$$= \frac{N}{N_x}\sum_{i=1}^{n-1} x^i(1-x)[2+(n-i-1)(1-x)] + \frac{N}{N_x}x^n = 1 - x + \frac{x}{n} \quad (2c)$$

as found from the equations derived in the appendix of Ref. 5. The correction term for finite n and x is simply x/n.

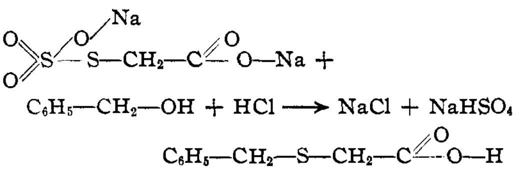
By preparing different samples of the copolymer having different molecular weights, and different chlorine contents, it should be possible to test these considerations and the assumptions involved. It may be noted that (2b) was derived by assuming that the reaction rates for 1–2 and 1–3 pairs are equal, and reactions between 1–4 substituents do not occur. The condition that 1–2 reactions proceed much more rapidly or much more slowly than 1–3 reactions, does not alter the result. This was shown by Flory. Wall[8] proved this to be true for any value of the relative rate of reaction of 1–2 and 1–3 pairs.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.
RECEIVED JANUARY 10, 1941

Preparation of S-Benzylmercaptoacetic Acid

BY GEORGE G. STONER AND GREGG DOUGHERTY

Certain alcohols can be condensed readily with mercaptans to yield sulfides. For example S-benzylmercaptoacetic acid was isolated in 72% yield after equimolar quantities of benzyl alcohol and mercaptoacetic acid had reacted in 2 N hydrochloric acid.[1] It has now been found that the same end can be achieved more directly and conveniently by using the Bunte salt, disodium S-carboxymethyl thiosulfate, prepared from chloroacetic acid and sodium thiosulfate.



$$\mathrm{NaO{-}SO_2{-}S{-}CH_2{-}C({=}O){-}O{-}Na} + \mathrm{C_6H_5{-}CH_2{-}OH} + \mathrm{HCl} \longrightarrow \mathrm{NaCl} + \mathrm{NaHSO_4} + \mathrm{C_6H_5{-}CH_2{-}S{-}CH_2{-}C({=}O){-}O{-}H} \quad (1)$$

Experimental Part

Solution of S-Carboxymethyl Thiosulfuric Acid.—Chloroacetic acid (9.5 g., 0.1 mole) was neutralized by sodium carbonate in 25 cc. of water, a solution of 25 g. (0.1 mole) of sodium thiosulfate in 40 cc. of water was added, and the resulting solution was kept at 100° for an hour. After cooling, 50 cc. (0.6 mole) of concentrated hydrochloric acid was added. No sulfur precipitated, but about 1 g. of sodium chloride was filtered off.

S-Benzylmercaptoacetic Acid.—The above solution was refluxed for twenty hours with 10.8 g. (0.1 mole) of benzyl alcohol. The oily layer was neutralized by sodium carbonate solution and washed with ether. Then 9.1 cc. (0.11 mole) of concentrated hydrochloric acid was added and after standing one day at 5° a yield of 10 g. (55%) was obtained, m. p. 60–61°,[2] equivalent weight calcd. 182.2, found 183.

Racemic Benzylsulfinylacetic Acid.—To a solution of 0.91 g. (0.005 mole) of S-benzylmercaptoacetic acid in 40 cc. of acetone, 0.55 cc. (0.0055 mole) of 30% hydrogen peroxide was added. The beaker was left uncovered for five days, by which time the solvent had evaporated, leaving a quantitative yield of sulfoxide, m. p. 126–127° after recrystallization from benzene.

Anal. Calcd. for $C_9H_{10}O_3S$: equiv. wt., 198.2; S, 16.17. Found: equiv. wt., 201; S, 16.5.

Benzylsulfonylacetic Acid.—A solution of 0.91 g. (0.005 mole) of S-benzylmercaptoacetic acid in 10 cc. of water was oxidized at room temperature for five days by 32 cc. (20% excess) of 4% potassium permanganate solution. The mixture was filtered and 0.05 mole of sulfuric acid was added. The solution was shaken with three 50 cc. portions of ether, 100 cc. of benzene was added to the extract, which then was concentrated to 40 cc. After one hour, 0.65 g. (60% yield) of fine crystals formed, m. p. 137°.[3]

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[1] Holmberg, *J. prakt. Chem.*, **141**, 93 (1934).

[2] Berg and Holmberg, *Svensk Kem. Tids.*, **47**, 257 (1935), reported 60°; Holmberg, *loc. cit.*, and *Arkiv Kemi, Mineral. Geol.*, **12A**, No. 11 (1936), reported 61–63°.

[3] Rothstein, *J. Chem. Soc.*, 309 (1937), reported 139–140°.

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RECEIVED FEBRUARY 15, 1941

The Use of Sulfuric Acid in Purifying Saturated Hydrocarbons: Its Action on 2,2,4-Trimethylpentane

BY FRANK C. WHITMORE AND H. H. JOHNSON, JR.

The use of sulfuric acid as a wash in the purification of saturated hydrocarbons is widespread. Observation has long led us in this Laboratory to the suspicion that such treatment is questionable. We have now studied the action of cold concentrated sulfuric acid on 2,2,4-trimethylpentane, isooctane. After treatment for ten days with cold 95% acid, we find that over half of the starting material has been changed to other products. Although the nature of these products has not been determined, there is no doubt that sulfuric acid has brought about profound changes.

The extent to which reaction took place makes imperative a most careful fractionation of a saturated hydrocarbon following a sulfuric acid wash. This fact and the possible loss of expensive material raise a real question as to the desirability of this method of purification.

Of course, the reaction here described constitutes a limiting case in which the treatment with sulfuric acid of 2,2,4-trimethylpentane was allowed to proceed until no further action was noted. Less prolonged treatment would not lead to as great a destruction of the product.

Experimental

A sample of Röhm and Haas isooctane certified by the Bureau of Standards was fractionated through a column equivalent to 85 theoretical plates. All of the distilled material and the residue had $n^{20}\text{D}$ 1.3915–16. It was thus very pure 2,2,4-trimethylpentane.

In a 22-liter flask equipped with a sealed stirrer and reflux condenser attached to a trap cooled by dry-ice and acetone was placed 7836 g. of 2,2,4-trimethylpentane and 5 liters of 95% sulfuric acid (C. P. Baker "Analyzed"). A slow evolution of sulfur dioxide started after a few minutes and was very pronounced after three hours. The mixture was stirred for ten days at about 20°, after which time the evolution of sulfur dioxide had practically ceased.

The cold trap contained 610 g. of material about half of which was sulfur dioxide. The acid layer from the flask was removed and diluted with five times its volume of water and 1 kg. of black powder, presumably carbon, filtered off. The oil layer was washed, dried over potassium carbonate, and fractionated through a 15-plate column to give 39% of material boiling below 96° at 740 mm. and 31% boiling above 123°. Less than 25% of the starting material was recovered as fairly pure 2,2,4-trimethylpentane. The nature of the other products could not be determined even after painstaking fractionations through the 85-plate column. Indications were obtained, however, that neohexane and 2,2,4,4-tetramethylpentane were present.

SCHOOL OF CHEMISTRY AND PHYSICS
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

RECEIVED MARCH 31, 1941

NEW COMPOUNDS

3-Phenylphenyl Acetate

The method which was used for the preparation of this compound was the same as that reported previously for 4-phenylphenyl acetate,[1] except that after pouring the reaction mixture into water the ester was extracted with ether; the ethereal solution was dried with anhydrous sodium sulfate and filtered, and the ether was removed by distillation. The crude product was obtained as a light brown viscous oil in a 96.5% yield. After distillation at 135–136° (2 mm.), it solidified, m. p. 34.0–34.2° (cor.). (The melting point was determined from a freezing point curve; the thermometer which was used had been calibrated by the United States Bureau of Standards.)

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66. Found: C, 79.6; H, 5.76.

The 3-phenylphenol which was used in this preparation was generously furnished by the Dow Chemical Company, Midland, Michigan.

DEPARTMENT OF CHEMISTRY
STATE COLLEGE OF WASHINGTON
PULLMAN, WASHINGTON
STEWART E. HAZLET
HARRY A. KORNBERG

RECEIVED MARCH 14, 1941

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[1] Hazlet and Kornberg, THIS JOURNAL, 61, 3037 (1939).

1-Phenylcycloheptanol

To an ethereal solution of the Grignard reagent prepared from 31.4 g. of bromobenzene and 5 g. of magnesium, after fifteen minutes, 22.4 g. of cycloheptanone was added with cooling and the alcohol isolated as usual, distilled in a vacuum, and the water droplets thereby formed removed over anhydrous sodium sulfate. The product was a viscous, colorless, fragrant liquid: $n^{20}\text{D}$ 1.5515, D^{20} 1.049, M_D (calcd.) 57.97, M_D (obsd.) 57.83.

Anal. Calcd. for $C_{13}H_{18}O$: C, 83.0; H, 9.0. Found: C, 82.79; H, 9.30.

DEPARTMENT OF CHEMISTRY
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RICHARD D. KLEENE

RECEIVED JANUARY 24, 1941

Derivatives of Tetrahydrofurfuryl Alcohol

3-Nitrohydrogenphthalate.—This compound was prepared according to the directions of Nicolet and Sacks.[1] It was obtained as a crystalline white solid which was recrystallized from hot water, m. p. 175–177°.

Anal. Calcd. for $C_{13}H_{13}O_7N$: N, 4.75. Found: N, 4.88.

α-Naphthylurethan.—This compound was prepared according to the directions of Shriner and Fuson.[2] It was obtained as clusters of needles which were recrystallized from petroleum ether, m. p. 88–90°.

Anal. Calcd. for $C_{16}H_{17}O_3N$: N, 5.17. Found: N, 5.27.

The tetrahydrofurfuryl alcohol was furnished by the Quaker Oats Company, Chicago, and the analyses were performed by Dr. T. S. Ma.

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[1] Nicolet and Sacks, THIS JOURNAL, 47, 2348 (1925).

[2] Shriner and Fuson, "Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1935, p. 143.

CHEMISTRY DEPARTMENT
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SHERMAN FRIED

RECEIVED FEBRUARY 17, 1941

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m-Bromo-*n*-alkylbenzenes

***m*-Bromo-*n*-propylbenzene.**—The Grignard reagent prepared from 61 g. of ethyl bromide was treated with 92.5 g. of *m*-bromobenzaldehyde and the crude *m*-bromophenylethylcarbinol thus obtained was heated for five hours at 160° with 30 g. of freshly fused potassium bisulfate in a