[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE ACTION OF SULFUR ON NORMAL-HEPTANE AND NORMAL-BUTANE

BY R. B. BAKER[1] AND E. EMMET REID

RECEIVED JANUARY 11, 1929 PUBLISHED MAY 6, 1929

Introduction

The action of sulfur on organic compounds has been the subject of many investigations.[2] Friedmann[3] investigated the action of sulfur on *n*-octane when heated under pressure. He obtained a thiophene, $C_8H_{12}S$, and a thiophthene compound, $C_8H_8S_2$.

The Present Investigation

n-Heptane and *n*-butane were heated with sulfur. The results obtained, so far as they go, are analogous to those of Friedmann. Heptane gives a substituted thiophene and *n*-butane seems to give thiophene itself, though the yields from both hydrocarbons were very small.

Experimental

***n*-Heptane. Sealed Pyrex Tubes.**—Three g. of sulfur and 11 g. of heptane were heated in each tube at temperatures varying from 150 to 250° for periods of four to twenty-four hours. On cooling the tubes were placed in "dry ice" before opening. The liquid was fractionated and consisted mostly of unchanged heptane. A very small residue boiling above 100° was obtained.

Steel Bombs.—Much larger amounts of materials were used in the bombs, which were heated to temperatures of 300–350° for periods of twenty-four to forty-eight hours. A charge consisted of 12.8 g. of sulfur and 40 g. of heptane. The residues from the bombs, after distilling off the unchanged heptane, were not much greater in proportion than those obtained from the glass tubes. There is very little indication of reaction under these conditions. However, the various residues were combined and fractionated. A fraction (about 2 g.) boiling at 160–161° was collected. A few drops of this liquid when treated with alcoholic mercuric chloride gave a pale yellow precipitate (test for thiophenes). Reasoning from the results of Friedmann's work on *n*-octane, heptane should give a thiophene of the empirical formula $C_7H_{10}S$. A Parr bomb determination of sulfur gave the result: calcd. for $C_7H_{10}S$: S, 25.40; found: S, 24.89, 25.04. The density was $d_{4°}^{0°} = 0.9332$; $d_{4°}^{25°} = 0.9221$.

This liquid gave positive tests for thiophenes by the methods of Fletcher and Hopkins,[4] Bauer[5] (indophenin reaction), Laubenheimer[6] and Steensma.[7] Negative tests were obtained when the liquid was examined for mercaptans[8] and sulfides.[9]

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[1] From a part of the Ph.D. dissertation of R. B. Baker, 1928.

[2] See, for example, Steinkopf and Kirchoff, British patent 16,810, July 18, 1912; Capelle, *Bull. soc. chim.*, [4] **3**, 150 (1908); W. Friedmann, *Ber.*, **49**, 1551 (1916).

[3] Friedmann, *Ber.*, **49**, 1344 (1916).

[4] Fletcher and Hopkins, *Chem. Zentr.*, I, 1442 (1907).

[5] Bauer, *Ber.*, **37**, 1244, 3128 (1904).

[6] Laubenheimer, *ibid.*, **8**, 224 (1875).

[7] Steensma, *Chem. Zentr.*, I, 1492 (1908).

[8] Reid, Mackall and Miller, THIS JOURNAL, **43**, 2104 (1921).

[9] Steinkopf, *Ann.*, **403**, 1 (1914).

Considerable solid matter was left in the tubes after the removal of the liquid. This proved to be sulfur mixed with some carbon.

n-**Butane.**—Steel bombs were used with butane and sulfur, the charge being 32 g. of butane and 15 g. of sulfur. As butane is a gas at ordinary temperatures the bomb was first well cooled in an ice-salt mixture before adding the hydrocarbon. The charge was heated for twenty-one hours at 335°.

On opening the bomb (after again cooling in ice water), a considerable amount of hydrogen sulfide was given off and the unreacted butane was volatilized. The gas evolved smelled like a low-boiling gasoline high in sulfur content. Upon opening the bomb very little residue was left (less than 1 g.). This was taken up in ether, and gave all of the above-mentioned color tests for thiophene.

Conclusions

The results obtained are analogous to those obtained by Friedmann on octane. From heptane and sulfur a thiophene and sulfur of the formula $C_7H_{10}S$ is formed in small amounts.

Similar results were obtained with butane and sulfur.

BALTIMORE, MARYLAND

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THE CLAISEN ESTER CONDENSATION WITH ETHYL THIOLACETATE[1]

BY R. B. BAKER[2] AND E. EMMET REID

RECEIVED JANUARY 11, 1929 PUBLISHED MAY 6, 1929

Introduction

This investigation was undertaken with the idea in mind of comparing ethyl thiolacetate with ethyl acetate in the ordinary Claisen condensation. No sulfur esters have ever been subjected to such a reaction, and it appeared of interest to compare the products obtained with those resulting from the condensation of ethyl acetate with itself, and of ethyl acetate with a ketone and a nitrile.

Ethyl thiolacetate, $CH_3COSC_2H_5$, in the presence of sodium metal condenses in a manner quite similar to ethyl acetate, and forms a sulfur analog of acetoacetic ester, $CH_3COCH_2COSC_2H_5$. The yield of ester is rather low, being about 15% of the theoretical (calculated on the amount of ethyl thiolacetate used).

At ordinary temperatures ethyl acetothiolacetate contains about 31% of enol (determined by the bromo-titration method of Kurt Meyer),[3] as compared to about 7% in acetoacetic ester.

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[1] Presented at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] From a part of the Ph.D. dissertation of R. B. Baker, 1928.

[3] Kurt Meyer, *Ber.*, **44**, 2718 (1911).