

esters to form pyrimidines,<sup>7</sup> the synthesis of either isomer of dimethylthiouracil by systematic means does not appear likely.

### Discussion

The direct replacement of an oxygen atom of 1,3-dimethyluracil by sulfur has several interesting implications. The product of this reaction is not attainable by any other known synthetic method. Furthermore, the ultraviolet absorption spectrum of this compound has a bearing on the general problem of the relationship between absorption spectra and tautomerism in the pyrimidine series. If, as seems probable, the sulfur has been assigned correctly to the 4 position, the marked resemblance of the spectrum of this compound to that of 4-thiouracil would seem to imply that the sulfur in the 4 position of the latter also exists primarily in the double bound form, rather than in the sulfhydryl form.

In this experiment the direct substitution of doubly bound sulfur for oxygen must have occurred. The greater reactivity of the oxygen in the 4 position here is to be contrasted with the more ready substitution of the oxygen in the 2 position of the dialkylbarbiturates.<sup>5</sup> The tautomerism of the latter group of compounds conceivably might have some bearing on the order in which the oxygen atoms are replaced.

### Experimental

**6-Phenyl-2,4-dithiouracil.**—Three and one-half grams of 6-phenyl-2-thiouracil<sup>8</sup> was treated with phosphorus pentasulfide as indicated in Table I. The product was

(7) Johnson and Heyl, *Am. Chem. J.*, **37**, 628 (1907).

(8) Warmington, *J. prakt. Chem.*, [2] **47**, 208 (1893).

isolated by extraction with hot ethanol and was recrystallized from *n*-propyl alcohol, giving 2.75 g. (73%) of yellow needles, m. p. 264–268° (dec.): soluble in *ca.* 350 parts of hot ethanol, insoluble in cold ethanol, hot and cold water, ether and benzene.

*Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>ON<sub>2</sub>S: C, 54.5; H, 3.64; S, 29.1. Found: C, 54.8; H, 3.55; S, 28.6.

**1,3-Dimethyl-4-thiouracil.**—A mixture of 3 g. of 1,3-dimethyluracil<sup>9</sup> and 9 g. of phosphorus pentasulfide was refluxed in 25 ml. of xylene and 35 ml. of toluene (120°) for three and one-half hours. The product was found in both solvent and residue. After recrystallization from 50 parts of hot water the product weighed 2.15 g. (64.5%). The yellow needles, m. p. 132–133°, were soluble in ether, xylene, toluene and hot water and somewhat soluble in cold water.

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>ON<sub>2</sub>S: C, 46.7; H, 4.65; S, 20.5. Found: C, 46.6; H, 4.72; S, 21.1.

**2,4-Dimercaptoquinazoline.**—The residue from the phosphorus pentasulfide treatment was purified by solution in 0.4 N sodium hydroxide and precipitation with acetic acid. The yield was 85% of material decomposing 275–295°. Soxhlet extraction with absolute alcohol yielded yellow needles, m. p. 308–309° (dec.). Kötzt<sup>10</sup> reports a decomposition point of 260°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub>: C, 49.4; H, 3.09; S, 33.0. Found: C, 49.3; H, 2.59; S, 33.6.

### Summary

In a variety of 2,4-substituted pyrimidines, oxygen or alkylmercapto groups can be replaced by sulfur by treatment of the compound with phosphorus pentasulfide at elevated temperatures. The formation of a monothiodimethyluracil from 1,3-dimethyluracil indicates that the reaction can proceed through replacement of a doubly bound oxygen atom by a sulfur atom.

(9) Davidson and Baudisch, *THIS JOURNAL*, **48**, 2379 (1926).

(10) Kötzt, *J. prakt. Chem.*, [2] **47**, 303 (1893).

TUCKAHOE, N. Y.

RECEIVED FEBRUARY 10, 1947

[CONTRIBUTION FROM THE HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

## The Acid Catalyzed Isomerization of $\alpha$ -Pinene<sup>1</sup>

BY WILLIAM A. MOSHER<sup>2</sup>

It has been known for many years that  $\alpha$ -pinene is readily converted into monocyclic terpenes and terpene alcohols when treated with dilute mineral acids.<sup>3</sup> The technical process for the production of synthetic pine oil practiced in this country and in Europe is based on this reaction. On the other hand, the course of this reaction has not been adequately explained; in fact, the literature does not offer any definite explanation, although general usage suggests the rupture of the cyclobutane ring by the direct addition of water.<sup>4</sup> However,

(1) Presented in part before the Division of Organic Chemistry, American Chemical Society, Atlantic City, New Jersey, April, 1946.

(2) Present address: Department of Chemistry, University of Delaware, Newark, Delaware.

(3) Armstrong and Tilden, *Ber.*, **12**, 1752 (1879); Wallach, *Ann.*, **239**, 34 (1885).

(4) Wagner and Ginsberg, *Ber.*, **27**, 1644, 2270 (1894); **29**, 1195 (1896).

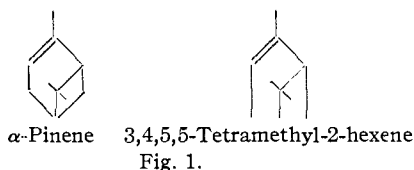
the reaction takes place readily in the absence of water, although no alcohols are formed in this case. Heat alone gives dipentene, presumably other monocyclic hydrocarbons, the acyclic terpene *allo*-ocimene, and the pyrenones resulting from cyclization of the *allo*-ocimene.<sup>5</sup> Anhydrous organic acids also give monocyclic terpenes and the esters of the acids used.<sup>6</sup> Anhydrous hydrogen chloride as employed in the old camphor process gives considerable by-product monocyclic terpenes in addition to "pinene hydrochloride."<sup>7</sup> Active earths such as vermiculite give camphene as the principal product but also the monocyclic

(5) (a) Berthelot, *Ann. chim.*, (iii) **37**, 223 (1853); **39**, 9 (1854); (b) Wallach, *Ann.*, **227**, 282 (1885); (c) Conant and Carlson, *THIS JOURNAL*, **51**, 3466 (1927); (d) Goldblatt and Palkin, *ibid.*, **66**, 655 (1944); (e) Fugitt and Hawkins, *ibid.*, **67**, 224 (1945); (f) Savieh and Goldblatt, *ibid.*, **67**, 2027 (1945).

(6) Reisman, *Bull. soc. chim.*, (iv) **41**, 94 (1927).

(7) Cf. Meerwein, *Ber.*, **53**, 1825 (1920).

terpenes, dipentene, terpinenes, and terpinolenes to the extent of about thirty per cent.<sup>8</sup>



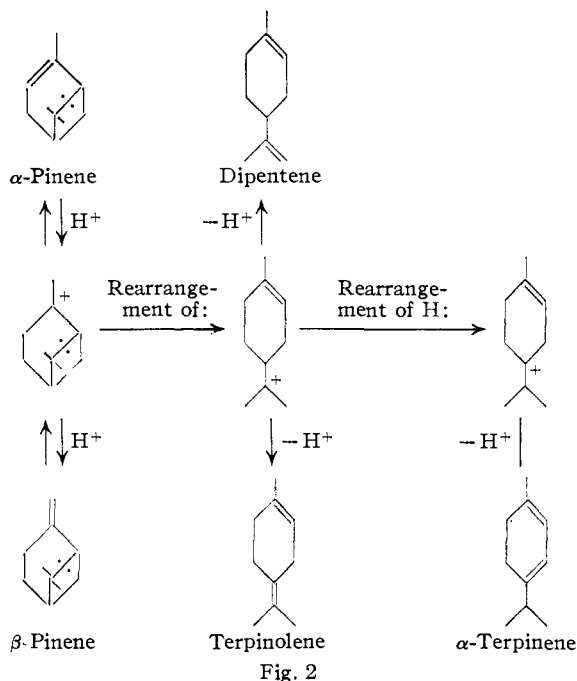
The object of the present work is to compare this acid catalyzed reaction of pinene with the previously studied behavior of an aliphatic olefin of similar structural relationships: 3,4,5,5-tetramethyl-2-hexene. As indicated in Fig. 1, the relative positions of groups are identical, disregarding the ring systems. This decene was first identified by Drake, Kline and Rose<sup>9</sup> in the dimer obtained when methylisopropylcarbinol is treated with 75% sulfuric acid at 80°. This was confirmed by Whitmore and Mosher.<sup>10</sup> The most unusual reaction of the above decene is the ease with which a carbon-to-carbon single bond is broken to give products of lower molecular weight when treated with 1-chloro-4-naphthalenesulfonic acid.<sup>11</sup>

Both 3,4,5,5-tetramethyl-2-hexene and  $\alpha$ -pinene on addition of a proton from any sufficiently acid catalyst should give the critical carbonium ion for depolymerization,  $R_3C-C-C^+$ , as proposed by Whitmore and Stahly.<sup>12</sup> By the application of the Whitmore-Stahly principle 3,4,5,5-tetramethyl-2-hexene should give isobutylene and 3-methyl-2-pentene, as actually found,<sup>10</sup> by the rearrangement of the pair of electrons between carbons 5 and 6 without simultaneous migration of the *t*-butyl group.

The treatment of  $\alpha$ -pinene with 1-chloro-4-naphthalene sulfonic acid is complicated by the fact that any monocyclic products formed boil at a higher temperature than the more symmetrical pinene and, therefore, considerable polymerization results; in the case of the analogous aliphatic compound, the products of splitting are rapidly removed from the catalyst and polymerization is minimized. The yield of monocyclic terpenes obtained from pinene in this manner is about 30%, and dipentene, terpinolene,  $\alpha$ -terpene and *p*-cymene have been identified in the mixture. Some *p*-menthane and  $\gamma$ -terpinene are probably present, but the detection of these is uncertain. The essential fact is the formation of monocyclic terpenes from  $\alpha$ -pinene, employing a mechanism identical with one strongly indicated for a related change in an aliphatic compound. The mechanism of the isomerization of  $\alpha$ -pinene is summarized in Fig. 2.

Although this work has not yet been extended to  $\beta$ -pinene, its related structure and the fact that it gives substantially the same reactions with

acid as does  $\alpha$ -pinene<sup>13</sup> indicates a similar mechanism.  $\alpha$ - and  $\beta$ -Pinene would yield the same carbonium ion on the addition of a proton. The fact that the thermodecomposition of  $\beta$ -pinene yields myrcene, whereas  $\alpha$ -Pinene yields *allo*-cimene,<sup>5d,e,f</sup> would indicate that the pyrolytic reaction does not proceed through a carbonium ion mechanism.



### Experimental

**Materials.**— $\alpha$ -Pinene (b. p. 155–156° (760 mm.),  $n_D^{20}$  1.4658) was obtained by distilling commercial pinene from wood turpentine (Hercules Pinene 111) through a column of 30 theoretical plates. The 1-chloro-4-naphthalenesulfonic acid was kindly supplied by Dean Frank C. Whitmore of the Pennsylvania State College.

**Isomerization of Pinene.**—Five moles (680 g.) of the above pinene dried over sodium was refluxed with 5 g. of the sulfonic acid for six hours, precautions being taken to exclude moisture. The product was neutralized with sodium carbonate solution and steam distilled to separate the monoterpenes from polymer. The steam volatile portion weighed 286 g. after drying over potassium carbonate.

**Identification of Products.**—The terpene mixture was distilled at a reflux ratio of 50–1 through a 30-plate column packed with  $3/32$ " stainless steel helices to give the following fractions: (1) 150–160° (760 mm.),  $n_D^{20}$  1.4620–1.4668, 68 g.; (2) 160–170°, 1.4684, 11 g.; (3) 170–180°, 1.4698–1.4753, 153 g.; (4) 180–185°, 1.4672–1.4840, 9 g.; (5) 185–190°, 1.4875–1.4904, 25 g.; residue 15 g.<sup>14</sup> Cut no. 1 was identified as unchanged  $\alpha$ -pinene by its physical properties and the preparation of the nitrosochloride, m. p. 112°, mixed m. p. 110°. Cut no. 2 was intermediate material and was not identified. Cut no. 3, the "dipentene cut," was divided into aliquots and

(13) Delépine and Adida, *Bull. soc. chim.*, **39**, 782 (1926); F. P. Austerweil, *ibid.*, **37**, 585, 686 (1924); **39**, 621, 954, 1643 (1926).

(14) The very close boiling points of menthanes, dipentane, *p*-cymene, and  $\alpha$ -terpinene, all between 170 and 178°, make sharp separation impracticable even with 100 theoretical plates. Dipentene and *p*-cymene also form an azeotrope as may also be the case with other components.

(8) U. S. Patent 2,129,323 (1938).

(9) Drake, Kline and Rose, *THIS JOURNAL*, **56**, 2076 (1934).

(10) Whitmore and Mosher, *ibid.*, **63**, 1120 (1941).

(11) Whitmore and Mosher, *ibid.*, **68**, 281 (1946).

(12) Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).

treated as follows: The addition of bromine to a cold petroleum ether solution gave solid dipentene tetrabromide, m. p. after recrystallization from ethyl acetate 126°, mixed m. p. unchanged. A second portion was treated with maleic anhydride after the method of Birch<sup>15</sup>; the distillate indicated 10%  $\alpha$ -terpinene based on the steam volatile fraction. The maleic anhydride adduct of  $\alpha$ -terpinene was isolated. A third portion was oxidized with cold neutral permanganate to give 17% of the steam volatile product as a saturated oil identified as *p*-cymene by the aroyl benzoic acid, m. p. and mixed m. p. 123.1° Cut no. 4 was not identified. Cut no. 5 gave terpinolene tetrabromide, m. p. and mixed m. p. 116–117°,<sup>17</sup> in 63%

(15) Birch, *Proc. Roy. Soc. N. S. Wales*, **71**, 54–59 (1937); *C. A.* **31**, 8109 (1937).

(16) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, 1935, pp. 76–77.

(17) Wallach, *Ann.*, **227**, 283 (1884).

yield based on the cut 5 indicating a high proportion of terpinolene. The residue was not investigated.

### Summary

1. The cyclobutane ring in  $\alpha$ -pinene is broken by treatment with 1-chloro-4-naphthalene sulfonic acid in an analogous fashion to 3,4,5,5-tetramethyl-2-hexene.

2. This reaction, and the general acid catalyzed isomerization of  $\alpha$ -pinene, and presumably  $\beta$ -pinene as well, to monocyclic terpenes is discussed from the point of view of the Whitmore mechanism with which it appears to be in complete harmony.

WILMINGTON, DELAWARE

RECEIVED APRIL 24, 1947

[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

## Substituted Styrenes. II. The Preparation of *p*-Iodo-, *p*-Nitro- and *p*-Dimethylaminostyrene and $\alpha$ -Vinylthiophene

BY ROGER W. STRASSBURG,<sup>1</sup> R. A. GREGG AND CHEVES WALLING

In connection with copolymerization studies<sup>2</sup> it has been found necessary to synthesize a number of substituted styrenes in this Laboratory.<sup>3</sup> This paper reports the preparation of the hitherto undescribed *p*-iodostyrene and new syntheses of *p*-nitrostyrene and  $\alpha$ -vinylthiophene. New physical constants are also reported for *p*-nitrostyrene and *p*-dimethylaminostyrene.

*p*-Iodostyrene has been prepared in three steps from commercially available *p*-aminoacetophenone by diazotization and conversion to *p*-iodoacetophenone (52% yield), reduction with aluminum isopropylate (92.5%), and dehydration over potassium acid sulfate (60%) in an over-all yield of 29%.

*p*-Nitrostyrene has been prepared by the treatment of  $\beta$ -bromo- $\beta$ -(*p*-nitrophenyl)-propionic acid with sodium carbonate solution.<sup>4</sup> We have followed what appears to be a more practical two-step synthesis from  $\beta$ -phenylethyl bromide by nitration followed by dehydrobromination in aqueous triethanolamine. We have, however, been unable to confirm the melting point previously reported for this styrene.<sup>4</sup>

*p*-Dimethylaminostyrene was prepared from *p*-dimethylaminobenzaldehyde and methylmagnesium bromide by a method similar to that employed by Marvel, Overberger, Allen and Saunders,<sup>5</sup> but in larger quantity. Our physical constants differ somewhat from theirs.

$\alpha$ -Vinylthiophene has been prepared by the de-

hydration of methyl- $\alpha$ -thienylcarbinol.<sup>6,7</sup> We have prepared the material in 28.7% yield by the reaction of  $\alpha$ -thienylmagnesium bromide with vinyl chloride in the presence of cobaltous chloride in a manner analogous to the synthesis of styrene reported by Kharasch and Fuchs.<sup>8</sup> An attempt to prepare *m*-methoxystyrene from *m*-iodoanisole by the same method, however, was unsuccessful.

### Experimental

***p*-Iodoacetophenone.**—Diazotization of 270 g. (2 moles) of *p*-aminoacetophenone with sulfuric acid and sodium nitrite, treatment of the diazo compound with excess potassium iodide solution, and vacuum distillation of the resulting oil gave 245 g. (52%) of light yellow *p*-iodoacetophenone, b. p. 137–140° (9 mm.), m. p. 83–84° (lit. 85°).

***p*-Iodophenylmethylcarbinol.**—In a 5-liter round bottom flask equipped with a 1 meter helices-packed fractionating column was placed 235 g. (0.96 mole) of *p*-iodoacetophenone and 2900 cc. of dry isopropyl alcohol in which 40 g. (1.48 moles) of aluminum had been dissolved, and the mixture slowly distilled. After several hours, when the distillate no longer gave a test for acetone with 2,4-dinitrophenylhydrazine, the excess alcohol was distilled off and, after cooling, the residue decomposed with 350 cc. of concentrated hydrochloric acid and 1000 g. of ice. After standing overnight the mixture was extracted with benzene, the benzene dried by azeotropic distillation, and then distilled off. The residue was vacuum-distilled at 2 mm. through a 6-in. Vigreux column until the forerun had been removed, and then without a column. There was obtained 211 g. (92.5%) carbinol, b. p. 99–120° (2–5 mm.), m. p. 40–42°. Inadvertently all of the carbinol was used before a sample was set aside for analysis. However, its method of preparation and subsequent reaction leaves little doubt as to its identity.

***p*-Iodostyrene** was prepared by dehydrating the carbinol over potassium acid sulfate essentially as described by Brooks<sup>9</sup> for similar compounds. Employing 211 g.

(1) Present address, University of Minnesota, Minneapolis, Minn.

(2) Walling, Briggs, Wolfstirn and Mayo, unpublished work.

(3) For the first paper in this series, see Walling and Wolfstirn, *THIS JOURNAL*, **69**, 852 (1947).

(4) Basler, *Ber.*, **16**, 3003 (1883).

(5) Marvel, Overberger, Allen and Saunders, *THIS JOURNAL*, **68**, 736 (1946).

(6) Mowry, Renoll and Huber, *ibid.*, **68**, 1105 (1946).

(7) Kuhn and Dann, *Ann.*, **547**, 293 (1941).

(8) Kharasch and Fuchs, *THIS JOURNAL*, **65**, 504 (1943).

(9) Brooks, *ibid.*, **66**, 1295 (1944).