steam-bath. The residue was taken up in ether and shaken, first with dilute hydrochloric acid, and then with water. The ether was distilled and the residue (19.5 g.) was esterified with diazomethane in the usual manner.

The solvents were removed under reduced pressure and the residue was taken up in methyl alcohol. The solution was cooled to 0° and water was added until the solution became cloudy. On standing several days at 0° the crystalline methyl ether of dehydroabietic acid was deposited. By addition of more water to the filtrate a semi-crystalline deposit was obtained. The supernatant liquid was decanted and the methyl alcohol distilled under reduced pressure.

Nine grams of the resulting oil was refluxed for three hours with 90 cc. of *n*-butyl alcohol and 9 g. of potassium hydroxide. The butyl alcohol was removed by steam distillation. When the residue was cooled an amorphous potassium salt separated. Ether was added to the mixture and the aqueous layer was removed. This aqueous layer did not contain an appreciable amount of potassium salt of dihydroabietic acid. The ether solution was then shaken out with 0.25 *N* sodium hydroxide. The aqueous extract was shaken twice with fresh ether and then the dihydroabietic acid was isolated by addition of dilute hydrochloric acid, extraction with ether and evaporation of the solvent.

Eight grams of this light yellow product was dissolved in 35 cc. of alcohol and 50 cc. of 0.4 *N* ammonium hydroxide. On standing overnight 1.3 g. of stout prisms separated. The free acid was liberated as outlined above and the residue was recrystallized from alcohol. The final product melted at 174-176° and gave a yellow color with tetranitromethane: $[\alpha]^{20}_D$ +108°; *c*, 2.043% in absolute alcohol.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60; neut. equiv., 304.3. Found: C, 78.70, 79.00; H, 10.55, 10.32; neut. equiv., 310.

52.1 mg. of substance was dissolved in 10 cc. of alcohol and directly titrated with 0.1 *N* sodium hydroxide against phenolphthalein: neutralization equivalent, 310; calcd., 304.3.

Hydroxytetrahydroabietic Acid.—A solution of 50 mg. of the lactone in 10 cc. of 10% *n*-butyl alcoholic potassium hydroxide was refluxed for five hours. The butyl alcohol was removed by steam distillation, the aqueous solution diluted with water and extracted three times with ether to remove any neutral material. The aqueous solution was then made acid to litmus and neutral to congo red by addition of dilute acetic acid. The crystalline precipitate which separated was extracted with ether, the ether solution washed with water and the solvent evaporated. The residue after recrystallization from dilute methyl alcohol had a melting point of 164–165°.

Anal. Calcd. for $C_{20}H_{34}O_3$: C, 74.47; H, 10.63. Found: C, 74.25; H, 10.88.

Summary

A dihydroabietic acid of high positive rotation has been isolated from so-called "α-pyroabietic acid" prepared by the catalytic method.

Another compound of the same elemental composition, previously thought to be a dihydro compound, was found to be a lactone.

Washington, D. C. Received July 29, 1938

[Contribution from the Chemical Laboratory of the University of Illinois]

Vinyl Halide Polysulfones. Peracetic Acid as a Catalyst for the Reaction between Sulfur Dioxide and Olefins[1]

By C. S. Marvel and F. J. Glavis

Polysulfones have been obtained from many common olefins and olefin derivatives and sulfur dioxide by using various organic peroxides to catalyze the reaction. However, up to this time no descriptions of the polysulfones prepared from vinyl chloride and vinyl bromide have appeared. Solonina[2] and Staudinger and Ritzenthaler[3] report failures to obtain the addition reaction between vinyl chloride and sulfur dioxide. Recently Frey, Fitch and Snow[4] intimate that the reaction occurs readily although they do not give the details of the preparation or a complete description of the product.

We have found that vinyl chloride and vinyl bromide will combine with sulfur dioxide to give polysulfones which have two vinyl units for each sulfur dioxide unit. In this respect they differ from all other olefins, olefin derivatives, or acetylenes which have been examined previously.

The addition reaction appears to require an especially effective catalyst and in our early experiments could only be brought about in the presence of an unusually "active" sample of paraldehyde which contained peroxides.

A closer examination of the paraldehyde samples which were tried as catalysts showed that the ones which would cause the reaction to run smoothly not only contained peroxides but also were strongly acidic and showed absorption

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[1] Paper No. VIII. For the seventh communication see This Journal, **60**, 1450 (1938).

[2] Solonina, *J. Russ. Phys.-Chem. Soc.*, **30**, 826 (1898); *Chem. Zentr.*, **70**, I, 248 (1899).

[3] Staudinger and Ritzenthaler, *Ber.*, **68B**, 455 (1935).

[4] Frey, Fitch and Snow, U. S. Patent 2,114,292 (1938).

in the ultraviolet at 2400 Å. Other samples of paraldehyde which did not show all of these properties were relatively non-effective as catalysts. This combination of properties suggested to us that the active constituent in the aged paraldehyde was peracetic acid.

A sample of peracetic acid in acetic anhydride was prepared by the method of Böeseken, Cohen and Kip[5] and without attempting to purify it was tested as a catalyst for the vinyl chloride–sulfur dioxide reaction. The reaction took place quickly and gave a good yield of polymer. This result is especially significant as it is now possible to bring about the addition reaction with a catalyst which can be prepared readily whereas previously it was necessary to examine many samples of paraldehyde before finding one that was effective.

Peracetic acid also proved to be an effective catalyst to bring about the addition of sulfur dioxide to allyl chloride as well as for the simple olefins and acetylenes which have been reported in earlier papers[1] as condensing when active paraldehyde was used as a catalyst. However, no polysulfones could be obtained from allyl bromide, 1,2,3-trichlorobutene or 1-bromoheptene.

Several structural formulas seem quite possible for the vinyl chloride polysulfone but as yet it is impossible to decide which one is correct. The polymer is a white, amorphous, insoluble, high-melting compound. On heating it loses sulfur dioxide. When treated with liquid ammonia it is not degraded to a cyclic disulfone as are most of the polysulfones from the other olefins[1] which have been studied. Vinyl chloride polysulfone reacts with liquid ammonia to produce a nitrogen-containing polymer with the approximate composition $[(CH_2CHNH_3Cl)_2SO_2]_x$. Aniline also reacts with vinyl chloride polysulfone to yield a product which contains nitrogen. Treating the polysulfone with hot aqueous sodium hydroxide solution removes about one-third of the chlorine as hydrogen chloride, leaving a black insoluble polymer. Boiling the polysulfone with 7% sodium hydroxide and distilling with steam at the same time, causes the polymer to darken instantaneously and gives a distillate which contains very small quantities of an aldehyde. A 2,4-dinitrophenylhydrazone of this aldehyde melting at 127–129° has been isolated and analyzed. The analysis indicates that this derivative has one C_3H_5 unit for each dinitrophenylhydrazone residue. The product is apparently not the 2,4-dinitrophenylhydrazone of acetone (m. p. 128°).[6]

Further work must be done to characterize this compound and to establish the way in which the two vinyl chloride units are combined with one sulfur dioxide unit in the polymer. It should be mentioned that vinyl bromide polysulfone gives essentially the same reactions as the chloride in all cases which have been examined.

Some copolymers of vinyl chloride, 1-pentene and sulfur dioxide have been obtained using ascaridole as a catalyst although ascaridole will not cause vinyl chloride and sulfur dioxide to combine in a reasonable time. Benzoyl peroxide did not bring about the formation of a copolymer. Analysis of this copolymer indicated that the ratio of constituents may be one mole of vinyl chloride to one mole of 1-pentene to two moles of sulfur dioxide. A copolymer prepared from a mixture of vinyl chloride and phenylacetylene with sulfur dioxide seemed to have these constituents present in the ratio of two moles to one mole to two moles, respectively.

Some rather rough freezing point determinations of solutions of styrene, 1-pentene, 10-hendecenoic acid and vinyl chloride in liquid sulfur dioxide showed that there was apparently no compound formation in the absence of a catalyst in the first three cases. Styrene and sulfur dioxide mixtures showed a eutectic at 27 mole per cent. of styrene, and 10-hendecenoic acid and sulfur dioxide mixtures showed a eutectic at 4 mole per cent. of the acid. 1-Pentene and sulfur dioxide mixtures gave a complex melting point curve similar to that observed by Seyer and Hugget[7] in their careful study of the system 1-hexadecene–sulfur dioxide. On the other hand, vinyl chloride and sulfur dioxide mixtures showed eutectics at 37 mole per cent. of vinyl chloride and 98 mole per cent. of vinyl chloride and a peak indicating compound formation at approximately 40 mole per cent. of vinyl chloride. While it is impossible to relate this compound to the composition of the polysulfone which is obtained in the presence of a catalyst, it is of interest that only in the case of vinyl chloride was compound formation noted in the solution, and this is the only olefin derivative to combine in a two to one ratio with sulfur dioxide to yield a polysulfone.

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[5] Böeseken, Cohen and Kip, *Rec. trav. chim.*, **55**, 815 (1936).

[6] Curtius and Dedichen, *J. prakt. Chem.*, [2] **50**, 266 (1894).

[7] Seyer and Hugget, *Trans. Roy. Soc. Can.*, **18**, 213 (1924).

Experimental Part

Vinyl Chloride Polysulfone.—To a mixture of equal volumes of liquid vinyl chloride and liquid sulfur dioxide was added about a half volume of active paraldehyde and one-fifth volume of 95% ethanol. The ice-cold mixture was sealed in a pressure bottle and allowed to warm to room temperature. The reaction apparently was complete in one hour and longer standing did not increase the yield. The polymer separated as an insoluble powder as it formed. The reaction flask was cooled and opened and the contents were poured into ether. The polymer was isolated by filtration and was purified by repeated washing with alcohol. Unless the product was washed thoroughly it would turn dark on standing. The dark material had very nearly the same analysis as the white product. The yields varied with the effectiveness of the catalyst from about 5 to 30%. The reaction goes so quickly that practically the same yields are obtained by running the reaction in an open vessel. Addition of larger amounts of catalyst did not increase the yield, but when the reaction was carried out under conditions which permitted recovery of the unused vinyl chloride, it was found that the recovered material gave as good results as the original material when a fresh charge of catalyst was added.

When ascaridole and benzoyl peroxide were tried as catalysts for the addition reaction, no polysulfone was obtained in six hours. Over a longer period some dark colored material was obtained from reaction mixtures containing ascaridole. With benzoyl peroxide no product was obtained even after twenty-four hours. When 15 cc. of the solution of peracetic acid prepared from 97.3 g. of acetic anhydride, 20 g. of 30% hydrogen peroxide and 1 g. of *p*-toluenesulfonic acid[5] was used as a catalyst the polymer formed in 30% yields within one-half hour.

The polysulfone was a white amorphous powder. It darkened at 135–140° and melted at 250–275°. It was insoluble in common organic solvents except dioxane in which it was very slightly soluble.

Anal. Calcd. for $(C_4H_6Cl_2SO_2)_x$: C, 25.40; H, 3.17; S, 16.93; Cl, 37.57. Found: C, 26.42; H, 3.67; S, 17.62, 16.83, 16.53; Cl, 38.19.

Vinyl Bromide Polysulfone.—Using 10 cc. of liquid sulfur dioxide, 10 cc. of liquid vinyl bromide, 5 cc. of active paraldehyde and 2 cc. of 95% ethanol there was obtained 1–2.5 g. of polysulfone. It was isolated and purified as described for the chlorine analog. The product melted with decomposition at 200–225°.

Anal. Calcd. for $(C_4H_6Br_2SO_2)_x$: S, 11.51; Br, 57.55. Found: S, 10.92; Br, 54.13.

Reactions of Vinyl Chloride Polysulfone

With Liquid Ammonia.—When 1 g. of vinyl chloride polysulfone was dissolved in 100 cc. of liquid ammonia a deep blue solution formed. Evaporation of the ammonia left 0.5 g. of dark colored residue insoluble in organic solvents and acetic acid.

Anal. Calcd. for $(C_4H_{12}Cl_2N_2SO_2)_x$: C, 21.52; H, 5.38; S, 14.38; N, 12.55. Found: C, 23.19, 22.50; H, 6.09, 7.39; S, 13.32, 15.79, 15.42, 13.55, 15.32; N, 12.46.

With Aniline.—One gram of the polysulfone was dissolved in 25 cc. of aniline and the solution allowed to stand at room temperature for fifteen hours. Most of the aniline was removed by distillation under reduced pressure. When about 5 cc. of solution remained, the residue was poured into 100 cc. of 95% ethanol. The precipitate was collected on a filter and washed with ethanol. The residue weighed about 1 g.

Anal. Calcd. for $(C_{10}H_{12}NClSO_2)_n$: C, 48.9; H, 4.9; S, 13.1; Cl, 14.5. Found: C, 51.3; H, 5.5; S, 13.4; Cl, 14.0.

Action of Heat.—A weighed sample of vinyl chloride polysulfone was placed in 75 cc. of dioxane. A stream of air purified by leading it through an "ascarite" tube was led through the apparatus and then through standard potassium dichromate solution. The dioxane was heated to boiling for various lengths of time with different samples and the amount of sulfur dioxide liberated was determined by titration of the standard dichromate solution. In three hours using about 0.1 g. of polysulfone about 75–85% of the calculated amount of sulfur dioxide was given off. With five hours of heating the sulfur dioxide evolved amounted to 97%.

With Alkali.—When a weighed sample of polysulfone (about 0.1 g.) was suspended in standard sodium hydroxide solution and heated to boiling the mixture turned black. After six hours this mixture was acidified and titrated for chloride ion, and it was found that about one-third of the chlorine in the polymer had been removed. A reaction mixture which was refluxed for twenty-four hours gave the same result.

A mixture of 2 g. of the polymer with 75 cc. of 7% aqueous sodium hydroxide solution was distilled with steam. The distillate was collected in a solution of 2,4-dinitrophenylhydrazine. The distillate gave a positive test with fuchsin aldehyde reagent. A small amount of 2,4-dinitrophenylhydrazone was obtained. It melted at 127–129° after recrystallization from alcohol.

Anal. Found: C, 45.19; H, 3.85; N, 23.21, 23.35.

This product gave a depression in melting point when mixed with the 2,4-dinitrophenylhydrazone of acetone (m. p. 128°). While the analysis checks for $[(C_3H_6)(NNHC_6H_3(NO_2)_2)]_x$ it has not been identified further.

Vinyl Bromide Polysulfone and Liquid Ammonia.—This reaction was carried out exactly as described for the chloride analog. The product was analyzed for sulfur.

Anal. Calcd. for $(C_4H_{12}Br_2N_2SO_2)_x$: S, 10.25. Found: S, 9.25.

Freezing Point–Composition Diagrams of Solutions of Olefins in Liquid Sulfur Dioxide.—Freezing point curves were taken on solutions of styrene, 10-hendecenoic acid, 1-pentene and vinyl chloride in liquid sulfur dioxide. The olefin was introduced into a weighed glass tube and the amount thus introduced determined by weight difference. Liquid sulfur dioxide was then added and the tube weighed again. Temperature measurements were made by means of a copper–constantan thermocouple with the reference end held at 0° by an ice–water mixture. These measurements are not considered to be of great accuracy but do give some evidence of the nature of the mixtures. The freezing point–composition curves are given in Figs. 1–4.

Vinyl Chloride-1-Pentene-Sulfur Dioxide Copolymer.—An equimolecular mixture of vinyl chloride and 1-pentene

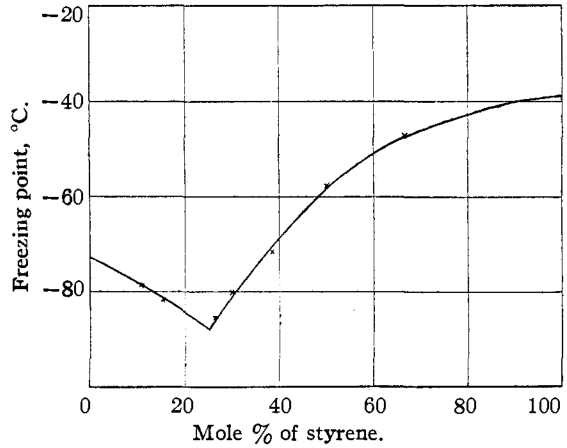


Fig. 1.—Sulfur dioxide–styrene freezing point–composition diagram.

was treated with an equal volume of liquid sulfur dioxide, catalyst and 95% ethanol and placed in a pressure bottle. The usual reaction mixture consisting of 10 parts of olefin, 10 parts of sulfur dioxide, 1/2 part of catalyst and 2 parts of ethanol was used. Two catalysts, ascaridole and a mixture of ascaridole and active paraldehyde, were used without significant change in yield or properties of the product. The yield was about 50% of a polymer which melted with decomposition at 200–225°. The polymer was insoluble in common organic solvents.

Anal. Calcd. for $[C_5H_{10}C_2H_3Cl(SO_2)_2]_x$: S, 24.6; for $(C_5H_{10}SO_2)_x$: S, 23.88; for $(C_2H_3ClSO_2)_x$: S, 25.29. Found: S, 24.57, 24.07.

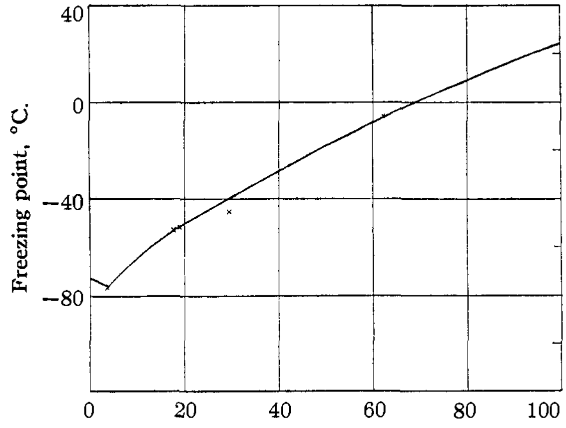


Fig. 2.—Sulfur dioxide–10-hendecenoic acid freezing point–composition diagram.

Vinyl Chloride–Phenylacetylene–Sulfur Dioxide Copolymer.—Two mixtures of vinyl chloride and phenylacetylene were treated with sulfur dioxide in the presence of ascaridole and alcohol in the usual ratios. Ten cubic centimeters of a mixture containing 13 moles of vinyl chloride for 5 moles of phenylacetylene gave 5.5 g. of a polymer which melted with decomposition at 280–285°.

Anal. Calcd. for $[(CH_2{=}CHCl)_2(C_6H_5C{\equiv}CH)(SO_2)_2]_x$: S, 18.03. Found: S, 17.97.

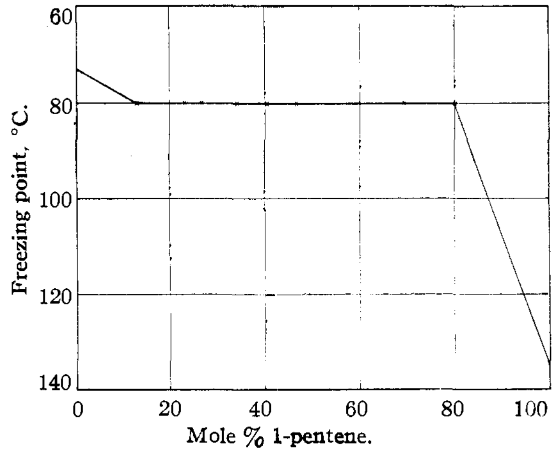


Fig. 3.—Sulfur dioxide–1-pentene freezing point–composition diagram.

Ten cubic centimeters of a mixture containing 8 moles of vinyl chloride for 5 moles of phenylacetylene gave 4 g. of polymer which melted with decomposition at 285–290°.

Anal. Found: S, 18.47.

Both polymers were insoluble in common organic solvents.

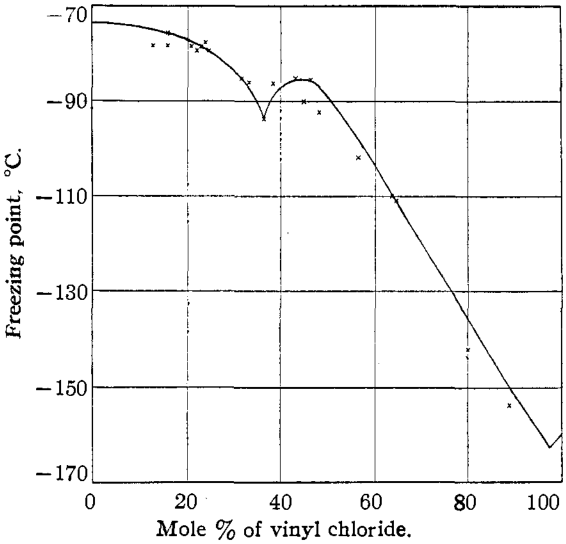


Fig. 4.—Sulfur dioxide-vinyl chloride freezing point–composition diagram.

Allyl Chloride Polysulfone.[4]—From 15 cc. of allyl chloride, 10 cc. of sulfur dioxide, 2 cc. of ethanol and 5 cc. of active paraldehyde, 2.5 g. of polymer was obtained in one hour. The polymer was slightly soluble in acetone and dioxane but insoluble in other common solvents. It melted at 185–215° and decomposed at 225–275°. Peracetic acid solution was equally effective as a catalyst for this preparation.

Anal. Calcd. for $(C_3H_4ClSO_2)_x$: S, 22.93. Found: S, 22.55.

Summary

1. The catalytic activity which certain samples

of aged paraldehyde have shown in promoting the reaction between olefins and sulfur dioxide can be obtained by use of peracetic acid solutions.

2. Vinyl chloride and vinyl bromide combine with sulfur dioxide in the presence of active paraldehyde or peracetic acid to give a polymer of the composition $[(CH_2{=}CHX)_2SO_2]_n$, rather than the usual one to one type of polymer. A preliminary study of the reaction of the vinyl halide polymer has not indicated its structural unit.

3. Freezing point–composition curves for solutions of styrene, 1-pentene and 10-hendecenoic acid in liquid sulfur dioxide offer no evidence of compound formation. But vinyl chloride and liquid sulfur dioxide form a compound containing approximately 40 mole per cent. of vinyl chloride.

URBANA, ILLINOIS RECEIVED AUGUST 1, 1938

[CONTRIBUTION OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Electronegativities of Highly Branched Aliphatic Groups

BY FRANK C. WHITMORE AND HERBERT BERNSTEIN

Since the well-known Kharasch table of relative electronegativities of univalent organic groups consists chiefly of aromatic groups,[1] we decided to place in the table some of the highly branched aliphatic groups available in this Laboratory. Following the method of Kharasch, the mixed dialkyl mercury compounds were treated with alcoholic hydrogen chloride.

$$R{-}Hg{-}R' + HCl \longrightarrow RHgCl + R'H$$

This result would place R′ above R in relative electronegativity. Of the fifteen mixed dialkyl mercury compounds used in the present study, four gave mixtures of R′HgCl and RHgCl. The groups involved in these cases are thus indistinguishable by Kharasch's method. With ten of the other compounds a clear distinction in the relative electronegativity of the groups was obtained.

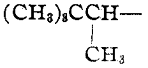
The results are given in Tables I and II.

TABLE I

ORDER OF DECREASING ELECTRONEGATIVITY

Phenyl
Methyl
Ethyl
n-Propyl
{ *n*-Butyl, $(CH_3)_3CCH_2CH_2$—
{ *n*-Hexyl, $(CH_3)_3CCH_2CH_2CH_2$—

$CH_3CH_2CH(CH_3)$—



$(CH_3)_3CCH(CH_3)$—

. . . .

Benzyl
$(CH_3)_3C$—, $(CH_3)_3CCH_2$—

Groups on the same line or bracketed are not distinguishable by this method. The dotted line above the benzyl group indicates that its relation to the groups immediately above it has not been determined experimentally.

The most interesting feature of this table is the position held by the *t*-butyl and neopentyl groups. Both are less electronegative than the benzyl, which, according to Kharasch, is less electronegative than any alkyl group which he tested. Furthermore, their electronegativities approximate each other. This corresponds to the inertness of *t*-butyl chloride and neopentyl chloride in certain metathetical reactions.[2]

Also of interest is the relationship between the pinacolyl and the secondary butyl groups. The *n*-hexyl and *n*-butyl groups have the same relative electronegativity. However, the pinacolyl, a group very susceptible to rearrangement,[3] is distinctly less electronegative than the secondary butyl group.

Experimental

Neopentyl chloride was prepared by the chlorination of neopentane.[2]

1-Chloro-3,3-dimethylbutane was prepared by slowly adding 29.8 g. (0.25 mole) of thionyl chloride to a solution of 21.7 g. (0.21 mole) of neopentylcarbinol in 19.7 g. (0.25 mole) of pyridine cooled on an ice-bath. A thick white solid formed. When the addition was complete, the ice-bath was removed and the temperature of the flask raised. Decomposition of the solid occurred between 94–133°. The residue was added to a mixture of 45 g. of ice and 30 g. of concentrated hydrochloric acid, the organic layer was separated from the aqueous layer and the latter was extracted with ether. Upon distillation, 15.5 g. of

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[1] Kharasch and Marker, THIS JOURNAL, **48**, 3140 (1926); Kharasch and Flenner, *ibid.*, **54**, 685 (1932).

[2] Conant and Hussey, *ibid.*, **47**, 479 (1925); Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).

[3] Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933)