

about 4 to 1. The sample was sealed under nitrogen. The sample had the following properties: boiling point at 66 mm. pressure, 69.5°; freezing point, -7.5°; refractive index, n_D at 25°, 1.5350."

Five calorimetric combustion experiments were performed.^{1,2,3} The mass of hydrocarbon used in each experiment was about one gram and the amount of reaction was determined from the mass of carbon dioxide produced in the combustion. No evidence of incomplete combustion was found in any of the experiments. The following results were obtained:

For the reaction of combustion, C_8H_8 (liquid, 1,3,5,7-cyclooctatetraene) + 10 O₂ (gas) = 8CO₂ (gas) + 4H₂O (liq.), the heat of combustion at 25° is $-\Delta H_{298.16}^\circ = 4537.84 \pm 1.16$ int. kj./mole or 1084.75 = 0.28 kcal./mole.

For the reaction of formation, 8C(solid, graphite) + 4H₂(gas) = C₈H₈(liq., 1,3,5,7-cyclooctatetraene), the heat of formation at 25° is $\Delta H_{298.16}^\circ = 247.10 \pm 1.23$ int. kj./mole or 59.07 = 0.29 kcal./mole.

For this calculation, the recently reported selected values of the heats of formation of carbon dioxide and water were used.^{4,5}

For the reaction of isomerization, in the liquid state, of cyclooctatetraene to styrene, C₈H₈ (liq., 1,3,5,7-cyclooctatetraene) = C₈H₈ (liq., styrene), the heat of isomerization at 25° is $\Delta H_{298.16}^\circ = -34.35 \pm 0.34$ kcal./mole. For this calculation, the value for the heat of formation of liquid styrene at 25° reported by Prosen and Rossini was used.⁶

These data indicate definitely that the cyclooctatetraene ring does not possess the stability inherent in the benzene ring, since, from the standpoint of the energy content, cyclooctatetraene is less stable than styrene by 34 kcal./mole.

(4) E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Research Natl. Bur. Standards*, **33**, 447 (1944).

(5) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945).

(6) E. J. Prosen and F. D. Rossini, *ibid.*, **34**, 59 (1945).

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RECEIVED MAY 1, 1947

Modified Synthesis of Ethyl Trifluoroacetate¹

By JAMES C. REID

The straightforward synthesis of ethyl trifluoroacetate by esterification of trifluoroacetic acid² involves the somewhat tedious process of isolating the acid from the reaction mixture in which it is formed. This paper describes the direct esterification of the acid without isolating it from the reaction mixture. This is possible de-

(1) This paper is based on work performed under Contract #W-7405-Eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory and the Department of Chemistry, University of California.

(2) Henne, Alderson and Newman, *THIS JOURNAL*, **67**, 918-919 (1945).

spite the large amount of water present because of the formation of a low boiling ternary azeotrope consisting of alcohol, water, and ester. The azeotrope contains 88 wt. per cent. of ester and boils at 54°.

Experimental

The quantities of materials specified are based on an oxidation of one mole of trichlorotrifluoropropene.

The oxidation mixture containing potassium trifluoroacetate filtered free of manganese dioxide is acidified with fourteen moles of sulfuric acid, then 1160 cc. of 95% ethanol is added and the mixture is fractionated through a thirty-plate column. About two-thirds of the ester can be distilled out as the azeotrope at 55-57° using a reflux ratio of 15:1. The head temperature then starts to climb and the ratio is increased to 30:1.

The temperature gradually reaches 78° and distillation is continued after this point has been reached until the total volume of distillate is half that of the alcohol used. The distilling time is ten hours.

Experiments with a sixty-plate column operating at a reflux ratio of 60:1 show that it is still necessary to distill out considerable alcohol after the temperature reaches 78° to get all the ester and so the more convenient thirty plate column is employed.

The distillate contains no hydrogen chloride but does contain sulfur dioxide if an excess has been used in reducing the excess permanganate employed in the oxidation.

The distillate is now redistilled through a thirty-plate column which separates the azeotrope from excess alcohol. The product coming over between 54-60° is collected as crude ester. A small amount of ester remains in the alcohol in the pot, which can be saved and used in the next esterification.

The alcohol and water are removed from the azeotrope by mixing it with half its volume of concentrated sulfuric acid, while cooling in an ice-bath, then distilling the ester out in a simple distillation apparatus. No water or alcohol escapes from the acid if the pot temperature does not exceed 120°.

The yield of purified ester is 73%, based on trifluoro-trichloropropene.

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RECEIVED MARCH 24, 1947

The Reaction of Thiuram Disulfide with Halomethyl Ketones

By J. J. RITTER AND H. SOKOL¹

In an attempt to prepare bis-(thiazyl-2) disulfides by the condensation of halomethyl ketones with thiuram disulfide, it was found that phenacyl bromides reacted smoothly with thiuram disulfide in acetone. Instead of the expected disulfides, however, excellent yields of 2-phenacylthio-4-arylthiazoles were obtained. This was particularly interesting in view of the fact that chloroacetone yielded no analogous product in an alcohol medium.²

When an acetone solution of thiuram disulfide and chloroacetone was allowed to stand overnight

(1) Abstracted from a portion of the thesis submitted to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Buchman, Reims and Sargent, *J. Org. Chem.*, **6**, 764 (1941).

at room temperature, sulfur and ammonium chloride precipitated from the reaction mixture; evaporation of the solvent gave only a tarry residue. With phenacyl bromides, however, the reaction appeared to follow a different course. The ammonium ion was not produced and 2-phenacylthio-4-arylthiazoles precipitated directly from the reaction mixtures as relatively pure hydrobromides. They were hydrolyzed to the free bases by washing with water.

Experimental³

Thiuram Disulfide.—Ammonium dithiocarbamate was prepared according to the general procedure of Miller,⁴ except that butyl or amyl alcohol was used instead of the ether-alcohol mixture. The crude product was oxidized directly by the method of Freund and Bachrach.⁵ Highest yields of the disulfide were obtained (60%) when small quantities of ammonium dithiocarbamate were used and the oxidation carried out rapidly.

Reaction of Phenacyl Bromides with Thiuram Disulfide.—In a typical experiment, a solution of 1.84 g. (0.01 mole) of thiuram disulfide and 3.98 g. (0.02 mole) of phenacyl bromide in 30 ml. of acetone was allowed to stand at room temperature, with occasional shaking, for seventy-two hours. Precipitation began within two hours. The copious precipitate was separated by filtration, washed on the filter with 10 ml. of cold acetone and finally with water until the washings gave a negative test for bromide. There was obtained 2.9 g. (93%) of 2-phenacylthio-4-phenylthiazole, which crystallized from 95% ethanol in fine white needles, m. p. 118°. No change in melting point was observed when a mixed melting point was run with a sample prepared according to the method of Buchman.²

Anal. Calcd. for C₁₇H₁₃ONS₂: N, 4.50; S, 20.58. Found: N, 4.63; S, 20.78.

The 2,4-dinitrophenylhydrazone was prepared in methanol, m. p. 151–153°.

Anal. Calcd. for C₂₃H₁₇O₄N₅S₂: N, 14.26. Found: N, 14.13.

In a similar manner, from *p*-bromophenacyl bromide and thiuram disulfide in acetone there was obtained a 94% yield of 2-(*p*-bromophenacylthio)-4-(*p*-bromophenyl)-thiazole, which crystallized as silky white needles from absolute ethanol, m. p. 146–147°.

Anal. Calcd. for C₁₇H₁₁ONBr₂S₂: N, 2.98; Br, 34.09. Found: N, 3.06; Br, 34.28.

The 2,4-dinitrophenylhydrazone was prepared in methanol, m. p. 179–181°.

Anal. Calcd. for C₂₃H₁₅O₄N₅Br₂S₂: N, 10.78. Found: N, 10.90.

(3) Melting points uncorrected.

(4) Miller, *Contrib. Boyce Thompson Inst.*, **5**, 31 (1933).

(5) Freund and Bachrach, *Ann.*, **285**, 201 (1895).

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RECEIVED DECEMBER 18, 1946

The Decarboxylation of Opianic Acid

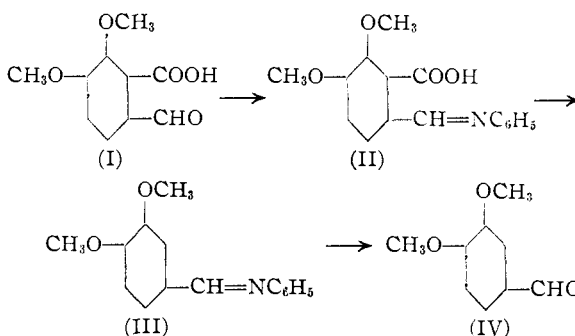
BY JOHN WEIJLARD, ELEANOR TASHJIAN AND MAX TISHLER

Opianic acid (I), a degradation product of hydrastine and narcotine, has been demonstrated to be 2-carboxy-3,4-dimethoxybenzaldehyde by con-

version into both veratraldehyde and hemipinic acid.¹

According to the literature the decarboxylation of opianic acid to veratraldehyde is difficult and the yield is poor. Under the drastic conditions employed by the previous investigators, cleavage of the ether groups occurs with the formation of vanillin, isovanillin and protocatechuic aldehyde as by-products. It is probable that lactol formation between the carboxyl and the neighboring aldehyde group is responsible for the decarboxylation difficulty.

Recent experiences in this Laboratory with the conversion of 2-carboxyindole-3-aldehyde into indole-3-aldehyde² prompted us to apply the same method to opianic acid. Accordingly, the aldehyde group of opianic acid was protected by conversion into the phenylimino derivative (II), the latter was decarboxylated to veratraldehyde anil (III) which was then hydrolyzed to veratraldehyde (IV). In this way, veratraldehyde was obtained from opianic acid in yields of around 90%.



Experimental

3,4-Dimethoxy-2-carboxy-(1)-phenyliminomethyl Benzene; Opianic Acid Anil.³—To a solution of 63 g. of opianic acid (0.3 mole) in a mixture of 300 cc. of alcohol and 300 cc. of 4% aqueous sodium hydroxide at 70° was added 28 g. of aniline (0.3 mole). The mixture was stirred five minutes at this temperature and then cooled to 3°. About 110 cc. of 10% hydrochloric acid was then added in a thin stream with efficient stirring. The anil precipitation was complete when the reaction was slightly acid to congo red. The product was filtered, washed free from chloride with water and dried at 70° to constant weight; yield 81.0 g. (94.6%), m. p. 188–190°. After recrystallization from alcohol, the compound melted at 191.5–192.5°.

Anal. Calcd. for C₁₆H₁₅O₄N: N, 4.91. Found: N, 5.03.

3,4-Dimethoxy-1-phenyliminomethylbenzene; Veratraldehyde Anil.—A mixture of 50 g. of the unrecrystallized opianic acid anil and 2 g. of powdered copper bronze was held at 195–205° for ten minutes, at which time the carbon dioxide evolution was complete. The cooled reaction mixture was used for the hydrolysis step.

For analytical purposes the product from a 1-g. run was dissolved in 20 cc. of boiling absolute alcohol, the solution

(1) Beckett and Wright, *J. Chem. Soc.*, **29**, 281 (1876); Wegscheider, *Monatsh.*, **3**, 356 (1882); Schorigin, Issaguljanz and Below, *Ber.*, **64**, 274 (1931).

(2) Shabica, Howe, Ziegler and Tishler, *THIS JOURNAL*, **68**, 1156 (1946). See also Boyd and Robson, *Biochem. J.*, **29**, 555 (1935).

(3) Although the anil was previously prepared [Liebermann, *Ber.*, **19**, 2284 (1886)], our procedure is recorded as it is different.