was added portionwise to two equivalents of the appropriate amine in dioxane. The mixture was then heated on the steam bath for 1 hr. The dioxane was removed under reduced pressure and dilute ethanol was added to the residue. The solution was treated with carbon if necessary and then filtered. The products were crystallized by concentrating the solution and cooling. The 3-amino-1,2-benzisothiazole-1,1-dioxides were purified by crystallization from ethanol or aqueous ethanol.

N-Substituted-o-sulfamylbenzamides (Table II). Saccharin (0.10–0.20 mole) was added to chlorobenzene to which one equivalent of the appropriate amine had been added. The mixture was refluxed for 8 hr. and then the solvent was removed under reduced pressure. The residue was acidified by the addition of dilute hydrochloric acid and cooled. The material which crystallized was collected and recrystallized from dilute ethanol. The *o*-sulfamylbenzamides were purified by crystallization from aqueous ethanol.

N-Substituted-o-methylsulfamylbenzamides (Table II). *N*-Methylsaccharin[3] (0.05–0.10 mole) was added to excess alkyl- or aralkylamine boiling at least at 130°. The mixture was refluxed for 8 hr. and then as much of the excess amine as possible was removed under reduced pressure. Dilute hydrochloric acid was added to the residue and the acidic solution was cooled to induce crystallization. The material which crystallized was collected and recrystallized from dilute ethanol. The *o*-methylsulfamylbenzamides were purified by crystallization from aqueous ethanol.

o-Sulfamylbenzoylhydrazine. Eighteen grams (0.10 mole) of saccharin was heated on the steam bath for 5 hr. with 5 g. (0.10 mole) of 100% hydrazine hydrate in 250 ml. of dioxane. After the mixture had become homogeneous most of the dioxane was removed under reduced pressure and the crystalline residue was collected. The product was crystallized from ethanol to yield 16.5 g. (77%) of material. The *o*-sulfamylbenzoylhydrazine was purified by crystallization from ethanol, m.p. 180° dec.

Anal. Calcd. for $C_7H_9N_3O_3S$: C, 39.06; H, 4.21; N, 19.53. Found: C, 39.06; H, 4.10; N, 19.81.

o-Methylsulfamylbenzoylhydrazine. Twenty grams (0.10 mole) of *N*-methylsaccharin was added to 150 ml. dioxane. Five grams (0.10 mole) of 100% hydrazine hydrate was added to the solution and the mixture was heated on the steam bath for 4 hr. The dioxane was removed under reduced pressure and the residue was dissolved in ethanol and filtered. The product was crystallized by concentrating the ethanol solution and cooling. The *o*-methylsulfamylbenzoylhydrazine was purified by crystallization from ethanol to yield 17 g. (74%) of material, m.p. 140°.

Anal. Calcd. for $C_8H_{11}N_3O_3S$· C, 41.91; H, 4.84; N, 18.33. Found: C, 42.04; H, 4.92; N, 18.18.

N-Acetylsaccharin. Five grams of *o*-sulfamylbenzoylhydrazine was warmed on the steam bath with 40 ml. acetic anhydride to dissolve the solid. The mixture was allowed to stand overnight at room temperature. The excess acetic anhydride was removed under reduced pressure and the residue was dissolved in ethanol. The ethanol solution was concentrated and cooled to yield 3 g. of material with m.p. 191° (lit.[4] m.p. 193°) after recrystallization from ethanol. The infrared spectrum of this material was identical with that of an authentic sample of *N*-acetylsaccharin.

Anal. Calcd. for $C_9H_7NO_4S$: C, 48.00; H, 3.12; N, 6.23. Found: C, 47.84; H, 2.82; N, 6.07.

1-Acetyl-2-(o-sulfamylbenzoyl)hydrazine. Five grams of *o*-methylsulfamylbenzoylhydrazine was warmed on the steam bath with 35 ml. acetic anhydride and then allowed to stand overnight at room temperature. The excess acetic anhydride was removed under reduced pressure and the residue was dissolved in ethanol. Concentration of the solution and cooling yielded 3.5 g. of material. The 1-acetyl-2-(*o*-sulfamylbenzoyl)hydrazine was recrystallized from ethanol m.p. 164°.

Anal. Calcd. for $C_{10}H_{13}N_3O_4S$: C, 44.27; H, 4.83; N, 15.49. Found: C, 44.17; H, 4.97; N, 15.78.

Acknowledgement. The authors thank R. M. Hughes, H. L. Hunter, and G. Maciak for the microanalyses. Harold Boaz and Donald Woolf gave valuable aid in establishing the structures and interpreting the physical data of the compounds reported.

INDIANAPOLIS, IND.

---

[3] H. L. Rice and G. R. Pettit, *J. Am. Chem. Soc.*, **76**, 302 (1954).

[4] H. Eckenroth, *Chem. Zentr.*, I, 235 (1897).

[CONTRIBUTION NO. 1587 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Electron Exchange Polymers. XIII. The Preparation of β-Vinylanthraquinone[1]

MIGUEL FERNANDEZ-REFOJO, YUE-LIANG PAN, KENNETH A. KUN, AND HAROLD G. CASSIDY

Received October 5, 1959

The synthesis of β-vinylanthraquinone (2-ethenylanthraquinone) from 2-methylanthraquinone is described. 2-Methylanthraquinone is oxidized to the 2-aldehyde which is converted to anthraquinone-2-acrylic acid. This yields β-vinylanthraquinone upon decarboxylation. The vinyl compound is characterized by physical and chemical methods. It appears possible to polymerize the vinyl compound and to prepare copolymers with styrene, with α-methylstyrene, and with maleic anhydride using free-radical initiators. The yields are low, and the products have not been characterized.

Anthraquinone has been shown not to interrupt the polymerization of styrene, as the presence of anthraquinone during polymerization has no effect on the molecular weight of the polystyrene produced.[2] Anthraquinone is also reported not to react with free radicals from azodiisobutyronitrile.[3] Moreover, three vinylanthracenes have been pre-

---

[1] This work was supported in part by a research grant G 3207 from The Division of Research Grants of The National Institutes of Health, Public Health Service, and in part by a grant from Research Corporation, both of which we acknowledge with pleasure.

[2] B. A. Dolgoplosk and S. Sh. Korotkina, *Zhur. Obshcheĭ Khim.*, **27**, 2546 (1957). (Through *Chem. Abstr.*, **52**, 7218^i.)

[3] F. J. L. Aparicio and W. A. Waters, *J. Chem. Soc.*, **1952**, 4666.

pared: the 1-, 2- and 9-compounds;[4] it is observed that they polymerize. These findings show that under the conditions of the experiments neither the reducibility of anthraquinone nor the size of the parent anthracene molecule prevent vinyl polymerization. It thus seemed feasible to prepare a vinylanthraquinone, and from it to prepare a polyvinylanthraquinone which would contribute an additional type of ring system to our class of oxidation reduction, or electron exchange polymers.[5] The preparation and properties of β-vinyl anthraquinone (2-ethenylanthraquinone) are reported here, as well as some attempts at polymerization.

EXPERIMENTAL

Anthraquinone-2-aldehyde diacetate.[6] Twenty-five grams of 2-methylanthraquinone was dissolved in a hot mixture of 625 ml. glacial acetic acid and 925 ml. acetic anhydride. The mixture was held at 5–10° while 25 ml. of concentrated sulfuric acid, followed by a solution of 30 g. chromic oxide in 30 ml. acetic acid, were added. The addition of the chromic solution should be done with vigorous stirring and should be completed in 2 hr. The mixture was stirred for about 4 more hr. at 5–10° then allowed to warm to room temperature. The greenish solution was poured into ice water, and the resulting precipitate filtered, washed five times with distilled water, and dried. Extraction with chloroform removed the desired product and left as a residue the byproduct, anthraquinone-2-carboxylic acid. Removal of the chloroform yielded a solid which was recrystallized twice from 95% ethyl alcohol. Pure anthraquinone-2-aldehyde diacetate so produced formed yellow, crystalline leaflets, m.p. 145–146° (corr.); yield 22.5 g., (59%).

Anthraquinone-2-aldehyde.[6] Twenty-eight grams of anthraquinone-2-aldehyde diacetate was dissolved in 650 ml. warm acetic acid, and 280 ml. conc. hydrochloric acid was added. The mixture was refluxed 10–15 min. and allowed to cool to room temperature. As the long, light yellow needles which formed are sensitive to light, becoming gray on exposure, the material was kept in the dark and handled in dim light. The crystalline product, dried *in vacuo* over sodium hydroxide pellets, melts at 187–188°, yield: 17.5 g. (89.6%). The filtrate, poured into ice water, yielded about 2 g. of nearly pure aldehyde, m.p. 185–188°, as a light yellow solid, apparently not sensitive to light.

Anthraquinone-2-acrylic acid. When this substance was prepared by the method of Eckert,[7] using a Perkin reaction, the yield was only fair, and the crude product was difficult to purify. The procedure of Hershberg and Fieser[8] gave excellent results. In a 250 ml. round bottom flask, 9.6 g. anthraquinone-2-aldehyde (0.040 mole), 15 g. malonic acid (0.144 mole), and 50 ml. pyridine were refluxed gently (oil bath). At first, the solids dissolved, then in 2 or 3 min. with increased gas evolution and foaming, the mixture set suddenly to a pasty mass. The mixture was heated for 1 hr. with occasional shaking, then 7.5 g. (0.072 mole) of malonic acid and 15 ml. pyridine were added and the mixture heated 1 hr. longer. The mixture was allowed to cool, and was filtered and the yellow solid washed thoroughly with pyridine five times and then with ethyl alcohol. Soluble impurities were thus removed, leaving a yellow solid which, vacuum dried, melted at 333–335°, and weighed 10.5 g. Yield 92.8%.

2-Vinylanthraquinone. Catalytic decarboxylation methods were used to prepare vinylanthraquinone from anthraquinone-2-acrylic acid.[8,9] Ten parts of the acid were heated with 1 part of catalyst in 7 to 8 parts of quinoline at its boiling point (230–240°). After 20 to 30 min., when the evolution of gas had stopped (longer heating decreases the yield), the brown solution containing some solid particles was cooled and extracted with ether. The extract was washed with 4*N* hydrochloric acid (care) four or five times, and with water. Upon drying the ether solution over anhydrous sodium sulfate and removing the ether, a crude 2-vinylanthraquinone was obtained, which could be purified by vacuum sublimation. Alternatively, the brown solution may be poured into excess 2*N* hydrochloric acid to form the soluble quinoline salt. The product was washed free of acid and dried. The charcoal-gray solid remaining was extracted with hot 95% ethyl alcohol. Removal of the alcohol from the extract, by distillation, left crude 2-vinylanthraquinone. Both methods gave nearly the same yields.

The catalysts used were: copper powder, yield 21.4%; basic cupric carbonate, yield 22.8%. When the latter catalyst was added to the boiling solution of anthraquinone-2-acrylic acid in quinoline a slightly improved yield of 25.7% of theory was obtained.

Vacuum-sublimed 2-vinylanthraquinone still smelled of quinoline. Two recrystallizations from ethyl acetate gave a product almost free from quinoline. This formed clusters of yellow crystals, m.p. 175–177°. The substance is slightly soluble in carbon tetrachloride, ether, and glacial acetic acid. It is soluble in toluene, in ethylene dichloride and in warm alcohol, and very soluble in chloroform. The substance shows the —C═C— stretching vibration at 6.11 μ in the infrared region.

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.05; H, 4.30. Found: C, 82.25; H, 4.32.

Bromination with pyridine sulfate dibromide[10] calculated for 1.00 double bond; found: 0.88. Hydrogenation in ethyl acetate, using platinum oxide to yield the ethylanthrahydroquinone gave the following results: 0.0523 g. should consume 10.01 ml. hydrogen (S.T.P.). Found: 11.8 ml. A control with 0.1691 g. ethylanthraquinone calcd. 16.03 ml. Found: 18.2. Evidently the hydrogenation easily goes further—possibly to anthranol. The hydrogenation product from vinylanthraquinone is oxidized by air[11] to 2-ethylanthraquinone, with disappearance of fluorescence. The product was shown to be identical with an authentic sample of 2-ethylanthraquinone: m.p. 104.4–107.3°; authentic sample, 107.4–108.3°; mixed m.p. 106.4–108.3°. Infrared spectra were superimposable.

Ozonization of 2-vinylanthraquinone under the conditions used by Hawkins[4a] yielded as the final product anthraquinone-2-carboxylic acid, m.p. 288–290°; authentic sample 290–291°; mixture 290–291°. Infrared spectra were superimposable.

N.M.R. examination. An examination of the nuclear magnetic resonance spectra of vinyl- and ethylanthraquinone produced the expected results. Measurements were made with Varian V-4300 high-resolution N.M.R. spectrometer operating at a frequency of 60 Mc./sec. and a field strength of approximately 14,000 gauss. The anthraquinones were

---

(4) (a) E. G. E. Hawkins, *J. Chem. Soc.*, 1957, 3858. (b) E. D. Bergmann and Dov Katz, *J. Chem. Soc.*, 1958 (3216).

(5) H. G. Cassidy, *J. Am. Chem. Soc.*, **71**, 402 (1949); H. J. Harwood and H. G. Cassidy, *J. Am. Chem. Soc.*, **79**, 4360 (1957); I. D. Robinson, M. Fernandez-Refojo, and H. G. Cassidy, *J. Polymer Sci.*, **39**, 47 (1959); Y-h. Chen, M. Fernandez-Refojo, and H. G. Cassidy, *J. Polymer Sci.*, **40**, 433 (1959).

(6) F. Ullmann and K. L. Klingenberg, *Ber.*, **46**, 712 (1913).

(7) A. Eckert, *Monatsh.*, **35**, 289 (1914).

(8) E. B. Hershberg and L. F. Fieser, *J. Am. Chem. Soc.*, **63**, 2561 (1941).

(9) C. Walling and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **69**, 852 (1947); W. S. Emerson, *Chem. Rev.*, **45**, 347 (1949); B. R. Brown, *Quart. Rev.*, **5**, 131 (1951).

(10) K. W. Rosenmund and W. Kuhnhenn, *Ber.*, **56**, 1262 (1923); M. Yasuda, *J. Biol. Chem.*, **94**, 401 (1932).

(11) W. Manchot, H. Gall, *Ber.*, **58**, 486 (1925).

dissolved in deuterochloroform using tetramethylsilane as an internal reference for a scale of shielding values.[12] Vinylanthraquinone showed the twelve strong lines of the ABC (approximately ABX) system,[13] $—CH_X{=}CH_AH_B$, which comprise three symmetrically split quartets centered at values of τ[12]: (X) 3.16, (A) 4.00, and (B) 4.50 with splittings: (X) 10.2 and 17.4 cps., (A) 1.2 and 17.4 cps., and (B) 1.2 and 10.2 cps. Coupling between geminal protons A and B within trigonally hybridized methylene is expected to be small as in styrene and *p*-methylstyrene.[14]

Ethylanthraquinone showed the typical spectrum for an ethyl group with the methylene quadruplet centered at 7.28 τ and the methyl triplet centered at 8.70 τ. Both compounds showed a pair of complex peaks for the aromatic hydrogens which centered at 1.77 and 2.25 τ.

Attempted polymerization of vinylanthraquinone. The folowing experiments were carried out in a flask with adapter carrying a two-way stopcock so that when monomer, solvent, and catalyst had been introduced the flask could be repeatedly evacuated and filled with nitrogen.

a. *With azobisisobutyronitrile.* 2-Vinylanthraquinone (referred to as monomer) 0.1019 g., 0.001 g. azodiisobutyronitrile, and 10 ml. reagent toluene were heated under nitrogen at 80° for 18 hr. There was neither turbidity nor apparent viscosity change. A further portion of 0.0034 g. catalyst (total 4.32% based on monomer) was added and after 23 hr. the mixture was seen to be turbid. Methanol precipitated 0.0073 g. solid, softening point 190–210°. The infrared spectrum showed the main peaks of anthraquinone but lacked the vinyl absorption at 6.12 μ. Residue from the mother liquors also lacked this peak.

b. *With benzoyl peroxide.* Benzoyl peroxide, 0.004 g., monomer 0.1037 g. in 10 ml. toluene, heated under nitrogen at 80° produced a turbidity after 4 hr., and a precipitate at 24 hr. The solid, removed and washed, weighed 0.0171 g. and softened at 320–330°. To the mother liquors 0.003 g. of catalyst was added and after 32 hr. 0.0164 g. of solid had precipitated. Its characteristics were the same as those of the first product. Again 0.003 g. catalyst was added to the filtrate and after 23 hr. at 80° under nitrogen, a turbid solution was present. Methanol in excess precipitated 0.013 g. solid, with a softening point of 210–220°. Infrared spectra indicated the same anthraquinone structure as the previous fractions. Total product 0.0465 g. (44.8%).

c. *With titanium tetrachloride.* To a solution of 0.1029 g. monomer in 10 ml. ethylene dichloride at −30° was added 0.05 to 0.07 ml. 99.5% titanium tetrachloride. An orange precipitate formed at once. After 2 hr. at low temperature the mixture was brought to room temperature and 95% ethanol added. The orange colored material gave way to a clear yellowish solution. Removal of solvents and working up the products yielded 0.0893 g. (86.78%) of monomer, identified by m.p. and IR.

d. *With sodium.* To a blue solution of 0.0106 g. sodium in *ca.* 20 ml. ammonia at its boiling point, 0.1024 g. monomer in 10 ml. toluene was added. The blue color remained unchanged. After several hours a reddish precipitate had formed on the wall of the flask. Finally, 0.5 g. ammonium chloride was added, the blue color being discharged at once. The ammonia was allowed to evaporate and the product worked up to yield 0.089 g. (86.9%) of monomer, identified by m.p. and infrared.

e. *Copolymerization with styrene* was attempted using 0.1 g. monomer, 0.5 g. freshly distilled styrene, (molar ratio 1:11), 0.006 g. benzoyl peroxide, in 10 ml. toluene. After 24 hr. at 80° under nitrogen there was no apparent increase in viscosity. Methanol in excess precipitated 0.051 g. yellow-white powder, softening at 138–148°, and exhibiting in the infrared peaks characteristic of anthraquinone, and the aromatic absorption of benzene at 6.69 and 6.89 μ.

f. *Copolymerization with α-methylstyrene* was attempted using 0.1 g. monomer, 0.5 g. α-methylstyrene (molar ratio 1:11) and 0.006 g. benzoyl peroxide in 10 ml. toluene. After 19 hr. at 80° under nitrogen, the mixture was cooled and excess methanol added to precipitate 0.0101 g. (1.8% of both monomers) of a solid softening at 165–195°, showing bands in the infrared at 3.47, 6.69, 6.82, 6.93 μ and a small band at 5.80 μ.

g. *Copolymerization with maleic anhydride* was attempted using 0.234 g. monomer, 0.099 g. maleic anhydride (molar ratio 1:11) and 1% benzoyl peroxide in 20 ml. toluene. After 23 hr. at 80° under nitrogen a precipitate was present. Methanol in excess was added, to precipitate 0.046 g. solid (13.8% on both monomers). Using a similar mixture but heating at 100° for 17 hr. produced 0.043 g. (12.9%) of similar product. Using a preparation containing a monomer-maleic anhydride ratio of 1:10, and 2% benzoyl peroxide based on monomer, for 41 hr. at 80°, under nitrogen, 0.0383 g. (11.5% if monomers react 1:1) of product was obtained, softening point 245–257°. The infrared of these products exhibits the characteristic carbonyl groups of both monomers: 5.94 μ for anthraquinone, 5.40 and 5.60 μ for the anhydride.

RESULTS

2-Vinylanthraquinone has been prepared starting with 2-methylanthraquinone. It appears to be homopolymerized in poor yield by radical techniques, and may be copolymerized, also in poor yield, with styrene, α-methylstyrene, and maleic anhydride. The polymerization of styrene seems to be inhibited by the anthraquinone derivative. That the reaction with maleic anhydride is not of the Diels-Alder type may be assumed from the observation that no reaction occurs in the absence of catalyst and that the Diels-Alder reaction is unaffected by initiators or inhibitors.[15]

That no polymerization occurred with the cationic initiator (which functions best when electrons can be released at the double bond) is consistent with the electron-withdrawing effect of the carbonyl group, which is expected readily to remove electrons from the vinyl group. Further, anthraquinone can combine with one or two molecules of aluminum trichloride. The latter complex is insoluble in ethylene dichloride, and is orange in color.[16] The behavior of monomer with titanium tetrachloride presents an analogy. The Lewis acid, attached to the oxygen(s) of the vinylanthraquinone would be expected further to deactivate the vinyl group toward a cationic initiator.

Acknowledgment. We acknowledge with pleasure the advice given us in connection with interpreting the N.M.R. data by Dr. Harold Conroy.

NEW HAVEN, CONN.

---

(12) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(13) H. J. Bernstein, J. H. Pople, and W. G. Schneider, *Canadian J. Chem.*, **35**, 65 (1957).

(14) H. J. Bernstein, J. H. Pople, and W. G. Schneider, *High-resolution Nuclear Magnetic Resonance*, McGraw-Hill Book Co., Inc., New York, 1959, p. 238.

(15) A. Wasserman, *J. Chem. Soc.*, **1935**, 828; P. H. Hermans, *Introduction to Theoretical Organic Chemistry*, Elsevier Publishing Co., 1954, p. 312.

(16) S. Coffey, *Chem. and Ind.*, **1953**, 1068.