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-cycloöctatetraene) + 10 O_2 (gas) = 8CO_2 (gas) + 4H_2O (liq.), the heat of combustion at 25° is $-\Delta Hc^\circ_{298.16}$ = 4537.84 ± 1.16 int. kj./mole or 1084.75 ± 0.28 kcal./mole.

For the reaction of formation, 8C(solid, graphite) + 4H_2(gas) = C_8H_8(liq., 1,3,5,7-cycloöctatetraene), the heat of formation at 25° is $\Delta Hf^\circ_{298.16}$ = 247.10 ± 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 cycloöctatetraene to styrene, C_8H_8 (liq., 1,3,5,7-cycloöctatetraene) = C_8H_8 (liq., styrene), the heat of isomerization at 25° is $\Delta H^\circ_{298.16}$ = −34.35 ± 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 cycloöctatetraene ring does not possess the stability inherent in the benzene ring, since, from the standpoint of the energy content, cycloöctatetraene is less stable than styrene by 34 kcal./mole.

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(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).

THERMOCHEMICAL LABORATORY
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WASHINGTON, D. C.

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Modified Synthesis of Ethyl Trifluoroacetate[1]

BY JAMES C. REID

The straightforward synthesis of ethyl trifluoroacetate by esterification of trifluoroacetic acid[2] 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 despite 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 trifluorotrichloropropene.

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[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).

The Reaction of Thiuram Disulfide with Halomethyl Ketones

BY J. J. RITTER AND H. SOKOL[1]

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

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(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).