; one had previously been isolated by Harries (16). Von Kostanecki and Rossbach (17) treated benzalacetophenone with warm alkali and obtained ϕCOCH(CH₂ϕCH₂COϕ)₂ in two forms, m.p. 198° and 256°.

[3] The addition of II to simple aldehydes and ketones was not investigated, since the products of these reactions would have been benzyl-type alcohols. Preliminary work with such compounds prepared according to Miller, Amidon, and Tawney (6) had shown that they were unsatisfactory monomers. In view of Wright's results (9), it is likely that II would have reacted fairly well with formaldehyde, acetone, etc.

[4] Melting points are uncorrected, unless otherwise stated. Analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois, Geller Microanalytical Laboratory, Hackensack, New Jersey, and Anna Griffin in this Laboratory.

tillers Chemical Corporation for a gift of this dispersion. Since we had stored the sample
for some time and the particles might have coalesced appreciably, it is possible that even
better results might have been obtained with a freshly prepared dispersion; laboratory
dispersing equipment has recently become available. It is possible that the toluene used in
this dispersion might have been metalated during these reactions, but no evidence for the
presence of benzylsodium was found. An atmosphere of dry nitrogen (Linde prepurified)
was maintained at all times.

G. F Wright (private communication) suggested that it was unnecessary to use finely
divided sodium as long as the coordinating reaction solvent was sufficiently pure. We did
not try massive sodium.

A sodium dispersion (3.7 g., 0.0735 atom of sodium) was added to 100 ml. of tetrahydro-
furan (THF) in a 300-ml. three-necked flask equipped with a drying tube, mercury-sealed
stirrer, and a gas inlet tube. After stirring for 0.5 hr., 6.56 g. (0.0368 mole) of I was added
in one portion. Within 30 seconds, the mixture became deep blue. (With sodium shot as
usually prepared, 10–30 minutes were required.) An additional 50 ml. of THF was added
and the mixture was stirred at ambient temperature for 2 hours.

Carbonation of II. cis-9,10-Dihydroanthracene-9,10-dicarboxylic acid. The flask contain-
ing II was connected by a goose-neck tube to a second flask containing a vigorously stirred
suspension of powdered Dry Ice in 300 ml. of ethyl ether. The solution of II then was poured
into the Dry Ice slurry by rotating its container around the goose-neck; a nitrogen atmos-
phere was maintained at all times. After the white curdy mixture was stirred overnight,
100 ml. of water was added and the mixture was made basic with a little sodium hydroxide
solution. The aqueous layer was washed with two 25-ml. portions of ethyl acetate, and the
combined organic layers were dried and evaporated. The residue, 0.88 g., m.p. 208–211°,
was I, as proved by recrystallization and mixture melting point.

The ice-cold aqueous layer was acidified with hydrochloric acid. Successive crops of
acid were taken: A, 4.70 g., m.p. 250–254° dec., N.E. 167; B, 3.21 g., m.p. 283–286.5°, N.E.
149; C, 0.74 g., m.p. 279–281°, N.E. 140. Neutral equivalents were determined by the method
of Fritz and Lisicki (11). By calculation from the weights and neutral equivalents, the re-
action yielded 69% of diacid, 17% of monoacid, and 13.5% of recovered I.

The mono- and di-acid were separated semi-quantitatively by partition chromatography
on silicic acid using ethyl acetate-water and Liddel and Rydon's (12) indicator. The diacid
was shown to be the *cis* isomer by its m.p. 282–283° in agreement with the literature value
(8, 13). Mathieu (13) has made a thorough study of the properties of *cis-* and *trans*-IV and
their separation from V.

Reaction of II with ethylene oxide. An ice-cold solution of II prepared as described from
7.99 g. of I was treated dropwise at 0° with a solution of ethylene oxide (redistilled) in
THF during 50 min. (In this and in subsequent reactions, two moles of reagent were used
per mole of I.) The white suspension was stirred at 0° for an additional hour, then treated
with 5 ml. of ethanol followed by excess saturated ammonium chloride solution. The organic
layer was separated, dried, and evaporated at room temperature in a vacuum. The amber
glass crystallized partially when maintained at 35°. Several crops were taken by triturating
the mixture with a small volume of cold ethyl ether, filtering, evaporating, and repeating
the process. Crop A, 4.86 g., m.p. 113–116.5°; B, 0.68 g., m.p. 112–125°; C, 0.10 g., m.p. 275–
279°; D, 0.47 g., m.p. 151–156°; E, 0.39 g., gummy solid. Crop A could not be obtained pure
by crystallization or by chromatography on alumina, but its infrared spectrum showed
hydroxyl absorption at 3350 cm⁻¹.

Reaction of II with propylene oxide. Redistilled propylene oxide (Dow) was added drop-
wise to an ice-cold solution of II from 6.07 g. of I during 5 min. The white suspension was
stirred at 0° for 30 min., then hydrolyzed with water. The semicrystalline oil obtained from
the organic layer was boiled with methanol, leaving 0.52 g. of I. No additional solid could
be obtained by crystallization techniques, so the residue was evaporated in a molecular
still at 0.04 mm. Gummy material was obtained with a block temperature of 145–177°.
Fractions A, block 176–195°, 0.69 g., m.p. 122–154°; B, block 195–205°, 0.54 g., m.p. 144–163°;

C, block 205–214°, 1.84 g., m.p. 115–150°, were obtained subsequently. Fraction B could be crystallized from ethylene chloride; after three crystallizations, the colorless rhombic crystals melted at 169–171.5°.

Anal. Calc'd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16.

Found: C, 79.75; H, 8.10.

This substance appears to be contaminated with some polyoxide material.

Reaction of II with epichlorohydrin. Epichlorohydrin was added in 20 min. to the solution of II at −30 to −50°. After reaction for 1.5–4.5 hr. at 25°, impure I was recovered in small amount. When the mixture was refluxed at 68° for 0.5 hr., an intractable brown-black oil was obtained (14).

Reaction of II with allyl chloride. A solution of allyl chloride (10.00 g., 0.131 mole) in tetrahydrofuran was added at 0.5° during 1 hr. to a stirred solution of II from 5.82 g. (0.0327 mole) of I. The color changed from blue to brown, green, pink, and finally white. After an additional 2 hr. of stirring at 0.5°, the mixture was hydrolyzed with saturated ammonium chloride. The chilled organic layer deposited 1.59 g. of I. The residual oil obtained by evaporating the organic layer at 100° (20 mm.) weighed 6.01 g. A portion (3.83 g.) was chromatographed on alumina and eluted with 10% benzene in petroleum ether. The colorless oil weighed 3.13 g., n_D^{24} 1.5881. The oil was twice distilled, b.p. 128° (0.30 mm.), n_D^{23} 1.5910. The refractive index corresponds to C_{17}–C_{18}.

Anal. Calc'd for $C_{17}H_{16}$: C, 92.68; H, 7.32.

Found: C, 92.08; H, 6.47.

It was possible to elute traces of yellow crystals from the column by increasing the percentage of benzene in the eluting solution.

Reaction of II with ethyl haloacetates. Two runs were made with ethyl bromoacetate, one at 0° for 1 hr., one at 25° for 11 hr. Small amounts of material melting over a wide range were obtained, and from them could be isolated 10–15% of I but no other pure substance. Two similar runs with ethyl iodoacetate gave similar results. In a third run in which addition was made in 0.5 hr. at 40°, the resulting black tar yielded *dihydro*anthracene (III) upon chromatography.

Reaction of II with chloroacetone. Chloroacetone was added in 5 min. at −30° to the suspension of II. The color changed to green, then deep red. After 6 hr. at room temperature, the mixture was hydrolyzed and the organic layer was processed to yield 7% of I and 38% of III.

Reaction of II with benzoyl chloride. Benzoyl chloride in THF was added to II at 0.5° during 1 hr. After 2 hr. at room temperature, the mixture was poured into water. From the insoluble yellow paste there was isolated, with the aid of chromatography, 56% of I. The remainder was a dark oil.

Reaction of II with benzalacetophenone. Benzalacetophenone in THF was added at 0° to the II from 5.17 g. of I. A sharp color change to green occurred after 74% (9.04 g.) of the theoretical 2 moles had been added, so addition was discontinued and the mixture was stirred for 1 hr. at 0–5°. The now black solution was treated with ethanol and water, then filtered. Crop A was collected, 4.34 g., m.p. 202–207.5°, Crop B from partial evaporation of the organic layer weighed 3.30 g., m.p. 156–176°; crop C was obtained by complete removal of the solvent, 4.65 g., m.p. 165–180°. Crop A was mostly I, but a substance, m.p. 265.5–267.5°, was isolated by crystallization from dioxane-water as needles, 0.28 g. The analytical sample melted at 268°. The infrared spectrum showed carbonyl absorption at 1670 cm^{-1}.

Anal. Found: C, 86.42; H, 6.58.

Crop B was crystallized several times from ethyl acetate-water-methanol mixture, then from benzene-petroleum ether to give, besides I, colorless needles, m.p. 206.0–207.5°.

Anal. Found: C, 86.47; H, 5.99.

The expected product from 2 benzalacetophenone and 1 anthracene would have: C, 88.56; H, 6.08. It is evident that both these materials, possibly stereoisomers, are derived from

benzalacetophenone itself; a dimeric reduction product would have: C, 86.09; H, 6.26.[2] No further attempt was made to identify these products.

Reaction of II with acrylonitrile. In one case, addition of acrylonitrile to II during 1 hr. at 0–5°, followed by immediate hydrolysis, gave III and traces of compounds melting at 263–272° and 220–255° dec. When such a mixture was allowed to stand 24 hr. at room temperature, another material, m.p. 190–230°, was isolated in small amount, accompanied again by III. In each case, only small amounts of polyacrylonitrile were formed.

Reaction of II with β-propiolactone. A large excess of β-propiolactone was added at 0–5°. During the addition, the color changed through dark green to tan and yellow. After 30 min., the mixture was hydrolyzed. The organic layer contained a nearly quantitative amount of III and the aqueous layer a trace of gummy acid, doubtless polyhydracrylic acid.

SUMMARY

1. A rapid, convenient method has been developed for addition of sodium to anthracene by the use of a high-surface sodium dispersion and tetrahydrofuran solvent.

2. Carbonation of the disodio adduct affords *cis*-9,10-dihydroanthracene-9,10-dicarboxylic acid in 70% yield.

3. The disodio adduct reacts with a variety of reagents, such as acrylonitrile, benzoyl chloride, benzalacetophenone, and β-propiolactone, by hydrogen abstraction or by transmetalation.

4. The disodio adduct appears to have synthetic value only in its reactions with alkyl halides, carbon dioxide, and (possibly) aldehydes and ketones.

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