N, 10.15. Found: C, 51.99; H, 8.72; N, 10.02.[19] Calcd. for $C_6H_{11}NO_2$: C, 55.79; H, 8.58; N, 10.85. Calcd. for $C_6H_{11}NO_2{\cdot}H_2O$: C, 48.96; H, 8.90; N, 9.52.

The phthaloyl derivative was prepared by heating with phthalic anhydride[20] and had a melting point of 140.5–141° after recrystallizing from 50% ethanol.

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05. Found: C, 64.71; H, 5.04.

The infrared absorption spectrum of I was determined in mineral oil using sodium chloride prisms and plates in a Perkin–Elmer model 12C infrared spectrometer.[1]

Cyclopropylcarbinylaminomalonic Acid.—Twenty-five and seven-tenths grams (0.1 mole) of the malonic ester was hydrolyzed by boiling with 250 ml. of 15% potassium hydroxide for 6 hours. The hydrolysate was diluted to one liter and run several times through a Duolite C-10 cation exchange column as it was very difficult to remove every trace of potassium from the compound. The solution was then concentrated under reduced pressure and crystallized from ethyl alcohol to give 14 g. of product which decomposed with the evolution of a gas at 210°. *Anal.* Calcd. for $C_{17}H_{11}NO_4$: N, 8.09. Found: N, 8.12.

The compound gave a weak ninhydrin test, was very soluble in water and insoluble in absolute alcohol. When refluxed with 10% hydrobromic acid, carbon dioxide was evolved and caught in a barium hydroxide trap, and upon purification of the product *via* the Duolite A-2 anion exchange column, Compound I was isolated as determined by the strong ninhydrin test, melting point and mixed melting point.

Acknowledgment.—The authors wish to thank the University of Colorado Council on Research and Creative Work for financial support of this research.

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[19] Nitrogen analyses were performed by Mrs. D. E. Ramey, University of Colorado.

[20] J. H. Billman and W. F. Hartung, This Journal, **70**, 1473 (1948).

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The Oximes of 9-Anthraldehyde

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A 9-anthraldoxime was first reported by Hinkel, Ayling and Beynon[1] as being prepared "readily—by the usual methods" and melting at 187°.[2] Fieser and Hartwell prepared 9-anthraldoxime in 93% yield and obtained a melting point of 165° (I).[3]

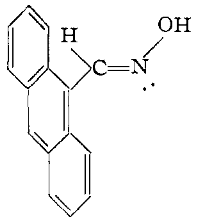
No difficulty was experienced in repeating Fieser and Hartwell's work, in which hydroxylamine hydrochloride neutralized with sodium carbonate was allowed to react with 9-anthraldehyde.

When hydroxylamine hydrochloride was used in 50% ethanolic pyridine[4] an oxime melting at 218–220° (II) was obtained. This compound could also be made by heating I in ethanol at 75° in the presence of a trace of hydrochloric acid. Compound I could be dissolved in hot 5% sodium hydroxide and reprecipitated with hydrochloric acid. Only a trace of II dissolved when heated on a steam-bath for a half-hour with 5% sodium hydroxide.

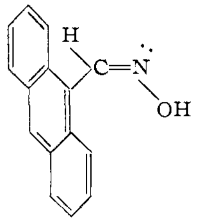
When compound I was warmed with acetic anhydride for 10 minutes the acetate was formed. Similar treatment of II gave 9-cyanoanthracene.

When I and allyl chloride were warmed with sodium hydroxide in aqueous ethanol a yellow compound presumably the O-allyl derivative (III) was formed. II upon similar treatment gave some orange colored resin and 9-cyanoanthracene.

On the basis of the above evidence I is believed to be *syn*-9-anthraldoxime (a) and II the *anti* isomer (b).



a



b

anti Forms of aldoximes upon treatment with a dehydrating agent of any kind generally lose water to yield a nitrile[5a] and it is to be noted that acetic anhydride and sodium hydroxide did convert II to a nitrile under conditions which convert I to the acetate and O-allyl derivatives. The *syn* form usually has the lower melting point and a higher ionization constant[5b] which again is in accord with our assignment of structures. The oxime with the more hindered group as in b should be more difficultly soluble in base since the resulting negative ion would be harder to solvate.

Compound I gave an allyl derivative with allyl chloride and base while II did not. This may again be due to the lack of salt formation with the less acidic oxime. The fact that the allyl derivative was yellow showed that the compound was an anthracene derivative and not an ethanoanthracene resulting from an intramolecular Diels–Alder reaction. If the O-allyl compound was derived from structure b, it should easily undergo an intramolecular Diels–Alder reaction and probably not be isolable. If III were derived from structure a, it could not give an intramolecular Diels–Alder reaction but at best an intermolecular reaction leading to a dimer, trimer or polymer. When III was heated at 200° for 10 minutes some III was recovered and an intractable oil was obtained.

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[1] L. E. Hinkel, E. E. Ayling and J. H. Beynon, *J. Chem. Soc.*, 339 (1936).

[2] This melting point for an oxime of 9-anthraldehyde has not been reported again in the literature. Hinkel, Ayling and Beynon report that after crystallizing 9-anthraldehyde, m.p. 105°, in the light it melted over a range up to 135°. It is not likely that they used this material containing the photodimer to prepare their oxime, m.p. 187°. The photodimer of 9-anthraldehyde melts at 187° also according to F. D. Greene, S. L. Misrock and J. R. Wolfe, Jr., This Journal, **77**, 3852 (1955). Greene in a private communication reported that his group has not yet made the oxime of this dimer and their preparation of the oxime of 9-anthraldehyde gave 88% of I with a trace of higher melting material, possibly our oxime, m.p. 220°.

[3] L. F. Fieser and J. L. Hartwell, This Journal, **60**, 2555 (1938).

[4] Two usual methods for preparing oximes are given by R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 202. The first of these uses sodium hydroxide instead of sodium carbonate and less alcohol, but otherwise resembles Fieser and Hartwell's method. The second procedure using pyridine and ethanol is the one leading to our oxime.

[5] (a) E. F. Degering, "An Outline of Organic Nitrogen Compounds," University Lithoprinters, Ypsilanti, Michigan, 1945, p. 182; (b) p. 175.

Attempts to prepare Diels–Alder adducts of either oxime were unsuccessful.

Experimental

syn-**9-Anthraldoxime.**—When 7 g. of hydroxylamine hydrochloride and 15 g. of 9-anthraldehyde were used as in Fieser and Hartwell's procedure,[3] 15.5 g. (96%) of *syn*-9-anthraldoxime was obtained, m.p. 160–165°. Recrystallization from ethanol gave long yellow needles, m.p. 165–166°, lit.[3] 165–165.5°. This compound was readily soluble in hot 5% sodium hydroxide.

anti-**9-Anthraldoxime.**—A mixture of 5 g. (0.024 mole) of 9-anthraldehyde and 5 g. (0.073 mole) of hydroxylamine hydrochloride in 25 ml. of pyridine and 25 ml. of anhydrous ethanol was heated on the steam-bath for 1.5 hours. The pyridine and ethanol were then removed by heating on the steam-bath for 4 more hours while blowing a jet of air into the reaction flask. The solid residue was ground with 25 ml. of water, filtered and washed with 10 ml. of water. The crude product (m.p. 211–214°) was recrystallized from ethanol (750 ml. was necessary for complete solution). Upon cooling, 5.2 g. (97%) of product was obtained, m.p. 218–220°. When 2 g. of this material was heated on the steam-bath in 50 ml. of 5% sodium hydroxide for 0.5 hour only a trace of it dissolved.

Anal. Calcd. for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.46; H, 5.12; N, 6.04.

In a further experiment, 0.200 g. of *syn*-9-anthraldoxime, m.p. 165°, was placed in 10 ml. of ethanol containing 2 drops of concentrated hydrochloric acid and heated at 75° for 17 hours. Upon cooling, 0.150 g. of material (75%) was separated, m.p. and mixed m.p. with the *anti*-oxime 218–220°.

Treatment of I and II with Acetic Anhydride.—In an effort to compare the ease of dehydration of I and II, 0.22 g. of each was placed in 2 ml. of acetic anhydride and warmed on the steam-bath for 10 minutes. Each solution was then made basic with 2 g. of sodium carbonate in 10 ml. of water and heated on the steam-bath for 10 minutes, cooled, diluted with 20 ml. of water and filtered.

Compound I was converted to a material melting at 132–133°; Fieser and Hartwell[3] give the melting point of the oxime acetate as 131.5–132°. II was converted to a compound melting at 173–174° and a mixed m.p. with 9-cyanoanthracene gave no depression. Refluxing I for 15 minutes with acetic anhydride will also produce 9-cyanoanthracene.[3]

Treatment of I and II with Allyl Chloride.—A mixture of 1.1 g. (0.005 mole) of I, 0.5 ml. (0.005 mole) of allyl chloride and 0.2 g. (0.005 mole) of sodium hydroxide in 2 ml. of water and 10 ml. of ethanol was heated under a reflux condenser to 80° and then allowed to cool. Since the allyl chloride seemed to be evaporating, 0.5 ml. more was added, the mixture was heated to 70° and allowed to cool. A very small amount of precipitate formed so 25 ml. of water was added. A precipitate melting at 75–78° was then formed. Upon dissolving in hot ethanol, diluting with water to the cloud point and allowing to cool, the melting point of the yellow compound O-allyl-*syn*-9-anthraldoxime was raised to 85–86°.

Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79. Found: C, 82.70; H, 5.60.

About 0.4 g. of the above material was obtained along with a low melting, polymer-like material. Upon heating 0.1 g. of O-allyl-*syn*-9-anthraldoxime in an oil-bath at 200° for ten minutes, 0.04 g. was recovered unchanged, while the remainder of the material was converted to an oil which could not be made to crystallize.

A mixture of 1.1 g. (0.005 mole) of II, 2 ml. (0.02 mole) of allyl chloride and 0.2 g. (0.005 mole) of sodium hydroxide in 2 ml. of water and 50 ml. of ethanol was refluxed for 20 minutes. Ten milliliters of water was added to the hot solution and 0.90 g. of yellow crystals were obtained in three crops: 1st crop, 0.22 g., m.p. 167–173°; 2nd crop, 0.33 g., m.p. 135–155°; 3rd crop, orange-colored resin 0.35 g. Recrystallization of crops I and II gave only 9-cyanoanthracene as isolable products.

Attempted Diels–Alder Reactions.—Compound I gave little evidence of adduct formation when heated under a reflux condenser with allyl alcohol, acrylic acid in sodium hydroxide solution, allyl chloride or acrylyl chloride, and upon refluxing with acrylamide in xylene.

When 1.1 g. of I dissolved in 10 ml. of 5% sodium hydroxide and 6 ml. of allyl alcohol was refluxed for 21 hours almost 1.1 g. of solid, m.p. 175–176°, was obtained and was identified as 9-cyanoanthracene by its color and mixed melting point.

II gave no evidence of adduct formation in reactions under reflux conditions with allyl chloride and acrylyl chloride by heating in a sealed tube reaction with acrylonitrile, or by heating with acrylamide in xylene.

Acrylyl chloride led to 9-cyanoanthracene with both oximes.

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The Preparation and Decarboxylation of Some α-Alkyl-β,β-dimethylglycidates

BY HORTON H. MORRIS AND RAYMOND H. YOUNG, JR.[1]

RECEIVED JULY 28, 1955

The nature of the products obtained by thermal decarboxylation of various α-substituted glycidic acids has been the subject of previous reports[2] from this Laboratory. In order to further establish that ketones, and not aldehydes, result when glycidic acids containing alkyl groups in the α-position undergo decarboxylation, and in continuation of our study of the glycidic ester condensation, an homologous series of previously unreported ethyl α-alkyl-β,β-dimethylglycidates has been prepared, where the alkyl group varies from methyl through nonyl.

The presence of an unsaturated, hydroxy-containing contaminant was detected by means of the infrared spectra in the initial preparations of the α-hexyl, α-heptyl and α-octyl glycidic esters. A report by Johnson, *et al.*,[3] and work to be reported later from this Laboratory strongly suggests that the impurity is the corresponding ethyl α-hydroxy-α-alkyl-β-methyl-β,γ-butenoate. The preparations were repeated, taking special precautions to maintain anhydrous conditions, and the glycidic esters so obtained were easily purified and showed no trace of the contaminant.

The corresponding glycidic acids decarboxylated under the influence of heat to yield the expected 2-methyl-3-alkanones in yields of 50–75%. The structures of the ketones, several of which are new, have been established by alternate syntheses and the determination of mixed melting points of derivatives.

An empirical relationship between the reciprocal of the molecular weight of an organic liquid and its refractive index exists and has proved to be a useful tool in this Laboratory. The general equation is $n^{20}\mathrm{D} = A/M + 1.4704 \pm 0.0006$, where A is a homology constant and M is the molecular weight. The A values for the homologous series reported

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[1] From the thesis submitted by Raymond H. Young, Jr., in partial fulfillment of the requirements of the degree of Master of Science in Chemistry, June, 1955.

[2] H. H. Morris and C. J. St. Lawrence, THIS JOURNAL, **77**, 1692 (1955), and previous papers.

[3] W. S. Johnson, J. Belew, L. Chinn and R. Hunt, *ibid.*, **75**, 4995 (1953).