tures probably do not make a significant contribution.[14]

Application of a crude method of calculating resonance energies suggested by Wheland[15] shows that the resonance energy of tropolone should be less than the sum (40–52 kcal. mole^{-1}) of the resonance energies of these two hybrid structures. This calculation gives 24 kcal. mole^{-1} for the resonance energy of tropone, 24 kcal. mole^{-1} for the carboxylic acid vinylog and 30 kcal. mole^{-1} for tropolone. Although this calculation is not intended for non-hydrocarbons, it shows clearly the effect of superimposing two resonance hybrids. The observed resonance energy (36 kcal. mole^{-1}) is quite reasonable for a hybrid of the tropone and carboxylic acid vinylog structures.

(14) In phenol these structures account for a 7 kcal. mole^{-1} increase in the resonance energy over that of benzene. These structures (c) are certainly less important than structure (b) since the cycloheptatriene nucleus is a poorer electron acceptor than the carbonyl group or a phenyl group.

(15) G. W. Wheland, "Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 79 *ff.*

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Reactions of Pivalyl, 2-Thenoyl and 2-Furoyl Chlorides with Cyclopentene[1]

BY L. H. KLEMM[2] AND THEODORE LARGMAN

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Treatment of a mixture of pivalyl chloride and cyclopentene in carbon disulfide with anhydrous stannic chloride (as catalyst) and subsequent dehydrohalogenation of the intermediate product by means of refluxing diethylaniline yielded an impure oil which reacted further with 2,4-dinitrophenylhydrazine to give a crystalline compound assigned the structure of 1-pivalylcyclopentene 2,4-dinitrophenylhydrazone. This structure was further substantiated by observation of the ultraviolet absorption spectrum of the oil which exhibited an intense maximum at 239 mμ (E 1.55, c 150 mg./liter) and a much weaker one at *ca.* 310 mμ (E 0.02) characteristics of an α,β-unsaturated ketone with two alkyl substituents variously attached to the available positions on the α- and β-carbons.[3] The oil proved to be inactive as an antibiotic[4] in *in vitro* tests with Gram-negative *E. coli* and Gram-positive *B. mycoides*.

Reaction of 2-thenoyl chloride with cyclopentene according to the procedure used with pivalyl chloride or with substitution of phosphorus pentoxide for the stannic chloride gave small amounts of 2-thenoic acid as the only isolable product, while use of anhydrous aluminum chloride as the catalyst gave excessive condensation to produce a small amount of yellow non-acidic crystalline material for which elemental analyses indicated the empirical formula $C_{13}H_{14}O_2S$. Anhydrous antimony pentachloride, a Lewis acid of strength intermediate between that of aluminum chloride and stannic chloride,[5] however, produced a small yield of an unstable oil which gave a positive isatin test and formed a crystalline derivative (with 2,4-dinitrophenylhydrazine reagent) of composition corresponding to that expected for 1-(2-thenoyl)-cyclopentene 2,4-dinitrophenylhydrazone.

With 2-furoyl chloride and cyclopentene, stannic chloride gave at least termolecular condensation to a colorless crystalline product of empirical formula $C_{14}H_{16}O_3$ which showed a positive pine splinter test for the presence of the furan nucleus.

Experimental[6]

Reaction of Pivalyl Chloride.[7]—A solution of 42 g. (0.161 mole) of anhydrous stannic chloride in 100 ml. of purified[8] carbon disulfide was cooled to −15° and treated with a solution of 11 g. (0.162 mole) of cyclopentene and 21.3 g. (0.177 mole) of pivalyl chloride, added dropwise with stirring. After one additional hour of stirring and four more hours in a refrigerator the viscous mixture (which had changed from light yellow to black during the course of reaction) was poured onto crushed ice and stirred to decompose the complex present. The organic layer was separated, washed with water, dried and evaporated. The resultant residue was refluxed for five hours at 185° with 20 ml. (0.125 mole) of purified[9] diethylaniline. The cooled mixture was diluted with ether, washed successively with excess 5% hydrochloric acid and 5% aqueous sodium hydroxide, dried, evaporated and fractionally-distilled; yield 7.7 g. of faintly yellow liquid, b.p. 63–68° (7 mm.), not obtained analytically pure. Treatment of a portion of this liquid with 2,4-dinitrophenylhydrazine[10] gave **1-pivalylcyclopentene 2,4-dinitrophenylhydrazone**, crystallizing from alcohol in yellow-orange needles, m.p. 144°.

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: C, 57.83; H, 6.07; N, 16.85. Found: C, 57.81; H, 6.02; N, 16.87.

The ultraviolet absorption spectrum of another portion of the yellow liquid was determined by means of a Beckman quartz spectrophotometer, model DU, using matched silica cells of 1-cm. path length and absolute methanol as a solvent. The oil obeyed Beer's law in the range 15–1500 mg./liter tested.

A third portion was used for tests on antibacterial activity by means of the agar diffusion method.[11] Solutions of 1–100 mg. of the oil in 0.3 ml. of methanol showed no apparent inhibition of growth for either *Escherichia coli* or *Bacillus mycoides*.

Reaction of 2-Thenoyl Chloride.—A mixture of 6 g. (0.088 mole) of cyclopentene, 13.5 g. (0.092 mole) of 2-thenoyl chloride, and 100 ml. of purified[8] carbon disulfide was cooled to 0° in a flask fitted with a calcium chloride drying tube and was treated slowly, with stirring, with 26.6 g. (0.089 mole) of anhydrous antimony pentachloride. The brown solution was stirred 30 minutes longer and then poured into a mixture of crushed ice and concentrated hy-

(1) From the Ph.D. thesis of Theodore Largman.

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(3) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941). Compare data for 1-acetylcyclopentene, I. Heilbron, *et al.*, *J. Chem. Soc.*, 1827 (1949).

(4) For data and theories on the antibacterial action of α,β unsaturated ketones see W. B. Geiger and J. E. Conn, THIS JOURNAL, **67**, 112 (1945); H. Rinderknecht, *et al.*, *Biochem. J.*, **41**, 463 (1947).

(5) O. C. Dermer, *et al.*, THIS JOURNAL, **63**, 2881 (1941). See also K. Bodendorf and H. Böhme, *Ann.*, **516**, 1 (1935); N. O. Calloway, *Chem. Revs.*, **17**, 327 (1935).

(6) Microanalyses were performed by B. Jarvis and A. Rosen. Melting points were determined by means of an Eimer and Amend melting point block and are uncorrected.

(7) Preparative procedure adapted from that of R. Robinson and co-workers, *J. Chem. Soc.*, 1285 (1935); 763 (1936), for 1-acetylcyclopentene.

(8) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 365.

(9) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 550.

(10) Procedure of R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 143.

(11) S. A. Waksman, "Microbial Antagonisms and Antibiotic Substances," 2nd Ed., The Commonwealth Fund, New York, N. Y., 1947 p. 75.

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).

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Preparation of Radioactive Iodotriphenylethylene[1]

BY D. C. MORRISON

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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.[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%.

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

Polarography of 8-Quinolinol-5-sulfonic Acid

BY J. P. PHILLIPS AND QUINTUS FERNANDO

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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.[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).