

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<sup>12</sup> 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<sup>8</sup> 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  $C_{14}H_{16}O_2$ : 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).

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## Preparation of Radioactive Iodotriphenylethylene<sup>1</sup>

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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.<sup>2</sup> 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.)

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

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.<sup>2</sup> 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  $\mu$ c./mg. was obtained. In a similar experiment using inactive iodine, 2 g. of bromotriphenylethylene gave 1.573 g. of iodo compound or 68.8%.

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## Polarography of 8-Quinolinol-5-sulfonic Acid

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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.<sup>1</sup> Since the sulfonic acid group apparently does not reduce at the dropping mercury cathode,<sup>2</sup> and the reduction of quinoline sulfonic acids by chemical means appears little different from the unsubstituted quinolines,<sup>3</sup> 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).