[Contribution from the Chemistry Department of the University of Colorado]

Diels-Alder Reactions of 9-Substituted Anthracenes. III.[1] Methyl and Allyl Acetals of 9-Anthraldehyde

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Attempts to prepare the allyl acetal of 9-anthraldehyde were unsuccessful due to the occurrence of an intramolecular Diels-Alder reaction. The methyl acetal of 9-anthraldehyde when condensed with methyl acrylate gave both possible Diels-Alder adducts of which the major one was of the *ortho*-type.

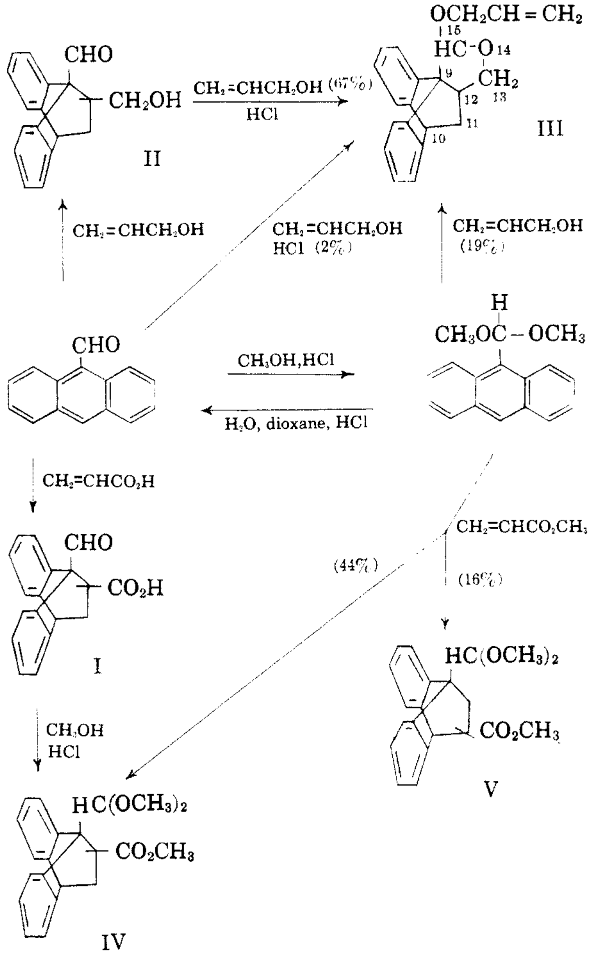
Previous work[2] has shown that 9-anthraldehyde has given only *ortho*-type 12-substituted-9,10-ethanoanthracene-9-carboxaldehydes with acrylic acid (I), acrylonitrile, and allyl alcohol (II). The oximes of 9-anthraldehyde were found to be unreactive as dienes[3] but other derivatives of 9-anthraldehyde, such as the acetals, are of interest.

The methyl acetal group is electron-rich, has one hydrogen atom capable of hyperconjugation, and should have quite a different polarizing effect on the anthracene nucleus than an aldehyde group. Being electron-rich it might aid Diels-Alder reactions in comparison to the aldehyde group but the greater bulk of the acetal group might sterically hinder the reaction. However, the increased hindrance did not prevent formation of adducts and the dimethylacetal was comparable to the aldehyde in reactivity as a diene.

The allyl acetal would have similar features but in addition would be expected to be capable of undergoing an intramolecular Diels-Alder reaction to give III.

This was found to be the case and efforts to obtain the allyl acetal of 9-anthraldehyde rather than compound III were unsuccessful. Compound III was identified by synthesizing it from the adduct of 9-anthraldehyde and allyl alcohol (II) and it was also prepared by the action of allyl alcohol on 9-anthraldehyde methyl acetal.

The methyl acetal of 9-anthraldehyde was prepared by recrystallizing 9-anthraldehyde in methanol to which a drop of hydrochloric acid was added. The high yield and ease of preparation was in marked contrast to the reaction of allyl alcohol with 9-anthraldehyde which gave only a very small yield. The alcohols higher than methanol appear to be too sterically hindered to react readily with 9-anthraldehyde. Recrystallizations from ethanol and 1-propanol did not give acetals. The methyl acetal was colorless but on standing it gradually darkened and took on the color of 9-anthraldehyde. The appearance of this yellow color was delayed by keeping the acetal tightly stoppered. When treated with acidified aqueous dioxane the methyl acetal was converted quantitatively to 9-anthraldehyde under conditions which failed to affect its methyl acrylate adduct.



Heating methyl acrylate and 9-anthraldehyde methyl acetal gave both possible isomers (IV and V). The major one was found to be the *ortho*-type adduct by synthesizing it from the known adduct[2] of 9-anthraldehyde and acrylic acid.

EXPERIMENTAL

9-Anthraldehyde methyl acetal.[4] A solution of 1.00 g.

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[1] Previous paper in this series: Meek and Dann, *J. Am. Chem. Soc.*, **78**, in press (1956).

[2] Meek and Poon, *J. Am. Chem. Soc.*, **74**, 761 (1952).

[3] Meek and Dann, *J. Am. Chem. Soc.*, **77**, 6677 (1955).

[4] This compound was prepared for the first time by Mrs. David E. Ramey.

(0.00485 mole) of 9-anthraldehyde (m.p. 104°) in 10 ml. of methanol acidified with one drop of concentrated hydrochloric acid was refluxed for 10 minutes and then left in a stoppered flask overnight. The methyl acetal separated in white plates and weighed 0.98 g. (79%), m.p. 145–146°.

Anal. Calc'd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.00; H, 6.32.

A 2-g. portion (0.00795 mole) of the methyl acetal of 9-anthraldehyde was placed in a flask with 25 ml. of water, 0.5 ml. of concentrated hydrochloric acid, and 10 ml. of dioxane. The mixture was heated for 30 minutes at 90°. Upon cooling, 1.65 g. (100%) of yellow crystals was obtained, m.p. 104–105°. A mixture m.p. with 9-anthraldehyde gave no depression.

Methyl 9-dimethoxymethyl-9,10-ethanoanthracene-12- and -11-carboxylate (IV and V). A mixture of 5.0 g. (0.02 mole) of the methyl acetal of 9-anthraldehyde, 17.2 g. (0.20 mole) of methyl acrylate, and 0.2 g. of hydroquinone was heated in a sealed tube at 120° for 17 hours. The excess methyl acrylate was evaporated and the sticky residue was dissolved in methanol. Upon cooling, 1.1 g. (16%) of crystals melting at 152–154° and 3 g. (44%) of crystals melting at 120–125° was obtained. Upon very slow recrystallization from methanol the melting points were raised to 135–136° (IV) and 155–156° (V).

Anal. Calc'd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: Low-melting isomer, C, 74.65; H, 6.73. High-melting isomer, C, 74.46; H, 6.46.

One gram of the higher-melting isomer (m.p. 152–153°) of the above adduct was placed in a flask with 25 ml. of water, 0.5 ml. of concentrated hydrochloric acid, and 10 ml. of dioxane. The mixture was heated for 30 minutes at 85–90°. Upon cooling, the starting material was recovered unchanged.

One gram of the adduct[2] of 9-anthraldehyde and acrylic acid (m.p. 211–212°) was dissolved in 20 ml. of methanol, one drop of concentrated hydrochloric acid was added, and the solution was saturated with dry hydrogen chloride. The container was stoppered and left standing for 19 hours. Upon evaporating some of the methanol, 0.5 g. of crystals was obtained, m.p. 135–136° and a mixture m.p. with the lower-melting isomer of the adduct of the acetal of 9-anthraldehyde and methyl acrylate was not depressed and showed that this isomer was methyl 9-dimethoxymethyl-9,10-ethanoanthracene-12-carboxylate.

15-Allyloxy-9,12-methanoxymethano-9,10-ethanoanthracene (III). (*a*). A mixture of 2.0 g. (0.0097 mole) of 9-anthraldehyde (m.p. 104–105°), 10 ml. (0.21 mole) or allyl alcohol, and 2 drops of concentrated hydrochloric acid was heated at 93° under a reflux condenser for 3 hours. The excess allyl alcohol then was distilled and the yellow residue was recrystallized from ethanol. A total of 1.8 g. of 9-anthraldehyde was recovered and also 0.06 g. (2%) of white solid crystals (III) which melted at 117–118° after recrystallization from ethanol.

Anal. Calc'd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.67; H, 6.65.

In an effort to improve the yield of III, the above procedure was changed so as to use 0.001 mole of calcium chloride, instead of hydrochloric acid as the catalyst, but only 0.05 g. (1.6%) of the acetal was obtained after heating for 24 hours at 87°.

(*b*). A mixture of 0.0478 g. (0.000194 mole) of 12-methylol-9,10-ethanoanthracene-9-carboxaldehyde,[2] m.p. 170–171°, and 5 ml. of allyl alcohol containing one drop of concentrated hydrochloric acid was heated at 90° for 15 hours. The excess allyl alcohol was removed and the residue was recrystallized from benzene and gave 0.0480 g. of white crystals, m.p. 100–105°. A second recrystallization from ethanol gave 0.0402 g. (67%), m.p. 115–117°. The mixture melting point with III was 115–117°.

(*c*). A mixture of 0.95 g. (0.0037 mole) of the methyl acetal of 9-anthraldehyde (m.p. 145–146°), 10 ml. of allyl alcohol, and 0.1 g. of hydroquinone was heated under a reflux condenser at 90° for 23 hours. Upon removing the excess allyl alcohol, yellow 9-anthraldehyde, 0.135 g., m.p. 100–103° was recovered along with 0.223 g. of white crystals, m.p. 116–117°. A mixture m.p. of these crystals with the material obtained from the action of allyl alcohol and acid upon the adduct of 9-anthraldehyde and allyl alcohol was not depressed.

A 25-mg. portion of III, 5 ml. of ethanol, 5 ml. of water, and 1 drop of concentrated hydrochloric acid was left standing for one month. The material which was separated from the solution at that time was unchanged from the starting material, m.p. 117–118°.

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