drochloric acid. The organic layer was separated, washed, dried and evaporated. Dehydrohalogenation and further purification were conducted as mentioned before, yield 3 g. of orange viscous liquid which rapidly darkened on standing and gave a positive isatin test (blue-green like that given by thiophene but not blue-black like that for 2-acetylthiophene), b.p. 128–130° (5 mm.). Treatment with 2,4-dinitrophenylhydrazine reagent[12] produced **1-(2-thenoyl)-cyclopentene 2,4-dinitrophenylhydrazone**, crystallizing in blood-red clusters from alcohol, m.p. 148–149°.

Anal. Calcd. for $C_{16}H_{14}N_4O_4S$: N, 15.63; S, 8.94. Found: N, 15.61; S, 9.27.

Repetition of the foregoing procedure except using anhydrous aluminum chloride instead of antimony pentachloride gave a small quantity of yellow platelets on crystallization from alcohol, m.p. 121–122°. The product was insoluble in 10% aqueous sodium hydroxide, showed no halogen present by both the Beilstein and sodium fusion tests, gave a negative isatin test, and depressed the melting point of an authentic sample of 2-thenoic acid upon admixture therewith.

Anal. Calcd. for $C_{13}H_{14}O_2S$: C, 66.63; H, 6.02; S, 13.67. Found: C, 66.46, 66.70; H, 5.96, 5.86; S, 12.96.

Reaction with 2-Furoyl Chloride.—A mixture of 10 g. (0.147 mole) of cyclopentene, 20 g. (0.153 mole) of 2-furoyl chloride and 90 ml. of purified[8] carbon disulfide was cooled to 2° and treated with 40 g. (0.154 mole) of anhydrous stannic chloride added dropwise over a 20-minute period during which time the color changed from orange to dark blue. After refrigeration overnight, the mixture was hydrolyzed and the intermediate product was collected as before and dehydrohalogenated by means of diethylaniline (23 g.). Fractional distillation of the resultant mixture gave an orange-red liquid, b.p. 120–200° (4–8 mm.), which solidified on cooling. Treatment of an absolute ethanolic solution of the solid with charcoal and crystallization from this solvent produced 3 g. of colorless rhombs, m.p. 124–125°. The crystals showed a positive pine splinter test (emerald green) and negative tests for halogen by both the Beilstein and sodium fusion methods.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.50, 72.58; H, 6.43, 6.76.

(12) Procedure of G. D. Johnson, THIS JOURNAL, **73**, 5888 (1951).

DEPARTMENT OF CHEMISTRY
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Preparation of Radioactive Iodotriphenylethylene[1]

BY D. C. MORRISON

RECEIVED APRIL 14, 1952

It was desired to prepare the iodine analog of the biologically active bromotriphenylethylene, containing radioiodine as tracer, for work on synthetic estrogens. This radioactive iodotriphenylethylene was used for uptake studies in human and animal tumors. The iodotriphenylethylene was prepared by a modification of the method of Koelsch.[2] The method was adapted to a smaller scale with some variations and radioiodine(I^{131}) was employed. An attempt to obtain the compound by iodination of triphenylethylene using iodine chloride in glacial acetic acid failed.

Experimental

Experimental work was done behind lead and Lucite shields in a hood.

Preparation of Radioiodine. (This method was suggested by Dr. Earl Hoerger).—The sodium iodide carrier (0.3 g.) was dissolved in water in a separatory funnel and the desired amount of I^{131} (as sodium iodide, Oak Ridge isotope) activity added. An equal volume of benzene was added and then 0.4 g. of sodium nitrite in concentrated aqueous solution. The mixture was treated dropwise with shaking with 6 *N* nitric acid until an excess was present. The contents were agitated vigorously behind a lead shield. If the aqueous phase (after separation of layers) was still colored by an additional drop of acid, more of the latter was added until the aqueous layer remained colorless. After standing 20 minutes, the layers were separated carefully and the organic layer washed once by extraction with water. The benzene solution of radioiodine could then be added to the Grignard reagent, with or without previous drying over sodium sulfate.

The radioiodine was also generated in some runs by the reaction of active iodide with potassium iodate and dilute sulfuric acid, but the above method was preferable. Any excess of either iodide or iodate seemed to cause retention of activity in the aqueous layer. This was probably caused, in the case of excess iodate, by an exchange reaction.

Preparation of Iodotriphenylethylene.—One gram of magnesium was treated in a nitrogen atmosphere with 0.3 ml. of ethyl bromide in 25 ml. of ether. After the reaction was well under way, 1 g. of bromotriphenylethylene (m.p. 114°) was added in a few portions during 10–15 minutes. No iodine was used as a primer as Koelsch recommends.[2] This mixture was refluxed for 2.5 hours. After cooling, the gray solution (yellow if air has been admitted) was treated with the I^{131} solution. Solid inactive iodine was then added until its color was permanent. It was thought best to use an insufficient amount of carrier iodine for the reaction, and then to destroy the remaining Grignard reagent with inactive iodine in order to utilize as much activity as possible. The mixture was now hydrolyzed by a mixture of ice and 1 *N* hydrochloric acid.

The ether–benzene layer was washed with bisulfite solution and with water and was then evaporated. The residue in ether–petroleum ether solution was decolorized with Nuchar and the solvents removed. The crystalline residue was extracted with four small portions of cold petroleum ether by grinding under this solvent. This removes a small amount of oil. The iodo compound could be used as such or recrystallized from boiling petroleum ether or from alcohol. One recrystallization from the former gave a product with m.p. 125.5–127°. Koelsch gives 126–127°. A specific activity of 23 μc./mg.was obtained. In a similar experiment using inactive iodine, 2 g. of bromotriphenylethylene gave 1.573 g. of iodo compound or 68.8%.

Acknowledgment.—The author expresses gratitude to Drs. K. G. Scott, J. G. Hamilton, W. M. Garrison and E. Hoerger for advice received during this work.

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(1) The work described in this paper was sponsored by the Atomic Energy Commission. It was supported in part by a grant from the Henry, Laura and Irene B. Dernham Fund of the American Cancer Society and the Christine Breon Fund.

(2) C. F. Koelsch, THIS JOURNAL, **54**, 2045 (1932).

Polarography of 8-Quinolinol-5-sulfonic Acid

BY J. P. PHILLIPS AND QUINTUS FERNANDO

RECEIVED MARCH 18, 1952

An interpretation of the polarograms of 8-quinolinol is made difficult in acid solutions by catalytic waves that obscure the reduction waves, and in neutral solutions pronounced maxima distort the curves.[1] Since the sulfonic acid group apparently does not reduce at the dropping mercury cathode,[2] and the reduction of quinoline sulfonic acids by chemical means appears little different from the unsubstituted quinolines,[3] the polarographic behavior of 8-quinolinol-5-sulfonic acid should be very similar to that of 8-quinolinol.

(1) J. T. Stock, *J. Chem. Soc.*, 586 (1949).
(2) S. Wawzonek, *Anal. Chem.*, **21**, 64 (1949).
(3) K. V. Bokil, *J. Indian Chem. Soc.*, **13**, 404 (1936).

It was found, however, that 8-quinolinol-5-sulfonic acid gave a catalytic wave in acid solutions at more negative potentials than did 8-quinolinol, so that at least one of the reduction waves prior to the catalytic wave could be analyzed (Fig. 1). Logarithmic analysis of this reduction wave indicated a one-electron process. Additional waves were masked by the catalytic wave.

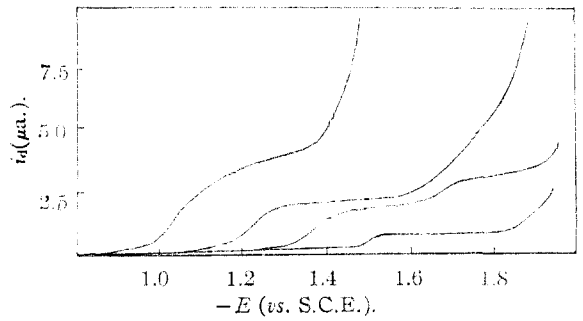

Fig. 1.—Polarograms of 8-quinolinol-5-sulfonic acid; from left to right: *p*H 3.75, 6.50, 8.90, 11.10; concentration 4.73×10^{-4} *M*.

In approximately neutral solutions 8-quinolinol-5-sulfonic acid was remarkably free from maxima, in contrast to 8-quinolinol.[1] The reduction wave found in acid solutions decreased in height with increasing *p*H. At a *p*H of 9 a well-defined double wave is obtained without indication of any following catalytic wave.

In alkaline solutions (*p*H 10–11.5) a single wave decreasing in height with increasing *p*H was obtained; the half-wave potential followed the equation $E_{1/2} = -0.77 - 0.059$ *p*H. Evidently the reaction is a one-electron reduction similar to 8-quinolinol.

In stronger alkali (*p*H 12) 8-quinolinol-5-sulfonic acid was not reducible. The double negative charge on the ion in such solutions may prevent the acquisition of further electrons.

The behavior of 8-hydroxyquinaldine-5-sulfonic acid was also investigated; in most respects it resembled 8-quinolinol-5-sulfonic acid fairly closely. The half-wave potential in alkaline solutions obeyed the equation $E_{1/2} = -0.97 - 0.050$ *p*H.

In view of the smoother waves obtained from these sulfonic acid derivatives in acid and neutral solutions they would seem to be better suited for analytical use than 8-quinolinol which has a usable reduction wave only in alkaline solution.

Experimental

A Sargent Model XXI Polarograph and an H-type cell kept at 25 ± 0.01° were employed for all determinations. Measurements were made against a saturated calomel electrode. The characteristics of the dropping mercury electrode, determined in 0.1 *N* potassium chloride on open circuit, were: $m = 2.30$ mg./sec., $t = 4.00$ sec.

Polarograms were run on each compound at six or more *p*H values between 2 and 12 and at concentrations ranging from 0.0001 to 0.001 *M*. Britton and Robinson buffers (consisting of acetic, phosphoric and boric acids with sodium hydroxide) were used after polarographic examination for reducible impurities. Oxygen was removed from the solutions with nitrogen. An instrument sensitivity of 0.100 was usually suitable.

Acknowledgments.—This work was supported in part by a grant from the Research Corporation. We are grateful to the Joseph E. Seagram's Distilleries for the use of their polarograph.

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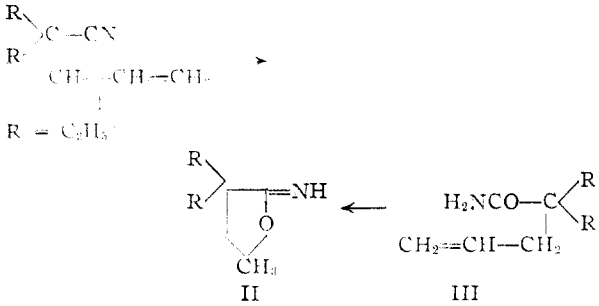
The Cyclization of Disubstituted Pentenoic Acid Derivatives

BY ROBERT F. RAFFAUF[1]

RECEIVED FEBRUARY 23, 1952

The conversion of substituted pentenoic acids to lactones, and of α-benzylpentenoic acid to a tetrahydronaphthalene derivative by means of sulfuric acid had been studied by Darzens some years ago.[2] More recent expression of interest in the cyclization of these acids[3] prompts us to record a similar series of observations with reference to the facile cyclization of 2,2-diethyl-4-pentenenitrile (I) which was carried out in these laboratories independently.

When I was dissolved in cold (0–5°) concentrated sulfuric acid and the solution was allowed to come to room temperature gradually (3–5 hr.) there was obtained, after dilution with water and neutralization with sodium hydroxide an 80% yield of a basic substance which, according to the observations of Schultz[4] and Easton,[5] we formulated as 2-imino-3,3-diethyl-5-methyltetrahydrofuran (II). The compound was surprisingly stable; it distilled with no evidence of decomposition as a colorless liquid (b.p. 80–82° (10 mm.)). *Anal.* Calcd. for $C_9H_{17}NO$: N, 9.02. Found: N, 8.80, 8.90.[6] It formed a crystalline benzenesulfonyl derivative, colorless needles from ethanol, m.p. 113–115°. *Anal.* Calcd. for $C_{15}H_{21}NO_3S$: N, 4.74; S, 10.85. Found: N, 4.68, 4.67; S, 10.80, 10.82. Hydrolysis in dilute mineral acid, or in alcoholic alkali followed by acidification, yielded



II III

a neutral, nitrogen-free product (b.p. 108–112° (19 mm.)) whose properties agreed with those expected for a lactone. *Anal.* Calcd. for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 68.8, 68.4; H, 10.2, 10.3. The same product was obtained from 2,2-diethyl-4-pentenoic amide (III); however, the solution of this compound in sulfuric acid was not strongly exothermic and could be conducted without external cooling. Craig's proposed mechanism[3] offers, in this case, a plausible description of the course of the reaction. In the case of the nitrile, however, this course is not as obvious; clearly an atom of oxygen must be introduced into the molecule to account for the product. Whether this is accomplished by initial and rapid hydrolytic attack of the CN-group followed by cyclization, or by preliminary addition of sulfuric acid to the allylic double bond followed by cyclic

(1) Research Associate, National Cancer Institute; present address: Smith, Kline and French Laboratories, Philadelphia 1, Pa.

(2) G. Darzens, *Compt. rend.*, **183**, 748, 1110 (1926).

(3) P. N. Craig, THIS JOURNAL, **74**, 129 (1952).

(4) E. M. Schultz, C. M. Robb and J. M. Sprague, *ibid.*, **69**, 2454 (1947).

(5) N. R. Easton, J. H. Gardner and J. R. Stevens, *ibid.*, **69**, 2941 (1947).

(6) Microanalyses by Mr. S. Alpert.